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Application of Photoclick Chemistry for the Synthesis of Pyrazoles via 1,3-Dipolar Cycloaddition between Alkynes and Nitrilimines Generated In Situ

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Abstract: The photochemical extrusion of gaseous nitrogen from 2,5-disubstituted tetrazoles to generate reactive nitrilimines in situ represents an efficient and attractive way to form dipoles that can be used to provide useful chemicals via 1,3-dipolar cycloadditions. The concept of "photoclick chemistry" already inspired numerous researchers, who exploited photochemical processes involving alkenes for the synthesis of adducts or the functionalization of biocompatible materials. The approach requires bioorthogonality, ease of access to the starting materials and operational simplicity. We report herein our investigations toward a photoclick reaction involving 2,5-disubstituted tetrazoles and alkynes as the dipolarophile for the synthesis of pyrazole derivatives. In addition to the numerous reports recently published on the synthesis of pyrazoles, we wish to add to the list a photochemical procedure that represents a mild and atom-economical alternative. Moreover, considering that such nitrilimines precursors can be accessed in one step from inexpensive and abundant starting materials and given the commercial availability of a broad spectrum of alkynes, we examined the scope of the photoclick reaction with respect to reactive partners, enabling the synthesis of a library of useful heteroaromatics.

Introduction

Pyrazoles are prominent members of the family of aromatic heterocycles and are useful as pharmaceutical agents,[1] ligands in catalyzed cross-coupling reactions[2] and as agronomical agents.[3] Their multiple uses in a broad range of domains drove the development of elaborate pathways to furnish this high-value heterocycle. Typically, they are obtained through condensation of hydrazine with 1,3-dicarbonyl compounds (Knorr synthesis).[4] Despite the overall efficiency of this method, it usually requires the use of expensive metal catalysts and/or hazardous hydrazine derivatives, and suffers from limitations with respect to the substrate scope, regioselectivity and yield. To overcome these drawbacks, research was performed over the last decade through exploration of this multicomponent condensation reaction by modifying and optimizing the reactants and the reaction conditions to access pyrazole ring derivatives.[5] More recently and in a more atom-economic fashion, catalytic procedures have been published. Glorius and co-workers reported an NHC-catalyzed [4+1] annulation between α,β-unsaturated aldehydes and hydrazones.[6] Ir- and Ru-based photoredox-catalyzed procedures were reported for the synthesis of pyrazoles combining either hydrazine and alkene derivatives[7] or hydrazones and α-bromoketones.[8]

As the major alternate pathway, 1,3-dipolar cycloadditions between diazo- or hydrazonoyl-compounds and unsaturated systems have been widely explored. The application of this reaction mode with olefins, at first affording pyrazoline or pyrazolidine rings, has been performed with alkenes to allow further access to aromatized heterocycles through the release of various leaving groups[9] or through oxidative post-treatment.[10] In a more straightforward and atom-economical approach, [3+2] cycloadditions between diazo species or hydrazonoyl dipoles with alkynes as dipolarophiles have been reported.[9a,11] Among these numerous reports, studies on the cycloaddition of alkynes with nitrilimines, generated through thermal breakdown of 2,5-disubstituted tetrazoles or through basic treatment of hydrazonoyl chloride, have been investigated.[12] However, to our knowledge, such reaction between alkynes and nitrilimines, generated photochemically through nitrogen extrusion of 2,5-disubstituted tetrazoles, has not been explored in detail.

Indeed, with the notable exception of control experiments reported by Padwa[10a] and Heimgartner[10b] on the photochemical extrusion of nitrogen from 2,5-disubstituted tetrazoles and later reaction with dimethyl acetylenedicarboxylate (DMAD) as the dipolarophile, we are not aware of other studies exploring thoroughly the synthetic potential of this route (Scheme 1).

This lack of precedent provides an attractive field of investigation by pursuing the elaboration of a simple, atom-economic, environmental-friendly and efficient photochemical synthesis of high-value pyrazoles starting from commercially available alkynes and easily accessible 2,5-tetrazole precursors by using known procedures. In this study, we were interested in investigating and adding a photochemical alternative to the list of synthetic pathways leading to the synthesis of useful pyrazole

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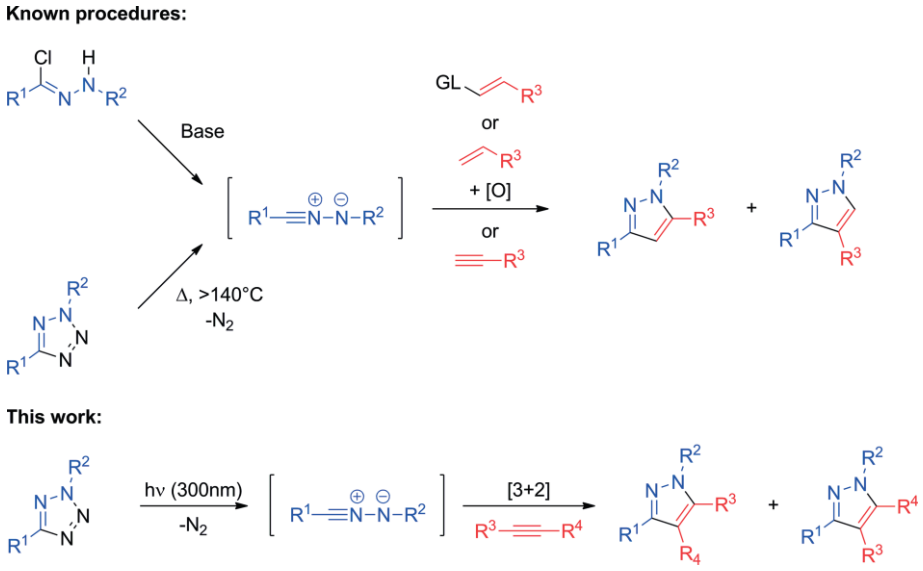


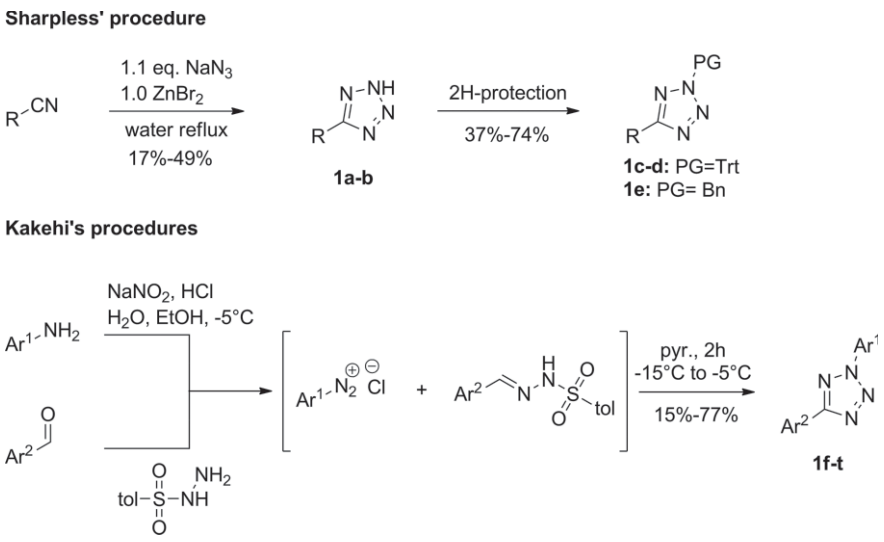
Scheme 1. Synthesis of pyrazoles through 1,3-dipolar cycloaddition of alkynes with nitrilimines.

rings, which could not be formed as efficiently by using other known methods. We sought to explore the scope of the reactants available for this strategy as well as to determine the influence of various parameters on the yield and regioselectivity. In addition to the elaboration of new compounds of possible medicinal use, a goal of this work is to extend the application of the biocompatibility of this "photoclick" reaction demonstrated by Lin et al.[13] in their work on photochemical in vivo transformation of tetrazole-containing proteins with alkenes.

Results and Discussion

We first prepared 2,5-tetrazole derivatives according to procedures developed by Sharpless[14] and Kakehi.[15] We selected these two methods for their ability to provide easily and efficiently a wide spectrum of nitrilimine precursors bearing various functional groups on both positions with inexpensive and commercially available starting materials. The former cited work[14] enables the synthesis of 1*H*-tetrazoles in refluxing water by the addition of sodium azide to nitriles, in the presence of zinc bromide. This method gives tetrazoles bearing alkyl or aryl chains on the 5-position of the heterocycle and allows further functionalization at the 2-position. The synthesis of 2,5-diaryltetrazoles was performed by using the latter reported method,[15] consisting of reacting aryl diazonium salts with tosyl-hydrazones. Both reactive partners can be generated simultaneously and react in cold pyridine in a sequential addition procedure (Scheme 2). As this was not the purpose of this study and the procedures are known, we did not attempt to optimize the reactions.

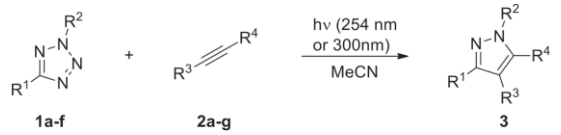
With a first series of tetrazole precursors in hand, we wished to determine the scope of this reaction in a qualitative manner



Scheme 2. Preparation of the tetrazole library.

using a combinatorial approach. We prepared solutions of a few milligrams (2–5 mg) of nitrilimine precursors **1a**–**f** in the presence of a few microliters of alkyne (one drop) in 2 mL vials equipped with a stir-bar and half-filled with acetonitrile (1 mL). We then exposed these test solutions to UV-light in a homemade photoreactor equipped with four UV-lamps either at 254 nm or 300 nm. The solutions contained in the vials were then directly injected after several increments of time in a UPLC-MS equipped with UV and ESI-MS detectors. The results of these preliminary tests are summarized in Table 1.

Table 1. Combinatorial tests for the photochemical synthesis of pyrazoles.[a]



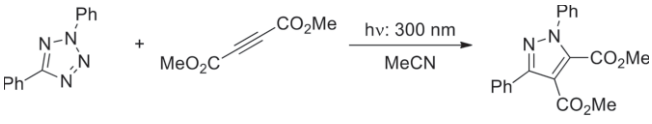
Reactants	1a	1b	1c	1d	1e	1f
2a	N.R.	N.R.	N.R.	N.R.	N.R.	+
2b	N.R.	N.R.	N.R.	N.R.	N.R.	Traces
2c	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
2d	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
2e	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
2f	N.R.	N.R.	N.R.	N.R.	N.R.	+
2g	N.R.	N.R.	N.R.	N.R.	N.R.	+

[a] N.R.: no reaction after 24 h of irradiation +: reaction proceeds under exposure to both wavelengths.

Confirming precedents in the literature,[10a,10b] the corresponding pyrazole resulting from **1f** and **2a** was obtained upon exposure to both 254 nm and 300 nm UV-light. Notably, irradiation with 300 nm light gave a cleaner reaction; analysis of the reaction performed at 254 nm showed the formation of degradation products. On the other hand, tetrazoles **1a**–**e** did not undergo conversion upon photolysis at any wavelength. Regarding alkynes **2a**–**g**, it seems that alkyl acetylenes are unreactive as dipolarophiles in the presence of the diphenyl-nitrilimine generated from **1f**. Indeed, only traces of the desired product were detected in the presence of TMS-acetylene, whereas the other candidates did not give any traceable results. Nevertheless, promising results were observed with **2a** and substituted propiolates **2f** and **2g**.

Based on these preliminary results, we turned our attention to a larger scale synthesis of these pyrazoles to determine the quality of this reaction and to fully characterize the structures detected in the previous tests. We began first by charging alkyne **2a** in excess (3 equiv.) with respect to 0.2 mmol (ca. 50 mg) of tetrazole **1f** in acetonitrile (5 mL). The reaction mixture was placed in a quartz vessel and exposed in a Rayonet® photoreactor equipped with 16 UV-Lamps emitting at 300 nm. After one hour of irradiation, analyses via UPLC-MS of the reaction mixture showed a maximal but incomplete consumption of the nitrilimine precursor. The removal of the volatiles and direct purification of the crude material by flash column chromatography afforded the desired pyrazole in excellent yield (Table 2, entry 1).

Table 2. Condition screening for the photochemical synthesis of pyrazoles.



entry	2a [equiv.]	Time [min.]	Conc. [M]	Yield [%][a]
1	3	60	0.045	86
2	4	60	0.045	69
3	3	60	0.075	63
4	3	90	0.045	74
5	3	60	0.010	83
6	3	1440	0.045	N.R.[b]

[a] Isolated yield of **3a**. [b] Experiment performed at 420 nm.

After altering a few experimental parameters, it appeared that the first applied conditions were better (Table 2, entry 1). The yield did not increase by raising the amount of alkyne (entry 2) or the concentration of the reaction medium (entry 3). We also tried to increase the time of exposure, to overcome the incomplete conversion of **1f**, which was always detected as traces in the shorter irradiation (entry 4). Lower concentration had no impact on the yield (entry 5). On the other hand, shifting the wavelength towards visible light inhibited the reaction (entry 6).

We then investigated the scope of both reacting partners needed for this reaction in a more systematic manner. We selected commercially and readily available alkynes to react with **1f** using the optimized conditions we set. Rapidly, we could confirm and identify a series of unreactive alkynes toward the generated nitrilimine (Figure 1).

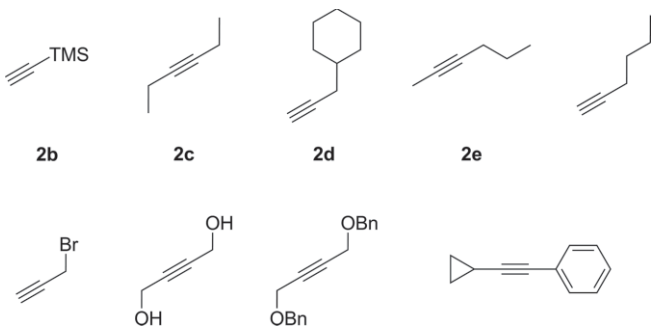
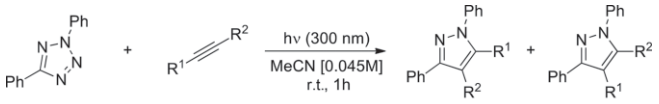


Figure 1. Non-reactive alkynes in the photochemical synthesis of pyrazoles.

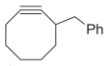
While non-isolable traces of the product with **2b** were detected via ESI-MS analysis of the reaction mixture (same as for preliminary tests), none of the corresponding pyrazoles, resulting from the reaction between the depicted alkynes in Figure 1 and the nitrilimine species generated from **1f**, could be isolated. All of the alkynes noted above were recovered after the reaction time necessary to consume the starting tetrazole, except for the cyclopropyl-bearing alkyne, which afforded a complex mixture from which we were not able to isolate any relevant side products. This is probably due to side reactions caused by the ring opening of the cyclopropyl-group upon photolysis.

Once on the right track regarding the starting materials reacting under these conditions, we performed the synthesis of a library of pyrazoles with **1f** as the nitrilimine precursor and a series of acetylenes to determine possible trends according to the features we could include on the alkyne reactive partner (Table 3).

Table 3. Varying the alkyne partner.



1f 3 equiv. **3a-h** **3a'-h'**

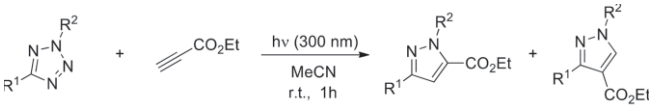
Entry	-R¹	-R²	Pyrazole	Ratio[a] (3/3')	Yield [%][b]
1	-CO_2Me	-CO_2Me	**3a**	–	86
2	-CO_2Et	-H	**3b/3b'**	8:2	89
3	-*p*CF_3Ph	-H	**3c/3c'**	1:1	86
4	-Ph	-H	**3d/3d'**	–[c]	63
5	-*p*OMePh	-H	**3e/3e'**	–[c]	7
6	-CO_2Me	-*p*CF_3Ph	**3f/3f'**	5:1	47
7	-CO_2Me	-*p*OMePh	**3g/3g'**	–	Traces
8			**3h/3h'**	1:1	95
9			**3i/3i'**	9:1	8
10	-*p*NO_2Ph	-H	**3j/3j'**	–[c]	7

[a] See Experimental Section for regioisomeric ratio determination. [b] Isolated yield. [c] Single isomer isolated.

According to the FMO-theory, the type-1 1,3-dipolar cycloaddition process involving the HOMO of the dipole and the LUMO of the dipolarophile in this reaction seems to be reflected in the yields obtained in this first series of isolated pyrazoles. Indeed, the lower LUMO of alkynes bearing EWG-substituents improves the efficiency of the reaction with the relatively electron-rich nitrilimine derived from **1f** (entries 1–3). In the case of reaction with electron-rich alkynes, we obtained lower yields of the desired products (entry 4, 5, 7). Interestingly, the reaction with 3-benzylcyclooctyne (entry 8) partially contradicts this trend. However, the ring strain present within this alkyne was found to be an effective driving force for the reaction.[16] At this stage, the regioisomeric ratios showed no particular trend that allows conclusions to be drawn. However, it should be noted that compound **3d** was the only isolated after purification by flash column chromatography. Indeed, no traces of the expected regioisomers **3d'** were detected or isolated. Difficulties in determining the ratio were encountered for compounds **3e** and **3g**, due to low yields and overlapping signals in the NMR spectra of inseparable mixtures. The poor performance of *p*-nitrophenyl acetylene in the reaction (entry 10) has to be pointed out. A quench of the excited state can be ruled out, because the tetrazole is fully photolyzed. The alkyne is also recovered intact at the end of the reaction, so a degradative photochemical process is also ruled out. The reason for such a low yield is thus so far unclear. In general, the reaction products are photostable: we exposed pyrazole **3a** to 300 nm UV-light for 24 h in MeCN and we observed no degradation at all. The photochemical nature of the reaction was confirmed by the absence of reaction of **1f** and 3-benzylcyclooctyne in refluxing acetonitrile for 3 hours.

To complement our study, we tested the reaction between various nitrilimines and ethyl propiolate by applying the same conditions (Table 4).

Table 4. Varying the tetrazole partner.

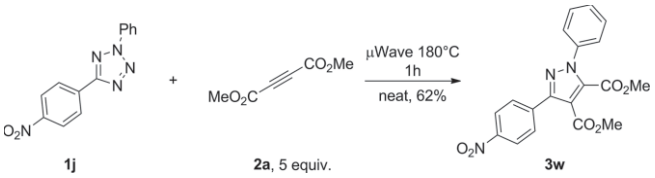


1g-r 3 equiv. **3i-t** **3i'-t'**

Entry	-R¹	-R²	Pyrazole	Ratio[a] (3/3')	Yield [%][b]
1	-*p*OMePh	-Ph	**3k/3k'**	8:2	97
2	-*o*BrPh	-Ph	**3l/3l'**	7:3	30
3	-*p*CNPh	-Ph	**3m/3m'**	9:1	45
4	-*p*NO_2Ph	-Ph	**3n/3n'**	–	0
5		-Ph	**3o/3o'**	9:1	81
6	-2-methylfuranyl	-Ph	**3p/3p'**	9:1	67
7	-CO_2Et	-Ph	**3q/3q'**	9:1	67
8	-Ph	-*p*NO_2Ph	**3r/3r'**	–	0
9	-Ph	-*p*FPh	**3s/3s'**	9:1	74
10	-Ph	-*m*ClPh	**3t/3t'**	9:1	99
11	-Ph		**3u/3u'**	9:1	30
12	-otoluidyl	-*p*OMePh	**3v/3v'**	8:2	87

To our satisfaction, a broad range of tetrazoles reacted efficiently with ethyl propiolate under the conditions we found. One can highlight the finding that EWGs on the nitrilimine partner has less influence than on alkynes with respect to the output of this reaction. An exception to this observation was found in nitro-substituted precursors, which showed total inhibition of the reaction process (Table 4, entries 4 and 8). Indeed, the 5-nitrophenyl tetrazole **1j** (precursor for **3n**/**3n'**) could not be generated upon photolysis; even after extended exposure time or change in the wavelength (exposure to 254 nm UV-light was tested). This was unexpected, given that UV/Vis analysis of the corresponding tetrazole showed high absorbance at 300 nm (ε_{300} = 34029 L mol^{-1} cm^{-1}/ε_{max} = ε_{295} = 34150 L mol^{-1} cm^{-1}). Regarding the 2-nitrophenyl tetrazole **1n** (targeting products **3r**/**3r'**), for which absorbance at the same wavelength is reduced to the half (ε_{300} = 15309 L mol^{-1} cm^{-1}/ε_{max} = ε_{304} = 15589 L mol^{-1} cm^{-1}), only a complex mixture was obtained from its reaction with ethyl propiolate by applying the same reaction conditions as for the other substrates. We believe that the nitro-group can shut down the photochemical reactivity of

the starting tetrazole by having a low-lying excited state, probably with significant charge-transfer character. To confirm our assumption, we performed their thermal breakdown in the presence of DMAD. This experiment gave us the desired pyrazole in good yield (Scheme 3).



Scheme 3. Thermal breakdown of tetrazole **1j** reacted with **2a**.

Overall, the regioisomeric ratios (r.r.) are in favor of the 5-substituted isomer. The prediction of the regioselectivity of such 1,3-dipolar cycloadditions has been demonstrated by DFT calculations to result from HSAB considerations, rather than FMO theory.[12d]

We then studied a possible solvent effect on the reaction efficiency and regioselectivity. We repeated the reaction between **1f** and ethyl propiolate in 1,4-dioxane, acetone, ethyl acetate and tetrahydrofuran (THF) by keeping constant the concentration and the equivalents of reactants. Globally, we observed a drop in both the yield and regioselectivity of **3b** and **3b′** with respect to the original experiment carried out in acetonitrile. In the case of THF, we were unable to precisely determine the yield and the r.r. due to difficulties in removing side products at the purification step. However, in benzene, a yield comparable to reactions run in acetonitrile was obtained, albeit with lower regioselectivity (Table 5).

Table 5. Solvent effect on the photochemical synthesis of pyrazoles.

Entry	Solvent	**3b/3b′** Yield [%][a]	**3b/3b′** (r.r.)[b]
1	MeCN	89	(8:2)
2	1,4-dioxane	51	(3.6:1)
3	Acetone	48	(4.5:1)
4	EtOAc	46	(3:1)
5	THF	Undet.[c]	(4:1)[c]
6	PhH	90	(3:1)

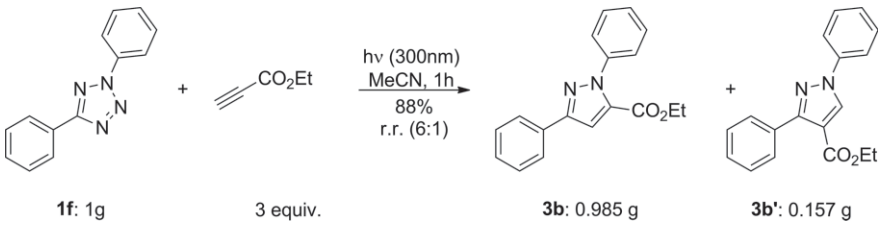
[a] Isolated yield. [b] Determined by ^{1}H NMR spectroscopic analysis of the isolated mixtures. [c] Mixtures of regioisomers, contaminated by side products.

We then performed experiments to examine the possibility to scale up this process and to apply the approach for the multistep synthesis of a complex product. To this end, we performed a gram-scale synthesis of compounds **3b**/**3b′** in a closed vessel sealed with a septum bearing a balloon capable of collecting the volume of extruded gas, which was visually detectable at this scale.

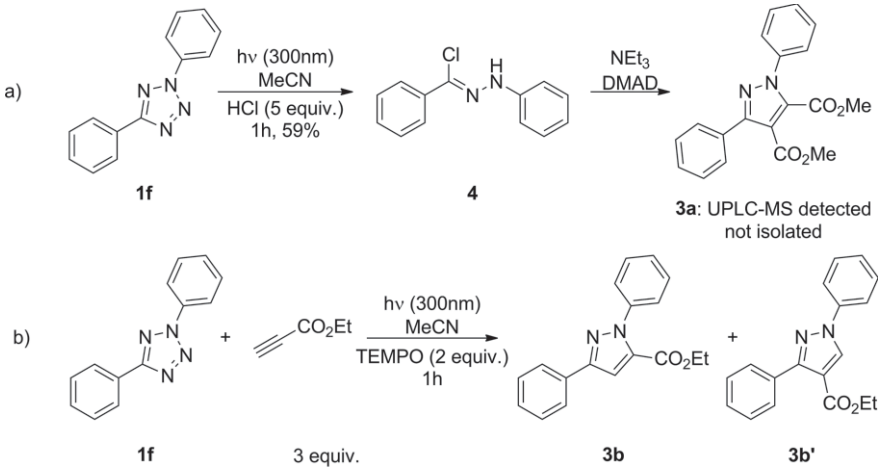
We were delighted to observe that the larger scale affected neither the yield nor the selectivity of the reaction (Scheme 4).

A series of experiments were then performed to investigate mechanistic aspects of the reaction. First, we wished to confirm the photochemical generation of the nitrilimine by trapping this intermediate in the presence of an excess of concentrated HCl. The second experiment involved determining the possible radical character along the path to the nitrogen extrusion (Scheme 5).

Pleasingly, we were able to isolate the trapped nitrilimine as the corresponding hydrazonoyl chloride **4** in satisfactory yield



Scheme 4. Gram-scale photochemical synthesis of pyrazoles **3b**/**3b′**.



Scheme 5. Mechanistic investigations.

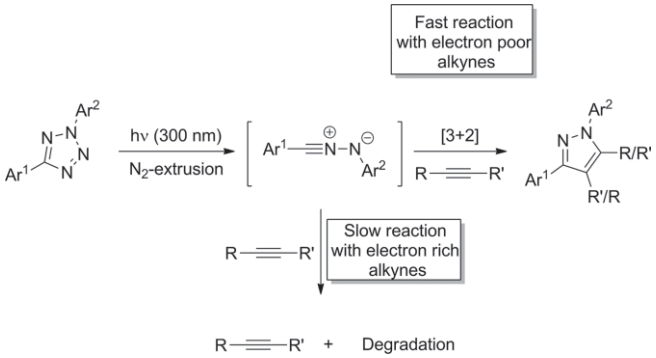
(Scheme 5, Eq. a). This intermediate was then reacted with DMAD in the presence of triethylamine to afford **3a**, the formation of which was detected by UPLC-MS analysis and comparison to samples obtained from previous experiments. From the second experiment, we can conclude that the chemical pathway involved in the generation of nitrilimines does not occur via radical intermediates (Scheme 5, Eq. b and Scheme 4). In fact, both the absence of isolated radical species trapped by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and the successful trapping of the nitrilimine by HCl suggest that nitrogen extrusion occurs either through heterolytic cleavage of the tetrazole ring or through very rapid and concerted intramolecular radical recombination followed by tautomerization of the generated nitrilimine. Despite being unable to give a precise yield for this reaction due to contamination of the isolated products with TEMPO even after column chromatography, we isolated both pyrazoles in an isomeric ratio and yield that were estimated to be close to the values obtained under normal synthetic conditions. This result was determined by NMR analysis and quantities of isolated mixture.

As shown by precedent studies regarding the photolysis of tetrazole derivatives,[17] the existence of six different fundamental structures for the ensuing nitrilimine intermediate has been postulated and is still under debate.[18] The photodecomposition could generate a plethora of subsequent byproducts[17] if this reactive species is not rapidly trapped or reacts with, for example, a dipolarophile. We used in this work 2,5-diaryl-nitrilimines, which are known to rearrange very rapidly into their corresponding carbodiimide upon photolysis.[18] Also, kinetic studies reported by Lin et al.[13e] demonstrated that the rate of a type-1 1,3-dipolar cycloaddition between a diaryl-nitrilimine and an alkene can be accelerated by raising the HOMO of the generated nitrilimine. Indeed, decreasing the HOMO–LUMO gap between the dipole (nitrilimine) and the dipolarophile (alkene or alkyne) is a fundamental parameter that can accelerate the reaction and thus prevent decomposition of the nitrilimine in the reaction mixture.

According to the results obtained in our experiments, it is consistent with the latter studies to consider the propargylic nitrilimine formed upon photolysis as the reactive species that is involved in our process. We can highlight the finding that the good yields obtained with electron-poor dipolarophiles could result from a rapid cycloaddition due to the small HOMO–LUMO gap between the two reactive partners, whereas the lower yields of electron-rich alkynes are the consequence of a slower reaction allowing degradation of the nitrilimine and the recovery of the alkynes (Scheme 6). On the other hand, the good yield and the regiospecificity observed with the relatively electron-rich phenylacetylene represent an interesting exception to this mechanistic assumption that shall be studied further.

Lastly, we wished to extend this reaction in an intramolecular fashion starting with suitable precursors **1s** and **1t**.

We were pleased to isolate **3x** in a satisfactory yield upon decreasing the reaction concentration. However, **3y** was only obtained in poor yield despite attempts to optimize the conditions. Dilution of the reaction medium by a factor of four was required to obtain the best yields in these intramolecular reactions, which went to maximal conversion of the starting material after one hour of irradiation (Scheme 7).



Scheme 6. Mechanistic rationale.

Conclusions

We demonstrated that the synthesis of pyrazoles via 1,3-dipolar cycloaddition between nitrilimines generated in situ photochemically from 2,5-tetrazoles in the presence of a slight excess of alkyne could be an efficient method to access valuable chemicals. We showed that this method allows efficient access to a large variety of pyrazoles bearing a broad range of versatile functionalities for further transformations and potential applications in the synthesis of elaborate structures. We also highlighted the possibility to perform this reaction either inter- or intramolecularly with moderate results under the latter mode. We established a simple, atom-economic and environmental-friendly process of reacting bench-stable and commercially available starting materials by only exposing them to UV-light in a solvent that does not require drying or degassing pretreatment. By using our method, we also obviate the need for multistep synthesis via the direct aromatization that occurs with alkynes instead of alkene derivatives that require further oxidative treatments or extrusion of leaving groups. Thus, this method also saves the use of multiple, sensitive expensive and sometimes toxic reactants. We also avoid the application of harsh conditions that are required, for example, for the thermal breakdown of tetrazole analogues and thus we simplified the purification and enhanced the yield and the regioselectivity of this cycloaddition. Finally, the bio-orthogonality of this method opens opportunities for the application of this process as a biocompatible material modification only with the help of UV-light.

Experimental Section

General Remarks: Thin-layer chromatography (TLC) analyses were performed using aluminum sheets coated with silica gel 60 F254 and were visualized with a UV-lamp and/or $KMnO_4$. Flash column chromatography (FC) was performed using Brunschwig silica gel (60 Å, 32–63 mesh). All ^1H NMR (300 or 360 MHz) and ^{13}C NMR (75 or 90 MHz) spectra were performed with Bruker Advance DPX 300 or 360. Data were treated with ACD labs software and all chemical shift are given in ppm and coupling constant in Hz (multiplicity: s = singlet, d = doublet, dd = doublet doublet, t = triplet, dt = doublet triplet, ddd = doublet doublet doublet, m = multiplet). The spectra

were calibrated with the following deuterated solvents: DMSO (2.50 for ^{1}H NMR and 39.52 for ^{13}C NMR), chloroform (7.27 for ^{1}H NMR and 77.00 for ^{13}C NMR) or dichloromethane (5.32 for ^{1}H NMR and 53.84 for ^{13}C NMR). IR spectra were recorded with a Fourier transform IR Bruker Tensor 27 spectrometer, neat; absorption bands are in cm^{-1}. ESI mass spectra were carried out with a Bruker FT/MS 4.7 T BioApex II spectrometer. Melting point measurements were performed with a Büchi Melting Point B-540 device.

5-Methyl-2*H*-tetrazole (1a): According to a reported procedure,[14] to a 100 mL reaction tube, a solution of acetonitrile (1.05 mL, 20 mmol), sodium azide (1.43 g, 22.00 mmol) and zinc(II) bromide (4.50 g, 20.00 mmol) was made in water (40 mL). The reaction mixture was heated at 170 °C for 24 h under vigorous stirring. HCl (3 N, 30 mL) and ethyl acetate (100 mL) were then added, and vigorous stirring was continued until no solid was present and the aqueous layer had a pH of 1. The organic layer was partioned and the aqueous layer was extracted with two portions of 100 mL of ethyl acetate. The combined organic layers were evaporated, 0.25 N NaOH (200 mL) was added, and the mixture was stirred for 30 min, until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension was filtered, and the solid was washed with 1 N NaOH (20 mL). To the filtrate was added 3 N HCl (40 mL) with vigorous stirring. The acidic solution was then saturated with $MgSO_4$ and extracted with EtOAc (6 100 mL). The solvent was removed under high vacuum to afford 5-methyl-2*H*-tetrazole (281.70 mg, 3.35 mmol, 17 % yield) as a white solid.

^{13}C NMR (75 MHz, [D_6]DMSO): δ 8.37 (CH_3), 129 (CH_3) ppm. Data recorded are in accordance to the reported ref.[14].

5-Phenyl-2*H*-tetrazole (1b): According to the reported procedure,[14] in a 250 mL flask, a solution of benzonitrile (2.06 mL, 20 mmol), sodium azide (1.43 g, 22.00 mmol) and zinc(II) bromide (4.50 g, 20.00 mmol) was made in water (40 mL). The reaction mixture was heated under reflux for 24 h under vigorous stirring. HCl (3 N, 30 mL) and ethyl acetate (100 mL) were then added, and vigorous stirring was continued until no solid was present and the aqueous layer had a pH of 1. The organic layer was partitioned and the aqueous layer was extracted with two portions of 100 mL of ethyl acetate. The combined organic layers were evaporated, 0.25N NaOH (200 mL) was added, and the mixture was stirred for 30 min, until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension was filtered, and the solid was washed with 1 N NaOH (20 mL). To the filtrate was added 3 N HCl (40 mL) with vigorous stirring causing a precipitate. This was filtered and washed with two portions of 20 mL of 3 N HCl and dried under high vacuum affording 5-phenyl-2*H*-tetrazole (1.43 g, 9.81 mmol, 49 % yield) as a white solid. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 7.55–7.63 (m, 3 H), 8.00–8.08 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 124, 126, 129, 131 ppm. Data recorded are in accordance with the reported ref.[14]

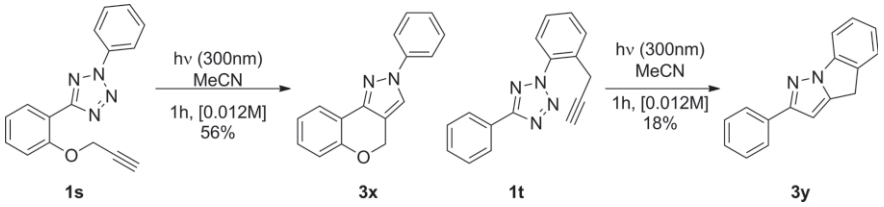
5-Methyl-2-trityl-2*H*-tetrazole (1c): According to the reported procedure,[19] in a 10 mL flask, 5-methyl-2*H*-tetrazole (100 mg, 1.19 mmol), (chloromethanetriyl)tribenzene (332 mg, 1.19 mmol), NaOH (1.25 mL, 1.25 mmol) and tetrabutylammonium bromide (77 mg, 0.24 mmol) were charged in DCM (2 mL). The solution was vigorously stirred at room temperature for 18 h. The reaction mixture was then diluted with an equivalent amount of water and extracted with DCM. The gathered organic layers were washed with water (two times), $NaHCO_3$ and brine, and dried with sodium sulfate. The solvent was removed under vacuum and the solid was purified by recrystallization in EtOAc (8 mL/g) to afford 5-methyl-2-trityl-2*H*-tetrazole (142.90 mg, 0.44 mmol, 37 % yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.58 (s, 3 H), 7.08–7.16 (m, 6 H), 7.29–7.40 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11, 82, 127.7, 127.9, 128.1, 128.2, 129, 130, 141, 161 ppm. Data recorded are in accordance with the reported ref.[19]

5-Phenyl-2-trityl-2*H*-tetrazole (1d): According to the reported procedure,[19] in a 25 mL flask, 5-phenyl-2*H*-tetrazole (500 mg, 3.42 mmol), (chloromethanetriyl)tribenzene (954 mg, 3.42 mmol), sodium hydroxide (3.59 mL, 3.59 mmol) and tetrabutylammonium bromide (221 mg, 0.68 mmol) were charged in DCM (9 mL). The solution was vigorously stirred at room temperature for 18 h. The reaction mixture was then diluted with an equivalent amount of water and extracted with DCM. The gathered organic layers were washed with water (two times), $NaHCO_3$ and brine, and dried with sodium sulfate. The solvent was removed under vacuum and the solid was purified by recrystallization in EtOAc (8 mL/g) to afford 5-phenyl-2-trityl-2*H*-tetrazole (568.80 mg, 1.46 mmol, 43 % yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.22 (m, 6 H), 7.31–7.40 (m, 9 H), 7.44–7.50 (m, 3 H), 8.13–8.20 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 83, 127.0, 127.7 (3 C), 128.3 (2 C), 128.7, 130.2, 130.3 (4 C), 141 ppm. Data recorded are in accordance to the reported reference.[19]

2-Benzyl-5-phenyl-2*H*-tetrazole (1e): According to the reported procedure,[20] a solution of 5-phenyl-2*H*-tetrazole (151.40 mg, 1.04 mmol) and *O*-benzyl S-prop-2-yn-1-yl carbonodithioate (345 mg, 1.55 mmol) was made in toluene (8 mL). The mixture was heated under reflux for 4 h. The solvent was then removed under vacuum and the crude material was purified by chromatography using pentane/EtOAc (8:1) as eluent to afford 2-benzyl-5-phenyl-2*H*-tetrazole (181.40 mg, 0.77 mmol, 74 % yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.82 (s, 2 H), 7.35–7.51 (m, 8 H), 8.11–8.20 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56, 126, 127, 128.3, 128.7, 128.8, 128.9, 130, 133, 165 ppm. Data recorded are in accordance to the reported ref.[20]

All the following 2,5-diaryltetrazoles were synthesized according to a procedure reported by Kakehi et al.[15] Unless modifications are mentioned, all compounds were purified by column chromatography using pentane/EtOAc (9:1) to (4:1) instead of recrystallization.

2,5-Diphenyl-2*H*-tetrazole (1f): Isolated as a pink solid (7.49 mmol, 70 %). Mp 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.63 (m, 6 H), 8.19–8.24 (m, 2 H), 8.25–8.31 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119, 127, 128, 129.60, 129.63, 130, 136, 165 ppm. HRMS:



Scheme 7. Intramolecular photochemical synthesis of pyrazoles and photochemical synthesis of indazole.

m/z calcd for $C_{13}H_{10}N_4 + H^+$ 223.0978; found: 223.0976. IR (neat): $\tilde{\nu}$ = 1595, 1530, 1496, 1471, 1447, 1368, 1281, 1215, 1184, 1136, 1073, 1016, 993, 924, 914, 788, 760, 728, 675 cm^{-1}. UV: ε_{300} = 5635 L mol^{-1} cm^{-1}.

5-(4-Methoxyphenyl)-2-phenyl-2*H*-tetrazole (1g): Isolated as a yellow solid (1.03 mmol, 63 %). Mp 104–106 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.90 (d, *J* = 0.55 Hz, 3 H), 7.01–7.08 (m, 2 H), 7.46–7.53 (m, 1 H), 7.54–7.62 (m, 2 H), 8.16–8.20 (m, 2 H), 8.20–8.23 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55, 114, 119, 128, 129.4, 129.6, 136, 161, 165 ppm. HRMS: *m/z* calcd for $C_{14}H_{12}N_4O + H^+$ 253.1084; found: 253.1085. IR (neat): $\tilde{\nu}$ = 3003, 2924, 2852, 1615, 1596, 1582, 1543, 1497, 1473, 1458, 1433, 1305, 1288, 1253, 1205, 1186, 1175, 1133, 1110, 1068, 1033, 1018, 1006, 991, 833, 750, 703, 671 cm^{-1}. UV: ε_{300} = 10206 L mol^{-1} cm^{-1}.

5-(2-Bromophenyl)-2-phenyl-2*H*-tetrazole (1h): Isolated as an orange solid (1.72 mmol, 60 %). Mp 71–73 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.41 (m, 7.35, 1 H), 7.43–7.66 (m, 4 H), 7.78–7.81 (dd, *J* = 1.2, 8 Hz, 1 H), 7.98–8.01 (dd, *J* = 1.8, 7.7 Hz, 1 H), 8.22–8.25 (m, 2 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 119, 122, 127, 129.6, 129.7, 131.4, 131.7, 134, 136, 164 ppm. HRMS: *m/z* calcd for $C_{13}H_9N_4Br + H^+$ 301.0083/303.0063; found: 301.0084/303.0069. IR (neat): $\tilde{\nu}$ = 1597, 1522, 1494, 1469, 1456, 1422, 1372, 1354, 1208, 1182, 1080, 1031, 1012, 992, 913, 828, 781, 757, 742, 677 cm^{-1}. UV: ε_{300} = 2155 L mol^{-1} cm^{-1}.

4-(2-Phenyl-2*H*-tetrazol-5-yl)benzonitrile (1i): Isolated as a red solid (5.90 mmol, 77 %). Mp 150–154 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.55 (m, 1 H), 7.55–7.61 (m, 2 H), 7.79 (d, *J* = 8.07 Hz, 2 H), 8.12–8.20 (m, 2 H), 8.30–8.38 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 113, 118, 119, 127, 129.6, 129.9, 131, 132, 136, 163 ppm. HRMS: *m/z* calcd for $C_{14}H_9N_5 + H^+$ 248.0931; found: 248.0933. IR (neat): $\tilde{\nu}$ = 2225, 1592, 1489, 1458, 1417, 1276, 1178, 1073, 1013, 996, 840 cm^{-1}. UV: ε_{300} = 11073 L mol^{-1} cm^{-1}.

5-(4-Nitrophenyl)-2-phenyl-2*H*-tetrazole (1j): Isolated as a red solid (1.58 mmol, 15 %). Mp 201 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.66 (m, 3 H), 8.17–8.25 (m, 2 H), 8.36–8.50 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119, 124, 127, 129, 130, 133, 136, 149, 163 ppm. IR (neat): $\tilde{\nu}$ = 3106, 2923, 2855, 1605, 1595, 1517, 1493, 1453, 1423, 1336, 1310, 1282, 1216, 1135, 1105, 1074, 1019, 1009, 997, 914, 858, 852, 759, 726, 677 cm^{-1}. UV: ε_{300} = 33509 L mol^{-1} cm^{-1}. No MS measurements were available by any methods.

2-Methoxy-6-(2-phenyl-2*H*-tetrazol-5-yl)phenyl acetate (1k): Isolated as a yellow-orange solid (2.87 mmol, 56 %). Isolated only through precipitation upon addition of water to the reaction mixture. The solid was then abundantly washed with water and dried to afford the pure final product. Mp 113–114 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.92 (s, 3 H), 7.14 (d, *J* = 8.31 Hz, 1 H), 7.38 (t, *J* = 8.07 Hz, 1 H), 7.52 (d, *J* = 7.09 Hz, 1 H), 7.55–7.62 (m, 2 H), 7.90 (d, *J* = 8.07 Hz, 1 H), 8.16 (d, *J* = 8.31 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20, 56, 114, 119, 120, 121, 126, 129, 136, 137, 152, 162, 169 ppm. HRMS: *m/z* calcd for $C_{16}H_{14}N_4O_3 + H^+$ 311.1139; found: 311.1139. IR (neat): $\tilde{\nu}$ = 1755, 1538, 1523, 1496, 1480, 1450, 1429, 1368, 1275, 1213, 1195, 1155, 1090, 1060, 1016, 997, 911 cm^{-1}. UV: ε_{300} = 6541 L mol^{-1} cm^{-1}.

5-(5-Methylfuran-2-yl)-2-phenyl-2*H*-tetrazole (1l): Isolated as a brown solid (1.75 mmol, 40 %). Mp 78–82 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.44–2.49 (m, 3 H), 6.20 (dq, *J* = 3.27, 0.93 Hz, 1 H), 7.13 (dd, *J* = 3.30, 0.37 Hz, 1 H), 7.48–7.61 (m, 3 H), 8.15–8.23 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155, 141, 129.7, 129.6, 120, 113, 108, 13 ppm. HRMS: *m/z* calcd for $C_{12}H_{10}N_4O + H^+$ 227.0927; found: 227.0930. IR (neat): $\tilde{\nu}$ = 2925, 2851, 1691, 1631, 1596, 1573, 1490, 1465, 1435, 1371, 1335, 1216, 1202, 1151, 1082, 1021, 995, 923 cm^{-1}. UV: ε_{300} = 14002 L mol^{-1} cm^{-1}.

Ethyl 2-Phenyl-2*H*-tetrazole-5-carboxylate (1m): Isolated as an orange solid (1.37 mmol, 28 %). Mp 65–68 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48 (t, *J* = 7.21 Hz, 3 H), 4.56 (q, *J* = 7.09 Hz, 2 H), 7.48–7.62 (m, 3 H), 8.14–8.22 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14, 62, 120, 129, 130, 136, 157 ppm. HRMS: *m/z* calcd for $C_{10}H_{10}N_4O_2 + Na^+$ 241.0696; found: 241.0698. IR (neat): $\tilde{\nu}$ = 3003, 1735, 1589, 1481, 1467, 1389, 1216, 1157, 1084, 1066, 1045, 1018, 1002, 916, 845 cm^{-1}. UV: ε_{300} = 544 L mol^{-1} cm^{-1}.

2-(4-Nitrophenyl)-5-phenyl-2*H*-tetrazole (1n): Isolated as a black solid (1.14 mmol, 16 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.59 (m, 3 H), 8.26–8.31 (m, 2 H), 8.42–8.51 (m, 4 H) ppm. UV: ε_{300} = 15371 L mol^{-1} cm^{-1}. Data in accordance with literature value.[21]

2-(4-Fluorophenyl)-5-phenyl-2*H*-tetrazole (1o): Isolated as a pink solid (1.36 mmol, 35 %). Mp 119–120 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.30 (m, 2 H), 7.43–7.58 (m, 3 H), 8.09–8.30 (m, 4 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 116.5, 116.7, 121.7, 121.8, 127.01, 127.03, 128, 130, 161, 164, 165 ppm. HRMS: *m/z* calcd for $C_{13}H_9N_4F + H^+$ 241.0884; found: 241.0889. IR (neat): $\tilde{\nu}$ = 1598, 1504, 1448, 1220, 1207, 1156, 1097, 1072, 1014, 995, 834 cm^{-1}. UV: ε_{300} = 4820 L mol^{-1} cm^{-1}.

2-(3-Chlorophenyl)-5-phenyl-2*H*-tetrazole (1p): Isolated as a pink solid (1.67 mmol, 45 %). Mp 89–90 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.59 (m, 5 H), 8.12 (dt, *J* = 7.82, 1.71 Hz, 1 H), 8.21–8.30 (m, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 117, 120, 126, 127, 128, 129, 130.72, 130.74, 135, 137, 165 ppm. HRMS: *m/z* calcd for $C_{13}H_9N_4Cl + H^+$ 257.0589; found: 257.0594. IR (neat): $\tilde{\nu}$ = 3108, 1593, 1528, 1478, 1449, 1362, 1210, 1167, 1098, 1073, 1017, 992, 868 cm^{-1}. UV: ε_{300} = 7238 L mol^{-1} cm^{-1}.

2-(Benzo[*d*][1,3]dioxol-5-yl)-5-phenyl-2*H*-tetrazole (1q): Isolated as a yellow solid (1.84 mmol, 48 %). Mp 133–134 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.10 (s, 2 H), 6.96 (d, *J* = 8.31 Hz, 1 H), 7.47–7.57 (m, 3 H), 7.67 (d, *J* = 2.20 Hz, 1 H), 7.72 (dd, *J* = 8.44, 2.08 Hz, 1 H), 8.17–8.30 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 101, 102, 108, 113, 126, 127, 128, 130, 131, 148.5, 148.6, 164 ppm. HRMS: *m/z* calcd for $C_{14}H_{10}N_4O_2 + H^+$ 267.0877; found: 267.0877. IR (neat): $\tilde{\nu}$ = 1612, 1501, 1447, 1266, 1242, 1210, 1178, 1108, 1040, 1015, 936, 891, 853 cm^{-1}. UV: ε_{300} = 7451 L mol^{-1} cm^{-1}.

2-(4-Methoxyphenyl)-5-(o-tolyl)-2*H*-tetrazole (1r): Isolated as a yellow solid (1.97 mmol, 24 %). Mp 71–73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.73 (s, 3 H), 3.90 (s, 3 H), 7.02–7.11 (m, 2 H), 7.31–7.45 (m, 3 H), 8.06–8.18 (m, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21, 55, 114, 121, 126.0, 126.3, 129.5, 129.9, 130, 131, 137, 160, 165 ppm. HRMS: *m/z* calcd for $C_{15}H_{14}N_4O + H^+$ 267.1240; found: 267.1242. IR (neat): $\tilde{\nu}$ = 1606, 1592, 1520, 1507, 1475, 1455, 1441, 1384, 1355, 1314, 1299, 1253, 1207, 1178, 1107, 1018, 831 cm^{-1}. UV: ε_{300} = 12724 L mol^{-1} cm^{-1}.

2-Phenyl-5-[2-(prop-2-yn-1-yloxy)phenyl]-2*H*-tetrazole (1s): Isolated as an orange solid (1.56 mmol, 15 % over two steps). Mp 50–51 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.55 (t, *J* = 2.45 Hz, 1 H), 4.89 (d, *J* = 2.45 Hz, 2 H), 7.19 (td, *J* = 7.58, 0.98 Hz, 1 H), 7.24–7.29 (m, 1 H), 7.47–7.54 (m, 2 H), 7.54–7.61 (m, 2 H), 8.11 (dd, *J* = 7.70, 1.83 Hz, 1 H), 8.19–8.26 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 57, 75, 78, 114, 117, 119, 122, 129.4, 129.5, 130, 131, 136, 155, 163 ppm. HRMS: *m/z* calcd for $C_{16}H_{12}N_4O + H^+$ 277.1084; found: 277.1082. IR (neat): $\tilde{\nu}$ = 3268, 2116, 1605, 1594, 1484, 1434, 1289, 1260, 1220, 1108, 1013 cm^{-1}. UV: ε_{300} = 7064 L mol^{-1} cm^{-1}.

5-Phenyl-2-[2-(prop-2-yn-1-yl)phenyl]-2*H*-tetrazole (1t): Isolated as an orange solid (1.37 mmol, 28 %). Mp 92–94 °C. ^1H NMR

(400 MHz, $CDCl_3$): δ = 2.14 (t, *J* = 2.69 Hz, 1 H), 3.87 (d, *J* = 2.69 Hz, 2 H), 7.47–7.61 (m, 5 H), 7.76 (dd, *J* = 7.82, 1.47 Hz, 1 H), 7.84 (dd, *J* = 7.70, 0.86 Hz, 1 H), 8.23–8.29 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22, 71, 79, 125, 127, 128.1, 128.9, 130.3, 130.6, 130.7, 165 ppm. HRMS: *m/z* calcd for $C_{16}H_{12}N_4 + H^+$ 261.1135; found: 261.1143. IR (neat): $\tilde{\nu}$ = 3247, 2120, 1528, 1494, 1469, 1449, 1414, 1365, 1282, 1211, 1164, 1139, 1073, 1014, 995 cm^{-1}. UV: ε_{300} = 977 L mol^{-1} cm^{-1}.

General Procedure for Photochemical Synthesis of Pyrazoles: In a quartz vessel, at room temp. a solution of tetrazole (ca. 0.2 mmol) and alkyne (3 equiv.) was made in acetonitrile [0.045 M]. The tube was plugged and irradiated for 1 h in a photochemical reactor (Rayonet®) equipped with 16 lamps emitting at 300 nm. Upon complete conversion, the solvent was removed under vacuum and the crude material was diluted with DCM, deposed on silica and purified with a FC Biotage Isolera system using pentane/Et_2O as eluent (5 % Et_2O on 3CV, 5 to 10 % on 7CV, 10 to 100 % on 6.5CV and finally 100 % on 9CV) to afford the desired pyrazoles. The regioisomeric ratios for non-separated isomers (r.r.) were determined based on the ^1H NMR spectrum of the isolated mixtures.

Dimethyl 1,3-Diphenyl-1*H*-pyrazole-4,5-dicarboxylate (3a): 2,5-Diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and dimethyl but-2-ynedioate (0.08 mL, 0.68 mmol) in acetonitrile (5.00 mL) afforded dimethyl 1,3-diphenyl-1*H*-pyrazole-4,5-dicarboxylate (65.20 mg, 0.19 mmol, 86 % yield) as a yellow solid. Mp 151–152 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 3.87 (s, 3 H), 7.40–7.58 (m, 8 H), 7.71–7.80 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52, 53, 114, 124, 128.2, 128.8, 128.9, 129.1, 129.2, 131, 136, 139, 151, 160, 163 ppm. HRMS: *m/z* calcd for $C_{19}H_{16}N_2O_4 + H^+$ 337.1183; found: 337.1177. IR (neat): $\tilde{\nu}$ = 1727, 1530, 1497, 1451, 1430, 1267, 1230, 1145, 1104, 1061, 987, 941, 834, 793, 759, 679, 634 cm^{-1}.

Ethyl 1,3-Diphenyl-1*H*-pyrazole-5-carboxylate (3b) and Ethyl 1,3-Diphenyl-1*H*-pyrazole-4-carboxylate (3b′): 2,5-Diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and ethyl propiolate (0.07 mL, 0.68 mmol) in acetonitrile (5.00 mL) afforded ethyl 1,3-diphenyl-1*H*-pyrazole-5-carboxylate (49.21 mg, 0.17 mmol, 75 % yield) and ethyl 1,3-diphenyl-1*H*-pyrazole-4-carboxylate (9.31 mg, 0.03 mmol, 14 % yield) as yellow solids [r.r. (8:2)].

Ethyl 1,3-Diphenyl-1*H*-pyrazole-5-carboxylate (3b): Mp 70–72 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.15 Hz, 3 H), 4.28 (q, *J* = 7.15 Hz, 2 H), 7.33–7.54 (m, 9 H), 7.86–7.93 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14, 61, 109, 125, 126, 128.3, 128.5, 128.6, 128.7, 132, 134, 140, 151, 159 ppm. HRMS: *m/z* calcd for $C_{18}H_{16}N_2O_2 + Na^+$ 315.1104; found: 315.1105. IR (neat): $\tilde{\nu}$ = 3062, 2977, 1728, 1597, 1540, 1497, 1456, 1432, 1356, 1282, 1233, 1199, 1109, 1080, 1040, 1025, 1005, 955, 907, 834, 817, 752, 714, 679 cm^{-1}.

Ethyl 1,3-Diphenyl-1*H*-pyrazole-4-carboxylate (3b′): Mp 68–69 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.15 Hz, 3 H), 4.31 (q, *J* = 7.15 Hz, 2 H), 7.32–7.54 (m, 6 H), 7.77–7.83 (m, 2 H), 7.85–7.91 (m, 2 H), 8.52 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14, 60, 113, 119, 127.4, 127.8, 128, 129.3, 129.5, 132.1, 132.2, 139, 154, 162 ppm. HRMS: *m/z* calcd for $C_{18}H_{16}N_2O_2 + Na^+$ 315.1104; found: 315.1108. IR (neat): $\tilde{\nu}$ = 3130, 3069, 2928, 1686, 1600, 1536, 1508, 1447, 1362, 1275, 1229, 1148, 1111, 1057, 1037, 1020, 956, 904, 873, 837, 750, 693, 684 cm^{-1}.

1,3-Diphenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (3c) and 1,3-Diphenyl-5-[4- (trifluoromethyl)phenyl]-1*H*-pyrazole (3c′): 2,5-Diphenyl-2*H*-tetrazole (40.30 mg, 0.18 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (0.03 mL, 0.18 mmol) in acetonitrile (5.00 mL) afforded 1,3-diphenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (27.00 mg, 0.07 mmol, 41 % yield) and 1,3-diphenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (30.00 mg, 0.08 mmol, 45 % yield) as yellow solids [r.r. (1:1)].

1,3-Diphenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (3c): Mp 110–112 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.90 (s, 1 H), 7.32–7.49 (m, 10 H), 7.56–7.63 (m, 2 H), 7.89–7.97 (m, 2 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 106, 125.88, 125.93, 125.98, 126.01, 126.05, 126.2, 128.4, 128.7, 129.29, 129.60, 129.66, 130.3, 130.6, 133, 134, 140, 143, 152 ppm. HRMS: *m/z* calcd for $C_{22}H_{15}F_3N_2 + H^+$ 365.1260; found: 365.1256. IR (neat): $\tilde{\nu}$ = 3067, 1619, 1594, 1554, 1495, 1458, 1429, 1360, 1321, 1164, 1119, 1066, 1018, 971, 955, 842, 805, 758, 692, 674, 609 cm^{-1}.

1,3-Diphenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole (3c′): Mp 145–146 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.44 (m, 7 H), 7.48–7.56 (m, 2 H), 7.62–7.69 (m, 4 H), 8.16–8.22 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 118, 127, 128.44, 128.60, 128.63, 129, 145 ppm. HRMS: *m/z* calcd for $C_{22}H_{16}F_3N_2 + H^+$ 365.1260; found: 365.1258. IR (neat): $\tilde{\nu}$ = 3067, 2924, 2847, 1596, 1494, 1474, 1460, 1441, 1374, 1322, 1292, 1267, 1169, 1125, 1072, 1018, 973, 919, 786, 758, 739, 692, 678, 636 cm^{-1}.

1,3,5-Triphenyl-1*H*-pyrazole (3d): 2,5-Diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and ethynylbenzene (0.07 mL, 0.68 mmol) in acetonitrile (5.00 mL) afforded 1,3,5-triphenyl-1*H*-pyrazole (42.20 mg, 0.14 mmol, 63 % yield) as an orange solid. Unique regioisomer isolated and characterized. Mp 128–129 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 6.86 (s, 1 H), 7.28–7.39 (m, 11 H), 7.42–7.47 (m, 2 H), 7.90–7.94 (m, 2 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 105, 125, 126, 127, 128.5, 128.8, 129.0, 129.2, 129.3, 129.4, 129.6, 130, 131, 133, 135.4, 135.5, 140, 145, 152 ppm. HRMS: *m/z* calcd for $C_{21}H_{16}N_2 + H^+$ 297.1386; found: 297.1389. IR (neat): $\tilde{\nu}$ = 2924, 2852, 1671, 1595, 1494, 1481, 1455, 1433, 1362, 1212, 1174, 1065, 1021, 971, 956, 919, 843, 813, 761, 690, 643 cm^{-1}.

5-(4-Methoxyphenyl)-1,3-diphenyl-1*H*-pyrazole (3e): 2,5-Diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and 1-ethynyl-4-methoxybenzene (89 mg, 0.68 mmol) in acetonitrile (5.00 mL) afforded 5-(4-methoxyphenyl)-1,3-diphenyl-1*H*-pyrazole (4.80 mg, 0.015 mmol, 7 % yield) as a brown semi-solid. Unique regioisomer isolated and characterized. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.78 (s, 1 H), 6.86 (d, *J* = 8.80 Hz, 2 H), 7.19–7.24 (m, 2 H), 7.30–7.47 (m, 8 H), 7.90–7.96 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55, 104, 113, 122, 125.2, 125.6, 127.2, 127.8, 128.5, 128.7, 129, 133, 140, 151, 159 ppm. HRMS: *m/z* calcd for $C_{22}H_{18}N_2O + H^+$ 327.1492; found: 327.1496. IR (neat): $\tilde{\nu}$ = 3066, 1612, 1595, 1519, 1493, 1456, 1392, 1360, 1293, 1248, 1174, 1067, 1027, 970, 834, 800, 762, 690 cm^{-1}.

Methyl 1,3-Diphenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole-5-carboxylate (3f) and Methyl 1,3-Diphenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole-4-carboxylate (3f′): 2,5-Diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and methyl 3-[4-(trifluoromethyl)phenyl]propiolate (154.00 mg, 0.68 mmol) in acetonitrile (5.00 mL) afforded methyl 1,3-diphenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole-5-carboxylate (39.00 mg, 0.09 mmol, 41 % yield) and methyl 1,3-diphenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole-4-carboxylate (6.00 mg, 0.01 mmol, 6 % yield) as two orange solids [r.r. (9:1)].

Methyl 1,3-Diphenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole-5-carboxylate (3f): Mp 146–147 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 3.59 (s, 3 H), 7.23–7.29 (m, 2 H), 7.31–7.36 (m, 3 H), 7.43–7.51 (m, 5 H), 7.60–7.66 (m, 2 H), 7.73–7.78 (m, 2 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 51, 112, 123, 125.5, 125.9, 126, 128.5, 128.8, 129.1, 129.5, 129.6, 131.1, 131.4, 131.5, 133, 134, 139, 145, 153, 164 ppm. HRMS: *m/z* calcd for $C_{24}H_{17}F_3N_2O_2 + Na^+$ 445.1134; found: 445.1132.

IR (neat): $\tilde{\nu}$ = 1720, 1496, 1460, 1434, 1322, 1245, 1160, 1126, 1066, 1021, 973, 852, 758, 699 cm^{-1}.

Methyl 1,3-Diphenyl-5-[4-(trifluoromethyl)phenyl]-1*H*-pyrazole-4-carboxylate (3f′): Mp 96–99 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 3.58 (s, 3 H), 7.28–7.30 (m, 2 H), 7.38–7.41 (m, 2 H), 7.45–7.55 (m, 8 H), 7.64 (dd, *J* = 8.68, 0.61 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 52, 123.01–123.07 (m), 125.5, 125.7, 128.73, 128.78, 128.92, 129.1, 129.4, 131, 132, 136, 140, 150 ppm. HRMS: *m/z* calcd for $C_{24}H_{17}F_3N_2O_2$ + Na^+ 445.1134; found: 445.1137. IR (neat): $\tilde{\nu}$ = 2958, 2922, 2855, 1724, 1592, 1495, 1438, 1324, 1217, 1153, 1110, 1096, 1065, 1019, 973, 922, 853, 766, 698, 654 cm^{-1}.

9-Benzyl-1,3-diphenyl-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*c*]-pyrazole (3h) and 4-Benzyl-1,3-diphenyl-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*c*]pyrazole (3h′): 2,5-Diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and 3-benzylcyclooct-1-yne (134.00 mg, 0.68 mmol) in acetonitrile (5.00 mL) afforded 9-benzyl-1,3-diphenyl-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*c*]pyrazole and 4-benzyl-1,3-diphenyl-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*c*]pyrazole as a yellow solid containing both non-separable regioisomers [83.50 mg, 0.21 mmol, 95 % yield, r.r. (1:1)]. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.59–2.01 (m, 12 H), 2.51–2.72 (m, 4 H), 2.75–3.00 (m, 6 H), 3.23–3.38 (m, 2 H), 6.75–6.82 (m, 2 H), 6.88–6.95 (m, 2 H), 7.08–7.20 (m, 7 H), 7.22–7.28 (m, 2 H), 7.31–7.52 (m, 15 H), 7.53–7.57 (m, 2 H), 7.60–7.65 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21, 23, 24, 25.2, 25.7, 25.9, 29.1, 29.4, 30, 34, 36, 37, 39, 40, 116, 119, 125.6, 125.8, 125.9, 126, 127.2, 127.5, 127.6, 127.8, 127.9, 128.03, 128.18, 128.20, 128.27, 128.82, 128.85, 128.9, 129, 134, 135, 139.7, 139.8, 140.4, 140.9, 143, 150, 151 ppm. HRMS: *m/z* calcd for $C_{28}H_{28}N_2$ + H^+ 393.2325; found: 393.2328. IR (neat): $\tilde{\nu}$ = 2918, 2858, 2841, 2208, 2169, 2140, 2036, 1985, 1596, 1497, 1452, 1359, 1157, 1112, 1070, 1023, 951, 916, 776, 735, 692 cm^{-1}.

1,3-Diphenyl-4-(thiophen-2-yl)-1*H*-pyrazole and 1,3-Diphenyl-5-(thiophen-2-yl)-1*H*-pyrazole (3i:3i′): 2,5-Diphenyl-2*H*-tetrazole (52.00 mg, 0.23 mmol) and 2-ethynylthiophene (76.00 mg, 0.70 mmol) in acetonitrile (5.00 mL) afforded a non-separable mixture of 1,3-diphenyl-4-(thiophen-2-yl)-1*H*-pyrazole and 1,3-diphenyl-5-(thiophen-2-yl)-1*H*-pyrazole (6.00 mg, 0.020 mmol, 8 % yield) as a brown semi-solid [r.r. (9:1)]. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.87 (dd, *J* = 3.55, 1.10 Hz, 2 H), 6.89 (s, 2 H), 6.97 (dd, *J* = 5.13, 3.67 Hz, 2 H), 7.30 (d, *J* = 0.98 Hz, 1 H), 7.31 (d, *J* = 0.98 Hz, 1 H), 7.33–7.38 (m, 2 H), 7.41–7.45 (m, 6 H), 7.45–7.48 (m, 4 H), 7.48–7.50 (m, 1 H), 7.90–7.91 (m, 1 H), 7.92–7.93 (m, 1 H), 8.05 (d, *J* = 1.47 Hz, 1 H), 8.08 (d, *J* = 1.22 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 104, 125, 126.2, 126.4, 127.2, 127.3, 128.0, 128.3, 128.6, 128.9, 129, 130, 131, 132, 134, 136.7, 136.8, 138, 139, 151 ppm. HRMS MALDI-TOF: *m/z* calcd for $C_{19}H_{15}N_2S$: 303.0950; found: 303.0835. IR (neat): $\tilde{\nu}$ = 3064, 1652, 1594, 1497, 1457, 1408, 1361, 1232, 1157, 1072, 956, 927, 848, 762, 689 cm^{-1}.

5-(4-Nitrophenyl)-1,3-diphenyl-1*H*-pyrazole (3j): 2,5-diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and 1-ethynyl-4-nitrobenzene (103.00 mg, 0.70 mmol) in acetonitrile (5.00 mL) afforded 5-(4-nitrophenyl)-1,3-diphenyl-1*H*-pyrazole (4.00 mg, 0.012 mmol, 7 % yield) as a pale-yellow solid. Unique regioisomer isolated and characterized. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.95 (s, 1 H), 7.33–7.43 (m, 6 H), 7.43–7.49 (m, 4 H), 7.91–7.93 (m, 1 H), 7.93–7.96 (m, 1 H), 8.16–8.18 (m, 1 H), 8.19–8.21 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106, 123, 125.4, 125.7, 128.1, 128.3, 128.7, 129.22, 129.29, 132.4, 132.9, 136, 139, 141, 147, 152 ppm. Data in accordance with literature.[22]

Ethyl 3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3k) and Ethyl 3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3k′): 5-(4-methoxyphenyl)-2-phenyl-2*H*-tetrazole (50.00 mg, 0.20 mmol) and ethyl propiolate (0.06 mL, 0.60 mmol) in acetonitrile (4.50 mL) afforded ethyl 3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate and ethyl 3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate as a yellow solid containing both non-separable regioisomers [61.90 mg, 0.19 mmol, 97 % yield, r.r. (8:2) determined via proton NMR measurement of the mixture]. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.13–1.19, 1.24, 3.74, 3.76, 4.17, 4.21, 6.82–6.92, 7.13–7.18, 7.31–7.43, 7.65–7.80, 8.39 ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13, 14, 29, 55.1, 55.2, 60, 61, 108, 113.2, 113.3, 114, 119, 124.5, 124.8, 126, 127, 127.2, 128, 129, 130, 132, 134, 139, 140, 151, 153, 159.1, 159.7, 160 ppm. HRMS: *m/z* calcd for $C_{19}H_{18}N_2O_3$ + Na^+ 345.1210; found: 345.1208. IR (neat): $\tilde{\nu}$ = 2997, 2978, 2935, 2835, 1725, 1616, 1599, 1547, 1499, 1431, 1295, 1255, 1231, 1172, 1103, 1036, 1025, 1005, 956, 912, 868, 833 cm^{-1}.

Ethyl 3-(2-Bromophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3l) and Ethyl 3-(2-Bromophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3l′): 5-(2-Bromophenyl)-2-phenyl-2*H*-tetrazole (50.00 mg, 0.17 mmol) and ethyl propiolate (0.05 mL, 0.49 mmol) in acetonitrile (3.70 mL) afforded ethyl 3-(2-bromophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (12.90 mg, 0.04 mmol, 21 % yield) and ethyl 3-(2-bromophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (5.70 mg, 0.02 mmol, 9 % yield) as two brown solids [r.r. (7:3)].

Ethyl 3-(2-Bromophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3l): Mp 110–111 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.31 (m, 3 H), 4.29 (q, *J* = 7.09 Hz, 2 H), 7.20–7.26 (m, 1 H), 7.37 (td, *J* = 7.58, 1.22 Hz, 1 H), 7.45–7.55 (m, 6 H), 7.69 (dd, *J* = 8.07, 1.22 Hz, 1 H), 7.80 (dd, *J* = 7.82, 1.71 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14, 61, 113, 122, 126, 127, 128.5, 128.7, 129, 131, 133.2, 133.5, 133.7, 140, 150, 159 ppm. HRMS: *m/z* calcd for $C_{18}H_{15}N_2O_2Br$ + H^+ 371.0390/373.0369; found: 371.0393/373.0368. IR (neat): $\tilde{\nu}$ = 3179, 2978, 2926, 1727, 1598, 1500, 1454, 1433, 1410, 1334, 1291, 1257, 1238, 1198, 1129, 1111, 1042, 1022, 1007, 831 cm^{-1}.

Ethyl 3-(2-Bromophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3l′): Mp 93–94 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 7.09 Hz, 3 H), 4.20 (q, *J* = 7.09 Hz, 2 H), 7.27–7.33 (m, 1 H), 7.34–7.42 (m, 2 H), 7.46–7.53 (m, 3 H), 7.67 (dd, *J* = 7.82, 0.98 Hz, 1 H), 7.76–7.81 (m, 2 H), 8.53 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13, 60, 119, 124, 126, 127, 129.5, 129.9, 130, 131, 132, 134, 139, 153 ppm. HRMS: *m/z* calcd for $C_{18}H_{15}N_2O_2Br$ + H^+ 371.0390/373.0369; found: 371.0395/373.0756. IR (neat): $\tilde{\nu}$ = 3119, 2918, 1849, 1695, 1596, 1540, 1502, 1439, 1364, 1282, 1256, 1223, 1144, 1066, 1021, 957, 913, 867 cm^{-1}.

Ethyl 3-(4-Cyanophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3m) and Ethyl 3-(4-Cyanophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3m′): 4-(2-Phenyl-2*H*-tetrazol-5-yl)benzonitrile (50.00 mg, 0.20 mmol) and ethyl propiolate (0.06 mL, 0.60 mmol) in acetonitrile (4.50 mL) afforded ethyl 3-(4-cyanophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate and ethyl 3-(4-cyanophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (4.30 mg, 0.01 mmol, 45 %) as a non-separable mixture of regioisomers (9:1) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.1 Hz 3 H), 1.35 (m, 1 H), 4.24–4.32 (m, 2 H), 7.38 (d, *J* = 0.49 Hz, 1 H), 7.47–7.52 (m, 4 H), 7.57–7.64 (m, 1 H), 7.68–7.74 (m, 2 H), 7.77–7.86 (m, 1 H), 7.99 (d, *J* = 8.07 Hz, 2 H), 8.05–8.12 (m, 1 H), 8.17–8.25 (m, 1 H), 8.33–8.42 (m, 1 H), 8.53 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13, 14, 60, 61, 109, 111, 114, 118.2, 118.7, 119.5, 119.8, 125, 126, 127, 128.6, 128.9, 129.6, 129.7, 129.9, 130.0, 131.2, 131.6, 132.5, 132.7, 135, 136, 140, 149, 158, 163 ppm. HRMS: *m/z* calcd for $C_{19}H_{15}N_3O_2$ + Na^+ 340.1056; found: 340.1053. IR (neat): $\tilde{\nu}$ = 3130, 2987, 2940, 2224, 1730, 1686, 1611, 1597, 1500, 1548, 1435, 1286, 1236, 1108, 1010, 839 cm^{-1}.

Ethyl 3-(2-Acetoxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3o) and Ethyl 3-(2-Acetoxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3o′): 2-Methoxy-6-(2-phenyl-2*H*-tetrazol-5-yl)phenyl acetate (60.00 mg, 0.19 mmol) and ethyl propiolate (0.06 mL, 0.58 mmol) in acetonitrile (4.30 mL) afforded ethyl 3-(2-acetoxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (53.00 mg, 0.14 mmol) as a yellow solid and a mixture of ethyl 3-(2-acetoxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate and traces of ethyl 3-(2-acetoxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (6.6 mg, 0.02 mmol) as a yellow solid. The overall yield is 81 % and r.r. (9:1) which was weighted according to the global mass of isolated product and determined via ^{1}H-NMR spectrum of the isolated mixture.

Ethyl 3-(2-Acetoxy-3-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3o): Mp 99–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.09 Hz, 3 H), 2.36 (s, 3 H), 3.90 (s, 3 H), 4.29 (q, *J* = 7.09 Hz, 2 H), 7.02 (dd, *J* = 8.19, 1.34 Hz, 1 H), 7.28–7.32 (m, 1 H), 7.33 (s, 1 H), 7.45–7.53 (m, 4 H), 7.55 (dd, *J* = 7.83, 1.47 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13, 20, 56, 61, 111.8, 111.9, 120, 125, 126.2, 126.5, 128.4, 128.5, 134, 137, 140, 147, 151, 158, 168 ppm. HRMS: *m/z* calcd for $C_{21}H_{20}N_2O_5$ + Na^+ 403.1264; found: 403.1261. IR (neat): $\tilde{\nu}$ = 3013, 1760, 1730, 1585, 1530, 1499, 1491, 1420, 1370, 1341, 1309, 1274, 1241, 1217, 1191, 1175, 1127, 1097, 1050, 1011, 981, 898 cm^{-1}.

Ethyl 3-(5-Methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3p) and Ethyl 3-(5-Methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3p′): 5-(5-Methylfuran-2-yl)-2-phenyl-2*H*-tetrazole (51.00 mg, 0.23 mmol) and ethyl propiolate (0.07 mL, 0.68 mmol) in acetonitrile (5.00 mL) afforded ethyl 3-(5-methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (40.80 mg, 0.14 mmol) purely isolated and a mixture (1:1) of 3-(5-methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate/ethyl-3-(5-methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-4-carboxylate (4.10 mg, 0.014 mmol) as respectively a yellow solid and an orange deposit. The overall yield is 67 % and r.r. (9:1), which was weighted according to the global mass of isolated product and determined via ^{1}H NMR spectrum of the isolated mixture.

Ethyl 3-(5-Methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3p): Mp 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23–1.29 (m, 3 H), 2.38 (d, *J* = 0.49 Hz, 3 H), 4.26 (q, *J* = 7.17 Hz, 2 H), 6.08 (dq, *J* = 3.15, 0.99 Hz, 1 H), 6.67 (d, *J* = 3.18 Hz, 1 H), 7.20 (s, 1 H), 7.42–7.49 (m, 5 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.6, 13.9, 61, 107.4, 107.8, 108, 126, 128.4, 128.6, 134, 140, 144, 145, 152, 158 ppm. HRMS: *m/z* calcd for $C_{17}H_{16}N_2O_3$ + H^+ 297.1234; found: 297.1236. IR (neat): $\tilde{\nu}$ = 1728, 1581, 1518, 1498, 1462, 1438, 1406, 1379, 1280, 1232, 1208, 1106, 1038, 1020, 949, 903 cm^{-1}.

Ethyl 3-(5-Methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3n) and Ethyl 3-(5-Methylfuran-2-yl)-1-phenyl-1*H*-pyrazole-4-carboxylate (3p′): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.09 Hz, 3 H), 2.44 (t, *J* = 0.73 Hz, 3 H), 4.36 (q, *J* = 7.25 Hz, 2 H), 6.14 (dd, *J* = 3.42, 0.98 Hz, 1 H), 7.37 (d, *J* = 7.58 Hz, 1 H), 7.45–7.48 (m, 3 H), 7.76–7.82 (m, 2 H), 8.45 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.7, 13.8, 60, 107.4, 107.7, 119, 126, 127, 128.5 (2 C), 128.7, 129, 132, 139, 144.3, 144.5, 153, 158 ppm. HRMS: *m/z* calcd for $C_{17}H_{16}N_2O_3$ + Na^+ 319.1053; found: 319.1048. IR (neat): $\tilde{\nu}$ = 2983, 2920, 2849, 1723, 1674, 1598, 1527, 1500, 1443, 1364, 1282, 1234, 1109, 1064, 1021 cm^{-1}.

Diethyl 1-Phenyl-1*H*-pyrazole-3,5-dicarboxylate (3q) and Diethyl 1-Phenyl-1*H*-pyrazole-3,4-dicarboxylate (3q′): Ethyl 2-phenyl-2*H*-tetrazole-5-carboxylate (61.00 g, 0.28 mmol) and ethyl propiolate (0.09 mL, 0.84 mmol) in acetonitrile (6.20 mL) afforded diethyl 1-phenyl-1*H*-pyrazole-3,5-dicarboxylate and diethyl 1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (54.00 mg, 0.19 mmol, 67 % yield) as an orange solid as an non-separable mixture of regioisomers r.r. (9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.28 (m, 3 H), 1.38–1.44 (m, 3 H), 4.25 (q, *J* = 7.17 Hz, 2 H), 4.41–4.49 (m, 2 H), 7.42–7.50 (m, 5 H), 7.52 (s, 1 H), 8.38 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13, 14, 61.3, 61.4, 114, 120, 126, 128, 129.2, 129.5, 134, 139, 143, 158, 161 ppm. HRMS: *m/z* calcd for $C_{15}H_{16}N_2O_4$ + Na^+ 311.1002; found: 311.0995. IR (neat): $\tilde{\nu}$ = 3144, 3066, 2982, 2936, 2905, 2873, 1723, 1599, 1254, 1499, 1483, 1465, 1366, 1282, 1227, 1136, 1084, 1022, 1007, 847, 760, 690 cm^{-1}.

Ethyl 1-(4-Fluorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3s) and Ethyl 1-(4-Fluorophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3s′): 2-(4-Fluorophenyl)-5-phenyl-2*H*-tetrazole (50.00 mg, 0.21 mmol) and ethyl propiolate (0.06 mL, 0.62 mmol) in acetonitrile (4.60 mL) afforded ethyl 1-(4-fluorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (40.40 mg, 0.13 mmol) and a mix (1:1) of ethyl 1-(4-fluorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate and ethyl 1-(4-fluorophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (7.00 mg, 0.02 mmol) respectively as a white solid and a yellow solid. The overall yield is 74 % and r.r. (9:1), which was weighted according to the global mass of isolated product and determined via ^{1}H NMR spectrum of the isolated mixture.

Ethyl 1-(4-Fluorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3s): Mp 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29–1.34 (m, 3 H), 4.22–4.33 (m, 2 H), 7.10–7.22 (m, 2 H), 7.31–7.34 (m, 1 H), 7.35–7.39 (m, 1 H), 7.41–7.53 (m, 4 H), 7.84–7.92 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14, 61, 109, 115.3, 115.5, 125, 127, 128.0, 128.4, 128.7, 132, 134, 136, 151, 159, 163 ppm. HRMS: *m/z* calcd for $C_{18}H_{15}N_2O_2F$ + H^+ 311.1190; found: 311.1190. IR (neat): $\tilde{\nu}$ = 3070, 2988, 1725, 1606, 1538, 1512, 1442, 1283, 1241, 1214, 1109, 1032, 845, 754 cm^{-1}.

Ethyl 1-(4-Fluorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3s) and Ethyl 1-(4-Fluorophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3s′): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (q, *J* = 7.09 Hz, 6 H), 4.30 (quin, *J* = 7.03 Hz, 4 H), 7.10–7.22 (m, 4 H), 7.34 (s, 1 H), 7.36–7.40 (m, 1 H), 7.41–7.53 (m, 7 H), 7.72–7.79 (m, 2 H), 7.83–7.92 (m, 4 H), 8.45 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14, 60, 113, 116.2, 116.5, 121.3, 121.4, 127, 129, 135, 154, 160, 161, 162, 163 ppm. HRMS: *m/z* calcd for $C_{18}H_{15}N_2O_2F$ + H^+ 311.1190; found: 311.1191. IR (neat): $\tilde{\nu}$ = 1726, 1628, 1538, 1512, 1442, 1363, 1281, 1232, 1214, 1158, 1110, 1056, 1025, 957 cm^{-1}.

Ethyl 1-(3-Chlorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3t) and Ethyl 1-(3-Chlorophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3t′): 2-(3-Chlorophenyl)-5-phenyl-2*H*-tetrazole (51.00 mg, 0.20 mmol) and ethyl propiolate (0.06 mL, 0.60 mmol) in acetonitrile (4.30 mL) afforded ethyl 1-(3-chlorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (57.40 mg, 0.18 mmol) isolated purely as a brown solid and a mixture of ethyl 1-(3-chlorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate/ethyl 1-(3-chlorophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (7.40 mg, 0.02 mmol) as an orange solid. The overall yield is 99 % and r.r. (9:1), which was weighted according to the global mass of isolated product and determined via ^{1}H NMR spectrum of the isolated mixture.

Ethyl 1-(3-Chlorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3t): Mp 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28–1.33 (m, 3 H), 4.31 (q, *J* = 7.09 Hz, 2 H), 7.34–7.37 (m, 1 H), 7.37–7.40 (m, 1 H), 7.41–7.48 (m, 5 H), 7.56 (dt, *J* = 2.08, 1.16 Hz, 1 H), 7.85–7.93 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14, 61, 109, 124, 125, 126, 128.5, 128.7, 129, 131, 134.1, 134.7, 141, 151, 158 ppm. HRMS: *m/z* calcd for $C_{18}H_{15}N_2O_2Cl$ + H^+ 327.0895; found: 327.0891. IR (neat): $\tilde{\nu}$ = 2981, 1726, 1592, 1483, 1431, 1357, 1285, 1236, 1200, 1119, 1098, 1077, 1036 cm^{-1}.

Ethyl 1-(3-Chlorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3t) and Ethyl 1-(3-Chlorophenyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3t′): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.37 (m, 10 H), 4.21–4.35 (m, 5 H), 7.32–7.36 (m, 3 H), 7.37–7.49 (m, 13 H), 7.54–7.58 (m, 1 H), 7.63–7.72 (m, 1 H), 7.82–7.92 (m, 6 H), 8.49–8.52 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.0, 14.2, 60, 61, 109, 117, 119, 124, 125, 126, 127.4, 127.8, 128, 129, 130, 131, 132 ppm. HRMS: *m/z* calcd for $C_{18}H_{15}N_2O_2Cl + H^+$ 327.0895; found: 327.0891. IR (neat): $\tilde{\nu}$ = 3140, 2982, 1726, 1703, 1593, 1535, 1483, 1431, 1359, 1285, 1119, 1096, 1037 cm^{-1}.

Ethyl 1-(Benzo[*d*][1,3]dioxol-5-yl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3u) and Ethyl 1-(Benzo[*d*][1,3]dioxol-5-yl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3u′): 2-(Benzo[*d*][1,3]dioxol-5-yl)-5-phenyl-2*H*-tetrazole (50.00 mg, 0.19 mmol) and ethyl propiolate (0.06 mL, 0.56 mmol) in acetonitrile (4.20 mL) afforded ethyl 1-(benzo[*d*][1,3]dioxol-5-yl)-3-phenyl-1*H*-pyrazole-5-carboxylate and ethyl 1-(benzo[*d*][1,3]dioxol-5-yl)-3-phenyl-1*H*-pyrazole-4-carboxylate (19.00 mg, 0.06 mmol, 30 %) as a non-separable mixture of regioisomers (9:1) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.09 Hz, 3 H), 4.30 (q, *J* = 7.09 Hz, 2 H), 6.04 (s, 0 H), 6.05 (s, 2 H), 6.86–6.91 (m, 1 H), 6.97 (d, *J* = 2.20 Hz, 1 H), 6.98–7.01 (m, 1 H), 7.29–7.32 (m, 1 H), 7.33–7.39 (m, 1 H), 7.40–7.47 (m, 2 H), 7.85–7.91 (m, 2 H), 8.39 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.0, 14.2, 60, 61, 101.7, 101.8, 101.9, 107.60, 107.66, 108, 109, 112, 119, 125, 127, 128.3, 128.5, 128.6, 129, 132.1, 132.3, 134.3, 134.6, 147.4, 147.8, 148, 151, 158, 162 ppm. HRMS: *m/z* calcd for $C_{19}H_{16}N_2O_4 + Na^+$ 359.1002; found: 359.1004. IR (neat): $\tilde{\nu}$ = 2905, 1718, 1494, 1451, 1434, 1367, 1343, 1290, 1091, 1028, 935 cm^{-1}.

Ethyl 1-(4-Methoxyphenyl)-3-(*o*-tolyl)-1*H*-pyrazole-5-carboxylate (3v) and Ethyl 1-(4-Methoxyphenyl)-3-(o-tolyl)-1*H*-pyrazole-4-carboxylate (3v′): 2-(4-Methoxyphenyl)-5-(*o*-tolyl)-2*H*-tetrazole (50.50 mg, 0.19 mmol) and ethyl propiolate (0.06 mL, 0.57 mmol) in acetonitrile (4.20 mL) afforded ethyl 1-(4-methoxyphenyl)-3-(*o*-tolyl)-1*H*-pyrazole-5-carboxylate (45.17 mg, 0.13 mmol, 71 % yield) and ethyl 1-(4-methoxyphenyl)-3-(*o*-tolyl)-1*H*-pyrazole-4-carboxylate (9.93 mg, 0.03 mmol, 16 % yield), respectively, as a pale-white solid and a transparent semi-solid [r.r. (8:2)].

Ethyl 1-(4-Methoxyphenyl)-3-(*o*-tolyl)-1*H*-pyrazole-5-carboxylate (3v): Mp 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.09 Hz, 3 H), 2.65 (s, 3 H), 3.97 (s, 3 H), 4.38 (q, *J* = 7.09 Hz, 2 H), 7.03–7.13 (m, 2 H), 7.32–7.41 (m, 3 H), 7.49–7.57 (m, 2 H), 7.68–7.76 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14, 21, 55, 61, 112, 113, 125, 127, 128, 129, 130, 131, 133.5, 133.7, 136, 151, 159.2, 159.5 ppm. HRMS: *m/z* calcd for $C_{20}H_{20}N_2O_3 + H^+$ 337.1547; found: 337.1545. IR (neat): $\tilde{\nu}$ = 3138, 2978, 2936, 1701, 1513, 1441, 1417, 1297, 1236, 1171, 1106, 1036, 1025, 954, 835 cm^{-1}.

Ethyl 1-(4-Methoxyphenyl)-3-(*o*-tolyl)-1*H*-pyrazole-4-carboxylate (3v′): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, *J* = 7.09 Hz, 3 H), 2.28 (s, 3 H), 3.85–3.88 (m, 3 H), 4.18 (q, *J* = 7.09 Hz, 2 H), 6.97–7.00 (m, 1 H), 7.00–7.02 (m, 1 H), 7.21–7.27 (m, 1 H), 7.27–7.38 (m, 3 H), 7.66–7.68 (m, 1 H), 7.68–7.71 (m, 1 H), 8.43 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14, 20, 55, 60, 114.6, 114.7, 121, 125, 128, 129, 130.1, 130.9, 132.4, 132.9, 137, 158, 162 ppm. HRMS: *m/z* calcd for $C_{20}H_{20}N_2O_3 + Na^+$ 359.1366; found: 359.1361. IR (neat): $\tilde{\nu}$ = 2979, 2933, 2836, 1717, 1533, 1514, 1463, 1249, 1216, 1172, 1136, 1107, 1054, 1026, 959, 831, 762 cm^{-1}.

Dimethyl 3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole-4,5-dicarboxylate (3w): In a microwave vial, 5-(4-nitrophenyl)-2-phenyl-2*H*-tetrazole (50.00 mg, 0.19 mmol) and dimethyl but-2-ynedioate (0.12 mL, 0.94 mmol) were mixed and heated neat at 180 °C for 1 h. The reaction progress was monitored via UPLC-MS analyses. Upon completion, the crude material was dissolved with DCM, deposed on silica and purified with a FC Biotage Isolera system using pentane/Et_2O as eluent (5 % Et_2O on 3CV, 5 to 10 % on 7CV, 10 to 100 % on 6.5CV and finally 100 % on 9CV) to afford dimethyl 3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4,5-dicarboxylate (44.10 mg, 0.12 mmol, 62 % yield) as a yellow solid. Mp 114–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 3.88 (s, 3 H), 7.48–7.57 (m, 5 H), 7.97–7.99 (m, 1 H), 7.99–8.01 (m, 1 H), 8.27–8.29 (m, 1 H), 8.29–8.32 (m, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 52, 53, 114, 123, 124, 129.3, 129.4, 129.8, 137.73, 137.78, 138, 147, 149, 160, 162 ppm. HRMS: *m/z* calcd for $C_{19}H_{15}N_3O_6 + Na^+$ 404.0853; found: 404.0852. IR (neat): $\tilde{\nu}$ = 2955, 1727, 1602, 1534, 1016, 1499, 1440, 1340, 1264, 1245, 1125, 1108, 999, 944, 854 cm^{-1}.

2-Phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole (3x): A solution of 2-phenyl-5-[2-(prop-2-yn-1-yloxy)phenyl]-2*H*-tetrazole (50.00 mg, 0.18 mmol) was made in acetonitrile (15.00 mL) in a quartz vessel and irradiated for 1 h at 300 nm. The solvent was removed under vacuum and the crude material was purified with a FC Biotage Isolera system using DCM/Et_2O (100 % DCM on 9CV, 5 % Et_2O on 7CV, 5 to 100 % Et_2O on 2CV and 100 % Et_2O on 4CV) as eluent to give 2-phenyl-2,4-dihydrochromeno[4,3-*c*]pyrazole (25.00 mg, 0.10 mmol, 56 % yield) as an orange semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.35 (d, *J* = 0.73 Hz, 2 H), 7.00 (dd, *J* = 8.19, 0.86 Hz, 1 H), 7.06 (td, *J* = 7.46, 1.22 Hz, 1 H), 7.22–7.27 (m, 1 H), 7.30 (tt, *J* = 7.40, 1.04 Hz, 1 H), 7.43–7.50 (m, 2 H), 7.69–7.76 (m, 3 H), 7.90 (dd, *J* = 7.70, 1.59 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 63, 114, 117, 118, 119, 121.6, 121.9, 122, 126, 129.4, 129.6, 129.8, 140, 145, 154 ppm. HRMS: *m/z* calcd for $C_{16}H_{12}N_2O + H^+$ 249.1022; found: 249.1028. IR (neat): $\tilde{\nu}$ = 3123, 3062, 2922, 2860, 1739, 1690, 1597, 1502, 1469, 1382, 1295, 1225, 1193, 1107, 1028, 983, 955, 828, 747 cm^{-1}.

2-Phenyl-4*H*-pyrazolo[1,5-*a*]indole (3y): A solution of 5-phenyl-2-[2-(prop-2-yn-1-yl)phenyl]-2*H*-tetrazole (51.30 mg, 0.20 mmol) was made in acetonitrile (15 mL) in a quartz vessel and irradiated for 1 h at 300 nm. The solvent was removed under vacuum and the crude material was purified with a FC Biotage Isolera system using DCM/Et_2O (100 % DCM on 9CV, 5 % Et_2O on 7CV, 5 to 100 % Et_2O on 2CV and 100 % Et_2O on 4CV) as eluent to afford 2-phenyl-4*H*-pyrazolo[1,5-*a*]indole (8.30 mg, 0.04 mmol, 18 % yield) as an orange semi-solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.93 (s, 2 H), 6.63 (t, *J* = 1.28 Hz, 1 H), 7.22 (dd, *J* = 7.61, 1.01 Hz, 1 H), 7.30–7.38 (m, 1 H), 7.38–7.50 (m, 4 H), 7.71 (d, *J* = 7.89 Hz, 1 H), 7.88–7.95 (m, 2 H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28, 98, 110, 124, 125, 127, 128.0, 128.6, 133, 145 ppm. HRMS: *m/z* calcd for $C_{16}H_{12}N_2 + H^+$ 233.1073; found: 233.1074. IR (neat): $\tilde{\nu}$ = 3296, 3061, 2921, 2850, 1781, 1718, 1623, 1597, 1545, 1473, 1454, 1399, 1303, 1054, 953, 762, 749, 691 cm^{-1}.

(*Z*)-*N*′-Phenylbenzohydrazonoyl Chloride (4): A solution of 2,5-diphenyl-2*H*-tetrazole (50.00 mg, 0.23 mmol) and HCl (0.11 mL, 1.35 mmol) in acetonitrile (5.00 mL) was irradiated for 1 h at 300 nm. Upon completion, the solvent was removed under vacuum and the crude material was purified by column chromatography using pentane/Et_2O (3:2) as eluent to give (*Z*)-*N*′-phenylbenzohydrazonoyl chloride (30.40 mg, 0.13 mmol, 59 % yield) as a yellow solid. Mp 128–131 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.96 (tt, *J* = 7.31, 1.13 Hz, 1 H), 7.19–7.24 (m, 2 H), 7.29–7.37 (m, 2 H), 7.39–7.47 (m, 3 H), 7.93–7.98 (m, 2 H), 8.11 (s, 1 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 113, 121, 125, 126, 129.0, 129.8, 129.9, 135, 144 ppm. IR (neat): $\tilde{\nu}$ = 3305, 1595, 1572, 1502, 1486, 1445, 1434, 1313, 1267, 1134, 1070, 941, 834, 753, 683, 654 cm^{-1}. No MS measurement available.

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