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General Synthesis of Tri-carbo-substituted N^2-Aryl-1,2,3-Triazoles via Cu-catalyzed Annulation of Azirines with Aryldiazonium Salts

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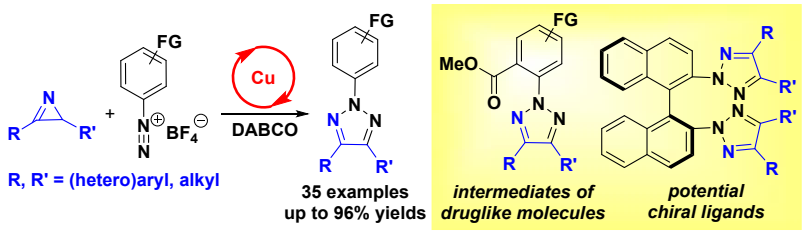
Supporting Information Placeholder

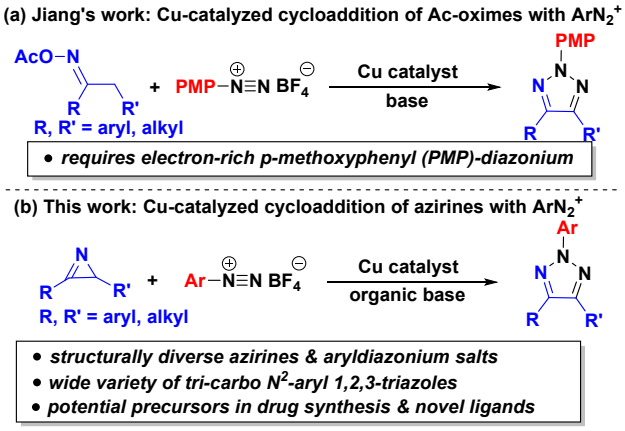


ABSTRACT: The general synthesis of fully substituted N^2-aryl-1,2,3-triazoles are hitherto challenging compared with the N^1-aryl counterparts. Herein we describe a Cu-catalyzed annulation reaction of azirines and aryldiazonium salts. This regiospecific method allows access to a broad spectrum of tri-carbo N^2-aryl-1,2,3-triazoles substituted with diverse aryl and alkyl moieties. Its utility is highlighted by the synthesis of several triazole precursors applicable in drug discovery, as well as novel chiral binaphthyl ligands bearing triazole moieties.

Introduction

1,2,3-Triazoles are prevalent functional compounds in medicinal and materials chemistry.[1,2] Among them, N^2-aryl-1,2,3-triazoles are important structural scaffolds found in numerous biologically active molecules in drug discovery, as exemplified in the orexin receptor antagonists, Suvorexant,[3] Nemorexant,[4] and Seltorexant,[5] for treating insomnia. Transition metal-catalyzed *N*-arylations have long been employed as the conventional methods to access the target N^2-aryl-1,2,3-triazoles,[6] but the concomitant formations of N^1-aryl regioisomeric side products are generally inevitable. Alternatively, annulation reactions using various synthetic synthons are the reliable strategies to deliver N^2-aryl-1,2,3 triazoles in regiospecific manners.[7,8] In this context, annulation reactions of nitrogen-based synthons with aryldiazonium salts have emerged as promising approaches to synthesize N^2-aryl-1,2,3-triazoles[8] thanks to the convenient preparations and broad scope of aryldiazonium salts.[9] Noteworthily, fully substituted N^2-aryl-1,2,3-triazoles are especially valuable heterocycles due to the multiple versatilities and functionalities governed by the possible existence of three distinct substituents attached to the triazole rings. To this end, streamlined and modular strategies based on the judicious use of suitable synthons for Cu-mediated or -catalyzed annulation with aryldiazonium salts were recently described by Tang,[8a] Yu,[8d] and our group[8e] to access a plethora of tri-substituted N^2-aryl-1,2,3-triazoles bearing aryl, thio, keto, and ester moieties. Importantly, Jiang and co-workers described a Cu-catalyzed annulation reaction of oxime acetates with electron-rich *p*-methoxyphenyl-diazonium salt in order to obtain tri-carbo N^2-aryl-1,2,3-triazoles in high yields[8b] (Scheme 1a). Recently, azirines, a class of reactive and readily accessible substrates capable of bearing di-aryl- or aryl-/alkyl-substituents, have been employed as atom-economic synthons to access a vast number of nitrogen heterocyclic compounds.[10] Based on our continuous endeavors in utilizing aryldiazonium salts for heterocycle synthesis,[8e,11] we envisioned that the annulation of azirines with aryldiazonium salts would also be feasible to access structurally diverse tri-carbo N^2-aryl-1,2,3-triazoles (Scheme 1b). This alternative strategy complements the precedented protocols, further extending the scope of tri-carbo N^2-aryl-1,2,3-triazole compounds. Herein we describe our discoveries based on this subject.

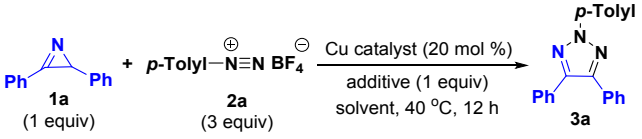
Scheme 1. Cu-catalyzed annulation of aryldiazonium salts for construction of tri-carbo N^2-aryl-1,2,3-triazoles.



Results and Discussions

Initially, 2,3-diphenyl-2*H*-azirine (**1a**) and 4-tolyldiazonium tetrafluoroborate (**2a**) were used as model substrates for study (Table 1). To our delight, **1a** reacted with 3 equivalents of **2a** in the presence of CuCl catalyst (20 mol %) and Li_2CO_3 (1 equiv) as base additive in toluene solvent at 40 °C in 12 h, furnishing the desired product, 4,5-diphenyl-2-(*p*-tolyl)-2*H*-1,2,3-triazole (**3a**), in 48% yield (Entry 1). Cu catalyst was crucial in this transformation, as no product was formed when CuCl was omitted (Entry 2). Base was also essential in the reaction, as the yield dropped in the absence of base (Entry 3). CuBr was found to be the superior Cu catalyst, slightly improving the yield to 50% (Entries 4-8). In the presence of organic base 1,4-diazabicyclo[2.2. 2]octane (DABCO), the yield of **3a** was enhanced to 75%, presumably owing to its moderate basicity and better solubility (Entry 9-13). Additionally, the yield of **3a** could be promoted to 93% using acetonitrile (MeCN) as the polar aprotic solvent (Entries 14-17). The reaction remained efficient at room temperature and in the presence of 2 equivalents of **2a** without loss of yield (Entry 18). Subsequent reducing the loadings of **2a**, base, and catalyst slightly diminished the yields accordingly (Entry 19-21).

Table 1. Optimizations of reaction conditions.[a]



Entry	Cu catalyst	base	Solvent	Yield (%)[b]
1	CuCl	Li_2CO_3	toluene	48
2	none	Li_2CO_3	toluene	0
3	CuCl	none	toluene	40
4	CuBr	Li_2CO_3	toluene	50
5	CuI	Li_2CO_3	toluene	8
6	CuTc	Li_2CO_3	toluene	48
7	CuOAc	Li_2CO_3	toluene	5
8	$CuCl_2$	Li_2CO_3	toluene	45
9	CuBr	Na_2CO_3	toluene	20
10	CuBr	K_2CO_3	toluene	18
11	CuBr	Et_3N	toluene	<5
12	CuBr	DBU	toluene	25
13	CuBr	DABCO	toluene	75
14	CuBr	DABCO	Et_2O	47
15	CuBr	DABCO	EtOH	74
16	CuBr	DABCO	CH_2Cl_2	89
17	CuBr	DABCO	MeCN	93
18[c,d]	CuBr	DABCO	MeCN	93
19[c,e]	CuBr	DABCO	MeCN	80
20[c,f]	CuBr	DABCO	MeCN	85
21[c,g]	CuBr	DABCO	MeCN	86

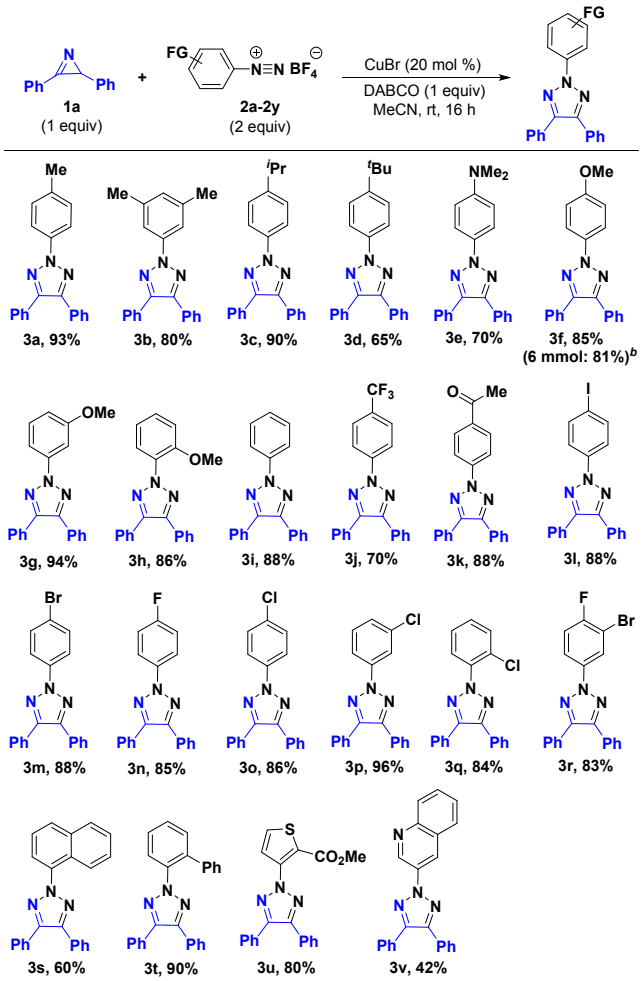
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Cu catalyst (20 mol %), additive, solvent (2 mL), argon atmosphere, 40 °C, 16 h. [b] Isolated yield. [c] Reaction was conducted at room temperature for 16 h. [d] **2a** (2 equiv.). [e] **2a** (1.5 equiv.). [f] DABCO (0.5 equiv.). [g] CuBr (10 mol %).

The optimized reaction protocol (Table 1, entry 17) proved to be versatile (Scheme 2). Electron-rich (**3a-3h**), electron-neutral (**3i**), and electron-deficient aryldiazonium salts (**3j-3r**) all reacted to give the corresponding N^2-aryl 1,2,3-triazoles in generally good to excellent yields (65%-96%). Likewise, *para*-, *meta*-, and *ortho*-substituted aryldiazonium salts underwent annulation to afford the triazoles in similar yields (**3f-3h, 3o-3q**). Additionally, di-halo-substituted diazonium salts (**3r**), as well as sterically bulky 2-naphthyl- (**3s**) and 2-phenylbenzene-diazonium salts (**3t**), were suitable reaction substrates to deliver the triazoles in good to high yields. Furthermore, thienyl (**3u**) and quinoline moieties (**3v**) could also be incorporated to the triazole products. A wide range of functional groups were compatible in this protocol, including amino (**3e**), trifluoromethyl (**3j**), keto (**3k**), iodo (**3l**), bromo (**3m**), fluoro (**3n**), chloro (**3o-3q**), and ester groups (**3u**). This protocol was amenable to the large-scale synthesis of triazole **3f** in equally high yield. However, monosubstituted 3-phenylazirine reacted to give a trace of triazole, suggesting that the additional substituent is necessary to assist the stabilization of reaction intermediates.

The protocol also allowed for the use of a variety of 2,3-di-sibstituted azirines, affording the unsymmetrical N^2-aryl-1,2,3-triazoles in good to excellent yields (Scheme 3). Electron-rich (**4a, 4f**) and electron-withdrawing aryl groups (**4b, 4c, 4g, 4i**), as well as heteroaryl groups (**4d**), could all be incorporated on both 2- and 3-positions of the azirine rings for triazole synthesis. Moreover, triazoles bearing methyl (**4h, 4m**), cyclopropyl (**4i**), *n*-pentyl (**4j**), 2-phenylethyl (**4k**), and 1-phenylethyl groups (**4l**) in either 3- or 4- positions were generated smoothly. Notably, the substituents at the 2- or 3-positions of azirine substrates were interchangeable, giving the identical triazole products in similar yields (**4a** and **4f**; **4c** and **4g**; **4h** and **4m**). Given the broad scope and ready accessibility of aziridines as well as the scalability of the protocol, the method could offer an expedient and convenient synthesis of N^2-aryl triazole for various industrial settings. Unfortunately, the monoalkyl-

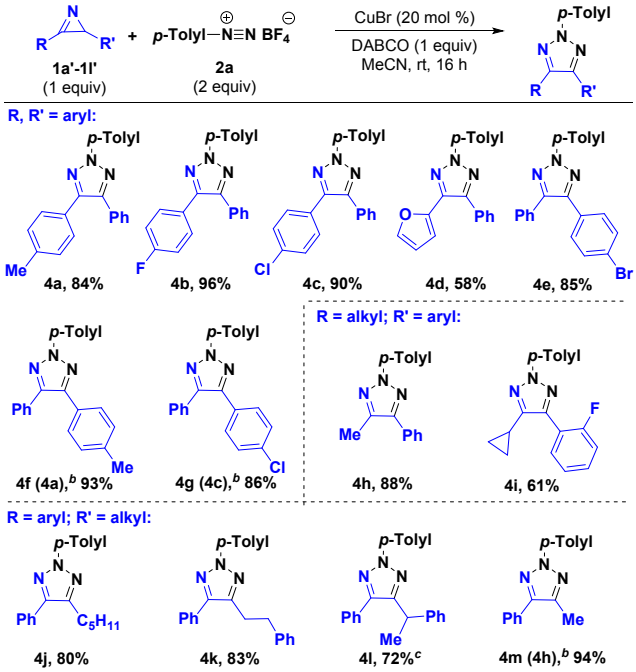
or dialkyl substituted azirines were either unstable or inaccessible for further study.

Scheme 2. Substrate scope of aryldiazonium salts.[a]



[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), CuBr (0.06 mmol), DABCO (0.3 mmol), MeCN (3 mL), argon atmosphere, rt, 16 h. Isolated yields were presented. [b] 1.16 g of **1a** was used.

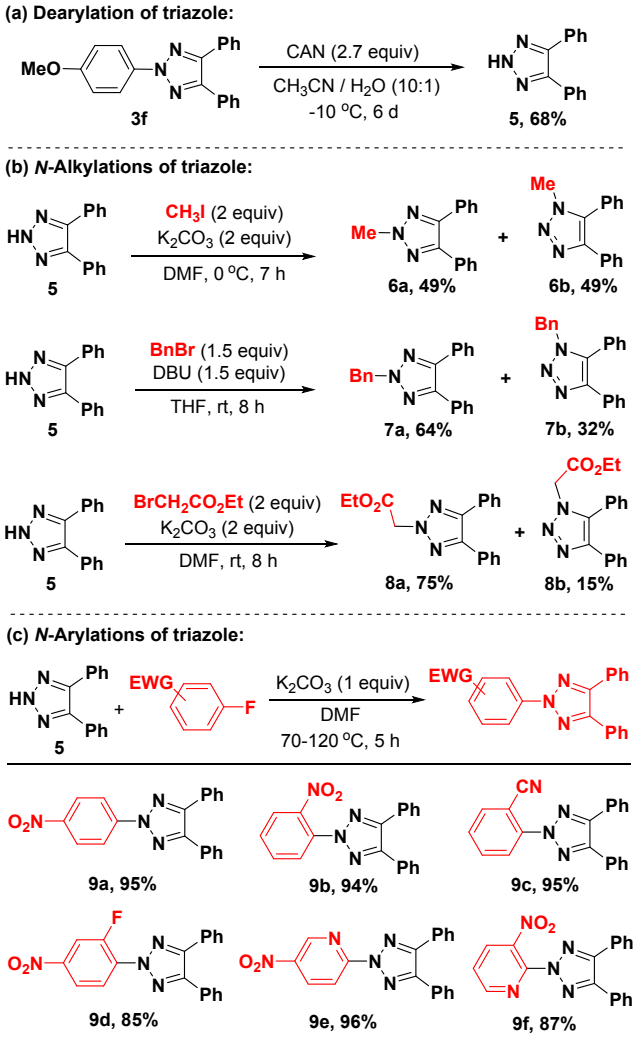
Scheme 3. Substrate scope of azirines.[a]



[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.6 mmol), CuBr (0.06 mmol), DABCO (0.3 mmol), MeCN (3 mL), argon atmosphere, rt, 16 h. [b] Identical products were formed using two different azirines. Isolated yields were presented. [c] Reaction was conducted at 40 °C.

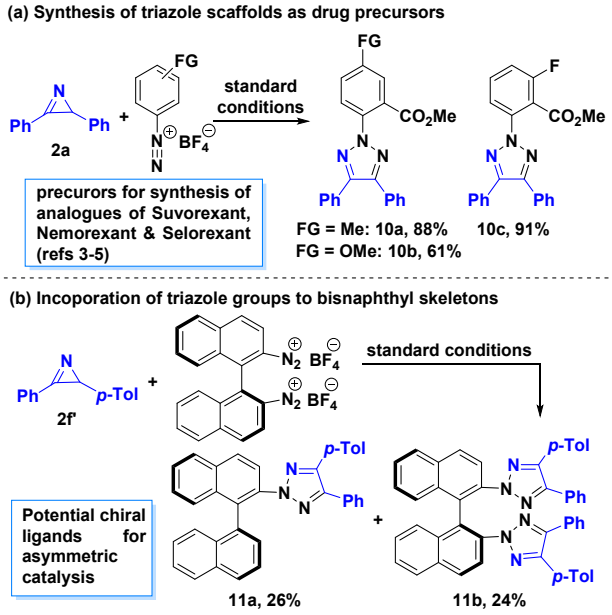
The derivatization of the tri-carbo N^2-aryl-1,2,3-triazole products were viable. Triazole **3f** could react with ceric ammonium nitrate (CAN)[12] to give the N^2-H free, 3,4-diphenyl 1,2,3-triazole **5** (Scheme 4a). **5** could further undergo various *N*-alkyations[13] to affords the corresponding N^2- and N^1-alkylated triazole congeners **6-8** (Scheme 4b). In addition, regiospecific N^2-arylation of **5** was accessible via nucleophilic aromatic substitution with various fluoroarenes to afford **9a-9f**,[14] allowing access to 1,2,3-triazole compounds with electron-deficient aryl groups and pyridyl groups at N^2-positions (Scheme 4c). Indeed, triazoles **6-9** were difficult to directly produce using the current protocol. Overall, this N^2-aryl triazole synthesis and *N*-dearylation strategy for elaborations would provide alternative routes to access a broad range of structurally and electronically diverse N^2-substituted and NH-free triazoles.[15]

Scheme 4. Derivatizations of the triazole products.



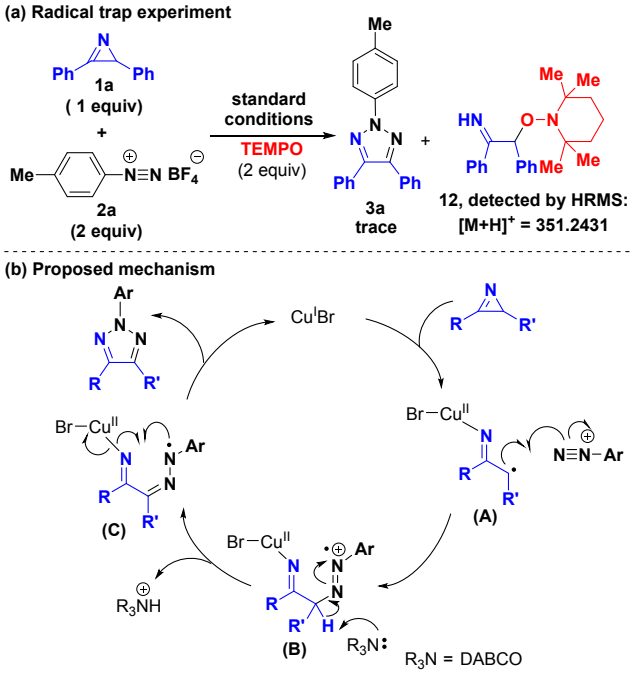
Under this protocol, several methyl 2-(4',5'-diaryl-2'-triazolyl)arenoate compounds **10a-10c** were readily synthesized using the corresponding azirines and aryldiazonium salts (Scheme 5a). These compounds could serve as precursors[16] towards the modular synthesis of the analogues of orexin receptor antagonists.[3-5] Moreover, (*S*)-[1,1'-binaphthalene]-2,2'-diamine was readily converted to the corresponding bis(diazonium) salt, which reacted with azirine **2a'** under the standard conditions to afford both mono- and bis-triazolyl substituted binaphthalenes, **11a** and **11b** (Scheme 5b). These novel class of chiral triazolyl-binaphthalenes would be potentially applicable in asymmetric transition metal-catalyzed transformations or photocatalysis.[17]

Scheme 5. Synthetic utility of the reaction protocol.



To probe the mechanism of the Cu-catalyzed annulation reaction, 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added as radical scavenger (Scheme 6a). The reaction became sluggish in the presence of 2 equivalents of TEMPO to form a trace of product **3a**. The adduct between TEMPO and azirine was also detected by HRMS analysis,[10d] indicating that radical pathways are likely involved in the reaction process. In the proposed reaction mechanism (Scheme 6b), CuBr catalyst initially cleaves the C-N single bond of azirine to form radical intermediate **A**,[10d] which further couples with aryldiazonium ion to form radical cation species **B**. Deprotonation of species **B** by DABCO furnishes radial species **C**, which then cyclizes to form the triazole product and regenerates CuBr for subsequent catalytic cycles.

Scheme 6. Probing of the reaction mechanism.



In conclusion, we have developed an annulation reaction of azirines with aryldiazonium salts. A diverse collection of tri-carbo N^2-aryl-1,2,3-triazoles substituted with both aryl and alkyl moieties can be accessed in association with good functional group tolerance. The triazole compounds are readily diversified to other derivatives. The protocol also allows expedient access to several potential precursors of druglike molecules as well as novel chiral binaphthyl ligands. Preliminary study suggests that a radical mechanism likely takes place. Further expansion of the substrate scope and the catalytic applications of chiral ligand **11a** and **11b** are underway in our laboratory.

Experimental Section

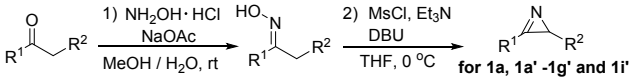
General information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), and 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external $CHCl_3$, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), and br (broad signal). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. Melting points were measured on a SGW X-4A digital melting point apparatus and are uncorrected. Optical rotations were determined using an Autopol IV automatic polarimeter. HPLC analyses were carried out on a HewlettPackard Model HP 1200 instrument. X-ray structural analysis was conducted on a Bruker APEX-II CCD instrument.

Tetrahydrofuran (THF), diethyl ether (Et_2O), and toluene were distilled from sodium/benzophenone prior to use; CH_2Cl_2 and CCl_4 was distilled from CaH_2; CH_3CN was distilled from P_2O_5. All purchased reagents were used without further purification. Thin-layer chromatography (TLC) was performed on precoated GF254 silica gel plates (Qingdao Marine Chemical Inc.) and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Inc.). Aryldiazonium salts **2**[11a] were prepared according to the reported procedures.

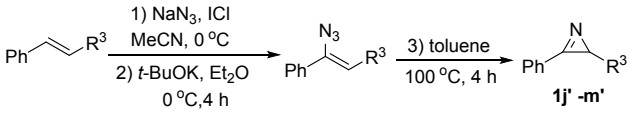
General procedure for synthesis of 2*H*-azirine (1).

(i) Method A (for synthesis of 1a, 1a' -1g' and 1i')[18]



Step 1: A solvent mixture of MeOH/H_2O (20:1) was added to a mixture of ketone (10 mmol, 1 equiv), $NH_2OH{\cdot}HCl$ (1.5 equiv) and sodium acetate (1.5 equiv) in a round bottom flask. The resulting solution was stirred at room temperature and the reaction was monitored by TLC. After the reaction was completed, the solvent was removed *in vacuo* and CH_2Cl_2 (30 mL) was then added. The mixture was washed with saturated $NaHCO_3$ solution followed by brine. The organic fraction was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give the oxime as the residue, which was used directly for the next step. **Step 2:** To a solution of the crude oxime (1 equiv, from step 1) in dry THF (30 mL) was added triethylamine (1.5 equiv) and methanesulfonyl chloride (1.5 equiv) sequentially at room temperature or at 0 °C. The solution became cloudy after the addition of methanesulfonyl chloride. The resulting mixture was stirred for 30 min, and DBU (1.5 equiv) was then added over 1 min. After stirring for additional 30 min, the reaction mixture was passed through a pad of silica gel and washed with Et_2O (30 mL x 3). The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography using peteroleum ether and ethyl acetate (20:1) as eluent to afford the 2H-azirine **1a, 1a'-1g' and 1i'**.

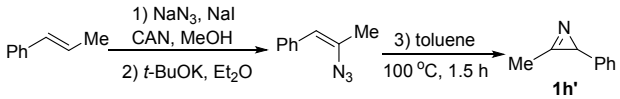
(ii) Method B (for synthesis of 1j' -1m')[19]



Step 1: To a suspension of NaN_3 (452 mg, 7.0 mmol, 2.5 equiv) in acetonitrile (2.2 mL) was added dropwise a solution of iodine monochloride (680 mg, 4.2 mmol, 1.5 equiv) in CH_2Cl_2 (3.6 mL) at -20°C, and the mixture was stirred at the same temperature. After 30 min, a solution of the corresponding alkene (2.8 mmol, 1.0 equiv) in CH_2Cl_2 (3.6 mL) was added slowly, and the mixture was stirred for additional 1 h. After the reaction, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL), and the reaction mixture were extracted with Et_2O (10 mL x 3). The combined organic fraction was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of solvent, the resulting crude material was used immediately for the next step without any further purification. **Step 2:** To a solution of the crude material (from step 1) in Et_2O (8 mL) was added *t*-BuOK (374 mg, 3.3 mmol, 1.2 equiv) at 0°C, and the mixture was stirred for 1 h at the same temperature. After the reaction, the reacion mixture was quenched with H_2O

(10 mL), and the organic materials were extracted with Et_2O (20 mL x 3). The combined organic fraction was washed with brine, dried over anydrous Na_2SO_4, and then dried *in vacuo*. The residue was purified by flash column chromatography using peteroleum ether and ethyl acetate (10:1) as eluent to give the corresponding vinyl azide. **Step 3:** A solution of the vinyl azide (from step 2) in toluene (15 mL) was heated at 100 ℃ for 4 h. After evaporation of solvent, the crude mixture was purified by flash column chromatography using peteroleum ether and ethyl acetate (20:1) as eluent to give the 2H-azirines **1j'-1m'**.

(iii) Method C (for synthesis of 1h')[19]



Step 1: To a mixture of alkene (6.0 mmol, 1.0 equiv), NaN_3 (390 mg, 6.0 mmol, 1.0 equiv), and NaI (900 mg, 6.0 mmol, 1.0 equiv) in methanol (9.0 mL) at 0 °C was added dropwise a solution of ceric ammonium nitrate (590 mg, 12.6 mmol, 2.1 equiv) in methanol (36 mL). Upon completion of the reaction as indicated by TLC, saturated aqueous $NaHSO_3$ (20 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (10 mL x 3) The combined organic fraction was washed with distilled water (24 mL) and saturated brine (24 mL), dried over anhydrous Na_2SO_4, and dried *in vacuo*. The resulting crude material was used immediately for the next step without any further purification. **Step 2:** To a solution of the crude material (from step 1) in dry Et_2O (20 mL) in an ice bath was added *t*-BuOK (1.34 g, 12.0 mmol, 2.0 equiv). The reaction mixture was stirred for 4 h at 0 °C and then washed with water (50 mL x 2). The combined organic fraction was dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The residue was purified by column chromatography using peteroleum ether and ethyl acetate as eluent (10:1) to give the crresponding vinyl azide. **Step 3:** A solution of the vinyl azide (from step 2) in toluene (15 mL) was heated at 100℃ for 1.5 h. After evaporation of solvent, the crude mixture was purified by flash column chromatography using peteroleum ether and ethyl acetate (20:1) as eluent to give the 2H-azirines **1h'**.

General procedure A: Annulation Reaction of 2*H*-Azirines 1 and aryldiazonium salt 2. An oven-dried 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with 2*H*-azirine (**1**, 1 equiv, 0.3 mmol), arene-diazonium salt (**2**, 2 equiv, 0.6 mmol), CuBr (20 mol%, 0.06 mmol), and DABCO (1 equiv, 0.3 mmol). The tube was evacuated under *vacuo* and then backfilled with argon (for three times). CH_3CN (3.0 mL) was transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere at room temperature for 16 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether / ethyl acetate) to give the desired N^2-aryl-1,2,3-triazole products **3** and **4**.

4,5-diphenyl-2-(p-tolyl)-2H-1,2,3-triazole (3a). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 86.8 mg (0.28 mmol), 93% yield, m.p. 105–107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 6.5, 3.1 Hz, 4H), 7.40 (dd, *J* = 4.9, 1.7 Hz, 6H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.8, 137.8, 137.4, 131.1, 129.9, 128.7, 128.7, 128.6, 118.9, 21.2. **HRMS** (ESI) m/z calcd. for $C_{21}H_{18}N_3^+$ 312.1501, found 312.1500 $[M+H]^+$.

2-(3,5-dimethylphenyl)-4,5-diphenyl-2H-1,2,3-triazole (3b). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 78.1 mg (0.24 mmol), 80% yield, m.p. 108–110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.66 (m, 4H), 7.45 – 7.33 (m, 6H), 7.00 (s, 1H), 2.42 (s, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.9, 139.8, 139.3, 131.0, 129.3, 128.7, 128.7, 128.6, 116.7, 21.5. **HRMS** (ESI) m/z calcd. for $C_{22}H_{20}N_3^+$ 326.1657, found 326.1658 $[M+H]^+$.

2-(4-isopropylphenyl)-4,5-diphenyl-2H-1,2,3-triazole (3c). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 93.8 mg (0.27 mmol), 90% yield, m.p. 108–110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.04 (m, 2H), 7.68 (s, 4H), 7.50 – 7.29 (m, 8H), 3.08 – 2.87 (m, 1H), 1.32 (d, *J* = 6.6 Hz, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 148.4, 145.8, 137.9, 131.1, 128.7, 128.7, 128.6, 127.3, 119.0, 33.9, 24.1. **HRMS** (ESI) m/z calcd. for $C_{23}H_{22}N_3^+$ 340.1814, found 340.1808 $[M+H]^+$.

2-(4-(tert-butyl)phenyl)-4,5-diphenyl-2H-1,2,3-triazole (3d). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 68.9 mg (0.20 mmol), 65% yield, m.p. 70–72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.65 (dd, *J* = 6.5, 3.1 Hz, 4H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.37 (m, 5H), 7.36 – 7.29 (m, 1H), 1.38 (s, 9H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 150.8, 145.8, 137.6, 131.1, 128.7, 128.7, 128.6, 126.3, 118.7, 34.8, 31.5. **HRMS** (ESI) m/z calcd. for $C_{24}H_{24}N_3^+$ 354.1970, found 354.1968 $[M+H]^+$.

4-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-N,N-dimethylaniline (3e). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.2), 71.5 mg (0.21 mmol), 70% yield, m.p. 145–147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9.1 Hz, 2H), 7.66 (dd, *J* = 7.4, 1.9 Hz, 4H), 7.46 – 7.29 (m, 6H), 6.80 (d, *J* = 9.1 Hz, 2H), 3.02 (s, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 150.0, 145.1, 131.4, 130.4, 128.7, 128.5, 128.5, 120.2, 112.4, 40.7, 40.5. **HRMS** (ESI) m/z calcd. for $C_{22}H_{21}N_4^+$ 341.1766, found 341.1768 $[M+H]^+$.

2-(4-methoxyphenyl)-4,5-diphenyl-2H-1,2,3-triazole (3f). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.2), 83.5 mg (0.26 mmol), 85% yield, m.p. 84–86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.1 Hz, 2H), 7.70 (dd, *J* = 6.5, 3.0 Hz, 4H), 7.50 – 7.35 (m, 6H), 7.05 (d, *J* = 9.1 Hz, 2H), 3.89 (s, 3H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 159.2, 145.7, 133.8, 131.2, 128.8, 128.7, 128.6, 120.4, 114.5, 55.8. **HRMS** (ESI) m/z calcd. for $C_{21}H_{18}N_3O^+$ 328.1450, found 328.1451 $[M+H]^+$. For the reacton based on 6 mmol (1.16 g) of 2*H*-azirines, the product **3f** was obtained in 81% yield (1.59 g).

2-(3-methoxyphenyl)-4,5-diphenyl-2H-1,2,3-triazole (3g). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.2), 92.3 mg (0.28 mmol), 94% yield, m.p. 100–102 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 2H), 7.75 – 7.62 (m, 4H), 7.42 (dd, *J* = 4.0, 2.8 Hz, 7H), 6.98 – 6.86 (m, 1H), 3.92 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 160.5, 146.1, 140.9, 130.9, 130.2, 128.8, 128.7, 128.6, 113.7, 111.2, 104.3, 55.7. **HRMS** (ESI) m/z calcd. for $C_{21}H_{18}N_3O^+$ 328.1450, found 328.1451 $[M+H]^+$.

2-(2-methoxyphenyl)-4,5-diphenyl-2H-1,2,3-triazole (3h). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.1), 84.5 mg (0.26 mmol), 86% yield, m.p. 92–94 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 6.4, 2.1 Hz, 5H), 7.50 – 7.41 (m, 1H), 7.38 (dd, *J* = 5.0, 1.7 Hz, 5H), 7.15 – 7.03 (m, 2H), 3.90 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 153.9, 145.7, 131.0, 130.6, 129.9, 128.7, 128.6, 128.6, 127.4, 120.8, 113.0, 56.5. **HRMS** (ESI) m/z calcd. for $C_{21}H_{18}N_3O^+$ 328.1450, found 328.1447 $[M+H]^+$.

2,4,5-triphenyl-2H-1,2,3-triazole (3i). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 78.5 mg (0.26 mmol), 88% yield, m.p. 93–95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 – 8.12 (m, 2H), 7.72 – 7.60 (m, 4H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.47 – 7.37 (m, 6H), 7.36 (d, *J* = 7.5 Hz, 1H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.1, 139.9, 130.9, 129.4, 128.8, 128.7, 128.6, 127.5, 118.9. **HRMS** (ESI) m/z calcd. for $C_{20}H_{16}N_3^+$ 298.1344, found 298.1349 $[M+H]^+$.

4,5-diphenyl-2-(4-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (3j). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.2), 76.7 mg (0.21 mmol), 70% yield, m.p. 107–109 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.70 – 7.56 (m, 4H), 7.50 – 7.37 (m, 5H), 7.36 – 7.29 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.31. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 147.3 (d, *J* = 261.7 Hz), 147.1, 142.1, 138.7, 130.3 (d, *J* = 43.6 Hz), 129.2, 128.8, 128.6, 128.4, 126.8 (q, *J* = 3.7 Hz). **HRMS** (ESI) m/z calcd. for $C_{21}H_{15}N_3F_3^+$ 366.1218, found 366.1218 $[M+H]^+$.

1-(4-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)phenyl)ethanone (3k). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.2), 89.6 mg (0.26 mmol), 88% yield, m.p. 140–142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H), 7.75 – 7.55 (m, 4H), 7.50 – 7.28 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 197.0, 147.1, 142.8, 135.7, 130.5, 129.9, 129.1, 128.8, 128.6, 118.5, 26.8. **HRMS** (ESI) m/z calcd. for $C_{22}H_{18}N_3O^+$ 340.1450, found 340.1458 $[M+H]^+$.

2-(4-iodophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3l). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.4), 111.7 mg (0.26 mmol), 88% yield, m.p. 138–140 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.71 – 7.58 (m, 4H), 7.48 – 7.33 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.4, 139.5, 138.4, 130.6, 128.9, 128.8, 128.6, 120.5, 92.1. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3I^+$ 424.0311, found 424.0316 $[M+H]^+$.

2-(4-bromophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3m). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.4), 99.3 mg (0.26 mmol), 88% yield, m.p. 117–119 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.54 (m, 6H), 7.52 – 7.29 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.5, 138.9, 132.5, 130.7, 128.9, 128.8, 128.6, 121.0, 120.3. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3Br^+$ 376.0449, found 376.0443 $[M+H]^+$.

2-(4-fluorophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3n). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 80.4 mg (0.26 mmol), 85% yield, m.p. 106–108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 – 8.05 (m, 2H), 7.73-7.56 (m, 4H), 7.49 – 7.36 (m, 6H), 7.19 (t, *J* = 8.6 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.71. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 161.9 (d, *J* = 246.9 Hz), 146.2, 136.2, 130.8, 128.9, 128.8, 128.6, 120.6 (d, *J* = 8.4 Hz), 116.2 (d, *J* = 23.1 Hz). **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3F^+$ 316.1250, found 316.1255 $[M+H]^+$.

2-(4-chlorophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3o). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.4), 85.6 mg (0.26 mmol), 86% yield, m.p. 83–85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.01 (m, 2H), 7.77 – 7.56 (m, 4H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.45 – 7.35 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.4, 138.3, 133.0, 130.7, 129.5, 128.9, 128.7, 128.6, 120.0. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3Cl^+$ 332.0955, found 332.0959 $[M+H]^+$.

2-(3-chlorophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3p). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.4), 95.6 mg (0.29 mmol), 96% yield, m.p. 76–78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (t, *J* = 1.9 Hz, 1H), 8.15 – 8.03 (m, 1H), 7.72 – 7.57 (m, 4H), 7.43 (dd, *J* = 9.6, 6.3 Hz, 8H), 7.37 – 7.28 (m, 1H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.6, 140.7, 135.3, 130.6, 130.5, 129.0, 128.8, 128.6, 127.4, 119.1, 116.9. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3Cl^+$ 332.0955, found 332.0948 $[M+H]^+$.

2-(2-chlorophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3q). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography

(petroleum ether/ethyl acetate = 30:1, R_f = 0.4), 83.6 mg (0.25 mmol), 84% yield, m.p. 78–80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 1H), 7.72 – 7.63 (m, 4H), 7.64 – 7.54 (m, 1H), 7.48 – 7.32 (m, 8H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.2, 138.1, 131.2, 130.7, 130.2, 129.5, 128, 128.7, 128.6, 127.7, 127.5. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3Cl^+$ 332.0955, found 332.0960 $[M+H]^+$.

2-(3-bromo-4-fluorophenyl)-4,5-diphenyl-2H-1,2,3-triazole (3r). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 98.2 mg (0.25 mmol), 83% yield, m.p. 82–84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 8.3 Hz, 1H), 7.69 – 7.58 (m, 4H), 7.51 (dd, *J* = 10.3, 2.0 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.42 – 7.34 (m, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.35. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 154.2 (d, *J* = 260.9 Hz), 146.9, 130.4, 129.0, 128.8, 128.6, 128.0 (d, *J* = 4.0 Hz), 127.7 (d, *J* = 9.0 Hz), 125.9, 121.8 (d, *J* = 8.3 Hz), 121.3 (d, *J* = 23.0 Hz). **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_3FBr^+$ 394.0355, found 394.0361 $[M+H]^+$.

2-(naphthalen-1-yl)-4,5-diphenyl-2H-1,2,3-triazole (3s). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 62.5 mg (0.18 mmol), 60% yield, m.p. 42–44 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 – 8.42 (m, 1H), 8.00 (d, *J* = 5.7 Hz, 1H), 7.96 (d, *J* = 6.5 Hz, 2H), 7.73 (dd, *J* = 6.5, 3.1 Hz, 4H), 7.64 – 7.57 (m, 3H), 7.49 – 7.36 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.1, 136.9, 135.0, 134.7, 130.9, 130.1, 129.6, 129.3, 129.3, 129.2, 128.9, 128.8, 128.7, 128.4, 127.6, 127.6, 126.8, 125.2, 124.0, 122.9. **HRMS** (ESI) m/z calcd. for $C_{24}H_{18}N_3^+$ 348.1501, found 348.1494 $[M+H]^+$.

2-([1,1'-biphenyl]-2-yl)-4,5-diphenyl-2H-1,2,3-triazole (3t). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.4), 100.8 mg (0.27 mmol), 90% yield, m.p. 82–84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 1H), 7.61 – 7.50 (m, 3H), 7.44 (dd, *J* = 6.6, 2.9 Hz, 4H), 7.39 – 7.29 (m, 9H), 7.23 (dd, *J* = 6.6, 2.9 Hz, 2H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.5, 139.1, 138.6, 137.9, 131.3, 130.9, 129.3, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.3, 126.0. **HRMS** (ESI) m/z calcd. for $C_{26}H_{20}N_3^+$ 374.1657, found 374.1660 $[M+H]^+$.

methyl 3-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)thiophene-2-carboxylate (3u). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 86.7 mg (0.24 mmol), 80% yield, m.p. 111–113 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.3, 2.8 Hz, 4H), 7.56 (d, *J* = 5.3 Hz, 1H), 7.48 (d, *J* = 5.3 Hz, 1H), 7.44 – 7.29 (m, 6H), 3.85 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 160.9, 146.2, 140.6, 130.6, 129.9, 128.8, 128.7, 128.6, 126.1, 124.4, 52.5. **HRMS** (ESI) m/z calcd. for $C_{20}H_{16}N_3O_2S^+$ 362.0963, found 362.0966 $[M+H]^+$.

3-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)quinoline (3v). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.1), 43.9 mg (0.13 mmol), 42% yield, m.p. 157–159 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.82 (d, *J* = 2.4 Hz, 1H), 8.85 (d, *J* = 2.1 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.74 (dd, *J* = 11.3, 4.0 Hz, 1H), 7.69 (dd, *J* = 6.5, 2.9 Hz, 4H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.34 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 147.2, 147.0, 142.7, 133.2, 130.5, 129.7, 129.7, 129.1, 128.9, 128.7, 128.3, 127.9, 127.7, 123.5. **HRMS** (ESI) m/z calcd. for $C_{23}H_{17}N_4^+$ 349.1453, found 349.1459 $[M+H]^+$.

4-phenyl-2,5-di-p-tolyl-2H-1,2,3-triazole (4a). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 82.0 mg (0.25 mmol), 84% yield, m.p. 90–92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.73 – 7.60 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.41 (ddd, *J* = 7.0, 6.2, 1.9 Hz, 3H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.9, 145.7, 138.6 , 137.8, 137.3, 131.2, 129.9, 129.4, 128.7, 128.6, 128.6, 128.5, 128.1, 118.8, 21.5, 21.2. **HRMS** (ESI) m/z calcd. for $C_{22}H_{20}N_3^+$ 326.1657, found 326.1650 $[M+H]^+$.

4-(4-fluorophenyl)-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4b). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 94.9 mg (0.29 mmol), 96% yield, m.p. 93–95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.62 (td, *J* = 5.3, 2.2 Hz, 4H), 7.41 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 – 6.97 (m, 2H), 2.42 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.80. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 248.2 Hz), 145.7, 144.9, 137.7, 137.5, 130.9, 130.4, 130.4, 130.0, 128.8, 128.6, 127.1 (d, *J* = 3.3 Hz), 118.8, 115.8 (d, *J* = 21.7 Hz), 21.2. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}N_3F^+$ 330.1407, found 330.1406 $[M+H]^+$.

4-(4-chlorophenyl)-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4c). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 93.4 mg (0.27 mmol), 90% yield, m.p. 109–101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.63 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.42 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.8, 144.6, 137.6, 137.6, 134.7, 130.8, 129.9, 129.8, 129.5, 129.0, 128.9, 128.8, 128.6, 118.8, 21.2. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}N_3Cl^+$ 346.1111, found 346.1109 $[M+H]^+$.

4-(furan-2-yl)-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4d). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 52.4mg (0.17 mmol), 58% yield, m.p. 58–60 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.81 – 7.65 (m, 2H), 7.54 (s, 1H), 7.51 – 7.40 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.56 – 6.36 (m, 1H), 2.42 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.8, 145.7, 143.1, 137.7, 137.6, 130.6, 129.9, 129.0, 128.8, 128.7, 119.0, 111.5, 109.8, 100.1, 21.2. **HRMS** (ESI) m/z calcd. for $C_{19}H_{16}N_3O^+$ 302.1293, found 302.1298 $[M+H]^+$.

4-(4-bromophenyl)-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4e). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 99.5 mg (0.26 mmol), 85% yield, m.p. 106–108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.62 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.53 (s, 4H), 7.46 – 7.37 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.42 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.9, 144.7, 137.7, 131.9, 131.6, 131.6, 130.8, 130.1, 130.0, 128.9, 128.9, 128.6, 122.9, 118.9, 21.2. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}N_3Br^+$ 390.0606, found 390.0608 $[M+H]^+$.

4-phenyl-2,5-di-p-tolyl-2H-1,2,3-triazole (4f). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 90.8 mg (0.28 mmol). 93% yield, m.p. 90–92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.73 – 7.60 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.41 (ddd, *J* = 7.0, 6.2, 1.9 Hz, 3H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.9, 145.7, 138.6 , 137.8, 137.3, 131.2, 129.9, 129.4, 128.7, 128.6, 128.6, 128.5, 128.1, 118.8, 21.5, 21.2. **HRMS** (ESI) m/z calcd. for $C_{22}H_{20}N_3^+$ 326.1657, found 326.1650 $[M+H]^+$. Compound **4f** was identidical as **4a**.

4-(4-chlorophenyl)-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4g). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 89.2 mg (0.26 mmol), 86% yield, m.p. 109–101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.63 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.42 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.8, 144.6, 137.6, 137.6, 134.7, 130.8, 129.9, 129.8, 129.5, 129.0, 128.9, 128.8, 128.6, 118.8, 21.2. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}N_3Cl^+$ 346.1111, found 346.1109 $[M+H]^+$. Compound **4g** was identidical as **4c**.

4-methyl-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4h). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 92.2 mg (0.26 mmol), 88% yield, m.p. 68–70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.90 – 7.73 (m, 2H), 7.51 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.45 – 7.36 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.61 (s, 3H), 2.43 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.2, 142.6, 137.8, 137.0, 131.2, 129.9, 128.9, 128.3, 127.5, 118.5, 21.2, 12.1. **HRMS** (ESI) m/z calcd. for $C_{16}H_{16}N_3^+$ 250.1344, found 250.1345 $[M+H]^+$.

4-cyclopropyl-5-(2-fluorophenyl)-2-(p-tolyl)-2H-1,2,3-triazole (4i). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 53.7 mg (0.18 mmol), 61% yield, m.p. 41–43 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.74 (t, *J* = 6.9 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.28 (m, 4H), 2.46 (s, 3H), 2.12 – 1.85 (m, 1H), 1.18 – 0.96 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.06. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 249.7 Hz), 149.9, 142.1, 137.8, 137.0, 131.6 (d, *J* = 3.1 Hz), 130.5 (d, *J* = 8.0 Hz), 129.8, 124.4 (d, *J* = 3.7 Hz), 119.2 (d, *J* = 14.7 Hz), 118.6, 116.3 (d, *J* = 21.7 Hz), 21.2, 8.6, 6.8. **HRMS** (ESI) m/z calcd. for $C_{18}H_{17}N_3F^+$ 294.1407, found 294.1411 $[M+H]^+$.

4-pentyl-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4j). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 48.9 mg (0.16 mmol), 80% yield, m.p. 40–42 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.21 (m, 2H), 3.03 – 2.87 (m, 2H), 2.43 (s, 3H), 1.84 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.48 – 1.34 (m, 4H), 0.95 (t, *J* = 7.0 Hz, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 147.0, 146.0, 137.9, 136.9, 131.4, 129.8, 128.8, 128.3, 127.7, 118.6, 31.8, 28.7, 26.1, 22.5, 21.1, 14.1. **HRMS** (ESI) m/z calcd. for $C_{20}H_{24}N_3^+$ 306.1970, found 306.1968 $[M+H]^+$.

4-phenethyl-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4k). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 84.5 mg (0.25 mmol), 83% yield, m.p. 77–79 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.80 – 7.66 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.46 – 7.38 (m, 1H), 7.38 – 7.18 (m, 7H), 3.35 – 3.23 (m, 2H), 3.21 – 3.10 (m, 2H), 2.44 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.2, 146.0, 141.5, 137.9, 137.0, 131.2, 129.9, 128.9, 128.6, 128.4, 127.7, 126.3, 118.7, 35.1, 28.3, 21.2. **HRMS** (ESI) m/z calcd. for $C_{23}H_{22}N_3^+$ 340.1814, found 340.1814 $[M+H]^+$.

4-phenyl-5-(1-phenylethyl)-2-(p-tolyl)-2H-1,2,3-triazole (4l). Following the geneal procedure **A**, the product was conducted at 40 °C with a heating mantle and obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 76.7 mg (0.22 mmol), 72% yield, m.p. 60–62 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.52 – 7.41 (m, 5H), 7.41 – 7.32 (m, 4H), 7.29 (d, *J* = 7.9 Hz, 1H), 4.51 (q, *J* = 7.2 Hz, 1H), 2.48 (s, 3H), 1.85 (d, *J* = 7.2 Hz, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 149.4, 146.3, 145.0, 138.0, 137.0, 131.0, 129.8, 128.7, 128.6, 128.4, 128.3, 127.7, 126.5, 118.7, 37.1, 23.3, 21.2. **HRMS** (ESI) m/z calcd. for $C_{23}H_{22}N_3^+$ 340.1814, found 340.1813 $[M+H]^+$.

4-methyl-5-phenyl-2-(p-tolyl)-2H-1,2,3-triazole (4m). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 98.5 mg (0.28 mmol), 94% yield, m.p. 68–70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.90 – 7.73 (m, 2H), 7.51 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.45 – 7.36 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.61 (s, 3H), 2.43 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 146.2, 142.6, 137.8, 137.0, 131.2, 129.9, 128.9, 128.3, 127.5, 118.5, 21.2, 12.1. **HRMS** (ESI) m/z calcd. for $C_{16}H_{16}N_3^+$ 250.1344, found 250.1345 $[M+H]^+$. Compound **4m** was identidical as **4h**.

Synthesis of 4,5-diphenyl-2H-1,2,3-triazole (5). A 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with **3f** (0.5 mmol) and

CAN (1.35 mmol). The tube was degassed and backfilled with argon (3 times). CH_3CN (5 mL) and H_2O (0.5 mL) was added into the tube via a syringe. The reaction mixture was cooled down to -10 °C, and was stirred under an argon atmosphere. The reaction was complete in 6 days (monitored by TLC). The resulting mixture was extracted with CH_2Cl_2 (15 mL × 3) and water (10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1 and then 5:1) to give **5**. The title compound was obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.2), 75.2 mg (0.34 mmol), 68% yield, m.p. 128–130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 4H), 7.36 (s, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 142.7, 130.2, 128.8, 128.7, 128.4. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}N_3^+$ 222.1031, found 222.1031 $[M+H]^+$.

Synthesis of Triazoles 6a and 6b via *N*-Methylations. A 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with 5 (44.2 mg, 0.2 mmol) and K_2CO_3 (55.2 mg, 0.4 mmol). The tube was degassed and backfilled with argon gas (3 times). DMF (1mL) was added into the tube via a syringe and the reaction mixture was cooled down to 0 °C. Then the addition of CH_3I (56.8 mg, 0.4 mmol) was added. The reaction mixture was stirred at 0 °C for 8 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 6:1) to give **6a** and **6b**.

2-methyl-4,5-diphenyl-2H-1,2,3-triazole (6a). Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.5), 23.1 mg (0.01 mmol), 49% yield, m.p. 58–60 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.4, 2.9 Hz, 4H), 7.42 – 7.29 (m, 6H), 4.27 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 144.7, 131.2, 128.7, 128.4, 128.3, 41.9. **HRMS** (ESI) m/z calcd. for $C_{15}H_{14}N_3^+$ 236.1188, found 236.1188 $[M+H]^+$.

1-methyl-4,5-diphenyl-1H-1,2,3-triazole (6b). Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.2), 23.1 mg (0.01 mmol), 49% yield, m.p. 122–124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.55 – 7.45 (m, 3H), 7.41 – 7.32 (m, 2H), 7.28 (d, *J* = 7.2 Hz, 3H), 3.94 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 144.5, 134.2, 131.1, 13.0, 129.8, 129.5, 128.6, 128.0, 127.8, 127.0, 35.4. **HRMS** (ESI) m/z calcd. for $C_{15}H_{14}N_3^+$ 236.1188, found 236.1190 $[M+H]^+$.

Synthesis of Triazoles 7a and 7b via *N*-Benzylations. A 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with **5** (55.3 mg, 0.25 mmol) and K_2CO_3 (69.1 mg, 0.5 mmol). The tube was degassed and backfilled with argon gas (3 times). Acetone (3mL) was added into the tube via a syringe. Then BnBr (64.1 mg, 0.38 mmol) was added and the resulting reaction mixture was stirred at room temperature for 12 h at 30 °C with a heating mantle. Upon completion of the reaction (monitored by TLC), the solvent was removed by rotary evaporator, the mixture was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 6:1) to give **7a** and **7b**.

2-benzyl-4,5-diphenyl-2H-1,2,3-triazole (7a). Obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.5), 49.8 mg (0.16 mmol), 64% yield, m.p. 79–81 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 6.5, 3.1 Hz, 4H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.45 – 7.31 (m, 9H), 5.68 (s, 2H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 144.9, 135.4, 131.2, 128.9, 128.6, 128.4, 128.4, 128.2, 58.9. **HRMS** (ESI) m/z calcd. for $C_{21}H_{18}N_3^+$ 312.1501, found 312.1504 $[M+H]^+$.

1-benzyl-4,5-diphenyl-1H-1,2,3-triazole (7b). Obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.2), 24.9 mg (0.08 mmol), 32% yield, m.p. 102-104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.35 – 7.22 (m, 6H), 7.23 – 7.14 (m, 2H), 7.07 (m, 2H), 5.45 (s, 2H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 144.6, 135.5, 134.0, 131.1, 130.2, 129.8, 129.3, 128.8, 128.5, 128.2, 128.0, 127.8, 127.6, 126.8, 52.2. **HRMS** (ESI) m/z calcd. for $C_{21}H_{18}N_3^+$ 312.1501, found 312.1503 $[M+H]^+$.

Synthesis of Triazoles 8a and 8b via *N*-alkylations. A 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with 5 (44.0 mg, 2 mmol) and K_2CO_3 (55.2 mg, 0.4 mmol). The tube was degassed and backfilled with argon gas (3 times). DMF (2mL) was added into the tube via a syringe. Then $BrCH_2CO_2Et$ (66.8 mg, 0.4 mmol) was added and the resulting reaction mixture was stirred at room temperature for 8 h. Upon completion of the reaction (monitored by TLC), the solvent was removed by rotary evaporator, the mixure was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 6:1) to give **8a** and **8b**.

ethyl 2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)acetate (8a). Obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.6), 46.0 mg (0.16 mmol), 75% yield, m.p. 101-103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.3 Hz, 4H), 7.36 (s, 6H), 5.27 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 166.9, 145.7, 130.9, 128.7, 128.6, 128.5, 62.3, 55.8, 14.3. **HRMS** (ESI) m/z calcd. for $C_{18}H_{18}N_3O_2^+$ 308.1399, found 308.1400 $[M+H]^+$.

ethyl 2-(4,5-diphenyl-1H-1,2,3-triazol-1-yl)acetate (8b). Obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.3), 9.2 mg (0.03 mmol), 15% yield, m.p. 42-44 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.54 – 7.45 (m, 3H), 7.31 – 7.27 (m, 2H), 5.99 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 166.6, 144.5, 134.7, 130.9, 130.1, 130.1, 129.6, 128.6, 128.0, 127.6, 127.0, 62.4, 49.4, 14.2. **HRMS** (ESI) m/z calcd. for $C_{18}H_{18}N_3O_2^+$ 308.1399, found 308.1403 $[M+H]^+$.

Generation Procedure B: Synthesis of 1,2,3-Traizoles bearing Electron-Deficient *N*-aryl groups (9). A 10 mL Schlenk tube equipped with a stirring bar and capped with

a rubber septum was charged with 5 (0.05 mmol), ArX (0.05 mmol) and K_2CO_3 (0.05 mmol). The tube was degassed and backfilled with argon gas (3 times). DMF (0.5 mL) was added into the tube via a syringe. The reaction mixture was stirred for 5 h at 70-120 °C with a heating mantle. Upon completion of the reaction (monitored by TLC), the solvent was removed by rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) to give **9**.

2-(4-nitrophenyl)-4,5-diphenyl-2H-1,2,3-triazole (9a). Following the Generation Procedure **B**, the reaction mixture was stirred for 5 h at 120 °C and the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 10:1, R_f = 0.5), 16.3 mg (0.05 mmol), 95% yield, m.p. 151–153 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 – 8.30 (m, 4H), 7.65 (dd, *J* = 6.5, 2.9 Hz, 4H), 7.51 – 7.33 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 147.9, 146.4, 143.7, 130.1, 129.4, 128.9, 128.6, 125.4, 118.9. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_4O_2^+$ 343.1195, found 343.1194 $[M+H]^+$.

2-(2-nitrophenyl)-4,5-diphenyl-2H-1,2,3-triazole (9b). Following the Generation Procedure **B**, the reaction mixture was stirred for 5 h at 70 °C and the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.6), 16.1 mg (0.05 mmol), 94% yield, m.p. 51–53 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.77 – 7.67 (m, 1H), 7.61 (dd, *J* = 6.5, 3.1 Hz, 4H), 7.55 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.46 – 7.33 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 147.5, 132.8, 132.3, 130.2, 129.2, 128.8, 128.7, 128.7, 125.0, 125.0, 99.8. **HRMS** (ESI) m/z calcd. for $C_{20}H_{15}N_4O_2^+$ 343.1195, found 343.1194 $[M+H]^+$.

2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)benzonitrile (9c). Following the Generation Procedure **B**, the reaction mixture was stirred for 5 h at 120 °C and the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.4), 15.3 mg (0.05 mmol), 95% yield, m.p. 99–101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.79 – 7.64 (m, 5H), 7.54 – 7.35 (m, 7H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 147.3, 140.5, 135.4, 133.7, 130.2, 129.2, 128.8, 128.7, 127.7, 122.2, 117.2, 104.6. **HRMS** (ESI) m/z calcd. for $C_{21}H_{15}N_4^+$ 323.1297, found 323.1297 $[M+H]^+$.

2-(2-fluoro-4-nitrophenyl)-4,5-diphenyl-2H-1,2,3-triazole (9d). Following the Generation Procedure **B**, the reaction mixture was stirred for 5 h at 90 °C and the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.6), 15.3 mg (0.04 mmol), 85% yield, m.p. 128–130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (t, *J* = 8.2 Hz, 1H), 8.27 – 8.17 (m, 2H), 7.64 (dd, *J* = 7.1, 2.4 Hz, 4H), 7.41 – 7.26 (m, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.50. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 153.0 (d, *J* = 261.9 Hz), 148.1 (d, *J* = 2.0 Hz), 146.7 (d, *J* = 7.6 Hz), 132.9 (d, *J* = 8.2 Hz), 129.9, 129.4, 128.9, 128.7, 124.3, 120.1 (d, *J* = 4.0 Hz), 114.3 (d, *J* = 25.2 Hz). **HRMS** (ESI) m/z calcd. for $C_{20}H_{14}N_4O_2F^+$ 361.1101, found 361.1109 $[M+H]^+$.

2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-5-nitropyridine (9e). Following the Generation Procedure **B**, the reaction mixture was stirred for 5 h at 80 °C and the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.4), 16.5 mg (0.05 mmol), 96% yield, m.p. 170–172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 2.5 Hz, 1H), 8.67 (dd, *J* = 9.1, 2.6 Hz, 1H), 8.35 (d, *J* = 9.1 Hz, 1H), 7.66 (dd, *J* = 7.6, 1.5 Hz, 4H), 7.51 – 7.33 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 153.4, 149.4, 145.7, 143.0, 134.4, 129.7, 129.6, 128.8, 113.6. **HRMS** (ESI) m/z calcd. for $C_{19}H_{14}N_5O_2^+$ 344.1147, found 344.1145 $[M+H]^+$.

2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-3-nitropyridine (9f). Following the Generation Procedure **B**, the reaction mixture was stirred for 5 h at 120 °C and the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.2), 14.9 mg (0.04 mmol), 87% yield, m.p. 126–128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71 – 7.58 (m, 4H), 7.55 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.7 – 7.32 (m, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 151.5, 148.6, 142.2, 139.5, 134.2, 129.7, 129.4, 128.9, 128.8, 123.5. **HRMS** (ESI) m/z calcd. for $C_{19}H_{14}N_5O_2^+$ 344.1147, found 344.1147 $[M+H]^+$.

methyl 2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-5-methylbenzoate (10a). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 97.5 mg (0.26 mmol), 88% yield, m.p. 105–107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 (dd, *J* = 6.5, 3.0 Hz, 4H), 7.56 (s, 1H), 7.47 – 7.32 (m, 7H), 3.78 (s, 3H), 2.45 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 168.2, 146.0, 138.5, 135.7, 132.3, 130.8, 130.3, 128.7, 128.7, 128.6, 128.5, 126.5, 123.5, 52.7, 21.1. **HRMS** (ESI) m/z calcd. for $C_{23}H_{20}N_3O_2^+$ 370.1556, found 370.1563 $[M+H]^+$.

methyl 2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-5-methoxybenzoate (10b). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 70.5 mg (0.18 mmol), 61% yield, m.p. 43–45 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.63 (dd, *J* = 6.4, 2.8 Hz, 4H), 7.47 – 7.34 (m, 6H), 7.31 – 7.26 (m, 1H), 7.13 (dd, *J* = 8.9, 2.8 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 167.4, 159.3, 145.8, 131.7, 130.9, 128.7, 128.5, 128.0, 125.6, 117.6, 114.6, 55.9, 52.7. **HRMS** (ESI) m/z calcd. for $C_{23}H_{20}N_3O_3^+$ 386.1505, found 386.1506 $[M+H]^+$.

methyl 2-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-6-fluorobenzoate (10c). Following the geneal procedure **A**, the product was obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 101.9 mg (0.27 mmol), 91% yield, m.p. 113–115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.63 (dd, *J* = 6.6, 2.9 Hz, 4H), 7.52 (td, *J* = 8.3, 6.0 Hz, 1H), 7.45 – 7.32 (m, 6H), 7.14 (t, *J* = 8.5 Hz, 1H), 7.14 (t, *J* = 8.5 Hz, 1H), 3.93 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.13. **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 164.6, 160.0 (d, *J* = 250.0 Hz), 146.6, 137.4 (d, *J* = 6.0 Hz), 131.5 (d, *J* = 9.4 Hz), 130.3, 129.1, 128.7,

128.5, 116.4 (d, J = 3.3 Hz), 115.1 (d, J = 23.0 Hz), 114.7, 114.5, 53.2. **HRMS** (ESI) m/z calcd. for $C_{22}H_{17}N_3O_2F^+$ 374.1305, found 374.1308 $[M+H]^+$.

Synthesis of 1,1'-Binaphthalene Scaffolds bearing 1,2,3-Triazoles (11a and 11b). An oven-dried 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with 2*H*-azirine (**1f'**, 0.3 mmol), arene-diazonium salt (0.6 mmol), CuBr (0.06 mmol), and DABCO (0.3 mmol). The tube was evacuated under *vacuo* and then backfilled with argon (for three times). CH_3CN (3.0 mL) was transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere at room temperature for 16 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether / ethyl acetate) to give the desired product **11a** and **11b**.

2-([1,1'-binaphthalen]-2-yl)-4-phenyl-5-(p-tolyl)-2H-1,2,3-triazole (11a). Obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 38.0 mg (0.01 mmol), 26% yield, m.p. 56–55 °C. $[\alpha]_D^{20}$ = –167.8 (*c* 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.9 Hz, 2H), 7.63 – 7.32 (m, 7H), 7.29 (d, J = 8.2 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.17 – 7.10 (m, 2H), 7.09 – 6.96 (m, 4H), 2.32 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.1, 144.9, 138.2, 136.9, 134.9, 133.8, 133.7, 133.5, 133.1, 132.0, 130.9, 129.3, 129.1, 128.8, 128.4, 128.3, 128.2, 128.1, 128.1, 127.8, 127.6, 127.1, 126.8, 126.9, 126.3, 125.8, 125.4, 122.6, 21.4. **HRMS** (ESI) m/z calcd. for $C_{35}H_{26}N_3^+$ 488.2127, found 488.2126 $[M+H]^+$.

2,2'-bis(4-phenyl-5-(p-tolyl)-2H-1,2,3-triazol-2-yl)-1,1'-binaphthalene (11b). Obtained as a yellow solid after column chromatography (petroleum ether/ethyl acetate = 30:1, R_f = 0.3), 51.9 mg (0.01 mmol), 24% yield, m.p. 110–112 °C. $[\alpha]_D^{20}$ = +123 (*c* 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.55 – 7.41 (m, 4H), 7.36 – 7.29 (m, 2H), 7.24 – 7.19 (m, 2H), 7.17 (d, J = 7.9 Hz, 3H), 7.13 (d, J = 7.7 Hz, 5H), 7.02 (d, J = 8.1 Hz, 4H), 6.96 (d, J = 8.1 Hz, 4H), 2.30 (s, 6H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 145.2, 145.0, 138.0, 136.9, 134.4, 132.8, 131.1, 129.3, 129.0, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.4, 127.3, 126.5, 121.9, 21.4. **HRMS** (ESI) m/z calcd. for $C_{50}H_{37}N_6^+$ 721.3080, found 721.3081 $[M+H]^+$.

Radical trap experiment. An oven-dried 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with 2*H*-azirine (**1a**, 0.3 mmol), aryldiazonium salt (**2a**, 0.6 mmol), CuBr (0.06 mmol), DABCO (0.3 mmol), and TEMPO (0.6 mmol). The tube was evacuated under *vacuo* and then backfilled with argon (for three times). CH_3CN (3.0 mL) was transferred into the tube via a syringe. The resulting mixture was stirred under an argon atmosphere at room temperature for 16 h and then subjected to HRMS analysis. The mass spectra presented a peak at m/z 351.2430, which likely corresponded to the TEMPO-trapped product **12**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental details and spectral data of all new compounds (PDF).

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Notes

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