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Synthesis of Functional 1,2,3-Triazoles and Its Applications in Transition Metal Catalysis

Wuming Yan
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Synthesis of Functional 1,2,3-Triazoles and Its Applications in Transition Metal Catalysis

Wuming Yan

**Dissertation submitted to the
Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Organic Chemistry**

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Morgantown, West Virginia
2012**

**Keywords: Functional 1,2,3-Triazoles, Transition Metal Catalysis, Allene,
Conjugated Enyne, Fluorophore, Planar-Intramolecular-Charge-Transfer, Iron
Chemistry, Photoredox Catalysis**

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ABSTRACT

Synthesis of Functional 1,2,3-Triazoles and Its Applications in Transition Metal Catalysis

Wuming Yan

Several new methodologies for synthesizing functional 1,2,3-triazoles which include arylation, vinylation, propargylation and allenation, have been successfully developed. These resulting new methods are of great benefit to the organic chemists who are working on the research fields related to 1,2,3-triazoles. Particularly, the iron catalyzed propargylation and allenation have initiated the iron chemistry with 1,2,3-triazoles as the ligand. For example, our efforts led to the discovery of a practical approach for the synthesis of conjugated enynes that is challenging through conventional methods. In the synthesis of conjugated enyne, 1,2,3-triazoles were revealed as the only ligand effectively promoting this important and challenging transformation (gave up to 95% yields). Other tested N-heterocycles, including the 1,2,4-triazole, tetrazole, and pyridine, all gave poor results (< 10%) even with similar binding pattern, which demonstrating the unique role of 1,2,3-triazole in iron catalysis.

In addition, the complexes $[\text{Ir}(\text{L}^{\wedge}\text{X})(\text{ArTriaz})_2]$ and $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$ have been successfully prepared through N-2-aryl-1,2,3-triazoles as the efficient binding ligands in coordination with iridium salt in excellent yields. These air and moisture stable Ir(III) complexes showed effective catalytic reactivity in photoredox catalysis.

The N-2-aryl-1,2,3-triazole derivatives (NATs) were developed as a new class of UV/blue-light-emitting fluorophores. Though both N-1-aryl-1,2,3-triazoles and N-2-aryl-1,2,3-triazoles gave strong photo absorption under excitation at 330 nm, only the N-2-analogue showed strong fluorescence emission in the UV/blue range with high efficiency in various solvents. The computational studies along with X-ray crystal structures indicated the significance of the effective conjugation between triazole ring and aryl groups on the N-2 position. The planar intramolecular charge transfer (PICT) mechanism was proposed, which was supported by solvent effect studies.

DEDICATED TO

My wife, Yalan XING, my daughter, Emma Jiayun YAN

My parents, Qingshen YAN, Baixiang YAN

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Chapter One: Synthesis of functional 1,2,3-triazoles

1.1 Introduction

1.1.1 Synthesis of precursor: *NH*-1,2,3-triazole

The 1,3-dipolar cycloaddition reaction between two unsaturated reactants gave an access to various five-membered heterocycles, which was developed by Huisgen in the early 1960's.¹ The cycloaddition of acetylenes and azides to synthesize 1,2,3-triazoles is by far the most useful member of this family. However, the 1,3-dipolar cycloaddition of terminal alkynes and organic azides afforded the 1,2,3-triazole as the mixture of 1,4-adduct and 1,5-adduct under thermal conditions (**Scheme 1**),² since the activation energies for the formation of both adducts were very close in this concerted process based on the mechanism study. In addition, the 1,4-adduct can be obtained only if the acetylene component is attached to an electron-withdrawing group (EWG), such as a carbonyl or cyano group (CN).³ However, these reactions usually required long reaction time and high temperature as alkynes are poor 1,3-dipole receptors.⁴

Scheme 1: Thermal 1,3-dipolar cycloaddition of acetylenes and azides.

To avoid these disadvantages of Huisgen azide-alkyne cycloaddition, Sharpless and co-workers have successfully discovered that the cycloaddition reaction is dramatically accelerated in the presence of copper catalyst, to give the 1,4-disubstituted 1,2,3-triazoles with excellent regioselectivity and high efficiency (yields are > 95%).⁵ Furthermore, this

copper catalyzed azide-alkyne cycloaddition (CuAAC), which is referred to as “click chemistry”, was well tolerant to various other functional groups and can be performed in various organic solvents, and water with a variety of (partially) miscible organic solvents, including DMSO, DMF, *t*BuOH and acetone (**Scheme 2**).

Scheme 2: The synthesis of 1,4-disubstituted 1,2,3-triazoles by Click chemistry.

Although several Cu(I) sources can be used directly in this process, such as copper(I) bromide (CuBr) or copper(I) iodide (CuI), the catalyst was better prepared in situ by the reduction of Cu(II) salts (e.g. CuSO₄) with reductants such as sodium ascorbate or ascorbic acid (**Scheme 3**). This transformation exhibited a broad substrate scope and produced the 1,4-disubstituted 1,2,3-triazoles in good to excellent yields with near perfect regioselectivity.

Scheme 3: Example of CuAAC reported by Shapless.

The reaction mechanism has been investigated using density functional theory calculations (DFT).⁶ The copper(I) species generated in situ formed a π -complex with the triple bond of a terminal alkyne. In the presence of a base, the terminal hydrogen, being the most acidic was deprotonated first to give a Cu(I) acetylide intermediate (therefore

indicated why internal alkynes failed to react by this process). Studies have shown that the transition state involved two copper atoms. One copper atom was bonded to the acetylide while the other Cu atom served to activate the azide. The metal center coordinated with the electrons on the nitrogen atom. The azide and the acetylide were not coordinated to the same Cu atom in this case. The ligands employed were labile and weakly coordinating. The azide displaced one ligand to generate a copper-azide-acetylide complex (CuAAC). At this point cyclization took place and followed by protonation; the source of proton being the hydrogen which was pulled off from the terminal acetylene by the base. The product was formed by dissociation of copper-azide-acetylide complex and the catalyst ligand complex was regenerated for further reaction cycles (**Figure 1**).

Figure 1: Proposed reaction mechanism of “Click chemistry”

Since the discovery of the CuAAC reaction in 2001, the 1,2,3-triazoles have been the subject of considerable research mainly due to their usefulness as the valuable synthetic intermediates in organic chemistry⁷ and also because of the important biological properties, which have found broad use in biology⁸ and medicinal chemistry.⁹ However,

despite being a very efficient method for the synthesis of N-substituted triazoles, one major limitation of the CuAAC was the lack of reactivity toward unsubstituted azides, such as NaN_3 and HN_3 . Therefore, to prepare *NH*-1,2,3-triazoles by CuAAC, the organic azides were usually applied with removable *N*-protecting groups followed by the deprotection (**Scheme 4**).¹⁰

Scheme 4: Synthesis of *NH*-1,2,3-triazoles through CuAAC.

Besides the CuAAC approach, the 1,3-dipolar cycloaddition between α -nitroalkene and sodium azide was considering another popular methodology for the synthesis of *NH*-1,2,3-triazoles and was first reported by Zefirov in 1971.¹¹ With DMSO as the solvent, the authors reported the formation of corresponding triazole at room temperature in roughly 60% yield along with “considerable quantities” of the corresponding byproduct 1,3,5-triarylbenzene (**Scheme 5**).

Scheme 5: The synthesis of *NH*-1,2,3-triazoles by Zefirov’s method.

However, Zard and co-worker re-examined this reaction in 2005 and discovered the above result was not reproducible.¹² As a result, they figured out the optimal condition

which involved a slow addition of α -nitroalkene to a hot solution of the excess amount of sodium azide (2-4 equiv.) at 80-90 °C (**Scheme 6**).

Scheme 6: Thermal condensation of α -nitroalkene and sodium azide (Zard's method).

Under the optimized condition, the *NH*-1,2,3-triazoles could be obtained in good to excellent yields (96% in one single case) with a very small amount of the byproduct 1,3,5-triarylbenzene. However, the challenging access of the olefin precursor α -nitroalkene significantly limited the application of this reaction.

Our group reported a Lewis base-catalyzed cascade nitroalkene-aldehyde-azide condensation for the synthesis of 4,5-disubstituted *NH*-1,2,3-triazoles in 2008 (**Scheme 7**).¹³ More than 25 new *NH*-1,2,3-triazoles were prepared in good to excellent yields under mild conditions. The C-5 vinyl group of triazole can be readily converted into other functional groups.

Scheme 7: Shi's Approach: Lewis base-catalyzed cascade nitroalkene-aldehyde-azide condensation.

The reaction mechanism was also investigated (**Figure 2**). The 1-aryl diene intermediate was produced by the Hertz reaction of nitroalkene and aldehyde, and then

quenched by azide anion (N_3^-) to give cycloaddition product triazole with elimination of the nitro group (NO_2^-).

Figure 2: Mechanism for synthesis of 4,5-disubstituted *NH*-1,2,3-triazoles.

1.1.2 Our strategy: How to reach the N-2 substitution of *NH*-1,2,3-triazoles?

To the best of our knowledge, the copper catalyzed azide-alkyne cycloaddition (CuAAC) gave N-1 substituted triazoles only (see **section 1.1.1**), due to the nature of azides. Alternatively, N-2 substituted triazoles may be accessed by the conversion of non-substituted *NH*-triazoles with appropriate electrophiles. However, as we know, before 2008, no effective strategy for regioselective N-2 substituted of 1,2,3-triazoles had been reported in the literature.

With a strong dipole moment and high electron density on the nitrogens, the *NH*-1,2,3-triazole could be a good nucleophile, which will react with electrophiles under suitable conditions. However, among the reported examples,¹⁴ the N-1 substituted triazoles were the dominant products. This was caused by the higher electron density associated with two terminal nitrogens (N-1 and N-3) than the internal nitrogen (N-2). Therefore, regioselective N-2 substitution was a big challenge in triazole derivatization.

To develop an efficient synthesis of N-2 substituted triazoles, our group has put numerous efforts and concluded successfully a strategy which was that the C-4 and C-5

substituent groups could deliver the necessary steric hindrance to provide N-2 as the preferred nucleophilic site (**Figure 3**).

Figure 3: Strategy for selective N-2 substitution (two bulky groups on C-4 and C-5).

To evaluate the effectiveness of this strategy, our group has developed successfully the N-2 alkylation of *NH*-1,2,3-triazoles (**Scheme 8**).¹⁵

Scheme 8: Synthesis of N-2-alkyl-1,2,3-triazoles.

As reported in the paper, the N-2 alkylation reactions usually gave very less amount of N-3 substituted triazoles. From the crystal structures,* the aryl group on the C-4 position was nearly coplanar with the triazole ring. The N-3 position was then blocked for electrophilic addition (**Figure 4**). Surprisingly, the benzyl ketone triazole gave excellent N-2 selectivity and even formed only the N-2 product in some cases (**Scheme 9**). Based on the conformational control analysis, the benzoyl group on C-5 position would like to be coplanar with the triazole ring to minimize the electronic repulsion

* Check the compounds **2a**, **N-1-3a**, **N-1-5a** and **N-2-4a** in the supporting information of N-2 alkylation published paper (see **ref. 15**).

between the keto oxygen and the N-1 nitrogen (**Figure 5**). Therefore, the phenyl group effectively blocked the N-1 position.

Figure 4: The C-4 aryl group was nearly coplanar with the triazole ring.

Scheme 9: The alkylation of benzyl ketone triazole.

Figure 5: Conformational control for selective N-2 substitution.

1.2 Efficient synthesis of N-2-aryl-1,2,3-triazole fluorophores via post-triazole arylation[†]

1.2.1 Reported method for synthesizing N-2-aryl-1,2,3-triazole

One important class of triazole derivatives is the N-2-aryl triazoles, where the two aromatic rings adopt a coplanar conformation. With the characteristic electron density distribution in the HOMO and LUMO, these bis-aromatic compounds give unique photonic properties. One example is the commercially available *o*-hydroxyphenyl benzotriazoles (such as Tinuvin P), which has been applied as an efficient light absorber to prevent polymer degradation from light radiation.¹⁶

Currently, the general approach for N-2-aryl triazole involves the hydrazine/ α -hydroxyketone condensation,¹⁷ as shown in **Scheme 10**. The need of various aryl hydrazines and α -hydroxyketones as starting materials significantly limited the application of this methods and only specific N-2 aryl triazole can be prepared with good yields. Therefore, an effective regioselective N-2 arylation approach will be of great importance for the triazole related research.¹⁸

Scheme 10: The hydrazine/ α -hydroxyketone condensation.

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1.2.2 Research Objective and Results

Our group has recently reported the synthesis of 4,5-disubstituted-NH-traizoles through Lewis base catalyzed process.¹³ With these compounds in hand, we recently reported a successful post-triazole N-2 alkylation through substrate conformation control.¹⁵ Encouraged by these results, we wondered if this strategy could be further extended to the regioselective N-2-arylation.

Table 1: Post-triazole arylation via S_NAr reactions^a

Entry	Triazole	Ar-X	Temp (°C)	Time (h)	Convsn (%) ^b	Yield (%) ^c	N-2 :N-1
1	1.2.1a	1.2.2a	rt	2	100	1.2.3a: 92	1:3
2	1.2.1b		rt	2	100	1.2.3b: 90	1.7:1 ^d
3	1.2.1c		rt	2	100	1.2.3c: 95	6:1
4	1.2.1d		rt	2	100	1.2.3d: 95	1:0
5	1.2.1c	1.2.2b: X = F; R = NO ₂	80	1	100	1.2.3e: 92	10:1
6	1.2.1c	1.2.2c: X = Cl; R = NO ₂	80	30	90	1.2.3e: 85	10:1
7	1.2.1c	1.2.2d: X = F; R = CN	80	30	66	1.2.3f: 62	10:1
8	1.2.1c	1.2.2b: X = Cl; R = CN	80	30	0	-	-

^a 1.2.1:1.2.2 = 1:1.5, c = 0.2 M; ^b based on the consumption of 1.2.1 by NMR; ^c isolated yields of all isomers; ^d structure of N-1-1.2.3b was determined by X-ray crystallography.

To evaluate the regioselectivity, the S_NAr substitution was first studied with a variety of 1,2,3-triazoles. The results are summarized in **Table 1**. Due to the absence of C-N bond exchange under the reaction condition in the arylation products **1.2.3**, the S_NAr reaction provided direct measurement of C-4 and C-5 groups influence on the regioselectivity. As indicated in **Table 1**, the benzotriazole **1.2.1a** gave modest selectivity with N-1 substituted triazole as the major product. On the other hand, the 4-phenyl triazole **1.2.1b** improved the N-2 selectivity, giving N-2 arylation as the major product, though with poor selectivity. To our pleasure, the application of 4,5-disubstituted triazole **1.2.1c** and **1.2.1d** gave N-2 arylation as the dominant products with excellent regioselectivity. As mentioned previously, the selectivity was driven by the conformation control of the C-4 and C-5 substitute groups. However, at higher temperature, the selectivity should be only driven by the steric effect. To our pleasure, increasing the reaction temperature (80 °C) gave improved N-2 selectivity (entry 5, 6 and 7), which suggested that the regioselectivity of post-triazole arylation could be achieved at higher temperature. Moreover, the less electron-deficient substrates were also suitable for this S_NAr transformation to form the corresponding N-2 arylation products as dominate products (entries 5-7). Although the S_NAr reaction of triazoles gave excellent N-2 regioselectivity, it only worked with electron-deficient aromatic halide substrates.

To extend the generality of N-2 arylation of 1,2,3-triazoles, we then explored the possible coupling strategy for aromatic systems with higher electron density. Numerous copper catalyzed N-aryl halide reactions have been reported in the last several years, but the reaction mechanism was not clear.¹⁹ The most likely mechanism involves a Cu(I) oxidative addition to Cu(III) intermediate followed by reductive elimination, which was

proposed by Buchwald, Hartwig and Stahl.²⁰ Hartwig also suggested that oxidative addition of the carbon halogen bond likely occurs in the catalytic cycles with strong ligand effects.^{20b} Based on these remarkable results, we rationalized that *NH*-1,2,3-triazole might be another good nitrogen source for copper mediated aryl halide amidation. With the focus on the ligand effect for optimal performance, reactions between *NH*-triazole **1.2.1c** and phenyl iodide **1.2.5a** were then carried out (**Table 2**).

Table 2: Screening reaction conditions for coupling with PhI^a

Entry	Cu cat	Ligand ^c	Solvent	Temp (°C)	Time (h)	Convsn (%) ^d	Yield (%) ^d
1	CuI	-	DMSO	110	24	low	0
2	CuI	proline	DMSO	110	24	100	71
3	CuCl	proline	DMSO	110	24	100	88
4	other ^b Cu cat.	proline	DMSO	110	24	<92	<79
5	CuCl	proline	other solvents ^b	110	24	<85	<74
6	CuCl	proline	DMSO	w 160	0.5	98	92
7	CuCl	glycine	DMSO	w 160	0.5	trace	trace
8	CuCl	Me-Gly	DMSO	w 160	0.5	60	30
9	CuCl	DMG	DMSO	w 160	0.5	98	86
10	CuCl	EDA	DMSO	w 160	0.5	53	29
11	CuCl	DMEDA	DMSO	w 160	0.5	70	47
12	CuCl	TMEDA	DMSO	w 160	0.5	trace	trace
13	CuCl	DACH	DMSO	w 160	0.5	53	44

^a **1.2.1c:1.2.4a** = 1:1.5, c = 0.2 M; ^b see supporting information; ^c Me-Gly: N-methyl glycine; DMG: N,N-dimethyl glycine; EDA: ethylenediamine; DMEDA: N,N'-dimethylethylenediamine; TMEDA: N,N,N',N'-tetramethylethylenediamine; DACH: *trans*-diaminohexane; ^d Based on the ¹H NMR with 1,3,5-trimethoxybenzene as internal standard.

Among all the tested reactions, the coupling product **1.2.5a** was not formed, if no ligands were applied. Different nitrogen containing ligands have been investigated in this Cu mediated amidation of *NH*-triazole, and we found proline was the best ligand for this transformation. To our satisfaction, excellent regioselectivity was received with N-2 arylation as the dominant product. Both Cu(I) and Cu(II) could effectively catalyze this reaction (entries 2-4). Screening of the solvents gave DMSO as the solvent choice. Considering of its low cost, good reaction performance and easy handling, CuCl was selected as the catalyst for this reaction. The optimal reaction condition is shown in entry 3. The use of microwave irradiation significantly shortened the reaction time from 24 hours to 30 minutes.

With the optimal reaction conditions, different *NH*-triazoles and aryl iodides were applied to evaluate the reaction substrate scope (**Table 3**). As shown in **Table 3**, benzotriazole **1.2.1a** gave the N-1 arylation as the dominant product with only 8% N-2 product isolated. The N-2 selectivity was increased while 4-phenyl substituted **1.2.1b** was applied, giving 60% N-2 isomer with another 15% N-1 isomer and only trace amount of N-3 isomer. Significant difference was observed when 4,5-disubstituted triazoles were used, where, as expected, in all cases only N-2 isomers were isolated with excellent yields. The substrate scope of this transformation covered different substituted groups on C-5 position of triazoles and various aryl iodides with EDG, EWG and pyridine. Due to the diminished reactivity of aryl bromides in the oxidative addition, application of aryl bromides resulted in significant decrease in the reaction conversion and yield. Moreover, this copper mediated aryl halide amidation of 1,2,3-*NH*-triazoles did not work well with a heterocyclic halide, because of the chelating interaction between heterocyclic structure

and copper catalyst. Notably, the substrate **1.2.1j** gave 45% of desired N-2 arylation product **1.2.5j** and 40% of N-3-arylation product N-3-**1.2.5j** (structures were determined by X-ray diffraction), which suggested the Cu-chelation between the phenol oxygen and triazole-N-3 position. The production of the steric disfavored N-3 arylation product strongly supports the Cu(III) reductive elimination mechanism.

Table 3: Substrate scope for Cu catalyzed triazole amidation^a

	ArI	yield (%) ^b		ArI	yield (%) ^b
1.2.1a	1.2.4a	1.2.5b: 8 ^c	1.2.1f	1.2.4a	1.2.5f: 60
1.2.1b	1.2.4a	1.2.5c: 68 ^d	1.2.1g	1.2.4a	1.2.5g: 85
1.2.1c	1.2.4a	1.2.5a: 87	1.2.1h	1.2.4a	1.2.5h: 87
1.2.1d	1.2.4a	1.2.5d: 85 ^e	1.2.1i	1.2.4a	1.2.5i: 80
1.2.1e	1.2.4a	1.2.5e: 85	1.2.1j	1.2.4a	1.2.5j: 45 ^{e,f}
1.2.1c	1.2.4b: R = <i>p</i> -Me	1.2.5k: 86	1.2.1c		1.2.4h 1.2.5r: 70
1.2.1d	1.2.4c: R = <i>p</i> -NO ₂	1.2.5l: 88	1.2.1c		1.2.4i 1.2.5s: 70
1.2.1c	1.2.4d: R = <i>p</i> -OMe	1.2.5m: 74	1.2.1d		1.2.4j 1.2.5t: 60
1.2.1i	1.2.4e: R = <i>o</i> -Me	1.2.5n: 70	1.2.1c		1.2.4j 1.2.5u: 70 ^e
1.2.1c	1.2.4f: R = <i>p</i> -I	1.2.5o: 67 ^{e,g}			
1.2.1c		1.2.4g 1.2.5p: 88			
1.2.1d		1.2.5q: 83 ^e			

^a **1.2.1:1.2.4** = 1:1.5, ^c 0.2 M; ^b Isolated yield; ^c N-1-**1.2.5b** 60% yield; ^d N-1-**1.2.5c** 11% yield. ^e Structure determined by X-ray crystallography. ^f N-3-**1.2.5j** 40% yield; ^g di-amidation product **1.2.5v** was formed in 10%.

The strong dependence on ligands of this transformation* initiated our interest in evaluating trans-metallation as an alternative pathway to further extend the substrate scope, especially for heterocyclic substrates. Therefore, the trans-metallation reactions between triazoles **1.2.1c** and phenyl boronic acid **1.2.6a** were investigated. Excitingly, transmetallation indeed produced the desired N-2 arylation product. Further screening of reaction conditions revealed THF as the best solvent (see other conditions in supporting information) (**Scheme 11**). To achieve the efficient turnover of the copper catalyst, oxygen gas was required.

Scheme 11: Copper catalyzed transmetalation between triazoles and boronic acids.

1.2.1c + Ph-B(OH)₂ 1.2.6a	$\xrightarrow{\text{conditions}}$	1.2.5a	conditions	yields (%)
			Cu(OAc) ₂ (1.5 equiv), DCM, rt, 12 h	88
			Cu(OAc) ₂ (0.2 equiv), THF, rt, 12 h	45
			Cu(OAc) ₂ (0.2 equiv), THF, 60 °C, 1 atm O ₂ , 12 h	89

Figure 6: Products from trans-metallation coupling with arylboronic acids.

Reaction conditions: **1.2.1c**:**1.2.6** = 1:1.5, c = 0.1 M, THF, 0.2 equiv. Cu(OAc)₂, 2 equiv, pyridine, O₂ 1 atm, 50 °C, 24 h.

* Check the detail in **Table 2** (entry 6-13).

With triazole **1.2.1c**, the N-2 isomer was the only product isolated, while **1.2.1a** and **1.2.1b** gave less than 40% N-2 isomers. We then focused on applying this strategy for the synthesis of N-2 aryl substrates that were difficult to be prepared from aryl iodide amidation. The results are summarized in **Figure 6**.

Finally, with a series of new N-2-aryl-1,2,3-triazoles in hand, the photonic properties which included UV absorption and fluorescence emission have evaluated. Besides the strong UV absorptions, the new triazole derivatives N-2-aryl-1,2,3-triazoles produced strong photonic luminescence and their emission pattern really depended on the substituted groups.

Figure 7: Comparison of photonic luminescence of selected N-1 and N-2-aryl triazoles (1.2.5b and 1.2.5c): the sample was measured in CH₃OH, *c* = 10 μM; λ_{ex} = 254 nm.

The importance of fluorescence active molecules has been well documented in various research fields.²¹ As shown in the **Figure 7**, both N-2 phenyl 1,2,3-triazoles (**1.2.5b** and **1.2.5c**) gave strong fluorescence emissions, while N-1 aryl analogues gave

weak emissions. These results suggested the N-2-aryl group is crucial for photonic emission. More importantly, the 4,5-disubstituted triazoles showed much stronger emission comparing to benzyl triazole derivatives (**Figure 8**). The N-2-aryl-1,2,3-triazoles as a new class of UV-Blue emitting fluorophores have been systematic investigated (see **Chapter Three**).²²

Figure 8: Photonic luminescence of N-2-aryl triazoles with different substituted groups on the C-5 position: the sample was measured in CH₃OH, *c* = 10 μM; λ_{ex} = 254 nm.

1.2.3 Conclusion

In conclusion, the first regioselective post triazole-arylation of *NH*-1,2,3-triazoles was developed through substrate controlled N-arylation. The importance of ligand effect in the copper mediated coupling with aryl iodide was observed and optimal condition allowed the formation of N-2 aryl products in excellent yields. Alternative approaches, including S_NAr and boronic acid transmetallations, have also been proved with excellent

regioselectivity. Moreover, the newly prepared N-2 aryl products gave interesting photonic luminescent emission, which re-emphasized the significance of the N-2-aryl-triazoles and reported methodologies.

1.3 Highly efficient synthesis of vinyl substituted triazoles by Au(I) catalyzed alkyne activation[†]

1.3.1 Reported methods for synthesis vinyl substituted triazoles

N-vinyl 1,2,3-triazole is a member of vinyl monomer family (**Figure 9**),²³ which provides the attractive features of thermal and chemical stability and functional handles from reactive groups in the synthesis of advanced materials. As we can see, in the N-vinyl triazole, it has a very unique structure, reminiscent of both styrene (aromaticity) and vinyl pyridine (lone pairs),²⁴ which displays a range of novel properties in the polymerization profiles similar to styrenic/acrylate systems.

Figure 9: Structures of N-vinyl 1,2,3-triazoles.

From the retrosynthetic analysis, the N-vinyl 1,2,3-triazole could be synthesized by the cycloaddition of alkynes with vinyl-substituted azides through either thermo conditions²⁵ or metal catalyzed 1,3-dipolar cycloadditions. However, specifically, the metal catalyzed cycloaddition between alkynes and vinyl-substituted azides has never been reported in literature, possibly due to the poor stability of vinyl-substituted azides (high-energy material) and existence of different resonance structures in vinyl-substituted azides (**Scheme 12**). As a result, the preparation of vinyl-triazole was very challenging.

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Scheme 12: Vinyl azide: challenging substrate for dipolar cycloaddition due to the existence of equilibrium.

Figure 10: Synthesis of N-vinyl 1,2,3-triazole via elimination of alkyl triazole.

Besides the elimination of alkyl substituted triazole approach (**Figure 10**), most two general methods have been reported in literature in the preparation of N-vinyl 1,2,3-triazoles. One was the elimination of alkyl halide (**Scheme 13**).²⁶ In this elimination approach, significant amounts of bis-triazole byproducts were usually formed and the substrate scope was very limited. Another one was the cyclization of vinyl azides with a highly reactive benzyne intermediate (**Scheme 14**).²⁷ The benzyne click chemistry provided an alternative strategy in preparing triazoles, however, again, it suffered poor yields and limited substrate scope.

Scheme 13: Elimination of alkyl halide.

Scheme 14: Benzyne click chemistry.

Therefore, efficient synthetic routes to access vinyl-triazoles are highly desirable. Considering the strong nucleophilicity of NH-1,2,3-triazole, we wondered whether the NH-triazole alkyne addition could be achieved as a new strategy for the synthesis of vinyl triazoles with high efficiency and a broad substrate scope.

1.3.2 Research Objective and Results

To optimize the reaction condition, the reactions between benzotriazole **1.2.1a** and phenylacetylene **1.3.2a** were performed in the presence of various catalysts (**Table 4**). Reactions at room temperature gave either very low yields or no reaction at all for all catalysts tested (included In(OTf)₃, AuCl, AuCl₃ and PPh₃AuCl). By increasing the reaction temperature, the Au(I) catalysts were identified as the best catalysts in activating the triple bond other than other metals catalysts as listed in the **Table 4**. With 5% loading of PPh₃AuOTf at 80 °C, the desired vinyl triazole **1.3.3a** was obtained in quantitative yield (entry 5). The reaction gave excellent regio-selectivity, where by only the N-1 substituted Markovnikov's product was observed. As indicated in entry 7, the product was obtained in excellent yield (92%) even with 0.2% loading of PPh₃AuOTf catalyst, though a longer reaction time (12h) required. Some other catalysts, such as In(OTf)₃, indicated modest reactivity (68% yield), but the superior efficiency of the PPh₃AuOTf catalyst made itself an ideal catalyst for this transformation. Different alkynes were then applied to the reaction to investigate the substrate scope. The results are summarized in **Table 5**.

Table 4: Screening of catalyst for triazole-alkyne addition.^a

Entry	Catalyst	Loading (%)	Temp (°C)	Time (hour)	Yields ^b (%)
1	AuCl	5	80	6	82
2	AuCl ₃	5	80	6	88
3	PPh ₃ AuOTf	5	rt	12	15
4	PPh ₃ AuOTf	5	50	20	60
5	PPh ₃ AuOTf	5	80	5	> 99%
6	PPh ₃ AuOTf	1	80	6	96
7	PPh ₃ AuOTf	0.2	80	12	92
8	CuI	5	80	12	N.R.
9	Cu(OAc) ₂	5	80	12	N.R.
10	Sc(OTf) ₂	5	80	12	< 5%
11	HOTf	5	80	12	10
12	In(OTf) ₃	5	80	12	68%
13	La(OTf) ₃	5	80	12	N.R.
14	AgOTf	5	80	12	20
16	Pd(OAc) ₂	5	80	12	N.R.

^a Reactions were carried out by dissolving **1.2.1a** (1.0 equiv), **1.3.2a** (1.5 equiv) and catalyst in toluene (0.2 M); ^b Determined by crude NMR.

From **Table 5**, the transformation was suitable for a variety of substituted alkynes. The terminal alkynes gave higher than 90% yields of only the Markovnikov's products even with 0.2% catalyst loading (**1.3.3a-d**). Impressively, the reaction also worked very well with symmetric internal alkynes, which are usually challenging substrates to be activated by metal catalysts. With 1% catalyst loading, the desired addition products were

prepared in good yields (**1.3.3e-g**). Notably, the reaction reached excellent double-bond selectivity and only the *trans*-addition products were formed in all cases, though the regio-selectivity of the asymmetric alkynes was poor (**1.3.3h**, **1.3.3i**). The double-bond stereochemistry was confirmed by NOE experiments. Meanwhile, both alkyl and aryl substituted alkynes were suitable for this reaction.

Table 5: Substrate scope of alkynes in the Au(I) catalyzed triazole addition.^a

$\text{1.2.1a} + \text{R}^3\text{—}\equiv\text{—R}^4 \xrightarrow[\text{Tol, 80 } ^\circ\text{C}]{\text{PPh}_3\text{AuOTf}} \text{1.3.3}$

Alkyne	Product	Cat. (%)	Time (h)	Yield ^b (%)	
<i>p</i> -Me-Ph—≡—H		1.3.3b : R ³ = <i>p</i> -Me-Ph	0.2	12	94
<i>p</i> -F-Ph—≡—H		1.3.3c : R ³ = <i>p</i> -F-Ph	0.2	10	96
<i>n</i> -Bu—≡—H		1.3.3d : R ³ = <i>n</i> -Bu	0.2	12	90
Ph—≡—Ph		1.3.3e : R ³ =R ⁴ =Ph	1.0	30	70
<i>n</i> -Pr—≡— <i>n</i> -Pr		1.3.3f : R ³ =R ⁴ = <i>n</i> -Pr	1.0	20	83
TMS—≡—Me		1.3.3g : R ³ =CH ₃ , R ⁴ =H	1.0	12	82
Ph—≡—Me	<p>1.3.3h: 1:1 of the two regio isomer</p>	1.0	20	84	
<i>n</i> -Pr—≡—Me	<p>1.3.3i: 1:1 of the two regio isomer</p>	1.0	20	81	

^a Reactions were carried out by dissolving **1.2.1a** (1.0 equiv), **1.3.2** (1.5 equiv) and PPh₃AuOTf in toluene (0.2 M) and heating at 80 °C. ^b Isolated yields.

Scheme 15: Substituted scope of different *NH*-1,2,3-triazoles.

^a Reactions were carried out by dissolving **1.2.1** (1.0 equiv), **1.3.2** (1.5 equiv) and PPh₃AuOTf in toluene (0.2 M) and heating at 80 °C. ^b Ratio of the two products were determined by NMR.

With this highly efficient catalytic triazole addition strategy, we then investigated the N-selectivity with different *NH*-1,2,3-triazoles (**Scheme 15**). All *NH*-triazoles were suitable for this transformation, giving the alkyne addition products in excellent yields. Only *trans* additions were observed, giving exclusive single double-bond isomers. The substituents on the triazoles showed a strong influence on the N-regio-selectivity, where most C-4-phenyl substituted triazoles gave N-2 isomers as the major products. Increasing the steric hindrance on the C-4 and C-5 positions did not show a dramatic difference towards the regio-selectivity. However, application of carbonyl-substituted *NH*-triazole

led to the formation of a single N-2 isomer (**1.3.4i**), similar to the results from N-2 alkylation¹⁵ and N-2 arylation (see **Section 1.2**) of NH-triazoles.

1.3.3 Conclusion

In conclusion, the first successful method in achieving vinyl substituted 1,2,3-triazoles through the Au(I) catalyzed alkyne additions was developed. Various vinyl-triazoles were prepared in good to excellent yields (up to 98%) with as low as 0.2% catalyst loading. Furthermore, excellent stereoselectivity of double bonds was achieved. Considering the great efficiency, excellent stereoselectivity of double bonds, broad substrate scope and controllable triazole nitrogen regioselectivity, it is our belief that the reported method provides a good strategy for the preparation of various vinyl-triazoles and thereby benefiting researches involving 1,2,3-triazoles as building blocks in material science and medicinal chemistry.

1.4 Iron catalyzed C-O bond activation for the synthesis of propargyl-1,2,3-triazoles and 1,1-bis-triazoles[†]

1.4.1 Examples of traditional propargylation

The propargylic moiety is a widely distributed structure in medicinal and organic chemistry due to the high synthetic value of the alkyne functionality.²⁸ The electron-rich triple bond, in combination with the fairly acidic character of the terminal acetylenic hydrogen atom, makes it a versatile entity for further chemical transformations.²⁹ In addition, various natural products, fine chemicals and pharmaceuticals containing propargylic subunits as components of their structures have been reported.³⁰

In general, the propargylation could be challenging since the nucleophiles would potentially attack the triple bond other than propargyl position, to give corresponding allene intermediates that further convert into other products, such as Meyer-Schuster rearrangement (**Scheme 16**).³¹

Scheme 16: Meyer-Schuster rearrangement and its mechanism.

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In last several years, many methods regarding propargylation have been reported. One attractive method was the Brønsted acid catalyzed propargylation.³² Among these reactions, two of most common nucleophiles were 1,3-diester³³ and allylsilane.³⁴ Another efficient way for making this propargylic moiety was the direct propargylation of arenes or heteroarenes with propargyl alcohols via transition metal catalyzed Friedel-Crafts³⁵ and ene-type³⁶ alkylation reactions (**Scheme 17**).

Scheme 17: Metal promoted propargylation of arenes.

With the fast-growing research applications of 1,2,3-triazoles, the effective methods in preparing diverse 1,2,3-triazole derivatives are strongly needed. Therefore, we are committed to the development of new strategies to introduce functional groups on the nitrogen of the triazole ring. At this time, we are focused on the propargylation of *NH*-1,2,3-triazoles with propargyl alcohols to synthesize propargyl-1,2,3-triazoles.

1.4.2 Research Objective and Results

To investigate the propargylation of *NH*-1,2,3-triazole, we first studied the $\text{S}_{\text{N}}2$ reaction between benzotriazole **1.2.1a** and propargyl bromide **1.4.2a** and obtained propargyl-

1,2,3-triazole **1.4.3a** in excellent yield (98%) as shown in **Scheme 18**. We then wondered whether the propargyl triazoles could be produced via simple S_N2 reactions of propargyl acetates. The propargyl acetate **1.4.2b** was reacted with benzotriazole **1.2.1a** to give no reaction at all with a base Cs₂CO₃ (**Scheme 19**). Treating the acetate under harsher conditions (DMSO and strong base) led to the formation of complex reaction mixtures with no desired propargyl triazole **1.4.3b** observed. Moreover, attempts in converting propargyl alcohol **1.4.4a** into propargyl tosylate or halide failed, which was likely caused by the undesired side reactions (such as Nazarov cyclization³⁷) associated with propargyl carbon cations (better leaving groups). We therefore deduced that one practical synthesis of propargyl triazoles could likely occur from the effective C-O bond activation of readily available propargyl alcohol.

Scheme 18: Synthesis of propargyl triazole **1.4.3a**.

Scheme 19: Challenges in the triazole propargylation.

A series of different commonly used Lewis acid catalysts were investigated in promoting the propargylation of triazole **1.2.1a** and propargyl alcohol **1.4.4a**. The results are summarized in **Table 6**.

Table 6: Catalyst screening.^a

	Catalyst	Loading (%)	Solv.	Temp (°C)	Time (h)	Conv. (%) ^b	Yield (%) ^c	N1:N2 ^c
1	FeCl ₃	20	DCE	60	17	100	90	8:1
2	Cu(OAc) ₂	20	DCE	60	17	57	<5	
3	CuI	20	DCE	60	17	22	<5	
4	PdCl ₂	20	DCE	60	17	13	<5	
5	RuCl ₃	20	DCE	60	17	69	49	1.1:1
6	IrCl ₃	20	DCE	60	17	96	65	2:1
7	Co(OAc) ₂	20	DCE	60	17	28	<5	
8	LaCl ₃	20	DCE	60	17	21	<5	
9	CeCl ₃	20	DCE	60	17	30	<5	
10	Ti(O- <i>i</i> Pr) ₄	20	DCE	60	17	52	<5	
11	AlCl ₃	20	DCE	60	17	26	<5	
12	TfOH	20	DCE	60	17	100	35	1.5:1
13	H ₃ PO ₄	20	DCE	60	17	73	9	1:1
14	FeCl ₃	20	THF	60	7	90	70	6:1
15	FeCl ₃	20	Toluene	60	7	100	40	2:1
16	FeCl ₃	20	MeOH	60	7	60	44	7:1
17	FeCl ₃	20	MeNO ₂	60	7	90	<5	
18	FeCl ₃	20	DMF	60	7	<5	<5	

19	FeCl ₃	20	DMSO	60	7	<5	<5	
20	FeCl ₃	20	MeCN	60	7	91	85	10:1
21	FeCl ₃	20	MeCN	rt	12	62	50	9:1
22	FeCl ₃	20	MeCN	90	5	100	93	11:1
23	FeCl ₃	10	MeCN	90	10	100	90	10:1
24	FeCl ₃	5	MeCN	90	12	90	82	9:1

^aStandard reaction condition: 1 equiv propargyl alcohol **1.1.4a**, 1.2 equiv triazole **1.2.1a**, 0.2 equiv catalyst and solvent; ^b conversions were determined based on the consumption of **1.4.4a**; ^c yields determined by NMR with 1,3,5-trimethoxybenzene as internal standard, and ratio determined by NMR of crude reaction mixtures.

As shown in **Table 6**, the significant decomposition of **1.4.4a** occurred with most of the Lewis acid catalysts. Some catalysts, such as RuCl₃ and IrCl₃, promoted this reaction in modest yields, but gave poor regioselectivities of 1:1 to 2:1 ratio of N1/N2 isomers (entry 5, 6, 12 and 13). Based on the observed performance of the various catalysts, FeCl₃ was revealed as the effective catalyst in promoting this transformation and gave the desired product **1.4.3b** in good yield with high regioselectivity, with an 8:1 ratio of N1/N2 isomers (entry 1). Further solvent screening revealed that this reaction was totally shut down in polar solvents, like DMSO, DMF. Surprisingly, the reaction gave almost no product formation with the 90% conversion of propargyl alcohol when MeNO₂ applied as the reaction solvent, because of the formation of α,β -unsaturated ketone product from Meyer-Schuster rearrangement (entry 17). Finally, we found the MeCN as the optimal solvent (entries 15-20) to give effective conversion even with decreased catalyst loading (entries 23-24). With the optimal condition in hand, different triazoles and propargyl alcohols were applied to investigate the reaction substrate scope (**Figure 11**).

Figure 11: Substrate scope of triazole propargylation.^a

^a Yields were determined by NMR with 1,3,5-trimethoxybenzene as internal standard, and ratios determined by NMR of crude reaction mixtures. The N-2 **1.4.3f** structure was confirmed by X-ray crystallography.

As shown in **Figure 11**, this Fe(III)-catalyzed propargylation was suitable for various different propargyl alcohols, which further enriched the available methods for effective post-triazole functionalization. Similar to our previously reported strategy (see

Section 1.1.2), the regioselectivity of 1,2,3-triazole strongly depends on the nature of triazole substrates. For example, the benzotriazole gave primarily N-1 substituted products, while keto-modified 4,5-disubstituted triazoles produced the dominant N-2 isomers (i.e., **1.4.3c**, **1.4.3g**). Meanwhile, the C-4 phenyl triazole gave a mixture of both N-1 and N-2 isomers with roughly 4:1 ratio, favoring the N-2 isomer.

The substituted groups on the propargyl position were critical for this transformation. The reaction generally worked well with aromatic substituted propargyl alcohols, except substrates with strong electron withdrawing groups (the *p*-nitrobenzene gave no reaction). No reactions were observed with aliphatic substituted propargyl alcohols due to the insufficient reactivity of C-O bond. Impressively, the reaction proceeded smoothly with vinyl-substituted substrate (such as **1.4.3r**), giving the corresponding triazole substituted enynes in excellent yields. Notably, Nazarov cyclization products were not observed in these reactions (**Figure 12**), which highlighted the rather mild conditions of the reported method.

Figure 12: Potential formation of Nazarov cyclization product with vinyl-substituted propargyl alcohols.

Excellent yields were generally received for internal alkynes with different substituted groups, including alkyl, aryl, TMS, and cyclopropyl. The reaction was also suitable for terminal alkynes and gave the corresponding propargyl triazoles in good yields based on NMR. Surprisingly, these substrates were not stable upon condensation for further purification purpose and gave complex mixtures (**Scheme 20**). We then thought the terminal propargyl triazoles would undergo further transformations in the presence of FeCl_3 . To remove the FeCl_3 factor, the deprotection of TMS protected propargyl triazole **1.4.3n** was carried out. Unfortunately, we obtained exactly the same result, which was the decomposition of terminal propargyl triazole upon condensation. One potential pathway could be triazole-alkyne 5-endo-dig cyclization which has been reported by Chen in our group.³⁸

Scheme 20: Unexpected decomposition of terminal propargyl triazole.

1.4.3 Application in synthesis of 1,1-bis-triazoles via ‘click’ chemistry

During the last four years, our group has been working on the development of 1,2,3-triazole derivatives as ligands in transition metal catalysis.³⁹ These triazole complexes have shown significant influence on the metal catalyst reactivity by serving as effective

nitrogen σ -donor. Our further studies of triazole-metal coordination initiated our interest in the synthesis the bis-triazole compounds as potential interesting bidentate ligands to coordinate with transition metal cations.

Scheme 21: Three Different Types of Bis-triazole Compounds.

Considering the different kind of substitution pattern, the bis-triazole compounds could be summarized in three different classes: N-N type,⁴⁰ C-C type,⁴¹ and N-C type (**Scheme 21**). While the N-N and C-C type bis-triazoles have been successfully synthesized from either post-triazole alkylation (**Scheme 21a**)¹⁵ or double click chemistry (**Scheme 21b**), the N-C type bis-triazoles have not been reported. These unsymmetrical N-C type bis-triazoles, especially the 1,1-bis-triazoles, are particularly interesting because of the presence of the stereocenter. A brief synthetic design of this type of compounds is shown in **Scheme 21c**, where the two triazole moieties are introduced by post-triazole propargylation and sequentially click chemistry. Although the retrosynthesis design looked straightforward, the actual preparation was much more challenging than we expected, especially the click chemistry of propargyl triazoles.

The click chemistry worked well with terminal alkynes rather than internal alkynes. However, the terminal propargyl triazoles undergo decomposition upon condensation, as we mentioned before. Therefore, we focused on searching a proper displacement of terminal propargyl triazole which can be applied in click chemistry, such as readily prepared TMS protected propargyl triazole.

Scheme 22: Synthesis of unsymmetrical N-C type bis-triazoles.^a

^a Isolated yields for all cases.

With the click chemistry of TMS protected alkynes, the universal procedures were TMS deprotection under basic condition first and subsequently ‘click’ chemistry in two individual steps. However, we have combined the TMS deprotection and click chemistry in one single step. Fortunately, the reactions between TMS protected propargyl triazoles

and corresponding azides gave the desired bis-triazoles (**1.4.5a-h**) in excellent yields under standard “click chemistry” condition (**Scheme 22**).

1.4.4 Conclusion

In conclusion, a highly efficient FeCl₃ catalyzed post-triazole propargylation method was developed, giving the desired propargyl triazole in excellent yields. Application of this strategy led to the synthesis of unsymmetrical 1,1-bis-triazoles. This study not only provided another efficient post-triazole functionalization strategy for the preparation of diverse triazole propargyl analogues, but provided entry to a new class of 1,1-bis-triazole compounds, which would likely be of interest for medicinal chemistry research, transition metal catalysis and material science.

1.5 Synthesis of allene triazole through iron catalyzed regioselective addition to propargyl alcohols[†]

1.5.1 Previous approaches for synthesis allene compounds

During last few decades, allene chemistry has received ample attention from organic and medicinal chemists, due to their synthetic potential in regio- and stereoselective C-C and C-X bond forming reactions⁴² and unique axis-to-center chirality transfer properties.⁴³ Moreover, allene subunits have been widely found in many natural products and pharmacologically active compounds.⁴⁴ Therefore, the allene chemistry has created the great demand of new methods for synthesis of any kind of allenes as precursors.

All the classical reaction types (addition,⁴⁵ elimination,⁴⁶ substitution⁴⁷ and rearrangement⁴⁸) have been applied to the synthesis of allenes and transition metal catalyzed allene synthesis have also been developed.⁴⁹ Among these methods, one of most convenient and general strategy for the synthesis of allenes was the nucleophilic S_N2' substitution of propargylic compounds with a leaving group. A variety of labile groups, including propargylic acetates, mesylates, carbonates, and halides, etc. have been used as leaving groups (**Figure 13**).

Figure 13: Most general method for synthesis allenes via nucleophilic S_N2' substitution.

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In the nucleophilic S_N2' substitutions, various types of nucleophiles, such as hydrides, halides, and organometallic reagents, have been employed. With hydride nucleophiles, most common hydride sources were aluminum hydride reagents, such as lithium aluminum hydride (LiAlH_4), and diisobutylaluminum hydride (DIBAL-H).⁵⁰ Recently, $\text{Cp}_2\text{Zr(H)Cl}$ has been applied to the *anti*- S_N2' -type reductive substitution of the *in situ* generated zinc or magnesium alkoxides of propargylic alcohols furnishing allenes in good yields and high ee's (**Scheme 23**).⁵¹ This approach provided stereospecific access to allenes directly from propargylic alcohols and then greatly improved the efficiency.

Scheme 23: $\text{Cp}_2\text{Zr(H)Cl}$ catalyzed preparation of chiral allenes.

Haloallenes were synthesized by the S_N2' substitutions of propargyl alcohols with halide nucleophiles which are useful substrates in substitution reactions⁵² and transition-metal catalyzed cross-coupling reactions.⁵³ The typical reaction condition for the preparation of haloallenes from propargyl alcohols was Appel-type reaction condition containing halide source (NXS or CBr_4) and appropriate OH activating reagent, such as phosphane-like PPh_3 , $(n\text{-Bu})_3\text{P}$ and trisubstituted amines (*i*-PrNEt) (**Scheme 24**).⁵⁴ Other conditions also have been reported. For example, treatment of propargyl diethanolamine boronates with N-halosuccinimides gave the corresponding allenyl halides in high yields (**Scheme 25**).⁵⁵ Moreover, the reaction of secondary or tertiary propargylic alcohols with NbBr_5 afforded allenyl bromides in moderate to good yields (**Scheme 26**).⁵⁶

Scheme 24: Appel-type reactions for synthesis haloallenes.

Scheme 25: Synthesis of haloallenes from propargyl diethanolamine boronates.

Scheme 26: Formation of bromoallenes by using NbBr_5 as the catalyst and bromide source.

Allenes can be synthesized *via* the direct $\text{S}_{\text{N}}2'$ addition of organometallic reagents, such as copper,⁵⁷ indium,⁵⁷ zinc⁵⁸ etc. to propargylic alcohols. Especially, diorganocopper reagents (Gilman's cuprates) have been widely used to prepare allenes from propargyl moieties with excellent chemoselectivity of $\text{S}_{\text{N}}2'$ substitutions rather than direct $\text{S}_{\text{N}}2$ reactions.⁵⁹ There are also many different organocopper catalysts involving a catalytic amount of a copper(I) salt (like CuBr) with an excess amount of organometallic reagents, which included organolithium,⁶⁰ Grignard reagents,⁶¹ organozinc,⁶² and organozirconium, have been reported in the literature (**Scheme 27**).⁶³

Scheme 27: Application of organometallic reagents in preparation of allenes.

1.5.2 Examples for allene as either ligand or catalyst.

It is well known that the allene compound has played an important role in the organic reactions as synthetic intermediate. However, there are only a few examples of allenes being used as catalysts or ligands have been reported in the literature. The first example was reported by Soai and co-workers in 2002. They have developed the asymmetric synthesis of pyrimidin-5-yl alkanol in the addition of $(i\text{-Pr})_2\text{Zn}$ to pyrimidine-5-carbaldehyde with excellent ee's by using chiral 1,3-disubstituted hydrocarbon allenes as catalysts (**Scheme 28**).⁶⁴ Later, they also pointed out the actual effectiveness of the allene as a chiral modulator was difficult to gauge because other experiments with the same system indicated that a strong nonlinear effect coupled with autocatalysis conspire to amplify even unmeasurable enantiomeric excesses.⁶⁵

Scheme 28: Enantioselective addition of $(i\text{-Pr})_2\text{Zn}$ to 2-(alkynyl)pyrimidine-5-carbaldehyde in the presence of chiral allenes.

In 2009, Ready and co-workers demonstrated that chirality of chiral allenes can be transferred to products in asymmetric catalysis. In the paper, they prepared a series of allene-containing biphosphine oxide catalysts, which were utilized in the asymmetric ring opening of *meso*-epoxides reactions with good enantioselectivities (**Scheme 29**).⁶⁶ The allene-containing biphosphine oxide catalysts revealed the very high efficiency in the reaction (0.1% loading only). Moreover, they successfully used chiral allene-containing biphosphine oxides as ligands in transition metal catalysis in 2011 (**Scheme 30**).⁶⁷

Scheme 29: Asymmetric ring opening of *meso*-epoxides with SiCl₄.

Scheme 30: Enantioselective addition of boronic acids to α -keto esters catalyzed by Rh^I(AllenePhos) complexes.

These studies opened the potential door of allenes compounds in the asymmetric catalysis. Considering the triazole binding pattern, we wondered whether the allenyl triazoles have the unique catalytic properties in transition metal catalysis. However, more

importantly, there is no effective method for synthesis of allenyl triazoles. We subsequently reported for the first time, the successful synthesis of allene triazoles through iron catalyzed regioselective triazole addition to the propargyl alcohol.

1.5.3 Research Objective and Results

Based on the literature reported strategies, two common approaches were proposed for the allene-triazole synthesis. One proposed pathway for synthesis of allene-triazole involves the deprotonation of propargyl triazoles at the propargyl position, followed by the treatment with H^+ or other electrophiles (**Scheme 31**).

Scheme 31: Proposed approaches from deprotonation of propargyl triazoles.

Unfortunately, the treatment of propargyl triazole **1.4.3a** with different base like *n*BuLi or KO^tBu followed by the quenching with either water or NBS gave a complex reaction mixture with no allene product formation. We then focused on alternative plausible S_N2' strategy, the triazole addition to propargyl alcohol derivatives. However, the reaction between propargyl acetate **1.5.2a** and benzotriazole **1.2.1a** gave no allene product even after the reaction mixture was refluxed for 10 hours with triazole anion

(**Scheme 32**). These results suggested that the synthesis of an allene-triazole was indeed a great challenge using conventional methods.

Scheme 32: Proposed S_N2' strategy of propargyl acetate with triazole anion.

Considering our previous success in the synthesis of propargyl triazoles through iron-catalyzed C-O bond activation, we decided to apply this process for the preparation of allene triazoles. According to literature, few examples have been reported for synthesis of allenes from propargyl alcohols by directly using Lewis acids as the catalysts (**Scheme 33**).⁶⁸

Scheme 33: Lewis acids activation strategy for synthesizing allenes.

As shown in **Figure 14**, the propargylation product can be formed if triazole substituted on the propargylic position (S_N2), while the allenation product will be produced if the triazole attacked the triple bond (S_N2'). Therefore, the di-substituted propargyl alcohols will be used with the hope to increase the steric hindrance at the propargyl position to direct the triazole to the alkyne based on our understanding of C-O bond activation. Although the di-substitution limited the reaction substrate scope, the

success of this strategy led to the first synthesis of the allene triazole and open the door for further development.

Figure 14: Iron-catalyzed C-O bond activation.

To test our hypothesis, diphenyl substituted propargyl alcohol **1.5.3a** was reacted with benzotriazole **1.2.1a** in the presence of FeCl_3 and MeCN as reaction solvent, both products from propargylation (**1.5.5a**) and allenation (**1.5.4a**) in a 1:3 ratio were obtained with 57% NMR yield (**Scheme 34**). The allene product **1.5.4a** has been characterized by X-ray crystallography.

Scheme 34: First reaction for investigation triazole allene product formation.

Encouraged by this result, the reactions between propargyl alcohol **1.5.3a** and benzotriazole **1.2.1a** have been investigated under various catalysts (**Table 7**). As shown in **Table 7**, the decomposition of propargyl alcohol **1.5.3a** occurred with most Lewis acids catalysts. However, we found FeCl_3 was the best choice of catalyst to give modest yield 57% and fair regioselectivity (3:1 ratio) for this transformation. Compared to other

transition metals, iron catalysts had many advantages, such as inexpensive, nontoxic and easy to handle.

Table 7: Catalyst screening^a

	Catalyst	Loading (%)	Sol. ^b	Temp (°C)	Time (h)	Tonv. (%) ^c	Yield (%) ^d	1.5.4a:1.5.5a ^d
1	FeCl ₃	10	MeCN	60	5	86	57	3:1
2	Cu(OAc) ₂	10	MeCN	60	5	<5	<5	-
3	CuI	10	MeCN	60	5	<5	<5	-
4	PdCl ₂	10	MeCN	60	5	30	<5	-
5	RuCl ₃	10	MeCN	60	5	82	36	1:1
6	IrCl ₃	10	MeCN	60	5	85	25	1:2
7	Fe(acac) ₃	10	MeCN	60	5	<5	<5	-
8	LaCl ₃	10	MeCN	60	5	19	<5	-
9	CeCl ₃	10	MeCN	60	5	25	<5	-
10	Bi(OTf) ₃	10	MeCN	60	5	71	42	2:1
11	AlCl ₃	10	MeCN	60	5	63	7	1:5
12	TfOH	10	MeCN	60	5	75	10	2:1
13	SnCl ₂	10	MeCN	60	5	69	29	1:1
14	FeCl ₂	10	MeCN	60	5	50	20	1:1
15	LiCl	10	MeCN	60	5	<5	<5	-

^a Standard reaction condition: 1 equiv propargyl alcohol (0.25 mmol), 1.3 equiv triazole (0.325 mmol), 0.1 equiv catalyst (0.025 mmol) and 2 mL solvent; ^b DCE: 1,2-dichlorethane, EtOAc: ethyl acetate; ^c conversions were determined based on the consumption of propargyl alcohol; ^d NMR yields of **4a** with 1,3,5-trimethoxybenzene as internal standard.

Table 8: Solvent screening^a

Reaction scheme: 1.5.3a + 1.2.1a $\xrightarrow[\text{Solvent}]{10\% \text{ FeCl}_3}$ 1.5.4a + 1.5.5a

	Catalyst	Loading (%)	Sol. ^b	Temp (°C)	Time (h)	Conv. (%) ^c	Yield (%) ^d	1.5.4a:1.5.5a ^d
16	FeCl ₃	10	Acetone	60	5	83	32	2:1
17	FeCl ₃	10	THF	60	5	73	42	2:1
18	FeCl ₃	10	Toluene	60	5	30	<5	-
19	FeCl ₃	10	MeOH	60	5	71	<5	-
20	FeCl ₃	10	MeNO ₂	60	5	78	60	4:1
21	FeCl ₃	10	DMSO	60	5	<5	<5	-
22	FeCl ₃	10	DMF	60	5	<5	<5	-
23	FeCl ₃	10	CHCl ₃	60	5	80	40	3:1
24	FeCl ₃	10	EtOAc	60	5	78	56	4:1
25	FeCl ₃	10	DCE	60	5	100	90 ^e	>20:1
26	FeCl ₃	10	DCE	rt	5	50	40	8:1

^a Standard reaction condition: 1 equiv propargyl alcohol (0.25 mmol), 1.3 equiv triazole (0.325 mmol), 0.1 equiv catalyst (0.025 mmol) and 2 mL solvent; ^b DCE: 1,2-dichlorethane, EtOAc: ethyl acetate; ^c conversions were determined based on the consumption of propargyl alcohol; ^d NMR yields of **4a** with 1,3,5-trimethoxybenzene as internal standard; ^e Isolated yield.

To further improve the regioselectivity of this reaction, different solvents was screened (**Table 8**). A polar solvent, such as DMSO, DMF, totally quenched the reaction.

To our surprise, the regioselectivity of the reaction, as indicated by the ratio of **1.5.4a** and **1.5.5a** increased dramatically (> 20:1 ratio) when 1,2-dichloroethane (DCE) was used as the reaction solvent. Interestingly, the ratio between **1.5.4a** and **1.5.5a** was dependent on the reaction temperature, where regioselectivity was dropped to 8:1 ratio at room temperature (entry 26).

With the optimal condition in hand, a series of different propargyl alcohols were investigated to explore the reaction substrate scope (**Figure 15**). As shown in **Figure 15**, the alkyne terminal R³ position could be tolerated TMS, *n*-Bu, *t*-Bu, vinyl and cyclopropenyl groups. Although a longer reaction time (12 h) was required, the bulky *t*-Bu group gave **1.5.4e** in 91% yield. No enyne decomposition (**1.5.4f**, **1.5.4r**) or cyclopropane ring opening (**1.5.4d**, **1.5.4s**) products were observed. The phenyl substituted alkyne gave the corresponding hydration product instead of the formation of desired triazole allene. The terminal alkynes (R³ = H) gave a complex reaction mixture under the optimal conditions. This limitation could be easily overcome by TMS deprotection.

Various substitutions on the propargyl position have also been investigated. The dialkyl substituted propargyl alcohols were unreactive enough even at higher temperature for longer time (60 °C, 24 h). The fact that aryl-alkyl substituted groups gave no allene triazole product was likely caused by the elimination of propargyl alcohols. For the electron-rich aryl substitution, higher yields were observed at room temperature (**1.5.4g-1.5.4k**). Heterocycles, such as thiophene (**1.5.4l**), were suitable for this reaction. Surprisingly, this transformation can tolerate a variety of functional group, such as the phenol substituted propargyl alcohols afforded the corresponding products (**1.5.4j**, **1.5.4k**) in good yields.

Figure 15: Reaction substrate scope^a

^a Isolated yield; ^b Room temperature; ^c Ratio(N2:N1) was determined by crude NMR of reaction mixture.

Substituents on the triazole indicated little influence on the reaction (**1.5.4m-1.5.4s**), likely due to the excellent overall nucleophilicity of the NH-triazole. Impressively, the alkyne-substituted propargyl alcohol was also suitable for this reaction, giving the conjugated alkyne-allene triazole in good yield. The structure of **1.5.4t** was confirmed by

X-ray crystallography. The electron-deficient aryl substituted propargyl alcohols did not work because the strong electron-withdrawing group on the benzene ring decreases the reactivity of C-O bond. Interestingly, although the triazole ring is a highly electron-deficient aromatic ring, the allene bis-triazole **1.5.4u** was obtained in modest yield under standard conditions, suggesting the potential triazole-Fe coordination in the activation of propargyl C-O bond.

Figure 16: Extending the substrate scope with propargyl acetate.^{a,b}

^a Reaction condition: 1 equiv propargyl acetate (0.25 mmol), 1.3 equiv triazole (0.325 mmol), 0.1 equiv catalyst (0.025 mmol) and 2 mL solvent;

^b Isolated yield; ^c Ratio(N₂:N₁) was determined by crude NMR of reaction mixture.

As we mentioned before, the electron-deficient aryl substituted propargyl alcohols were not suitable for this transformation, due to the lower reactivity of the C-O bond. To further extend the substrate group of electron-deficient ring, we have tuned the reactivity of propargyl alcohol derivatives. Therefore propargyl acetates **1.5.6** were prepared to react with triazoles. Excitingly, the desired allene triazoles (**1.5.4v-1.5.4z**) with electron-withdrawing group substituents were obtained in good to excellent yields, as shown in **Figure 16**.

Scheme 35: TMS-deprotection and X-ray crystal structures

Surprisingly, the allene-triazole shows significantly higher stability than the regular allene. For example, when the allene **1.5.4h** was treated with 2 equivalents of TfOH in wet DCM at room temperature, no allene decomposition (even the TMS deprotection) was observed after 12 hours based on the recovered yield of **1.5.4h** (97%). The TMS group could be readily removed by treatment with base as shown in **Scheme 35**.

The X-ray crystal structures not only confirmed the formation of the allene-triazoles, but also revealed the detailed configuration. Among all five allene-triazole crystal structures (**1.5.4a**, **1.5.4g**, **1.5.4u**, **1.5.4y** and **1.5.7a**), excellent conjugations between triazole ring and the allene π -bond were observed, even with bulky TMS group on the same carbon center. This extended conjugation likely accounted for the improved allene stability.

1.5.4 Conclusion

Herein, we reported the first synthesis of allene-substituted 1,2,3-triazole derivatives to fill the “missing piece” of triazole functionalizations. With the improved allene stability, the allene-triazoles are expected to exhibit potential new reactivity that may lead to

interesting chemical and physical properties, such as ligand development and material construction.

1.6 Mitsunobu reaction of 1,2,3-*NH*-triazoles: regio- and stereo-selective synthesis of triazole derivatives[†]

1.6.1 Two practical problems from previous 1,2,3-triazole functionalizations

Since 2008, our group have successfully reported five different functionalizations of 1,2,3-triazoles which included alkylation, arylation, vinylation, propargylation and allenation (Figure 17).

Figure 17: Five different functionalizations of 1,2,3-triazoles.

From these studies, we learned that the *N*-1 and *N*-2 selectivities of 1,2,3-triazoles heavily depended on the placement of substituents on the 1,2,3-triazoles, such as 4,5-disubstituted 1,2,3-*NH*-triazoles gave absolutely dominant *N*-2 substituted products and 4-substituted 1,2,3-*NH*-triazoles produced slightly dominant *N*-2 regioisomers, while

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benzotriazole gave N-1 substituted products as significantly major products in all functionalizations (**Figure 18**). Therefore, the **first** practical problem was carried out regarding the regioselective synthesis of N-2 triazoles. How can we improve the N-2 regioselectivity of 1,2,3-triazoles, especially for N-1 preferred triazoles, such as 1*H*-1,2,3-triazole and benzotriazole. Although some strategies which was focused on the development of the appropriate substituents on the C-4 and C-5 positions to reach good N-2 selectivity have been reported in literature,⁶⁹ new strategies that can encourage N-2 selectivity from “N-1-substitution favored” 1,2,3-*NH*-triazole were highly desired.

Figure 18: N-1 & N-2 selectivities of 1,2,3-*NH*-triazoles.

Scheme 36: The propargylation of benzotriazole with enantioenriched propargyl alcohol.

Due to the presence of a stereogenic center, the propargylation of triazoles gave the potential opportunity to synthesize chiral propargyl triazole derivatives. We then investigated the reaction between benzotriazole and an enantioenriched propargyl alcohol

(92% ee) (**Scheme 36**). Unfortunately, we obtained a racemic propargyl triazole product. This result suggested the chiral propargyl triazoles could not be synthesized via propargylation. Then the **second** practical challenge was the selective synthesis of enantioenriched triazole derivatives.

The N-1 nitrogen of 1,2,3-triazole is usually more basic (higher electron density) than the N-2 nitrogen, however, because the center N-2 nitrogen is much less steric hindered, N-2 substitution is kinetically favored. As a result, the highly stereochemistry sensitive Mitsunobu reactions could potentially favorer the kinetic product and increase the N-2 selectivity. Meanwhile, the rather high acidity (pKa around 8-10) and the excellent nucleophilicity of *NH*-1,2,3-triazoles make them suitable coupling partners with alcohols under Mitsunobu conditions. Moreover, the excellent stereoselectivity associated with the Mitsunobu reaction could be achieved, where complete inversion of alcohol stereogenic center occurred through S_N2 addition. Combining these two ideas, we postulated that the Mitsunobu reaction could be used to install chirality on the triazoles compounds.

1.6.2 Introduction of Mitsunobu reaction

The Mitsunobu reaction is an organic reaction which provides the substitution of primary or secondary alcohols with nucleophiles mediated by the combination of a trialkyl or triarylphosphine and a dialkyl azodicarboxylate (DEAD or DIAD).⁷⁰ Because of its scope, stereospecificity, and mild reaction conditions, the Mitsunobu reaction has played a critical role in organic synthesis and medicinal chemistry.⁷¹ A wide range of compounds can be synthesized using a Mitsunobu protocol, such as esters,⁷² amines,⁷³ azides,⁷⁴ ethers,⁷⁵ cyanides,⁷⁶ thiocyanides,⁷⁷ thioesters,⁷⁸ and thioethers⁷⁹. (**Scheme 37**).

Scheme 37: Mitsunobu reaction.

Although the Mitsunobu reaction is widely used in synthetic organic chemistry, the reaction mechanism of Mitsunobu reaction was fairly complex. The reaction intermediates have been the subject of debate.⁸⁰ A possible mechanism was shown in **Scheme 38**.

Scheme 38: Postulated mechanism for the Mitsunobu reaction.

The first step is the irreversible formation of the intermediate betaine **I** from the nucleophilic attack of phosphine (PR_3) upon dialkyl azodicarboxylate, which has been confirmed by NMR⁸¹ and ESI-MS.⁸² In the second step, the betaine **I** deprotonates the

hydrogen of the nucleophile to give the species **II**. The intermediate **II** then reacts with the alcohol to form the alkoxyphosphonium **III**. Finally, the desired product is produced by the attack of nucleophilic anion upon intermediate **III**. The byproducts of Mitsunobu reaction are phosphine oxide and dialkyl hydrazine-1,2-dicarboxylate.

1.6.3 An example: Improvement of regioselective N-2 isomers from ligand control.

Despite our successes on the application of conformational control strategy for the synthesis of regioselective N-2 substituted 1,2,3-triazoles (see **Section 1.1.2**), we realized this strategy is not effective for specific substrates, which were discussed in **Section 1.6.1**.

Scheme 39: N-2 arylation was reported by Shi and Buchwald.

In 2008, we reported the copper(I) mediated N-2 arylation of 1,2,3-*NH*-triazoles (**Section 1.2**). We obtained poor to moderate N-2 regioselectivity for both benzotriazole and 4-substituted 1,2,3-*NH*-triazoles. Recently, Buchwald⁸³ and coworkers described a

palladium-catalyzed N-arylation of 1,2,3-triazoles with exceptional levels of N-2 regioselectivity by using the very bulky biaryl phosphine ligand (**Scheme 39**). The ratios of N-2 and N-1 triazole regio-isomers were 1:7.5 and 6:1 for benzotriazole and 4-phenyltriazole individually by utilization of our approach, while they were 1:1 and 32:1 roughly from Buchwald's method. We therefore have known the N-2 selectivity of 1,2,3-triazoles could be improved significantly by using a bulky ligand.

1.6.4 Research Objective and Results

To verify our hypothesis as mentioned in the **section 1.6.1**, the reactions between benzyl alcohol **1.6.2a** and benzotriazole **1.2.1a** were performed under standard Mitsunobu reaction and alkylation conditions separately (**Scheme 40**).

Scheme 40: Mitsunobu reaction and alkylation of benzotriazole.

As shown in **Scheme 40A**, the dehydration product **1.6.3a** was obtained in excellent isolated yields (97%, combined N-1 and N-2 isomers) under Mitsunobu conditions. Compared to the alkylation reaction of benzotriazole, where only trace amount (< 5%) of N-2-**1.6.3a** was isolated (**Scheme 40B**), the Mitsunobu reaction provided significantly

better overall yields of the N-2 isomer. To verify how different alcohols influenced the reactivity and regioselectivity, alcohols **1.6.2** reacted with **1.2.1a**. The results were summarized in **Table 9**.

Table 9: Reaction substrate scope with benzotriazole (BTA)^a

1.2.1a	1.6.2		
		yields ^b (N-1 + N-2)	ratio ^c N-2 : N-1
1.6.3a		97%	1:1.6
1.6.3b		84%	1:1.3
1.6.3c		95%	1:1.9
1.6.3d		93%	1:1.8
1.6.3e		96%	1:1.7
1.6.3f		94%	1:1.5
1.6.3g		97%	1:1.2
	1.6.3h	88%	1.6:1
	1.6.3i	96%	1.6:1
	1.6.3j	93%	2:1
	1.6.3k	85%	1.8:1
	1.6.3l	80%	1.2:1
	1.6.3m	79%	2.6:1

^a Standard reaction condition: 1 equiv of alcohols **1.6.2**, 1.2 equiv of triazoles **1.2.1a**, 1.2 equiv of triphenylphosphine (PPh₃) and 1.2 equiv of diisopropyl azodicarboxylate (DIAD) were mixed in the distilled tetrahydrofuran (THF). ^b Isolated yields. ^c Ratios determined by NMR of crude reaction mixtures.

As shown in **Table 9**, the Mitsunobu reaction was suitable for a number of different alcohols **1.6.2**, giving the coupling products in excellent yields (> 85%). Significantly improved N-2 products (compared with the alkylation of 1,2,3-triazoles) were obtained in

all cases. The Mitsunobu reactions produced N-1 isomers as the dominant products in primary alcohols. However, compared to alkylation, they improved the regioselectivities significantly. Although secondary alcohols required longer reaction times (8 to 12 h), they gave the N-2 isomers as the major products, which supported our hypothesis that stereochemistry sensitive Mitsunobu reaction help the formation of kinetic N-2 addition even with highly N-1 preferred benzotriazole.

Table 10: Reaction substrate scope with various triazoles.^{a,b}

^a Standard reaction conditions: 1 equiv of alcohols, 1.2 equiv of triazoles, 1.2 equiv of triphenylphosphine (PPh₃) and 1.2 equiv of diisopropyl azodicarboxylate (DIAD) were mixed in the distilled tetrahydrofuran (THF). ^b Yields determined by NMR with 1,3,5-trimethoxybenzene as internal standard, and ratios determined by NMR of crude reaction mixtures.

Different *NH*-1,2,3-triazoles were subsequently used to investigate their influence on regioselectivity and also further extend the reaction substrate scope (**Table 10**). Among all the tested *NH*-1,2,3-triazoles, significantly improved N-2 selectivity was observed. For example, as we have reported in previous alkylation of triazoles, the reaction between the 4-phenyl-*NH*-1,2,3-triazole (**1.2.1b**) with benzyl bromide (PhCH₂Br) gave N-1 substituted benzyl **1.6.4a** as the major product (N-2:N-1 = 1:5 roughly).

Under the Mitsunobu conditions, the desired N-2 isomer became the major product (N-2:N-1 = 1.7:1). Good to excellent isolated yields of the N-2 isomers were obtained. The Mitsunobu reactions of *NH*-1,2,3-triazoles not only provided an alternative approach for *NH*-1,2,3-triazole functionalization, but also, more importantly allowed the N-2 functionalization through altering different alcohols instead of adjusting the substitution groups on 1,2,3-triazoles.

The significance of Mitsunobu reaction in altering the N-1/N-2 selectivity was further highlighted in the synthesis of bis-N-2-triazole derivatives as shown in **Scheme 41**. Generally speaking, the N-1/N-1-bis-triazoles could be readily prepared through the double click chemistry from di-alkynes. On the other hand, the N-2/N-2-bis-triazoles, were extremely challenging to prepare due to the unfavored statistic from mathematics calculation. For example, assuming the mono substitution gave N-1:N-2 = 5:1, the ratio of the double substitution of the same reaction would be N-1/N-1:N-1/N-2:N-2/N-2 = 25:10:1 ((N-1:N-2) * (N-1:N-2) = N-1/N-1:N-1/N-2:N-2/N-1:N-2/N-2 = 25:5:5:1, where N-1/N-2 = N-2/N-1). The theoretical yields for N-2/N-2 product would be only 2.7%. The Mitsunobu conditions, by altering the N-1 and N-2 selectivity, gave the great

opportunity to synthesize the N-2/N-2 isomer for the first time through the simple post triazole derivatization.

Scheme 41: Synthesis of challenging N-2-bis-triazoles.

As indicated in **Scheme 41**, bis-triazole **1.6.5a** which has been confirmed by X-ray crystallography was successfully prepared even with benzotriazole, which gives predominantly N-1 products (**Figure 19**). The yields of the N-2/N-2 isomers were significantly improved with the 4-phenyl-triazole (**1.6.5b**) and derivatives (**1.6.5d** and **1.6.5f**). Notably, only trace amount of the N-2/N-2 bis-triazoles were observed while treating the 4-phenyl-triazole with the di-chloro/bromo alkanes due to the unfavored statistic discussed above.

Figure 19: Crystal structure of **1.6.5a**

From above studies, the *NH*-1,2,3-triazoles have been confirmed as the good coupling partner of Mitsunobu reaction with good reactivities. We then investigated the stereoselectivity of this transformation. The Mitsunobu reaction can be transfer the complete inversion of alcohol stereogenic center to product via S_N2 addition. The *trans*-2-methylcyclohexanol **1.6.2b** and *trans*-2-methylcyclopentanol **1.6.2c** were reacted with benzotriazole (BTA) **1.2.1a** and phenyl-triazole (PTA) **1.2.1b**. As expected, excellent stereoselectivity were achieved with only the corresponding *cis*-products (**1.6.6a** - **1.6.6d**) observed via complete stereochemistry inversion (**Scheme 42**).*

Scheme 42: Complete stereochemistry inversion.

* The relative stereochemistries of **1.6.6a** - **1.6.6d** were determined by the NMR.

Encouraged by these exciting results, we synthesized enantiomeric pure 1,2,3-triazole derivatives through the coupling of triazoles and chiral alcohols under Mitsunobu conditions. As shown in **Scheme 43**, the chiral triazoles **1.6.7a** and **1.6.7b** were prepared from enantiomeric pure alcohol **1.6.2d** and quinine **1.6.2e** with excellent stereochemistry control. Under the Mitsunobu conditions, the enantiomeric pure alcohol **1.6.2d** gave near complete chirality transfer, forming the chiral triazole **1.6.7a** in 96% ee (determine by HPLC).*

Scheme 43: Asymmetric synthesis of chiral triazole derivatives.

Due to the large difference of polarity between N-1 and N-2 isomers, they were easily separated by column chromatography, which made this method very attractive strategy for the preparation of the enantiomeric pure triazoles. Similar to previous cases, the secondary alcohols improved the yields of the N-2 isomers even with benzotriazole.

* The ee of N-2-**1.6.7a** was not determined due to the difficulty in separation of the two enantiomers in HPLC. However, large optical rotation of N-2-**1.6.7a** was observed with $[\alpha]_D^{25} = -55.40$ (CH_2Cl_2 , c 1.0), which confirmed the likely similar excellent stereochemistry inversion was associated with the product.

The synthesis of **1.6.7b** (structure confirmed by X-ray crystallography) highlighted the strength of Mitsunobu reaction of *NH*-1,2,3-triazoles in the preparation of highly functional triazole analogous (**Figure 20**). To the best of our knowledge, these are the first examples of the synthesis of enantiomeric pure triazoles. We are expected that these compounds can certainly be applied as potential novel ligand and catalysis in asymmetric catalysis.

Figure 20: Crystal structure of **N-2-1.6.7b**.

1.6.5 Conclusion

In conclusion, the Mitsunobu reactions between *NH*-triazoles and alcohols is a practical strategy for 1,2,3-triazole functionalization with excellent yields under mild conditions. Unlike previous strategies reported in literature, where different substituents of triazoles were required to achieve good yields of *N*-2 isomers, the Mitsunobu conditions favored the formation of the kinetic product *N*-2 isomers, even with highly *N*-1 preferred 1,2,3-

triazoles (such as benzotriazole). Therefore, this method provided an alternative approach to achieve triazole N-2 substitution without changing the substituents on the triazoles. Moreover, with the excellent stereochemistry control, the reported method allowed asymmetric synthesis of enantiomeric pure triazole derivatives, which could certainly help the further development of 1,2,3-triazole as potential new ligands in transition metal catalysis.

Chapter Two: 1,2,3-triazoles applied as ligands in transition metal catalysis

2.1 Introduction

2.1.1 Substituted 1,2,3-triazoles as neutral ligands

The transition metal catalysis has revolutionized the traditional way synthetic chemists construct organic molecules in last several decades.⁸⁴ Compared to classical syntheses, transition metal catalysis provided new efficient and sustainable routes for organic synthesis and the production of fine chemicals. One key correlation of successful transition metal mediated catalysis was the fundamental understanding of ligand-metal coordination (referred as “ligand field theory”), which represented an application of molecular orbital theory to transition metal complexes.⁸⁵ In addition to the unique chemical properties of the individual metal elements, the binding ligand plays a crucial role in transition metal catalysis.⁸⁶ Besides providing the spatial arrangement (asymmetric synthesis) at the metal center, ligand influences the electronic environment, thus adjusting metal reactivity.⁸⁷ Ligand variation provide a powerful tool in transition metal catalysis, because key features of transition metal catalysts such as reactivity, selectivity, and stability may be tuned by the steric and electronic properties of the coordinated ligands.⁸⁸ Considerable effort has focused on the development of new novel metal binding ligands,⁸⁹ such as BINAP,⁹⁰ BOX,⁹¹ DuPhos,⁹² TADDOL⁹³ and salen.⁹⁴ All of these ligands which have been extensively and successful applied in organic synthetic chemistry (**Figure 21**).

Figure 21: Famous ligands in transition metal catalysis.

With the strong σ -donor and weak π -acceptor properties of the triazole ring, 1,2,3-triazoles offer attractive ligands for coordination with transition metals.⁹⁵ However, due to the limited access of functional triazole derivatives, only a few studies that utilize triazoles as ligands were reported in the literature before 2001.⁹⁶ Since the discovery of “click chemistry”, the application of 1,2,3-triazoles in several fields have been widely studied. However, these studies regarding the application of 1,2,3-triazoles as ligand in transition metal catalysis still remain undeveloped.

One of the earliest studies which revealed the excellent metal binding ability of 1,2,3-triazoles was reported by Sharpless in 2004. They synthesized the C_3 -symmetric polytriazolylamines as ligands for copper(I) catalyst. As they claimed, the loading of copper(I) catalyst can be decreased as low as 0.25-1 mol% (normally 5 mol% in standard condition of “click chemistry”), because these powerful ligands stabilize the copper(I) catalyst, by protecting it from oxidation and disproportionation, while enhancing its catalytic activity in the click chemistry (**Scheme 44**).⁹⁷ This new class of ligands is

capable of binding to the copper(I) species by forming a five member chelate between the N-3 nitrogen of triazole ring and the amine.

Scheme 44: Application of C₃-symmetric polytriazoles as the replacement of sodium ascorbate salt in click chemistry.

Table 11: Screening of various triazoles as stabilizing ligands for copper(I) catalyst.

Based on the screening of various ligands (**Table 11**), the best ligand was tris-(benzyltriazolylmethyl)amine (TBTA). Its tetradentate binding ability is believed to completely envelope the copper(I) center, leaving no free binding sites available for potential destabilizing interactions (**Figure 22**).⁹⁸ The tertiary amine and the 1,2,3-

triazole functionalities likely work in concert to make TBTA so efficient: the more basic and sterically encumbered nitrogen, accelerates the catalysis by providing additional electron density on the metal center, while the latter, being more labile, comes off the copper center only temporarily to allow the formation of the copper(I)-acetylide/ligand complex, which is then carried through the catalytic cycle.

Figure 22: Proposed structure of $\text{Cu}^{\text{I}}(\text{TBTA})$ complex.

In 2005, Zhang reported a new type of monophosphine ligand (ClickPhos) bearing a triazole heterocycle in the backbone, which was showing high reactivity in the Pd-catalyzed Suzuki-Miyaura coupling and amination reactions of aryl chlorides.⁹⁹ Later, van Marseveen and co-workers introduced a 1,2,3-triazoles as part of bidentate P,N-type ligand (ClickPhine),¹⁰⁰ which is an important class of ligands that have been applied in various catalytic transformations.¹⁰¹ In the ClickPhine ligand, the 1,2,3-triazole played the role of nitrogen donor. A series of ligands were synthesized from readily available starting materials to give several homogenous and heterogeneous dendritic and polymeric catalysts (**Scheme 45**).

According to the NMR studies of the precursor palladium chloride **IV** (when R = Ph), the ^1H NMR spectra gave broad signals for the allylic protons (except for the central proton) indicated isomerization via π rotation or π,σ -rearrangement. The ^{31}P NMR spectrum showed a broad signal at 20.6 ppm and revealed a monodentate binding of the

ClickPhine ligand with the chloride still coordinated to the palladium. After mixing compound **IV** with AgBF_4 , the formation of cationic palladium-allyl triazole complex in which the ligand shows bidentate P,N coordination, as confirmed by NMR data. The ^1H NMR signal of the triazole proton shifted 0.71 ppm to lower field (from 8.15 to 8.86 ppm) after ion exchange, and the CH_2 group gave rise to an AB pattern showing that these protons became inequivalent. In addition, the signal in the ^{31}P NMR spectrum shifted from 20.6 to 40.5 ppm and became sharper. This was the **first** example that provided direct evidence of triazole binding to a transition metal. Furthermore, preliminary experiments found the efficiency of these ClickPhine ligands in the Pd-catalyzed allylic alkylation reaction.

Scheme 45: Synthesis route of “ClickPhine” P,N-ligand and their Pd-complexes.

Additional examples of N-coordination of a 1,2,3-triazole to a metal was reported in 2007. Koten, Gebbink and co-workers reported the first examples of 1,4-disubstituted 1,2,3-triazoles as monodentate Lewis-basic ligands for cationic Pd- and Pt- pincer complexes with reported crystal structure (**Scheme 46**).¹⁰² The 1,2,3-triazole coordinated metal complexes were accessed by the addition of the triazole to the pincer Pd and Pt cations, which is generated in situ upon reaction with AgBF_4 . The single X-ray

crystallographic structure of the complex revealed an M(II) ion which is four coordinate with a distorted square-planar ligand environment by virtue of the donor atoms of the tridentate pincer ligand and the N-3 nitrogen of the triazole.

Scheme 46: 1,2,3-triazoles as monodentate Lewis-basic ligands for cationic Pd- and Pt-pincer complexes

A comparison study of relative coordination strength of 1,2,3-triazoles with respect to more traditional Lewis bases PPh₃, 1-methyl-imidazole, Et₂S, DMSO, aniline, MeCN and pyridine was performed by means of ¹H NMR spectroscopy which represented as the relative association constant, *K*_{ass} (**Scheme 47**).

Scheme 47: The definition of *K*_{ass}.

The experiments showed that 1,2,3-triazole **L1** is a stronger ligand than Et₂S, DMSO, H₂O and MeCN (**Table 12**), but is weaker than PPh₃, pyridine and *N*-methyl imidazole in strength. Entries 9-11 indicated that the coordination strengths of triazoles

ligands toward the pincer Pt cation can be tuned by the appropriate functionalization of 1,4-disubstituted triazoles.

Table 12: K_{ass} values for Lewis base coordination to Pt-pincer complex compared to **L1** for several competing ligands **Lx**.

Entry	Lx	K_{ass}	Entry	Lx	K_{ass}
1	H ₂ O	-	6	Pyridine	19.5
2	DMSO	0.002	7	PPh ₃	>> ^a
3	MeCN	0.02	8	<i>N</i> -methyl imidazole	>> ^a
4	Et ₂ S	0.03	9	1 <i>H</i> -1,2,3-triazole	4.16
5	Aniline	0.3	10	L2	6.47
			11	L3	18.5

^a Full conversion to **2Lx** occurred

Recently, 1,2,3-triazol-5-ylidenes were found to be the good alternative NHC ligands for forming complexes with transition metals,¹⁰³ such as gold,¹⁰⁴ silver,¹⁰⁵ rhodium,¹⁰⁶ ruthenium,¹⁰⁷ palladium¹⁰⁸ and copper¹⁰⁹ which have been applied in the some classical organic synthesis. For example, Fukuzawa and co-workers demonstrated the utility of their new PdCl₂(TMes)₂ complex in Suzuki reactions (**Scheme 48**), where the TMes (triazole-based NHC bearing mesityl groups).^{108b} Indeed, complex PdCl₂(TMes)₂ was successful in catalyzing the Suzuki reaction between aryl chlorides and various aryl boronic acids in good to excellent yields. Following their previous results with PdCl₂(TMes)₂ complex, they extended the chemistry of 1,2,3-triazolylidene ligands by synthesizing new copper complexes, such as CuCl(aNHC) and CuCl(TPh).¹⁰⁹ These complexes were evaluated as catalysts for the CuAAC azide-alkyne cycloaddition

reaction to give 1,4-substituted 1,2,3-triazoles in excellent yields at room temperature with short reaction times (**Scheme 49**). They also claimed complex $\text{CuCl}(\text{TPh})$ was particularly effective for the reaction between sterically hindered azides and alkynes. Moreover, Crowley¹⁰⁴ and co-workers disclosed the first gold ‘click’ 1,2,3-triazolylidene complex and its utility in gold(I)-catalysis (**Scheme 50**). The air and moisture stable gold(I) complex proved to be a good catalyst for carbene transfer reactions from diazo compounds into O–H, N–H and C–H bonds, hydroalkoxylation of allenes and enyne cyclizations. In 2011, Grubbs^{107b} applied the stabilized 1,3,4-triaryl-1,2,3-triazol-5-ylidene carbenes to displace the phosphine ligand of Hoveyda-Grubbs catalyst, generating a family of 1,3,4-triaryl-1,2,3-triazol-5-ylidene containing ruthenium metathesis catalysts (**Scheme 51**). These complexes were found to be active room-temperature catalysts for the ring-opening metathesis polymerization of cyclic olefins and for ring-closing olefin metathesis reactions. The catalytic properties of the Ru-1,2,3-triazolylidene complexes are strongly influenced by the nature of the MICs’ substituents.

Scheme 48: Suzuki couplings with aryl chlorides catalyzed by the Pd-1,2,3-triazolylidene complex $\text{PdCl}_2(\text{TMes})_2$.

Scheme 49: CuAAC reactions catalyzed by copper(I)-1,2,3-triazolyldene complexes

Scheme 50: Carbene transfer reactions from diazo compounds catalyzed by the gold(I)-1,2,3-triazolyldene complex.

Scheme 51: Ring opening and ring closing metathesis using Grubbs' 1,3,4-triaryl-1,2,3-triazol-5-ylidene containing ruthenium catalysts.

2.1.2 1,2,3-*NH*-triazoles as anionic ligands

Compared to N-substituted triazoles, the *NH*-triazoles provide acidic N-H protons ($pK_a < 10$),¹¹⁰ therefore, they can be applied as anionic ligands with multiple binding sites. On the basis of reported literatures so far, all efforts regarding triazole as anionic binding ligand have focused on benzotriazoles,¹¹¹ which decreased the overall interests in this class of complexes, due to limited functionality availability. In one of the earliest example of benzotriazole as a ligand, Oro and co-workers discovered the application of benzotriazole and benzotriazolate anion in Rh(I) complexes.¹¹² To investigate the structure and binding patterns of Rh(I)-triazole complexes, they successfully synthesized mono- and di nuclear rhodium complexes of the general formula $RhClL_2(btzh)$, $[Rh(\mu-btz)L_2]_2$, $Rh_2(\mu-btz)(\mu-N_3)(L_2)_2$ and $Rh_2(\mu-btz)(\mu-SCN)(COD)_2$ [L_2 = diolefin, $(CO)_2$ or $(CO)(PPh_3)$] (**Scheme 52**). For example, the addition of benzotriazole to $[Rh(\mu-Cl)(COD)]_2$ suspended in acetone resulted in the formation of $[RhCl(COD)(btzh)]$ complex as stable yellow solid in excellent yield (88%).

Scheme 52: Synthesis of $[Rh(btzh)(COD)]_2$ complexes reported by Oro.

Although the molecular structure of Rh(I)-triazole complex remains to be determined, a square planar arrangement was proposed with the benzotriazole coordinated through a pyridyl nitrogen atom. Moreover, the addition of triethylamine to a

solution of $[\text{RhCl}(\text{COD})(\text{btzH})]$ in methanol, led to elimination of the acidic proton of the benzotriazole ligand with the formation of $[\text{Rh}(\mu\text{-btz})(\text{COD})]_2$. A direct route to prepare $[\text{Rh}(\mu\text{-btz})(\text{COD})]_2$ complex, in high yield involved the reaction of $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ with benzotriazole and KOH. The molecular weight measurements on $[\text{Rh}(\mu\text{-btz})(\text{COD})]_2$ complex indicated a dinuclear complex (Rh-Rh 3.27 Å), therefore suggesting that the nitrogen atoms of the benzotriazolate ligand involved in coordination are adjacent to each other (**Figure 23**). This proposed dinuclear structure for these complexes was confirmed by the X-ray study of $[\text{Rh}(\mu\text{-btz})(\text{COD})]_2$.

Figure 23: Proposed dinuclear structure of Rh(I)-triazole complexes.

In addition, Oro and co-workers studied the only known example of a 4,5-disubstituted-(NH)-1,2,3-triazole coordination with Rh(I).¹¹³ Neutral bi- and mono-nuclear dicyanotriazolate (DcTz) complexes of formula $[\text{Rh}_2(\mu\text{-DcTz})_2\text{L}_2\text{L}'_2]$ ($\text{L}_2 = \text{L}'_2 =$ diolefin; $\text{L} = \text{CO}$, $\text{L}' = \text{PPh}_3$ or P(OPh)_3 ; $\text{L} = \text{L}' = \text{P(OPh)}_3$; $\text{L}_2 = \text{COD}$, $\text{L}' = \text{P(OPh)}_3$) and $[\text{Rh}(\text{DcTz})\text{L}_2\text{L}']$ ($\text{L}_2 =$ diolefin, $\text{L}' = \text{PPh}_3$; $\text{L} = \text{PPh}_3$, $\text{L}' = \text{CO}$) and the ionic derivative $[\text{Rh}(\text{dppe})_2][\text{DcTz}]$ have been synthesized. Based on the study by Rasmussen¹¹⁴ showing that the coordinating ability of the ligands can be influenced by the presence of cyan substituents on the heterocyclic ring, the authors investigated the coordinating ability of 4,5-dicyano-1,2,3-triazole (HDcTz). Treatment of $[\text{Rh}(\text{acac})(\text{COD})]$ with 4,5-dicyano-

1,2,3-triazolate led to the formation of the Rh(I) dicyanotriazole complex in high yields (**Scheme 53**).

Scheme 53: Synthesis of $[\text{Rh}(\mu\text{-DcTz})(\text{COD})]_2$ complex.

2.1.3 Achievements of our group by using 1,2,3-triazoles as the ligands

During the past several years, our group has been working on the development of new catalysts with 1,2,3-triazoles as ligands in transition metal catalysis. These efforts led to the discoveries of triazole-Rh and triazole-Au catalysts with interesting new reactivities.

On the basis of our success in the synthesis of 4,5-disubstituted-(*NH*)-1,2,3-triazoles through Lewis base-catalyzed cascade nitroalkene-aldehyde-azide condensation.¹³ Duan in our group examined the binding ability of a triazole anion with Rh(I) by treating the 4,5-disubstituted-(*NH*)-1,2,3-triazoles with $[\text{Rh}(\text{COD})\text{Cl}]_2$ under basic conditions (**Scheme 54**).¹¹⁵ As expected, the triazole anion effectively substituted the chloride (Cl^-) and triazole-Rh(I) complexes ($[\text{Rh}(\text{COD})(\text{Triaz})]_2$) were obtained in near quantitative yields. These complexes showed excellent stability towards both air and moisture, and can be purified by column chromatography. As a new class of transition metal complexes, these compounds display effective catalytic reactivity in the Pauson-Khand reaction.

Encouraged by the successful synthesis of triazole-Rh(I) complexes, we investigated triazoles as ligands for the synthesis of Au(I) complexes. In comparison with the more expensive NHC ligands,¹¹⁶ the simple triazoles are also known to possess a nitrogen σ -donor and a lower LUMO aromatic antibonding orbital for metal back-bonding. The triazole-Au(I) complexes were prepared successfully in quantitative yields using a preparation procedure similar to triazole-Rh(I) complexes (**Scheme 55**).¹¹⁷ Further studies revealed that the triazole-Au(I) catalyst gave excellent reactivity, selectivity and improved thermal stabilities in several organic transformations which included hydroamination and synthesis of Hashmi phenol,¹¹⁸ *E*- α -haloenones,¹¹⁹ enones¹²⁰ and allenes.¹²¹ Based on the synthesis of allenes from rearrangement of propargyl alcohols, we deduced one of unique properties of triazole-Au complexes was no further activation of allene intermediates with activation of triple bond only, while other regular gold catalysts can activate both (**Scheme 56**).^{121a}

Scheme 54: Synthesis of triazole-Rh(I) complexes and its application in Pauson-Khand reactions.

Scheme 55: Synthesis of triazole-Au(I) complexes.

Scheme 56: Asymmetric synthesis of substituted allenes.

2.2 Synthesis of $[\text{Ir}(\text{L}^{\wedge}\text{X})(\text{ArTriaz})_2]$ and $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$ complexes and their application in photoredox catalysis

2.2.1 Reported examples of triazole-Ir(III) complexes

1,2,3-triazoles have been extensively studied in the past decade due to the discovery of “click chemistry”. The synthesis of 1,2,3-triazole related chelate ligands was first described using the “click chemistry” of amino acid derived alkynes or azides in 2006.¹²² The resultant chelate ligands are bound through a primary amine and either the N-3 nitrogen or, in some cases, the N-2 nitrogen of the triazoles (**Figure 24**). Since then, several additional examples of this “click-to-chelate” approach have been reported, and this field has been reviewed.¹²³ The majority of examples use either 2-ethynyl pyridine,¹²⁴ which tends to give five-membered chelation (**Figure 24A**), or 2-picolylethyne,¹²⁵ which gives six-membered chelation (**Figure 24B**). Both of these ligands coordinate through N-3 nitrogen as expected, since DFT calculations have shown that N-3 nitrogen is a better donor than N-2 nitrogen.¹²⁶ However, coordination through N-2 nitrogen is also possible using ligands of type C,¹²⁷ but the complexes are less stable than those of type A, as has been confirmed experimentally and computationally for a series of palladium complexes.^{127c}

Figure 24: Chelating triazoles derived from 2-ethynyl pyridine (**A**), 2-picolylethyne (**B**), and 2-azidomethylpyridine (**C**).

The luminescence of pyridine triazoles is sensitive to the presence of metal ions,¹²⁸ and the ease of tuning the electronic properties of these ligands has been used to control the luminescence of biscyclometalated iridium(III) complexes (**Figure 25**).¹²⁹ Luminescent Ir(III) complexes have been used in various applications such as biological labeling reagents,¹³⁰ photosensitizers for light-driven catalytic water reduction,¹³¹ single oxygen sensitizers,¹³² and sensors.¹³³ Moreover, the most important application of the Ir(III) complexes is as emitters in electroluminescent devices including organic light-emitting devices (OLEDs)¹³⁴ and light-emitting electrochemical cells (LEECs).¹³⁵

Figure 25: Different kind of biscyclometalated iridium complexes.

The luminescent properties of biscyclometalated iridium(III) complexes significantly changed when 1,2,3-triazoles was the subunits of iridium(III) complexes structures. For example, Zysman-Colman reported the incorporation of 4-aryl-1-benzyl-1*H*-1,2,3-triazoles (atl) as cyclometallating ligands into new heteroleptic iridium(III) complexes containing diimine (N^N) ancillary ligands 2,2'-bipyridine (bpy) and 4,4'-ditert-butyl-2,20-bipyridine (dtBubpy) in 2011.¹³⁶ These complexes emit from the yellow to sky blue in acetonitrile (MeCN) solution at room temperature. Their photoluminescent quantum efficiencies are markedly higher (between 25 and 80%) than analogous

(C[^]N)₂Ir(N[^]N)⁺ type complexes, where C[^]N is a 2-phenylpyridine ligand (**Figure 26**). The results of a computational investigation suggested that for these complexes, the highest occupied molecular orbital (HOMO) is located on both the aryl fragment of the atl ligands and the iridium metal while the lowest unoccupied molecular orbital (LUMO) is located essentially exclusively on the ancillary ligand.

Figure 26: Enhanced luminescent Ir(III) complexes bearing aryltriazole cyclometallated ligands reported by Zysman-Colman.

Furthermore, De Cola and Fernández-Hernández synthesized and characterized two biscyclometalated Ir(III) complexes isomers depending on the reaction temperatures which are N,N-*trans*-[Ir-(dfptrBz)₂(dmbpy)]⁺PF₆⁻, with *cis*-C,C and *trans*-N,N arrangement of the C[^]N ligands at 140 °C, and N,N-*cis*-[Ir-(dfptrBz)₂(dmbpy)]⁺PF₆⁻, *cis*-C,C and *cis*-N,N C[^]N ligand orientation at 80 °C (dmbpy = 4,4'-dimethyl-2,2'-bipyridine and dfptrBz = 1-benzyl-4-(2,4-difluorophenyl)-1*H*-1,2,3-triazole).¹³⁷ More interestingly, both isomers showed significantly different photophysical and electroluminescent properties, depending on the mutual arrangement of the C[^]N ligands (**Figure 27**).

Figure 27: Control of the Mutual Arrangement of Cyclometalated Ligands in Cationic Ir(III) Complexes.

Although these triazole-Ir(III) complexes revealed the unique and important luminescent properties, the triazole-Ir(III) complexes have **not** yet been explored for use in homogeneous transition metal catalysis. Therefore, we develop new transformations using triazole-Ir(III) complexes as the catalysts to take advantage of their unique luminescent properties to develop systems that are capable of photoredox catalysis.

2.2.2 Synthesis of [Ir(L^X)(ArTriaz)₂] and [Ir(bbpy)(ArTriaz)₂]Cl complexes

These biscyclometalated iridium(III) complexes are generally synthesized through a two-step process, the first step being a reaction between the HC^N ligand and IrCl₃·nH₂O to form a dichloro-bridged dinuclear Ir(III) dimer, [Ir(C^N)₂(μ-Cl)]₂.¹³⁸ Further reaction of the dichloro-bridged dimer with a third cyclometalating ligand yields triscyclometalated complexes that can be homoleptic, [Ir(C^N)₃],¹³⁹ if the C^N are identical or heteroleptic, [Ir(C^N)₂(C^{N'})], if a different C^{N'} is used.¹⁴⁰ The chloride dimer can also react with chelating ligands, leading to a wide range of neutral bis-cyclometalated complexes [Ir(C^N)₂(L^X)] (L^X = anionic ligands as β-diketonates, picolinate, pyridineazolate,

etc.) or cationic complexes $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{L}')^+]^+$ (e.g. $\text{L}^{\wedge}\text{L}'$ = neutral ligands such as diimines, phosphines, etc.) (**Figure 28**).¹⁴¹

Figure 28: Four different kinds of biscyclometalated Ir(III) complexes.

With 4-aryl-1-alkyl-1*H*-1,2,3-triazoles as cyclometallating ligands ($\text{HC}^{\wedge}\text{N}$) into Ir(III) complexes, the triazoles can act as the directing group to facilitate C-H activation on the phenyl ring to form cyclometalated N,C chelates.¹⁴² Based on our previous study for the efficient synthesis of N-2-aryl-1,2,3-triazoles as mentioned in **Section 1.2**, our efforts turned to the application of these N-2-aryl-1,2,3-triazoles as new cyclometallating ligands in the preparation of iridium(III) complexes. As shown in **Figure 29**, these are three different potential binding sites $\text{N}(1)^{\wedge}\text{C}(6'')$, $\text{N}(3)^{\wedge}\text{C}(2'')$ and $\text{N}(3)^{\wedge}\text{C}(2')$ for the formation of iridium(III) complexes. Considering steric effects, the binding site $\text{N}(1)^{\wedge}\text{C}(6'')$ is less steric hindered than the other two sites $\text{N}(3)^{\wedge}\text{C}(2'')$ and $\text{N}(3)^{\wedge}\text{C}(2')$, we then expect the binding site $\text{N}(1)^{\wedge}\text{C}(6'')$ is more favored to bind with iridium(III) ion. To

evaluate this hypothesis, the reactions between IrCl_3 and 2,4-diphenyl-2*H*-1,2,3-triazole are carried out (**Scheme 57**). As we expected, each reaction gave only one single product which was the desired triazole-Ir(III) complexes binding with N(1)[^]C(6'') site in the triazole ligand in excellent yield. These new Ir(III) complexes showed excellent stability towards both air and moisture and could be easily purified by column chromatography.

Figure 29: Three different potential binding sites for forming Ir(III) complexes in the 1,2,3-triazole ligands.

Scheme 57: General method of synthesis for triazole-Ir(III) complexes.

On the basis of this developed procedure for the synthesis triazole-Ir(III) complexes, we have isolated four different $[\text{Ir}(\text{L}^{\text{X}})(\text{ArTriaz})_2]$ complexes in excellent yields (**Figure 30**). Single crystals of complexes **2.2.3b**, **2.2.3c** and **2.2.3d**, suitable for X-ray

crystallographic analysis, were successfully grown from dichloromethane (DCM) and are shown in **Figure 31**, **Figure 32** and **Figure 33** respectively.

Figure 30: Six different $[\text{Ir}(\text{L}^{\wedge}\text{X})(\text{ArTriaz})_2]$ complexes.

Figure 31: X-ray crystal structure for triazole bound Ir(III) complex **2.2.3b**.

Figure 32: X-ray crystal structure for triazole bound Ir(III) complex **2.2.3c**.

Figure 33: X-ray crystal structure for triazole bound Ir(III) complex **2.2.3d**.

UV absorption spectra were almost the same. This phenomenon is consistent to the reported literatures.^{141c}

Figure 35: UV absorption spectra of triazole-Ir(III) complexes. Sample preparation: 1.0×10^{-5} mol/L in MeOH and measured in 1 cm-length quartz cell).

Figure 36: Fluorescence spectra of triazole-Ir(III) complexes. Sample preparation: 1.0×10^{-5} mol/L in MeOH, excitation at $\lambda = 286$ nm with 2.5 nm slit.

Figure 37: Fluorescence spectra of triazole-Ir(III) complexes. Sample preparation: 1.0×10^{-5} mol/L in MeOH, excitation at $\lambda = 369$ nm with 2.5 nm slit.

2.2.3 Evaluation of catalytic reactivity

During the last decade, visible-light photoredox catalysis has shown great promise as a green and sustainable method. As a result of its high natural abundance, benign environmental impact, cleanliness, and sustainability,¹⁴³ photocatalysis using visible light is a reliable and powerful energy source.¹⁴⁴ In this context, there are several examples of its usefulness, including asymmetric alkylation of aldehydes,¹⁴⁵ [3+2] cycloaddition of aryl cyclopropyl ketones,¹⁴⁶ [2+2] cycloaddition of enones,¹⁴⁷ reductive dehalogenation,¹⁴⁸ Oxidation,¹⁴⁹ radical addition to unsaturated bonds,¹⁵⁰ and coupling reactions.¹⁵¹ Since 2010, Stephenson and co-workers reported the application of visible-light photoredox catalysis for the formation of C-C bonds between tertiary N-arylamines and nitroalkanes via an oxidative aza-Henry reaction. In the presence of 1 mol % Ir(ppy)₂(dtbbpy)PF₆, efficient coupling of nitroalkanes with in situ-generated iminium

ions provides the desired products in up to 96% yield (**Scheme 58**).¹⁵² Mechanistic studies suggest that reductive quenching of the Ir³⁺ excited state by the tertiary amine leads to the ammonium radical cation, with subsequent catalyst turnover (Ir²⁺ → Ir³⁺) likely affected by atmospheric oxygen (**Figure 38**).

Scheme 58: An oxidative aza-Henry reaction between tertiary N-arylamines and nitroalkanes.

Figure 38: Proposed mechanism for oxidative aza-Henry reaction by Stephenson.

To evaluate the catalytic reactivity of this new class of Ir(III) complexes, we have synthesized the iridium complex [Ir(bbpy)(ArTriaz)₂]Cl (**Scheme 59**). We then tested its reactivity in aza-Henry reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline.

Scheme 59: Synthesis of complex $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$.

Scheme 60: Aza-Henry reaction of 1,2,3,4-tetrahydroisoquinoline catalyzed by $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$ complex.

Surprisingly, we found this reaction was wavelength sensitive. As shown in **Scheme 60**, different light sources gave different efficiency of this transformation. At the same time, we have known $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$ complexes were the effective catalysts for photoredox catalysis. We then wondered whether the new methodology which combined crossed-conjugate addition and photoredox catalysis could be achieved for the synthesis of new novel nitroalkene derivative. The Lewis base activated crossed-conjugate addition of nitroalkene chemistry is well-known in our group.¹⁵³

Our initial attempts were to treat 2-phenyl-1,2,3,4-tetrahydroisoquinoline **2.2.5** and nitroalkenes **2.2.7** in the presence of the Lewis base L-proline. Unfortunately, no products were obtained (**Scheme 61**). Based on a proposed mechanism as shown in **Figure 38**, O_2 could be the oxidant to turn over the catalytic cycle of Ir catalyst. In our reaction system,

it failed to generate the iminium ion intermediate which suggests the nitromethane is very critical for the turnover catalytic cycle of iridium catalyst (**Figure 39**). We then tested the parallel reactions with different reaction solvents (**Scheme 62**).

Scheme 61: Aza-Henry reaction with nitroalkene activated by Lewis base.

Figure 39: Mechanistic insight of Aza-Henry reaction with nitroalkene.

Scheme 62: Solvent factor for reaction system.

As shown in **Scheme 62**, the product formed only from nitromethane as the reactant, while the activated nitroalkene was not involved in the reaction. These above results indicated the proper oxidant to make the effective turnover of iridium catalyst is vital for the Aza-Henry reaction with activated nitroalkene. Therefore, we need to put further efforts to investigate the optimal conditions for this new transformation.

2.2.4 Conclusion

In conclusion, we have successfully developed the synthesis and structural characterization of N-2-aryl-1,2,3-triazoles as cyclometallating ligands in coordination with Ir(III) salt to give $[\text{Ir}(\text{L}^{\wedge}\text{X})(\text{ArTriaz})_2]$ and $[\text{Ir}(\text{bbpy})(\text{Triaz})_2]\text{Cl}$ complexes in excellent yields. One of the first examples of X-ray structure of N-2-aryl-1,2,3-triazole as the ligands bound with iridium salt is presented. Although the new methodology for aza-Henry reaction with activated nitroalkene has yet to be demonstrated, these complexes showed effective catalytic activity in the aza-Henry reaction, indicating the potential of this Ir(III) triazole complexes as a new class of photoredox catalysts.

2.3 1,2,3-Triazole as Unique Ligand in Promoting Iron Catalyzed Propargyl Alcohol Dehydration for the Synthesis of Conjugated Enynes

2.3.1 General introduction of Iron chemistry

The development of efficient, fast, selective, and clean synthetic methods is highly desirable in organic chemistry. With this point, numerous metal-mediated catalysts have been developed and played vital roles in the organic syntheses. Many of them are derived from heavy or rare metals and their toxicity and prohibitive prices constitute severe drawbacks for large-scale applications. As we know, iron is one of the most abundant metals on earth which is closely related to the life of the human being, and consequently one of the most inexpensive and environmentally friendly ones.¹⁵⁴ Most importantly, many iron salts and complexes are commercially available,¹⁵⁵ or are reported in the literature.¹⁵⁶ Due to its advantages and significance, the development of iron-based chemistry in organic synthesis has led to various iron-catalyzed organic transformations, including nucleophilic additions,¹⁵⁷ substitutions,¹⁵⁸ reductions,¹⁵⁹ oxidations,¹⁶⁰ hydrogenations,¹⁶¹ cycloadditions,¹⁶² isomerizations,¹⁶³ rearrangements,¹⁶⁴ and polymerizations.¹⁶⁵

In the last decade, Fürstner's group explored several organoiron catalyzed cross coupling reactions with Grignard reagents (**Scheme 63**).¹⁶⁶ They showed that iron salts allow various types of electrophiles, such as aryl chlorides, aryl tosylates, alkyl halides, alkynyl epoxides, enol triflates and phosphates, acid chlorides and thioesters, to be activated under mild conditions. Such iron-catalyzed processes occur very rapidly even at low temperature and therefore are distinguished by broad functional group compatibility. Furthermore, recent advances in carbon-heteroatom bond formation and studies relevant

to the general reactivity of in situ generated and structurally defined “low-valent” iron complexes which have been confirmed by X-ray crystallography are presented (**Scheme 64**).¹⁶⁷ These complexes revealed the excellent catalytic reactivity for a variety of Alder-ene, [4+2], [5+2], and [2+2+2] cycloaddition and cycloisomerization reactions of polyunsaturated substrates which tolerate esters, ketones, sulfonamides, acetals, ethers, cyclopropanes, remote alkenes, amines and aryl halides (**Scheme 65**).

Scheme 63: Iron-catalyzed cross coupling reaction between organic halide/pseudohalide and Grignard reagents.

Scheme 64: Different “low-valent” iron complexes.

Scheme 65: One “low-valent” iron complex as the catalyst in a variety of transformations.

The C-H activation has gained many attentions from organic chemists, because it meets not only the efficient and sustainable requirement of organic transformations but also the understanding of the intrinsic features of the broadly existing C-H bonds in organic molecules.¹⁶⁸ Iron-containing enzyme-catalyzed C-H activation has been reported and suggested a potential application of iron catalysis in C-H activation.¹⁶⁹ Combining the advantages of both iron chemistry and C-H activation, the significance of iron-catalyzed C-H activation has stimulated rapid development in the past several years.¹⁷⁰

The C-H bond oxidation is one of the most common processes in C-H activation. In the synthetic field, iron-catalyzed systems for C-H oxidation can be traced back to one

century ago, and this was summarized as Gif chemistry¹⁷¹ and Fenton chemistry,¹⁷² as well as other non-heme mimic systems.¹⁷³ Recently, iron-catalyzed oxidation was mostly focused on sulfide oxidations,¹⁷⁴ epoxidation,¹⁷⁵ and olefin dihydroxylation.¹⁷⁶ In contrast, iron catalyzed C-H bond oxidation has had few significant breakthroughs for a rather long time, until recent years.

In 2007, White and co-worker made a significant improvement in the oxidation of general sp^3 C-H bonds.¹⁷⁷ They reported the iron catalyzed aliphatic C-H oxidation by using $[Fe(PDP)(SbF_6)_2]$ complex. In this report, a highly selective oxidation of nonactivated sp^3 C-H bonds via iron catalysis was well investigated (**Scheme 66**). Iron (PDP) complex [PDP = 2-((S)-2-[(S)-1-(pyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl)methyl]pyridine] was essential for this transformation and the higher rigid PDP ligand led to the increase of selectivity. This process was rather clean, since the oxidant was hydrogen peroxide, which was cheap, easily available, and frequently used in traditional iron-catalyzed Gif¹⁷¹ and Fenton¹⁷² chemistry. In this transformation, the electronic feature rather than the steric effect of C-H bonds plays an important role, since electron rich tertiary C-H bonds showed a higher reactivity than either secondary or primary C-H bonds. An electron-withdrawing group (EWG) on the α or β carbon of the C-H bond quenched the reactivity (**Figure 40**).

Scheme 66: Iron-catalyzed oxidation of unactivated sp^3 C-H Bonds.

Figure 40: Reactivity of different C-H bonds.

Considering the mechanistic insight among iron catalyzed transformations, the iron species generally could either serve as Lewis acid or as redox center through single electron transfer (SET) process. For example, various iron-containing domains of the enzymes showed their high catalytic abilities in C-H oxidations, in which the SET process was considered as a possible pathway to facilitate the C-H oxidation.¹⁷⁸

2.3.2 Research Objective and Results

Conjugated enynes are fundamental building blocks in biology,¹⁷⁹ material science¹⁸⁰ and fine chemical synthesis.¹⁸¹ As a result, the synthesis of enynes has received considerable attention during recent decades, and new methods for their preparation have been developed. Among these various methods, the metal-catalyzed dimerization of terminal alkynes was a straightforward approach (**Scheme 67A**, $R=R''$, $R'=H$).¹⁸² Unfortunately, the complicated regio- and stereoselectivity of the dimerization process significantly limited the wide application of this method. To minimize this drawback, the solution was the coupling of alkynes with structurally defined organometallic alkenes (**Scheme 67B**).¹⁸³ However, organometallic alkenes are usually difficult to handle and are very toxic in general, especially those that are volatile.

Scheme 67: Classical approaches for synthesizing conjugated enynes.

The most employed protocol for the synthesis of conjugated enynes has been the cross-coupling reactions between vinyl halides and terminal acetylenes catalyzed by palladium complexes and copper(I) iodide, namely, the Sonogashira reaction (**Scheme 67C**).¹⁸⁴ This elegant process does not require the stoichiometric amount of an organometallic reagent. However, the major limitation of this method was the preparation of the vinyl halide. In view of the limitations and shortcomings of these established methods, we believed that the simple and efficient methods that can install this unsaturated hydrocarbon moiety are highly desirable.¹⁸⁵

The catalytic propargyl alcohol dehydration, without any doubt, is one of most atom-economic and practical approaches for conjugated enyne synthesis. Although some methods related to propargyl alcohol dehydration strategy have been reported (**Scheme 68**), such as the phosphoric esters *syn*-elimination¹⁸⁶ and cyclopropane ring opening,¹⁸⁷ these methods only work for limited specific substrates. Therefore, this simple transformation is challenging and problematic.

Scheme 68: The dehydration propargyl alcohol for specific substrates in synthesis of conjugated enynes.

A) Cyclopropane ring opening strategy

B) Phosphoric esters syn-elimination

C) A general approach

To achieve alcohol elimination, a Lewis acid was generally required (for OH activation). However, the carbocation intermediate and conjugated enynes products are highly reactive under these conditions. This often leads to undesired decomposition and polymerization. As illustrated in **Table 13**, the commonly used Lewis acids all gave poor yields of enyne **2.3.2a**, even though most of the propargyl alcohol **2.3.1a** was consumed. Therefore, to fill this “missing methodology”, new catalysts need to be developed either by providing proper acidity (only activating the C-O bond without formation of “pure” carbocation) or by going through alternative reaction path (such as radical) to avoid the undesired decomposition. The recent studies on triazole-Au complex revealed excellent chemoselectivity of this triazole catalyst and the triazole-borane complexes suggested the ability of triazole to stabilize a single electron reaction center.¹⁸⁸ Additionally, in the

synthesis of triazole-allenes (**Section 1.5**), the higher yield and improved regioselectivity was obtained when we pre-mixed the FeCl₃ and triazole before the addition of propargyl alcohol (**Table 14**). On the basis of these results, we postulated that triazole ligands might provide the needed reactivity for this simple but important transformation.

Table 13: Direct propargyl alcohol dehydration: a challenging transformation.^a

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>2.3.1a</p> </div> <div style="text-align: center;"> $\xrightarrow{10 \text{ mol\% [cat], MeCN, 7 h}}$ </div> <div style="text-align: center;"> <p>2.3.2a</p> </div> </div>				
Entry	Catalyst	Temp (°C)	Convsn (%) ^b	Yield (%) ^c
1	TfOH	60	90	30
2	AlCl ₃	60	10	<5
3	Bi(OTf) ₃	60	90	21
4	NiCl ₃	60	22	<5
5	In(OTf) ₃	60	80	15
6	CeCl ₃	60	23	<5
7	LaCl ₃	60	26	<5
8	RuCl ₃	60	78	22
9	IrCl ₃	60	75	20
10	PdCl ₂	60	30	<5
11	Cu(OAc) ₂	60	52	<5
12	Co(OAc) ₃	60	26	<5
13	Ti(Oi-Pr) ₄	60	71	9
14	FeCl ₂	60	30	<5
15	FeCl ₃	60	95	29
16	Fe(acac) ₃	60	59	12
17	FeCl ₃	rt	32	11

^a General reaction conditions: **2.3.1a** (0.25 mmol, 1.0 equiv.) and Lewis acid catalyst (10 mol%) in MeCN (5 mL); ^b Conversions were determined based on the consumption of propargyl alcohol; ^c NMR yields of **2.3.2a** with 1,3,5-trimethoxybenzene as internal standard.

Table 14: A small detail from allenation of triazole.

Catalyst	Loading (%)	Sol. ^b	Temp (°C)	Time (h)	Conv. (%) ^c	Yield (%) ^d	1.5.4a:1.5.5a ^d
FeCl ₃ (w/o pre-coord.)	10	MeCN	60	5	86	57	3:1
LiCl	10	MeCN	60	5	90	70	6:1

Table 15: Screening of ligands^{a,b,c}

^a General reaction conditions: **2.3.1a** (0.25 mmol, 1.0 equiv.), ligands (10 mol%) and Lewis acid catalyst (10 mol%) in MeCN (5 mL); ^b Conversions were determined

based on the consumption of propargyl alcohol; ^c NMR yields of **2.3.2a** with 1,3,5-trimethoxybenzene as internal standard.

To test our hypothesis, various triazole-FeCl₃ mixtures were employed as the catalysts to react with **2.3.1a**. To ensure the consistency, all reactions were conducted under identical conditions and the reaction mixtures were measured after 7 hours (**Table 15**). To our surprise, the simple addition of N-methyl benzotriazole **L1** to FeCl₃ significantly decreased undesired decomposition of **2.3.1a**, giving the desired enyne **2.3.2a** in good yields. Screening the triazole ligands revealed even better reactivity of chelating ligands, giving enyne in excellent yields. On the basis of synthetic simplicity of triazole ligands, we have selected 2-(1*H*-benzo[d][1,2,3]triazol-1-yl)ethanol **L10** as the optimal ligand for this transformation.

Table 16: Screening of different heteroaromatic ligands^{a,b,c}

2.3.1a

$\xrightarrow[20 \text{ mol\% L, 60 } ^\circ\text{C, 7 h}]{10 \text{ mol\% FeCl}_3, \text{ MeCN}}$

2.3.2a

conv. 21%
yield <5%

conv. 87%
yield 8%

conv. 50%
yield 14%

conv. 21%
yield <5%

conv. 41%
yield <5%

conv. 35%
yield <5%

conv. 35%
yield <5%

L10
10 h
conv. 100%
yield 92%

FeCl ₃	L10	time	temp (°C)	conv.	yield
10%	10%	7 h	60	85%	72%
10%	20%	7 h	60	91%	82%
10%	30%	7 h	60	76%	60%
10%	40%	7 h	60	71%	56%
10%	20%	10 h	60	100%	92%

^a General reaction conditions: **2.3.1a** (0.25 mmol, 1.0 equiv.), ligands (10 mol%) and Lewis acid catalyst (10 mol%) in MeCN (5 mL); ^b Conversions were determined based on the consumption of propargyl alcohol; ^c NMR yields of **2.3.2a** with 1,3,5-trimethoxybenzene as internal standard.

Furthermore, we have investigated other heteroaromatic ligands, including pyridine, imidazole, tetrazole and 1,2,4-triazoles. Interestingly, they did not catalyze this transformation at all, even with very similar binding patterns, which demonstrated the unique properties of 1,2,3-triazoles as ligands in adjusting iron cation reactivity (**Table 16**).

Table 17: Reaction substrate scope.^{a,b}

^a General reaction conditions: **2.3.1a** (0.25 mmol, 1.0 equiv.), ligands **L10** (20 mol%) and Lewis acid catalyst (10 mol%) in MeCN (5 mL); ^b isolated yields.

The bi-dentate triazole-based ligands displayed better reactivity. Increasing the ligand loading revealed 2:1 (ligand/Fe) ratio as the optimal conditions, which was

consistent with the Fe^{3+} octahedral coordination (six coordination sites, requiring open coordination sites for OH binding in the transition state). Solvent screening revealed acetonitrile as the optimal solvent. Attempts in obtaining the iron-triazole complex crystal structure have been unsuccessful at this moment. Nevertheless, addition of readily available 1,2,3-triazole to FeCl_3 provided a practical and highly efficient catalyst system, which gave the critical chemoselectivity for the C-O bond activation. To the best of our knowledge, this is the first catalytic system reported that can effectively promote this important transformation.¹⁸⁹ Various functional propargyl alcohols were prepared to investigate the reaction substrate scope. The results are summarized in **Table 17**.

As indicated in **Table 17**, both terminal alkyne (**2.3.2r**) and internal alkyne were suitable for this reaction, giving the desired enynes in excellent isolated yields. The alkyne terminal can tolerate various substituted groups, including alkyl (**2.3.2a**, **2.3.2b**), aryl (**2.3.2e**), TMS (**2.3.2c**), cyclopropyl (**2.3.2g**) and even vinyl groups (**2.3.2d**). The propargyl position tolerates an aromatic ring with either electron donating (**2.3.2j**, **2.3.2k**) or electron withdrawing (**2.3.2s** to **2.3.2u**) groups. Elimination to the alkenes showed excellent stereoselectivity, with only one double bond isomer observed, which were unambiguously characterized by X-ray crystal structure (**2.3.2n**). Substrates **2.3.2n-2.3.2u** illustrated the good functional group tolerability of this method. The formation cyclohexenyl enyne **2.3.2i** indicated slower reaction rate caused by the lower reactivity of the C-O bond. However, the starting material propargyl alcohol could be fully recovered, indicating the excellent chemoselectivity of the 1,2,3-triazole/Fe catalysts. Enynes with 1,2-disubstituted alkenes could not be formed because of the low reactivity of C-O bond under the reaction conditions. Raising the reaction temperature caused decomposition of

the propargyl alcohols. However, the highly reactive 1,4-enediynes could be easily synthesized with this method (**Table 18**), which highlighted the benefits of the milder reaction condition and improved chemoselectivity of this catalyst.

Table 18: Synthesis of 1,4-enediynes^{a,b}

^a General reaction conditions: identical as above; ^b Isolated yields.

2.3.3 Tuning the reactivity of conjugated enynes in 1,4-bromolactonization.

Halogen-promoted addition of nucleophiles to alkenes and alkynes is one of the most fundamental reactions in organic synthesis.¹⁹⁰ Arguably, the halolactonization is very useful since the resulting lactone can easily be elaborated.¹⁹¹ To date, several 1,4-bromolactonizations of conjugated enynes to give the products synthetically valuable bromoallenes have been reported in natural product synthesis.¹⁹² Moreover, bromoallenes could be the important intermediates in organic transformations.¹⁹³ In 2009, Tang and co-workers reported a DABCO-catalyzed, highly regio- and diastereoselective 1,4-bromolactonization of conjugated enynes (**Scheme 69**).¹⁹⁴ In contrast to 1,2-addition to double bond in the conjugated enynes, where two adjacent stereogenic centers are created,

1,4-addition across conjugated enynes can produce a stereogenic center and an axially chiral allene simultaneously. However, in Tang's paper, the substrates were relatively limited. As shown in **Figure 41**, the substituted group on R₂ position was methyl or hydrogen only and also no substrate with an aromatic substituent on the R₃ position has been reported, likely caused by the difficult enyne synthesis.

Scheme 69: DABCO-catalyzed 1,4-Bromolactonization of conjugated enynes reported by Tang

Figure 41: Limited substrates from Tang's approach.

With our reported method here, these CO₂H or ester (CO₂Me) substrates could be readily prepared, we then tried to extend the substrate scope of Tang's approach which is

DABCO-catalyzed 1,4-Bromolactonization of conjugated enynes. Treating **2.3.2n**, **2.3.2o** with NBS in the presence of 2 mol% DABCO resulted in 6-endo-trig cyclization products, giving the lactones **2.3.3a** and **2.3.3b** in good yields (**Scheme 70**). With the terminal alkyne substrate (**2.3.2r**), it gave complex reaction mixture.

Scheme 70: The 6-endo-trig cyclization of conjugated enynyl acids.

Based on above results, we thought two factors, which are the energetic favorite of cyclization (based on ring strain, six-membered ring is most stable) and relative reactivities of double bond and triple bond in the enynes, may be affected the success of 1,4-bromolactonization of conjugated enynes. Both extended carbon chain substrates **2.3.2p** and **2.3.2q** have been subjected to the standard condition of 1,4-bromolactonization, unfortunately, no six-membered ring containing bromoallenes were

formed (**Scheme 71**). We then focused on tuning the reactivities of double bond and triple bond in conjugated enynes.

Scheme 71: The 7-endo-trig cyclization of conjugated enynyl acids.

The enediynyl acids **2.3.2y'** and **2.3.2z'**, which can be prepared in 3 steps, was reacted with NBS and gave no desired products. We thought that the formation of tertiary bromide generated the carbocation intermediate in situ, and then decomposed (**Scheme 72**). Despite these negative results, we learned that the reactivities of double bond and triple bond were very critical for this transformation at least. Finally, to tune the electronic effect of substituted pattern on the both double bond and triple bond, these enynes **2.3.2s**, **2.3.2t** and **2.3.2u** have been prepared successfully (**Scheme 73**). With our delight, the treatment **2.3.2s**, **2.3.2t**, **2.3.2u** with NBS resulted in either 6-endo-trig or 5-exo-trig cyclization, giving the lactone **2.3.3e** or bromoallenes (**2.3.3f**, **2.3.3g**) in excellent yields and diastereoselectivity ($>20:1$) (**Scheme 74**). Surprisingly, simply changing the substituted groups at the alkyne terminal, the 6-6-endo-trig or 5-exo-trig could be controlled with excellent stereoselectivity.

Scheme 72: The reactions with enediynyl acids as the reactants.

Scheme 73: Synthesis of enynes **2.3.2s**, **2.3.2t** and **2.3.2u**.

Scheme 74: Substituted group dependent enyne activation.*

2.3.4 Mechanistic study.

According to the literature, iron cation catalyzed reactions should undergo either Lewis acid electrophilic activation or single electron redox process.¹⁹⁵ To investigate the reaction mechanism of this triazole-ligand coordinated Fe^{3+} cation catalyst, the cyclopropane substituted propargyl alcohols (**2.3.4a**, **2.3.4b**) were prepared and treated with FeCl_3 under various conditions. As indicated in **Figure 42**, both Lewis acid catalyzed cyclopropane opening¹⁹⁶ and radical initiated ring opening¹⁹⁷ have been reported in literature. The NH-triazole nucleophile and radical trapper 1,4-cyclohexyldiene (CHD) were then used to investigate the mechanism of the triazole-Fe catalysts.

* Relative stereochemistry of compounds **2.3.3e**, **2.3.3f** and **2.3.3g** have been fully characterized through comprehensive 1D and 2D NMR analysis. Detailed spectra are provided in supporting information.

Figure 42: Mechanistic investigations.

The reaction of **2.3.4a** under the optimal conditions gave the chloro-enyne **2.3.5a** as the only enyne product isolated (82% yield, **Figure 42A**). With the addition of NH-triazole nucleophile (**Figure 42B**), triazole enynes **2.3.5b** and **2.3.5c** were isolated in 61% and 75% yield individually as the only double bond isomers (**2.3.5c** was confirmed by X-ray). Addition of the radical trapper CHD did not lead to the formation of H-quenched enyne **2.3.2b** (**Figure 42C**). Instead, the chloro-enyne **2.3.5a** was the only enyne product isolated. These results suggested the reaction proceeds via carbocation ring opening instead of radical mechanism, which is consistent with our hypothesis that 1,2,3-triazole ligands provided the required electronic effect in adjusting Lewis acidity of Fe³⁺ to achieve the required chemoselectivity for this transformation.

2.3.5 Conclusion

In conclusion, 1,2,3-triazoles were identified as unique ligands for iron mediated catalysis. The challenging catalytic dehydration of propargyl alcohols to conjugated enynes was

successfully achieved with this new iron-based catalytic system. The fact that 1,2,3-triazoles were the only heterocycles “working” among the tested ligands illustrate their ability in adjusting iron cation reactivity, thereby providing the foundation for further development of other important iron catalyzed transformations. Moreover, we have tuned the reactivity of conjugated enyne in the 1,4-bromolactonization reaction.

Chapter Three: N-2-aryl-1,2,3-triazoles: a new class of UV-Blue emitting fluorophores through Planar-Intramolecular-Charge-Transfer (PICT)[†]

3.1 Introduction

Photoactive molecules are important in chemistry, biology and material research.¹⁹⁸ The last two decades evidenced the great advance in this research area, where fluorescent active dyes have been applied to many different research fields, such as biological target imaging,¹⁹⁹ effective photosensors²⁰⁰ and novel photoactive materials.²⁰¹

Two key features of fluorescence emitting molecules are quantum efficiency and the wavelengths of excitation and emission. Although several fluorophores have been developed over the years, effective UV/blue light emitting small molecules are still rare²⁰² due to the relative high-energy gap required between the interactive orbitals, which may cause either poor photostability or low quantum efficiency.²⁰³ However, the fast growing research, such as OLED display²⁰⁴ and Förster resonance energy transfer (FRET)²⁰⁵ studies, in photoactive compounds generated increasing needs for effective UV/blue emitting molecules.

Two of main challenges in developing UV/blue emitting small molecules are the optical activity and photostability dilemma. As shown in **Scheme 75A**, although condensed polyaromatic structures have an effective aromatic conjugation, usually these compounds possess low energy gap between excited and ground states, thus giving emissions at a longer wavelength. Alternatively, bis-aromatic structures (**Scheme 75B**)

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could provide the needed larger energy gap for potential UV/blue emitting.²⁰⁶ However, the steric repulsions between the *ortho*-substituted groups cause poor conjugations between the two aromatic rings and therefore significantly decrease the photoactivity. To overcome this problem, extended aromatic systems have been developed to enhance the conjugations (**Scheme 75C**).²⁰⁷ Blue light emission has been observed with this type of molecules, such as the commercial available blue dye disodium 4,4'-bis(2-sulfostyryl)biphenyl (DSBP, **STD-1**).²⁰⁸ However, the photolabile C=C double bonds considerably limit the potential applications of these compounds.²⁰⁹

Scheme 75: Different types of UV/blue emitting small molecules.

3.2 Research Objective and Results

3.2.1 Initiation

Our interest in developing novel blue-emitting small molecules was initiated by our recent discovery (**Figure 43**). As shown in **Figure 43**, the N-2-phenyl triazole **3.1a** showed good emission at 362 nm when it was excited at 254 nm, while the N-1-aryl

isomer **3.1a'** gave almost no emission. This interesting finding suggested suggested that the N-2-aryl-triazoles (NATs) might be applied as new building blocks to reach effective UV/blue emission by overcoming the challenges associated with other small molecule systems. Therefore, a series of NATs were prepared by using the method which has been described in **Section 1.2** and the optical properties of these NATs were investigated as the new UV/blue dyes.

Figure 43: Photoluminescent spectra of N-2-aryl-1,2,3-triazole: sample preparation: 1.0×10^{-5} mol/L in MeOH, excitation at 254 nm with 5 nm slit, quantum yield of **3.1a** $\Phi = 0.154$, quantum yield of **3.1a'** $\Phi = 0.009$.

3.2.2 Influence of substituted groups on the C-4 and C-5 positions

To evaluate these new fluorophores, one key concern is whether the optical properties (efficiency, excitation and emission wavelengths) of the NATs could be adjusted while maintaining effective emission in the UV/blue range. The structures of NATs allowed

substitutions on three different positions: C-4, C-5 and N-2. Although the C-4 and C-5 substitutions are away from the N-2 aryl groups, they may strongly influence conjugation at the N-2 position through electronic effect. This concern was confirmed by the X-ray crystal structures of compounds **3.1b** and **3.1c** shown in **Figure 44**.

Figure 44: X-tray crystal structures of **3.1b** and **3.1c**.

As shown in **Figure 44**, the N-2-phenyl group in compound **3.1b** formed good conjugation with triazole ring with a dihedral angle 5.5° , which supported our proposed strategy that the N-2 aryl triazoles could provide much improved conjugations by avoiding the *ortho*-steric repulsion associated with typical bis-aromatic systems. The C-4-phenyl, on the other hand, showed poorer conjugation (dihedral angle 21.8°) in the solid state. This steric influence was further emphasized by the structure of compound **3.1c**, where a nearly perpendicular conformation was observed (dihedral angle 81.1°) at the C-4 position when the bulky cyclohexenyl group was placed at the C-5 position, even

with the possible formation of intramolecular hydrogen bonds (between phenol hydroxy and triazole N-2 nitrogen). Moreover, the conformation of the C-4-aryl group also showed the influence on the conjugation at the N-2 position, at least in the solid state: a much bigger dihedral angle was observed for compound **3.1c** (19.7°) than **3.1b** (5.5°). These crystal structures provided a strong foundation in rationalizing the photoactivity of the NATs. However, it was expected that free σ -bond rotations at N-2 and C-4 positions could occur while the compounds were dissolved in solution.

Table 19: Fluorescence emission of compounds with different C-5 substitutions.^a

	3.1d	3.1e	3.1f	3.1g	
	<hr/>				
	Absorption (nm)	Emission (λ_{max})	Φ^b	Fluorescence Intensity ($\times 10^3$) ^c	
3.1a	222 (0.127), 305 (0.222)	362	0.15	19.6	
3.1b	206 (0.128), 263 (0.250)	316	0.02	4.7	
3.1c	227 (0.257), 292 (0.268)	380, 400	0.06	10.8	
3.1d	220 (0.146), 296 (0.276)	348	0.09	23.0	
3.1e	220 (0.118), 294 (0.263)	347	0.35	46.3	
3.1f	220 (0.111), 290 (0.253)	342	0.45	56.6	
3.1g	221 (0.128), 285 (0.265)	342	0.30	52.4	
STD-1	207 (0.452), 234 (0.228), 349 (0.710)	402, 422	0.23	63.1	
STD-2	234 (0.423), 334 (0.068)	365	0.56	13.9	

^a Sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 254 nm with 5.0 nm slit; ^b Quantum yields (Φ) were determined based on 1.0×10^{-5} mol/L Quinine sulfate dihydrate (**STD-2**) in H₂O ($\Phi = 0.56$); ^c calculated photo emission integration from the original spectra. All fluorescence measured under identical conditions (see supporting information). **STD-1** = disodium 4,4'-bis(2-sulfostyryl)biphenyl (DSBP).

To evaluate how the various substituted groups on the C-4 and C-5 positions influenced the overall excitation and emission, compounds **3.1d** to **3.1g** were designed and prepared with different substituted groups on the C-5 positions. The absorptions and emissions of these compounds are summarized in **Table 19**.

Compared with N-2-phenyl benzotriazole **3.1a**, the C-4-N-2-diphenyl triazoles generally gave stronger emissions (**3.1e-3.1g**). All of these substrates emitted in the UV-blue range with λ_{max} around 350 nm. The photoquenching by strong electron withdrawing carbonyl group were observed (**3.1b**). Notably, the highly steric hindered compound **3.1g** gave similar strong emission for the much less hindered compound **3.1f**, which suggested the little influence of the bulkiness on the C-5 position for the light emission.

3.2.3 Variation on N-2-position

With the N-2-aryl moiety as the fluorophore core, it is expected that the N-2 substituted groups will surely influence the overall optical performance. We wondered if this could be used to adjust the fluorescence emissions and make NAT tunable dyes. Compounds with different substituted groups on the N-2-phenyl ring were prepared to investigate the substituent group effect on their optical properties.

As shown in **Table 20**, most of the N-2-substituted aromatic compounds **3.2** gave good UV/blue light emissions. The overall quantum efficiency of NATs is around 30%, which are comparable with commercial blue dyes (for example, DSBP $\Phi = 0.23$, measured under the identical conditions). These results suggested the promising future of these compounds as new UV/blue emitting fluorophores. Similar to other literature reports,²¹⁰ photoquenching by NO₂ (**3.2e**) and by a carbonyl group (**3.2f**) were observed.

Interestingly, a significant decrease of emission intensity was obtained with *ortho*-pyridine compound **3.2h**. Considering the similar electronic effect of *para*-pyridine **3.2g**, this result was rather surprising. The success in obtaining the X-ray crystal structures for both **3.2g** and **3.2h** helped to reveal the mechanistic reason behind this result (**Figure 44**).

Table 20: Substituted group effect on the N-2 position.^a

	Absorption (nm)	Emission (λ_{max})	Φ^b	Fluorescence Intensity ($\times 10^3$) ^c
1e	220(0.118), 294(0.263)	347	0.35	46.3
2a	224 (0.154), 309 (0.397)	350	0.31	138
2b	240 (0.056), 294 (0.212)	343	0.34	35.0
2c	298 (0.274)	344	0.35	72.1
2d	245 (0.041), 298 (0.226)	374	0.31	61.6
2e	225 (0.181), 336 (0.205)	342	<0.005	< 0.5
2f	228 (0.135), 250 (0.14), 317 (0.365)	343	<0.005	< 0.5
2g	220.5 (0.133), 300 (0.242)	341	0.28	52.2
2h	238 (0.156), 276 (0.093)	341	0.15	1.7
2i	222 (0.482), 260 (0.115), 296 (0.127)	375	0.27	29.6

^a Sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit; ^b Quantum yields (Φ) were determined based on 1.0×10^{-5} mol/L Quinine sulfate dihydrate in H_2O ($\Phi = 0.564$); ^c calculated photo emission integration from the original spectra. All fluorescence measured under identical conditions (see supporting information).

Figure 45: X-ray crystal structures of **3.2g** and **3.2h**.

As shown in **Figure 45**, the crystal structure of **3.2h** exhibited a larger dihedral angle between the pyridine ring and triazole ring, due to the electron repulsion between the lone pair electrons of the nitrogen atoms on triazole and pyridine rings. This result supports our hypothesis that effective conjugation between triazole ring and N-2 aryl groups is crucial for good fluorescence emission.

The quantum yield (Φ), which indicates the percentage photon emission, is based on the photons absorbed. Therefore, although quantum yield is a very important parameter used to evaluate fluorescent active molecules, it may not completely represent the performance of the fluorophores since molecules may absorb photons with different efficiency (different absorption ϵ). The fluorescence intensities of NATs were calculated (under the identical conditions) and shown in **Table 20**.

The emission intensities of NATs are compatible or higher than both commercial blue dyes quinine sulfate dihydrate and DSBP. Impressively, compounds **3.2a** gave very intense emission, which was more than two times stronger than quinine sulfate dihydrate dye; extending conjugation is known to enhance photoabsorption. However, this strategy usually does not work well for blue emitting dyes because conjugation gives a red shift, resulting in the emission at a longer wavelength. To our surprise, this

undesired red shift did not occur in the NAT system. For compound **3.2i**, only slight red shift (13 nm) was observed compared with compound **3.1e**. The compound **3.2a**, on the other hand, gave almost no red shift even with largely increased emission intensity. These unusual photoactivities highlighted the unique properties of these novel NAT dyes (also see computational studies in later section for the HOMO-LUMO distributions).

3.2.4 Substituent group electronic effect

To investigate substituent electronic effects, two series of compounds were compared with substituted groups either on the *para*-position of the N-2 phenyl or on the *para*-position of the C-4 phenyl. The photoluminance spectra are depicted in **Figure 46**.*

Figure 46: Photoluminescent spectra of N-2-aryl-1,2,3-triazole. Sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

(A)

* See the detailed excitation/emission data in supporting information.

(B)

The F-, Cl-, CN- and OMe-substituted NATs all gave strong emission. Interestingly, a very similar trend was observed with substituted groups on either the N-2 phenyl ring (**Figure 46A**) or on the C-4 phenyl ring (**Figure 46B**). The NATs with electron deficient substituted groups (F, Cl, CN) showed very little wavelength shifts. In contrast, the strong electron donating methoxy group, gave noticeable red shifts when placed on either N-2 (**3.2d**) or C-4 (**3.3f**) positions. The CN-substituted compound **3.2a** gave the highest emission intensity due to the more efficient light absorption through conjugation. Similar trends were also observed between F- and Cl-substituted NATs. Whereas similar quantum yields were observed, the Cl-substituted NATs gave higher fluorescence emission than F substituted NATs, which was due to the better resonance conjugation between lone pair electrons of Cl and the phenyl ring. The summarized absorption and emission data are shown in **Table 21**.

Table 21: Excitation and emission behavior of substituted NATs.^a

3.1e: R ¹ = H, R ² = H	3.3a: R ¹ = F, R ² = H	3.3f: R ¹ = OMe, R ² = H	3.3k: R ¹ = Cl, R ² = H
3.2a: R ¹ = H, R ² = CN	3.3b: R ¹ = F, R ² = CN	3.3g: R ¹ = OMe, R ² = CN	3.3l: R ¹ = Cl, R ² = CN
3.2b: R ¹ = H, R ² = F	3.3c: R ¹ = F, R ² = F	3.3h: R ¹ = OMe, R ² = F	3.3m: R ¹ = Cl, R ² = F
3.2c: R ¹ = H, R ² = Cl	3.3d: R ¹ = F, R ² = Cl	3.3i: R ¹ = OMe, R ² = Cl	3.3n: R ¹ = Cl, R ² = Cl
3.2d: R ¹ = H, R ² = OMe	3.3e: R ¹ = F, R ² = OMe	3.3j: R ¹ = OMe, R ² = OMe	3.3o: R ¹ = Cl, R ² = OMe

	Excitation (λ_{max})	Emission (λ_{max})	Φ^b	Fluorescence Intensity ($\times 10^3$) ^c	Stoke shift (nm)
3.1e	298	347	0.34	46.3	49
3.2a	312	350	0.31	138	38
3.2b	298	343	0.34	35.0	45
3.2c	292	344	0.35	72.1	52
3.2d	304	374	0.31	61.6	70
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3.3a	278	343	0.39	35.2	65
3.3b	305	351	0.51	99.1	46
3.3c	277	343	0.40	45.5	66
3.3d	279	343	0.25	79.6	64
3.3e	280	373	0.33	96.3	93
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3.3f	284	360	0.39	82.2	76
3.3g	318	401	0.32	111	83
3.3h	283	360	0.34	78.6	77
3.3i	287	364	0.34	89.8	77
3.3j	284	369	0.34	114	85
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3.3k	280	341	0.35	134	61
3.3l	306	352	0.45	174	46
3.3m	281	343	0.41	77.3	62
3.3n	283	345	0.36	99.0	62
3o	285	376	0.35	101	91

^a Sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit; ^b Quantum yields (Φ) were determined based on 1.0×10^{-5} mol/L Quinine sulfate dihydrate (STD-2) in H₂O ($\Phi = 0.56$); ^c calculated photo emission integration from the original spectra. All fluorescence measured under identical conditions (see supporting information).

3.2.5 NATs: Tunable UV/blue emitting small molecule dyes

The large number of NATs spectra allowed us to explore the key factors that control the optical properties of novel tunable NATs UV/blue dyes. First, the emission enhancement by CN and Cl groups were confirmed, where strong emissions were observed in all cases with these two groups. When both CN and Cl are present (triazole **3.31**), the highest emitting intensity was achieved with λ_{max} at 352 nm. Notably, though the fluorescence enhancement was believed to be a consequence of the extended conjugation, no significant red shift was observed. This UV emission was more than three times stronger than the commercial standard blue dye DSBP, which highlighted the superior photoactivity of these novel UV fluorophores.

Figure 47: Photoluminescent spectra of N-2-aryl-1,2,3-triazole. Sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

The electron donating OMe is an as the effective shift-tuning group for the NAT dyes. The red shifts were observed with OMe on either N-2 (**3.2d**) or C-4 (**3.3f**) positions. No further red shift occurred with OMe on both positions (**3.3j**), suggesting that cancellation of the inductive effects in **3.3j** resulted in no further red shift. This hypothesis was further supported by the emission of compound **3.3g**, where a red shift was achieved (emission λ_{max} at 401 nm) when combination of OMe and electron withdrawing CN were applied on the opposite sites of NATs (**Figure 47**).

Figure 48: Range of Stock shifts for N-2-aryl-1,2,3-triazole. Sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

Besides the significant influence on the fluorescence intensity and emission wavelength, the various substituents could also affect the Stock shift. As shown in **Table 21**, the Stock shifts for these tested compounds ranges from 38 nm to 93 nm (**Figure 48**). The CN modified NATs gave narrow emission band with smaller Stock shifts. Whereas the OMe substituted NATs gave broader emission bands with larger Stock shifts. The ability to modify the Stock shifts is consistent with good photoactivity of the NATs,

which allowed easy adjustment for the emission wavelength and the gap between excitation and emission.

3.2.6 Computational investigations

Time-dependent density function theory (TD-DFT) theoretical calculations were also carried out with the Gaussian 03²¹¹ packages by using the B3LYP/6-31G(d) model.²¹² Unlike the orbitals in other simple bis-aromatic compounds, the HOMOs and LUMOs of the NATs were very similar for all N-2 substituted triazoles with LUMO locate between triazole and N-2 aryl rings. Examples of compounds **3.2d** and **3.3g** are given in **Figure 49**.

The N-2-substituted NATs are much less polar compared with the N-1 analogous due to the homogenization of electron density through extended π -conjugation. The photoexcitation introduces a high extension of planarity to induce the homogeneous distribution of electron density throughout the triazole and N-2 aryl rings. This phenomenon, which has been well documented in the literature, is referred to as planar intramolecular charge transfer (PICT).²¹³

Figure 49: HOMO and LUMO orbitals of compounds **3.2d** and **3.3g**.

What makes the 1,2,3-triazole special comparing to other aromatic structures is the highly effective conjugation between triazole and N-2 aryl rings, even with the presence of theoretically free-rotatable N-C σ bonds. These co-planar structures were confirmed not only by the X-ray crystal structures, as shown in earlier discussions, but also indicated by the computational studies as the most stable conformations for these molecules. Solvent screenings of these dyes has been performed and indicated little change of the optical properties of these dyes in EtOAc, MeOH, CH₂Cl₂, THF or CH₃CN,²¹⁴ which supported the proposed intramolecular charge transfer mechanism. Moreover, the computational studies also indicated that the twisted non-planar conformation was the most energetic favored structures for N-1 isomers (**Figure 50**), which is consistent with the experimental observation that poor fluorescence emission was observed with all N-1 isomers.

Figure 50: The most stable conformation of **N-1-1e'** from computational studies: twisted N-1-aryl ring.

These computational studies revealed the unique features of the NATs (N-2 isomers), which allow them to be effective fluorophores for UV/blue light emitting. The calculated HOMO–LUMO gaps for **3.1e-3.3o** (**Table 22**) are around 3.60–4.78 eV, which

are in good agreement with the experimental values of 3.90-4.48 eV from optical absorption spectra.*

Table 22: Calculated HUMO-LUMO energy gaps.^a

	Eg (eV)	LUMO-HOMO (eV)		Eg(eV)	LUMO-HOMO (eV)
3.1e	4.16	3.95	3.3f	4.37	4.34
3.2a	3.97	3.60	3.3g	3.90	3.73
3.2b	4.16	4.06	3.3h	4.38	4.51
3.2c	4.25	4.06	3.3i	4.32	4.51
3.2d	4.08	3.94	3.3j	4.37	3.72
3.3a	4.46	4.29	3.3k	4.43	4.27
3.3b	4.07	3.94	3.3l	4.05	3.90
3.3c	4.48	4.78	3.3m	4.41	4.04
3.3d	4.44	4.77	3.3n	4.38	4.03
3.3e	4.43	4.21	3.3o	4.35	4.16

^a Optical HOMO–LUMO gaps (Eg) were derived from the onset absorption wavelength: $E_g \text{ (eV)} \approx 1240/\lambda_{\text{max}}$

3.2.7 Extended NAT fluorescence probes

Encouraged by the good optical activity of these NATs and the mechanistic insight for tuning optical emission, we prepared compounds **3.4a** and **3.4b** as two new molecular probes (**Scheme 76**). Considering the UV/blue emission was achieved through the extended conjugations between triazole and N-2 aryl groups, we postulated that the bis-triazoles should behave as good fluorophores with even stronger emission efficiency.

* See detailed computational results of all compounds **3.1e** to **3.3o** in the supporting information

Compound **3.4a** was prepared and tested. As expected, the two triazole rings provide good conjugation with the central phenyl groups (dihedral angle measured from X-ray crystal structure), giving significantly improved UV emission with quantum yield at 0.76. Notably, the emission λ_{max} is 390 nm, still in the UV/blue range even with the further extended conjugation. The fluorescence intensity of **3.4a** was more than 3 times stronger than the commercial blue dye DSBP, while measured at identical condition (excitations at both 254 nm and 310 nm). The styrene groups in **3.4a** gave the extra synthetic handle for any further modification, such as polymerization and metathesis coupling, making **3.4a** a promising UV probe for further investigation.

Scheme 76: Extended NAT probes.

Effective UV/blue dye for biological systems is rare since the protein substrates may quench the emission. To verify the biocompatibility of the NAT fluorophore, compound **3.4b** was synthesized through coupling NAT with protected lysine. The optical properties of this amino acid modified NAT were tested. We were pleased to find that no photoquenching was observed. Notably, compound **3.4b** possessed selected protected acid and amine groups, which made it easier to be coupled with biological targets through either the C-terminal or the N-terminal. Considering the unique UV/blue

emission of this NAT, It is expected that the amino acid modified NAT could be good new UV fluorescence probe for various chemical and biological studies.

3.3 Conclusion

We herein report the N-2-aryl-triazole (NAT) as a novel class of effective UV/blue emitting dyes. Through a comprehensive comparison of the substituted groups on C-4, C-5 and N-2 positions, a general trend was revealed regarding how to effectively adjust the photoactivity of these compounds. Both emission wavelengths (from 350 nm to 400 nm) and Stocks shift (from 38 nm to 98 nm) could be adjusted with various substituted functional groups. The computational studies and X-ray crystal structures confirmed the effective co-planar structures as the most stable conformation, which was unique to the N-2 isomers. This information could initiate the new strategies for future dye designs. Finally, further derivatizations gave highly efficient UV-emitting bis-triazoles and biocompatible amino acid NAT probes, thus supporting the potential use of these novel dyes in related chemical, material and biological applications.

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- 214 Solvatochromism studies of compound **3.1 e**, **3.2 a**, **3.2 d**, **3.2 e** have been carried out in various solvents. Detailed experimental results are shown in the Supporting Information, where little changes were observed in different solvent systems, strongly supported the proposed PICT mechanism. For example, for compound **3.2 a**, the quantum yield in different solvents are observed as following: in MeOH $\Phi = 0.31$; in dichloromethane $\Phi = 0.37$; in acetonitrile $\Phi = 0.34$; in ethyl acetate $\Phi = 0.37$; in THF $\Phi = 0.34$.

Supporting information

Chapter One: Synthesis of functional 1,2,3-triazoles

1.2 Efficient synthesis of N-2-aryl-1,2,3-triazole fluorophores via post-triazole arylation

General Information

Unless otherwise noted all commercial materials and solvents were obtained from commercial provider and used without further purification. Air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flamed-dried glassware and standard syringe/septa techniques. ^1H and ^{13}C NMR spectra were recorded with 600 MHz NMR spectrometer. The Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) or DMSO (δ 2.49 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) or DMSO (δ 39.5 ppm) for ^{13}C . Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. HRMS were recorded on LTQ-FTUHRA spectrometer. UV-visible spectra were obtained on a Shimadzu UV-2500. Fluorescence spectra for emission and excitation were obtained on a Hitachi 7000.

1*H*-benzo[*d*][1,2,3]triazole (**1.2.1a**) is commercial available. 4-Phenyl-2*H*-1,2,3-triazole (**1.2.1b**) was prepared according to Zard's procedure.¹ Other N-H triazoles (**1.2.1c**, **1.2.1d**, **1.2.1f-1.2.1j**) were prepared according to our procedures.^{2,3}

Procedure for synthesis of 4-benzyl-5-phenyl-2H-1,2,3-triazole (1.2.1e)

To a 100 mL round-bottom bottle was added phenyl(5-phenyl-2H-1,2,3-triazol-4-yl)methanol² (1.0 g), 10% Pd/C (0.4 g) and methanol (20 mL). The bottle was capped and filled with hydrogen and the reaction mixture was stirred at room temperature for 2d. After Pd/C was filtrated, the filtrate was concentrated. The residue was added water (15 mL) then extracted with ethyl acetate (3 x 15 mL). The combined organic phases were washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and flash silica gel chromatography (hexane-EtOAc, v/v = 4/1) gave the product. Yield 70%, ¹H NMR (600 MHz, CDCl₃): δ 7.62-7.59 (m, 2H), 7.41-7.33 (m, 3H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.22-7.17 (m, 3H), 4.24 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 144.0, 141.3, 138.1, 130.2, 128.7, 128.7, 128.5, 128.3, 127.6, 126.6, 31.1.

General procedure for S_NAr reaction of triazole with halobenzene

To a 50 mL round-bottom bottle was added triazole (1 mmol), fluoro or chloro-substituted benzene (1.5 mmol), potassium carbonate (2 mmol) and DMSO (2 mL). The reaction mixture was stirred at room temperature (or heated up to 80 °C) and monitored by TLC. After the reaction was completed, water (20 mL) was added. The mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic phases were washed with brine and dried with anhydrous Na₂SO₄. The solvent was removed under reduced pressure to get a residue, the residue was purified by recrystallization or flash silica gel chromatography gave the product.

General procedure for microwave assisted Cu-catalyzed coupling of triazoles with aryl iodide

To 10 mL microwave tube was successively added 4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole (1a) (98.8 mg, 0.4 mmol), base (0.8 mmol), copper catalyst (0.04 mmol), ligand (0.08 mmol), and iodobenzene (125 mg, 0.6 mmol) under N₂, and then anhydrous solvent (2 mL) was added by syringes. The tube was put into microwave reactor and heated to certain temperature for 30 min. After cool, to the reaction mixture was added 1,3,5-trimethoxybenzene (15-20 mg, accurate to 0.1 mg), water (15 mL), 10% HCl solution (1 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was used to NMR analysis directly. The data were listed in **Table S1** and **Table S2**.

Screening reaction conditions

Table S1.2-1: Screening of the reaction condition^a

Ent	Cat(10%)	Co-cat (20%)	Base (2.5eq)	Sol	T(°C)	t(h)	Conv. ^b	Yield ^b
1	CuI	-	K ₂ CO ₃	DMSO	110	24	0	0
2	CuI	L-proline	K ₂ CO ₃	DMSO	110	24	100	71
3	CuCl	L-proline	K ₂ CO ₃	DMSO	110	24	100	88
4	CuCl ₂	L-proline	K ₂ CO ₃	DMSO	110	24	64	42
5	CuSO ₄	L-proline	K ₂ CO ₃	DMSO	110	24	37	11
6	Cu(OAc) ₂	L-proline	K ₂ CO ₃	DMSO	110	24	92	79
7	CuCl	L-proline	K ₂ CO ₃	DMF	110	24	85	74
8	CuCl	L-proline	K ₂ CO ₃	CH ₃ CN	110	24	73	60
9	CuI	L-proline	K ₂ CO ₃	DMSO	mw110	0.5	62	32
10	CuCl	L-proline	K ₂ CO ₃	DMSO	mw110	0.5	82	68
11	CuCl ₂	L-proline	K ₂ CO ₃	DMSO	mw110	0.5	80	49
12	CuSO ₄	L-proline	K ₂ CO ₃	DMSO	mw110	0.5	low	trace
13	Cu(OAc) ₂	L-proline	K ₂ CO ₃	DMSO	mw110	0.5	81	51
14	CuCl	L-proline	K ₂ CO ₃	DMSO	mw140	0.5	96	87
15	CuCl	L-proline	K ₂ CO ₃	DMSO	mw160	0.5	98	92
16	CuCl	L-proline	Cs ₂ CO ₃	DMSO	mw160	0.5	84	55
17	CuCl	L-proline	KOH	DMSO	mw160	0.5	75	45
18	CuCl	L-proline	K ₂ CO ₃	DMF	mw160	0.5	87	64
19	CuCl	L-proline	Cs ₂ CO ₃	DMF	mw160	0.5	90	71
20	CuCl ^d	L-proline ^e	K ₂ CO ₃	DMSO	mw160	0.5	82	73
21 ^c	CuCl	L-proline	K ₂ CO ₃	DMSO	mw160	0.5	40	10
22 ^c	CuCl	L-proline	Cs ₂ CO ₃	DMSO	mw160	0.5	68	36
23 ^c	CuI	L-proline	Cs ₂ CO ₃	DMSO	mw160	0.5	85	53

^a **1.2.1c:1.2.4a** = 1:1.5, C=0.2 M; ^b Based on the consumption of **1.2.1c** and formation of **1.2.5a** using 1,3,5-trimethoxybenzene as internal standard; ^c use PhBr instead of PhI; ^d loading was decreased to 5%; ^e loading was decreased to 10%.

Table S1.2-2: Ligand Screening^a

Ent	Cat(10%)	Co-cat (20%)	Base (2.5eq)	Sol	T(°C)	t(h)	Conv. ^b	Yield ^b
12	CuCl	L-proline	K ₂ CO ₃	DMSO	mw160	0.5	98	92
24	CuCl	pyrrolidine	K ₂ CO ₃	DMSO	mw160	0.5	low	trace
25	CuCl	glycine	K ₂ CO ₃	DMSO	mw160	0.5	low	trace
26	CuCl	Me-GLY	K ₂ CO ₃	DMSO	mw160	0.5	60	30
27	CuCl	DMG	K ₂ CO ₃	DMSO	mw160	0.5	98	86
28	CuCl	EDA	K ₂ CO ₃	DMSO	mw160	0.5	53	29
29	CuCl	DMEDA	K ₂ CO ₃	DMSO	mw160	0.5	70	47
30	CuCl	TMEDA	K ₂ CO ₃	DMSO	mw160	0.5	low	trace
31	CuCl	DACH	K ₂ CO ₃	DMSO	mw160	0.5	53	44
32	CuCl	bipy	K ₂ CO ₃	DMSO	mw160	0.5	47	trace
33	CuCl	ABC	K ₂ CO ₃	DMSO	mw160	0.5	40	trace
34	CuCl	DMABC	K ₂ CO ₃	DMSO	mw160	0.5	48	7
35	CuCl	BDC	K ₂ CO ₃	DMSO	mw160	0.5	50	trace
36	CuCl	PDC	K ₂ CO ₃	DMSO	mw160	0.5	32	trace

^a **1.2.1c:1.2.4a** = 1:1.5, C=0.2 M; ^b Me-Gly: N-methyl glycine; DMG: N,N-dimethyl glycine; EDA: ethylenediamine; DMEDA: N,N'-dimethylethylenediamine; TMEDA: N,N,N',N'-tetramethylethylenediamine; DACH: 1,2-trans-diaminocyclohexane; bipy: 2,2'-bipyridine; ABC: 2-aminobenzoic acid; DMABC: 2-(dimethylamino)benzoic acid; DBC: 1,2-benzenedicarboxic acid; PDC: pyridine-2,6-dicarboxylic acid.

General procedure for microwave assisted Cu-catalyzed coupling of triazoles with aryl iodide

To 10 mL microwave tube was successively added N-H triazole (0.8 mmol), potassium carbonate (220 mg, 1.6 mmol), L-proline (18 mg, 0.16 mmol), copper (I) chloride (8 mg, 0.08 mmol) and iodobenzene (250 mg, 1.2 mmol) under N₂, and then anhydrous solvent (2 mL) was added by syringes. The tube was put into microwave reactor and heated to certain temperature for 30 min. After cool, to the reaction mixture was added water (15 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phases were washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and flash silica gel chromatography gave the product.

General procedure for Cu-catalyzed coupling of triazoles with arylboronic acid

To 25 mL round-bottom bottle was successively added N-H triazole (**1c**) (0.4 mmol), arylboronic acid (0.8 mmol), THF 10 mL, pyridine (125 mg, 0.8 mmol) and copper (II) acetate (14 mg, 0.08 mmol). The bottle was equipped with a condenser with an oxygen balloon on top of it. The reaction mixture was refluxed and monitored by TLC. After cool, the reaction mixture was concentrated and added water (15 mL) then extracted with ethyl acetate (3 x 20 mL). The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and flash silica gel chromatography gave the product.

General procedure for UV/VIS and Fluorescence measurements

UV/VIS absorption, fluorescence emission and excitation spectra were recorded in methanol solvents in 1 cm-length quartz cell. The solution concentrations were 3×10^{-6} M for absorption spectroscopy and fluorescence spectroscopy. Emission spectra were recorded with an excitation wavelength at 254 nm.

Reference

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2. Sengupta, S.; Duan, H.; Lu, W.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008**, 10, 1493.
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Compounds Characterization

1.2.3a

2-(2,4-dinitrophenyl)-2H-benzo[d][1,2,3]triazole 1.2.3a: yield 24%; m.p. 166-167 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.70 (d, J = 2.4 Hz, 1H), 8.60 (dd, J = 9.0 Hz, 2.4 Hz, 1H), 8.47 (d, J = 9.0 Hz, 1H), 7.87-7.85 (m, 2H), 7.46-7.44 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.8, 146.1, 143.4, 136.3, 129.0, 127.1, 126.7, 120.7, 118.7; UV (MeOH) λ_{max} 221 (ϵ = 36000), 321 (ϵ = 20000); HRMS Calculated for $[\text{C}_{12}\text{H}_7\text{N}_5\text{O}_4 + \text{H}]^+$: 286.05708, Found: 286.05725.

N-1-1.2.3a

1-(2,4-dinitrophenyl)-1H-benzo[d][1,2,3]triazole N-1-1.2.3a: yield 74%; m.p. 185-187 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.00 (d, J = 2.4 Hz, 1H), 8.70 (dd, J = 9.0 Hz, 2.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.63 (t, J = 8.4 Hz, 1H), 7.52 (t, J = 8.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.4, 146.3, 144.2, 134.3, 132.5, 129.8, 128.5,

128.4, 125.4, 121.8, 121.2, 108.8; UV (MeOH) λ_{max} 221 ($\epsilon = 48000$); HRMS Calculated for $[\text{C}_{12}\text{H}_7\text{N}_5\text{O}_4+\text{H}]^+$: 286.05708, Found: 286.05709.

2-(2,4-dinitrophenyl)-4-phenyl-2H-1,2,3-triazole 1.2.3b: yield 60%; m.p. 187-189 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 8.99 (d, $J = 2.4$ Hz, 1H), 8.86 (s, 1H), 8.68 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 8.41 (d, $J = 9.0$ Hz, 1H), 7.96-7.94 (m, 2H), 7.78-7.77 (m, 2H), 7.76-7.74 (m, 1H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 151.4, 146.7, 142.2, 137.2, 134.7, 130.7, 130.0, 128.83, 128.81, 127.0, 125.5, 121.8; HRMS Calculated for $[\text{C}_{14}\text{H}_9\text{N}_5\text{O}_4+\text{H}]^+$: 312.07273, Found: 312.07280.

1-(2,4-dinitrophenyl)-4-phenyl-1H-1,2,3-triazole N-1-1.2.3b: yield 38%; m.p. 202-204 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 9.30 (s, 1H), 8.98 (d, $J = 2.4$ Hz, 1H), 8.76 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 8.25 (d, $J = 9.0$ Hz, 1H), 7.91 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.54-7.46 (m, 2H), 7.40 (t, $J = 8.4$ Hz, 1H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 148.2, 148.1, 144.1, 133.5, 130.1, 129.8, 129.5, 129.4, 128.6, 126.2, 123.2, 122.1; HRMS Calculated for $[\text{C}_{14}\text{H}_9\text{N}_5\text{O}_4+\text{H}]^+$: 312.07273, Found: 312.07277.

1.2.3c

2-(2,4-dinitrophenyl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.3c: yield 84%; m.p. 156-158 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.62 (d, $J = 2.4$ Hz, 1H), 8.52 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 8.37 (d, $J = 9.0$ Hz, 1H), 7.64-7.61 (m, 2H), 7.37-7.34 (m, 2H), 7.32-7.25 (m, 6H), 5.98 (s, 1H), 5.66 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 149.6, 149.0, 145.6, 141.9, 138.1, 137.6, 135.2, 129.4, 128.55, 128.52, 128.51, 127.9, 126.9, 126.7, 124.3, 120.8, 120.2; UV (MeOH) λ_{max} 221 ($\epsilon = 116000$), 266 ($\epsilon = 83600$), 336 ($\epsilon = 33600$); HRMS Calculated for $[\text{C}_{22}\text{H}_{15}\text{N}_5\text{O}_4 + \text{H}]^+$: 414.11968, Found: 414.11997.

1.2.3d

(2-(2,4-dinitrophenyl)-5-phenyl-2H-1,2,3-triazol-4-yl)(phenyl)methanone 1.2.3d: yield 92%; m.p. 164-166 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 9.03 (d, $J = 2.4$ Hz, 1H), 8.73 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 8.49 (d, $J = 9.0$ Hz, 1H), 8.06 (d, $J = 7.3$ Hz, 2H), 7.81-7.67 (m, 3H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.47-7.45 (m, 3H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 186.7, 151.0, 146.9, 144.4, 142.1, 135.9, 134.4, 133.7, 130.2, 130.1, 128.71, 128.69, 128.5, 128.3, 127.8, 126.2, 121.2; UV

(MeOH) λ_{max} 221 ($\epsilon = 97600$), 266 ($\epsilon = 76900$); HRMS Calculated for $[\text{C}_{21}\text{H}_{13}\text{N}_5\text{O}_5+\text{H}]^+$: 416.09916, Found: 416.09895.

2-(4-nitrophenyl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.3e: yield 98%; m.p. 147-149 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.35 (d, $J = 9.6$ Hz, 2H), 8.32 (d, $J = 9.6$ Hz, 2H), 7.65-7.63 (m, 2H), 7.40-7.38 (m, 2H), 7.26-7.24 (m, 6H), 5.97 (s, 1H), 5.67 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 148.4, 147.7, 146.2, 143.5, 138.7, 128.0, 129.3, 128.9, 128.47, 128.42, 128.37, 127.8, 126.8, 125.1, 119.6, 118.8; UV (MeOH) λ_{max} 336 ($\epsilon = 28600$); HRMS Calculated for $[\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_2+\text{H}]^+$: 369.13460, Found: 369.13481.

4-(4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazol-2-yl)benzonitrile 1.2.3f: yield 62%; m.p. 134-135 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 8.26 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 8.4$ Hz, 2H), 7.65-7.62 (m, 2H), 7.42-7.26 (m, 8H), 6.12 (s, 1H), 5.66 (s, 1H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 147.1, 146.9, 141.5, 137.9, 137.5, 134.1, 129.0, 128.9, 128.6, 128.4, 127.3, 126.4,

120.0, 118.8, 118.2, 109.9; UV (MeOH) λ_{max} 210 ($\epsilon = 39100$), 314 ($\epsilon = 28600$); HRMS Calculated for $[\text{C}_{23}\text{H}_{16}\text{N}_4+\text{H}]^+$: 349.14477, Found: 349.14486.

2,4-diphenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.5a: yield 87%; oil; ^1H NMR (600 MHz, CDCl_3): δ 8.17 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.30-7.20 (m, 6H), 5.93 (s, 1H), 5.64 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.6, 145.9, 139.7, 139.2, 138.5, 130.2, 129.2, 128.35, 128.28, 128.13, 127.7, 127.4, 126.8, 118.9, 118.8; UV (MeOH) λ_{max} 297 ($\epsilon = 36300$), 266 ($\epsilon = 76900$); HRMS Calculated for $[\text{C}_{22}\text{H}_{17}\text{N}_3+\text{H}]^+$: 324.14952, Found: 324.14964.

2-phenyl-2H-benzo[d][1,2,3]triazole 1.2.5b: yield 8%; m.p. 109-110 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.36 (d, $J = 7.2$ Hz, 2H), 7.95-7.92 (m, 2H), 7.55 (t, $J = 7.2$ Hz, 2H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.44-7.40 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 145.0, 140.4, 129.4, 128.9, 127.2, 120.6, 118.4; UV (MeOH) λ_{max} 222 ($\epsilon = 48800$), 310 ($\epsilon = 29600$); HRMS Calculated for $[\text{C}_{12}\text{H}_9\text{N}_3+\text{H}]^+$: 196.08692, Found: 196.08691.

1-phenyl-1H-benzo[d][1,2,3]triazole N-1-1.2.5b: yield 60%; m.p. 85-87 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.14 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 7.8$ Hz, 2H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 1H); 7.42 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.4, 136.9, 132.2, 129.8, 128.6, 128.2, 124.3, 122.8, 120.2, 110.3; UV (MeOH) λ_{max} 222 ($\epsilon = 41400$); HRMS Calculated for $[\text{C}_{12}\text{H}_9\text{N}_3+\text{H}]^+$: 196.08692, Found: 196.08688.

2,4-diphenyl-2H-1,2,3-triazole 1.2.5c: yield 68%; m.p. 43-45°C; ^1H NMR (600 MHz, CDCl_3): δ 8.13 (d, $J = 8.4$ Hz, 2H), 8.04 (s, 1H), 7.89 (d, $J = 7.2$ Hz, 2H), 7.50-7.43 (m, 4H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 148.8, 139.9, 130.5, 130.0, 129.2, 128.9, 128.8, 127.4, 126.1, 118.8; UV (MeOH) λ_{max} 221 ($\epsilon = 44700$), 294 ($\epsilon = 34700$); HRMS Calculated for $[\text{C}_{14}\text{H}_{11}\text{N}_3+\text{H}]^+$: 222.10257, Found: 222.10262.

N-1-1.2.5c

1,4-diphenyl-1H-1,2,3-triazole N-1-1.2.5c: yield 11%; m.p. 186-187°C; ^1H NMR (600 MHz, CDCl_3): δ 8.19 (s, 1H), 7.93-7.90 (m, 2H), 7.82-7.78 (m, 2H), 7.50-7.43 (m, 2H), 7.48-7.44 (m, 3H), 7.37 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 148.4, 137.1, 130.3, 129.8, 128.9, 128.8, 128.4, 125.8, 120.5, 117.6; UV (MeOH) λ_{max} 222 ($\epsilon = 5100$); HRMS Calculated for $[\text{C}_{14}\text{H}_{11}\text{N}_3+\text{H}]^+$: 222.10257, Found: 222.10269.

1.2.5d

Phenyl(2,5-diphenyl-2H-1,2,3-triazol-4-yl)methanone 1.2.5d: yield 85%; m.p. 115-117°C; ^1H NMR (600 MHz, d_6 -DMSO): δ 8.14-8.10 (m, 4H), 7.87-7.83 (m, 2H), 7.74 (t, $J = 7.8$ Hz, 1H), 7.63 (t, $J = 7.8$ Hz, 2H), 7.60 (t, $J = 7.8$ Hz, 2H), 7.55-7.48 (m, 4H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 188.1, 150.3, 143.4, 139.3, 137.3, 134.6, 130.9, 130.5, 130.1, 129.6, 129.5, 129.3, 129.19, 129.18, 119.9; UV (MeOH) λ_{max} 210 ($\epsilon = 45200$), 263 ($\epsilon = 30600$); HRMS Calculated for $[\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}+\text{H}]^+$: 326.12879, Found: 326.12876.

4-benzyl-2,5-diphenyl-2H-1,2,3-triazole 1.2.5e: yield 85%; m.p. 93-95 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.14-8.11 (m, 2H), 7.69-7.65 (m, 2H), 7.50-7.45 (m, 2H), 7.42-7.24 (m, 8H), 7.23-7.18 (m, 1H), 4.31 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.9, 145.0, 139.8, 138.4, 130.6, 129.2, 128.7, 128.6, 128.5, 128.4, 127.7, 127.1, 126.5, 118.6, 31.7; UV (MeOH) λ_{max} 221 ($\epsilon = 37700$), 290 ($\epsilon = 29900$); HRMS Calculated for $[\text{C}_{21}\text{H}_{17}\text{N}_3+\text{H}]^+$: 312.14952, Found: 312.14965.

6-hydroxy-1-(2,5-diphenyl-2H-1,2,3-triazol-4-yl)hexan-1-one 1.2.5f: yield 60%; m.p. 73-75 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.18 (d, $J = 8.4$ Hz, 2H), 8.01 (d, $J = 7.2$ Hz, 2H), 7.53 (t, $J = 7.2$ Hz, 2H), 7.50-7.40 (m, 4H), 3.67 (t, $J = 6.6$ Hz, 2H), 3.21 (t, $J = 7.2$ Hz, 2H), 1.84-1.77 (m, 2H), 1.66-1.61 (m, 2H), 1.61-1.52 (br, 1H), 1.52-1.45 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 195.3, 149.5, 143.2, 139.2, 129.5, 129.43, 129.40, 129.3, 128.5, 128.2, 119.3, 62.7, 40.6, 32.5, 25.4, 23.6; UV (MeOH) λ_{max} 221 ($\epsilon = 40200$); HRMS Calculated for $[\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_2+\text{H}]^+$: 336.17065, Found: 336.17086.

2,4-diphenyl-5-(1-phenylethyl)-2H-1,2,3-triazole 1.2.5g: yield 85%; oil; ^1H NMR (600 MHz, CDCl_3): δ 8.17 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 7.2$ Hz, 2H), 7.49 (t, $J = 8.4$ Hz, 2H), 7.41-7.27 (m, 8H), 7.20 (t, $J = 7.2$ Hz, 1H), 4.43 (q, $J = 7.2$ Hz, 1H), 1.76 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 149.9, 146.7, 145.0, 140.2, 131.0, 129.4, 128.8, 128.75, 128.5, 128.4, 127.8, 127.2, 126.6, 118.9, 37.2, 23.3; UV (MeOH) λ_{max} 221 ($\epsilon = 48400$), 285 ($\epsilon = 34800$); HRMS Calculated for $[\text{C}_{22}\text{H}_{19}\text{N}_3+\text{H}]^+$: 326.16517, Found: 326.16535.

4-(naphthalen-1-yl)-2-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.5h: yield 87%; oil; ^1H NMR (600 MHz, CDCl_3): δ 8.19 (d, $J = 7.2$ Hz, 2H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.82-7.76 (m, 2H), 7.51-7.40 (m, 5H), 7.40-7.32 (m, 2H); 7.32-7.27 (m, 2H), 7.12-7.08 (m, 3H), 5.53 (s, 1H), 5.48 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.6, 146.3, 139.8, 139.0, 138.9, 133.6, 131.6, 129.2, 129.1, 128.3, 128.2, 128.1, 127.8, 127.7, 127.4, 127.3, 126.4, 125.9, 125.7, 125.0, 118.8, 118.7; UV (MeOH) λ_{max} 221 ($\epsilon = 96900$), 295 ($\epsilon = 34600$); HRMS Calculated for $[\text{C}_{26}\text{H}_{19}\text{N}_3+\text{H}]^+$: 374.16517, Found: 374.16535.

4-cyclohexenyl-2,5-diphenyl-2H-1,2,3-triazole 1.2.5i: yield 80%; oil; ^1H NMR (600 MHz, CDCl_3): δ 8.11 (d, $J = 7.8$ Hz, 2H), 7.74 (d, $J = 6.6$ Hz, 2H), 7.48-7.41 (m, 4H), 7.40-7.35 (m, 1H), 7.31 (t, $J = 7.2$ Hz, 1H), 6.12-6.11 (m, 1H), 2.43-2.39 (m, 2H), 2.19-2.14 (m, 2H), 1.80-1.74 (m, 2H), 1.73-1.65 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.9, 145.4, 139.8, 131.5, 130.1, 129.1, 128.6, 128.5, 128.3, 128.2, 127.0, 118.6, 27.6, 25.5, 22.7, 21.9; UV (MeOH) λ_{max} 221 ($\epsilon = 70800$), 290 ($\epsilon = 47300$); HRMS Calculated for $[\text{C}_{20}\text{H}_{19}\text{N}_3\text{-Ph}+2\text{H}]^+$: 226.13387, Found: 226.13388.

1-(5-cyclohexenyl-2-phenyl-2H-1,2,3-triazol-4-yl)naphthalen-2-ol 1.2.5j: yield 45%; m.p. 124-126 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.13 (d, $J = 7.8$ Hz, 2H), 7.84 (d, $J = 9.0$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.51-7.46 (m, 3H), 7.40-7.30 (m, 3H), 7.28 (d, $J = 9.0$ Hz, 1H); 6.55 (s, 1H), 5.83 (s, 1H), 2.40-2.36 (m, 2H), 1.88-1.84 (m, 2H), 1.64-1.58 (m, 2H), 1.53-1.48 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 152.4, 149.7, 139.5, 139.4, 132.3, 131.1, 130.1, 129.3, 128.9,

128.2, 127.7, 127.5, 126.7, 124.7, 123.6, 118.6, 117.9, 110.2, 26.5, 25.5, 22.4, 21.7; UV (MeOH) λ_{max} 227 ($\epsilon = 103000$), 292 ($\epsilon = 37400$); HRMS Calculated for $[\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}+\text{H}]^+$: 368.17574, Found: 368.17578.

4-cyclohexenyl-5-(2-phenoxynaphthalen-1-yl)-2H-1,2,3-triazole N-3-1.2.5j: yield 40%; m.p. 313-315 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 10.23 (s, 1H), 7.82 (d, $J = 9.0$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.32-7.17 (m, 8H), 7.00 (d, $J = 8.4$ Hz, 1H), 5.91 (s, 1H), 2.24-2.11 (m, 2H), 1.88-1.70 (m, 2H), 1.45-1.34 (m, 4H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 155.2, 147.2, 137.2, 133.9, 132.3, 129.6, 129.5, 129.0, 128.8, 128.4, 128.2, 128.1, 125.4, 124.6, 123.8, 123.3, 118.7, 107.6, 26.3, 25.4, 22.7, 22.2; HRMS Calculated for $[\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}+\text{H}]^+$: 368.17574, Found: 368.17588.

4-phenyl-5-(1-phenylvinyl)-2-*p*-tolyl-2H-1,2,3-triazole 1.2.5k: yield 86%; 70-72 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.04 (d, $J = 7.8$ Hz, 2H), 7.69-7.67 (m, 2H), 7.41-7.38 (m, 2H), 7.28-7.20 (m, 8H), 5.92 (s, 1H), 5.63 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.3, 145.6,

139.3, 138.6, 137.6, 137.3, 130.3, 129.7, 128.3, 128.26, 128.2, 128.1, 127.7, 126.8, 118.8, 118.7, 21.0; UV (MeOH) λ_{max} 296 ($\epsilon = 21700$); HRMS Calculated for $[\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}+\text{H}]^+$: 338.14517, Found: 338.16510.

(2-(4-nitrophenyl)-5-phenyl-2H-1,2,3-triazol-4-yl)(phenyl)methanone 1.2.5l: yield 88%; m.p. 151-153 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 8.46 (d, $J = 9.0$ Hz, 2H), 8.34 (d, $J = 9.0$ Hz, 2H), 8.11 (d, $J = 8.4$ Hz, 2H), 7.86-7.81 (m, 2H), 7.75 (t, $J = 7.2$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 2H), 7.52-7.48 (m, 3H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 187.2, 150.4, 146.6, 143.9, 142.5, 136.3, 134.2, 130.3, 129.8, 128.7, 128.6, 128.5, 128.4, 125.6, 119.9; UV (MeOH) λ_{max} 222 ($\epsilon = 48300$), 322 ($\epsilon = 31300$); HRMS Calculated for $[\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_3+\text{H}]^+$: 371.11387, Found: 371.11409.

2-(4-methoxyphenyl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.5m: yield 74%; oil; ^1H NMR (600 MHz, CDCl_3): δ 8.07 (d, $J = 9.0$ Hz, 2H), 7.69-7.66 (m, 2H), 7.41-7.39 (m, 2H), 7.28-7.20 (m, 6H), 7.98 (d, $J = 9.0$ Hz, 2H), 5.92 (s, 1H), 5.63 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 158.9, 146.1, 145.4, 139.2, 138.6, 133.5, 130.3, 128.32, 128.25, 128.13,

128.08, 127.6, 126.8, 120.2, 118.8, 114.3, 55.5; HRMS Calculated for $[C_{23}H_{19}N_3O+H]^+$: 354.16009, Found: 354.16012.

4-cyclohexenyl-5-phenyl-2-*o*-tolyl-2*H*-1,2,3-triazole 1.2.5n: yield 70%; oil; 1H NMR (600 MHz, $CDCl_3$): δ 7.78-7.72 (m, 2H), 7.66-7.64 (m, 1H), 7.45-7.40 (m, 2H), 7.40-7.35 (m, 1H), 7.34-7.27 (m, 3H), 6.13-6.10 (m, 1H), 2.47 (s, 3H), 2.45-2.39 (m, 2H), 2.18-2.13 (m, 2H), 1.79-1.74 (m, 2H), 1.71-1.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.2, 144.7, 139.5, 132.5, 131.61, 131.59, 129.7, 128.5, 128.4, 128.3, 128.1(may 2), 126.5, 125.0, 27.6, 25.5, 22.7, 21.9, 19.2; UV (MeOH) λ_{max} 221 (ϵ = 51700); HRMS Calculated for $[C_{21}H_{21}N_3+H]^+$: 316.18082, Found: 316.18098.

2-(4-iodophenyl)-4-phenyl-5-(1-phenylvinyl)-2*H*-1,2,3-triazole 1.2.5o: yield 67%; oil; 1H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.69 (dd, J = 7.8 Hz, 1.8 Hz, 2H), 7.38 (dd, J = 7.8 Hz, 1.8 Hz, 2H), 7.29-7.10 (m, 6H), 5.93 (s, 1H), 5.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 146.3, 139.4, 139.1, 138.4, 138.3, 129.9, 128.5, 128.4,

128.3, 128.2, 127.7, 126.8, 120.5, 119.1, 91.9; UV (MeOH) λ_{max} 220 ($\epsilon = 66200$), 304 ($\epsilon = 49900$); HRMS Calculated for $[\text{C}_{22}\text{H}_{16}\text{N}_3+\text{H}]^+$: 450.04617, Found: 450.04614.

2-(4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazol-2-yl)pyridine 1.2.5p: yield 88%; m.p. 103-105 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.64 (s, 1H), 8.16 (d, $J = 7.2$ Hz, 1H), 7.88 (t, $J = 7.8$ Hz, 1H), 7.76-7.70 (m, 2H), 7.40-7.36 (m, 2H), 7.32 (br, 1H), 7.28-7.20 (m, 6H), 5.96 (s, 1H), 5.70 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.7, 148.9, 147.8, 147.2, 138.9, 138.8, 128.3, 129.6, 128.5, 128.3, 128.2, 128.1, 127.9, 126.8, 122.8, 119.4, 113.8; HRMS Calculated for $[\text{C}_{21}\text{H}_{16}\text{N}_4+\text{H}]^+$: 325.14477, Found: 325.14470.

Phenyl(5-phenyl-2-(pyridin-2-yl)-2H-1,2,3-triazol-4-yl)methanone 1.2.5q: yield 83%; m.p. 133-135 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.64 (dd, $J = 4.8$ Hz, 1.2 Hz, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 8.12 (d, $J = 8.4$ Hz, 2H), 7.94-7.89 (m, 3H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 2H), 7.42-7.40 (m, 3H), 7.39 (dd, $J = 7.2$ Hz, 4.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 188.0, 150.8, 150.6, 149.1, 144.0, 139.0, 136.9, 133.7, 130.5, 129.5, 128.9, 128.8, 128.5, 128.4, 123.7,

114.4; UV (MeOH) λ_{max} 221 (ϵ = 39200), 289 (ϵ = 29900); HRMS Calculated for $[\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}+\text{H}]^+$: 327.12404, Found: 327.12404.

3-(4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazol-2-yl)pyridine 1.2.5r: yield 70%; 99-101 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.47 (s, 1H), 8.61 (s, 1H), 8.45-8.42 (m, 1H), 7.71-7.67 (m, 2H), 7.43 (dd, J = 7.8 Hz, 4.8 Hz, 1H), 7.41-7.37 (m, 2H), 7.31-7.23 (m, 6H), 5.96 (s, 1H), 5.66 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 148.2, 147.5, 146.8, 140.4, 138.9, 138.2, 136.1, 129.7, 128.5, 128.4, 128.35, 128.25, 127.7, 126.8, 125.8, 123.7, 119.3.; UV (MeOH) λ_{max} 221 (ϵ = 68500), 301 (ϵ = 28400); HRMS Calculated for $[\text{C}_{21}\text{H}_{16}\text{N}_4+\text{H}]^+$: 325.14477, Found: 325.14474.

4-(4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazol-2-yl)pyridine 1.2.5s: yield 70%; m.p. 107-108 °C; ^1H NMR (600 MHz, d_6 -DMSO): δ 8.80 (bs, 2H), 8.06 (br, 2H), 7.70-7.66 (m, 2H), 7.43-7.27 (m, 8H), 6.14 (s, 1H), 5.67 (s, 1H); ^{13}C NMR (125 MHz, d_6 -DMSO): δ 151.4, 147.3, 147.1, 144.5, 137.8, 137.5, 129.0, 128.9, 128.6, 128.5, 128.4, 127.3, 126.4, 120.0, 112.3; HRMS Calculated for $[\text{C}_{21}\text{H}_{16}\text{N}_4+\text{H}]^+$: 325.14477, Found: 325.14495.

Phenyl(5-phenyl-2-(pyridin-4-yl)-2H-1,2,3-triazol-4-yl)methanone 1.2.5t: yield 60%; m.p. 119-121 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.83 (br, 2H), 8.10 (d, $J = 8.4$ Hz, 4H), 7.90-7.84 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.46-7.41 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 187.5, 151.3, 151.1, 145.2, 144.3, 136.7, 133.9, 130.5, 129.8, 128.7, 128.67, 128.57, 128.52, 113.3; UV (MeOH) λ_{max} 221 ($\epsilon = 64300$); HRMS Calculated for $[\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}+\text{H}]^+$: 327.12404, Found: 327.12402.

2-(naphthalen-1-yl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.5u: yield 70%; m.p. 96-98 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.44 (d, $J = 8.4$ Hz, 1H), 7.98-7.90 (m, 3H), 7.74 (dt, $J = 6.6$ Hz, 1.8 Hz, 2H), 7.60-7.52 (m, 3H), 7.46 (dt, $J = 6.6$ Hz, 1.8 Hz, 2H), 7.30-7.22 (m, 6H), 5.96 (s, 1H), 5.72 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.6, 145.9, 139.2, 138.7, 136.6, 134.5, 130.2, 129.5, 128.4, 128.33, 128.31, 128.2, 128.16, 127.8, 127.43, 127.38, 126.9, 126.6, 125.0, 123.7, 122.7, 119.1; UV (MeOH) λ_{max} 222 ($\epsilon = 75300$); HRMS Calculated for $[\text{C}_{26}\text{H}_{19}\text{N}_3+\text{H}]^+$: 374.16517, Found: 374.16534.

4-phenyl-2-(4-(4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazol-2-yl)phenyl)-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.5v: yield 10%; m.p. 177-179°C; ^1H NMR (600 MHz, CDCl_3): δ 8.31 (s, 4H), 7.70 (dd, $J = 7.8$ Hz, 1.8 Hz, 4H), 7.42 (dd, $J = 7.8$ Hz, 1.8 Hz, 4H), 7.31-7.24 (m, 12H), 5.97 (s, 2H), 5.68 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.0, 146.3, 139.1, 138.5, 138.4, 130.0, 128.5, 128.42, 128.36, 128.2, 127.7, 126.9, 119.5, 119.2; UV (MeOH) λ_{max} 332 ($\epsilon = 63800$); HRMS Calculated for $[\text{C}_{38}\text{H}_{28}\text{N}_6+\text{H}]^+$: 569.24482, Found: 569.24498.

4-phenyl-5-(1-phenylvinyl)-2-(thiophen-2-yl)-2H-1,2,3-triazole 1.2.7a: yield 40%; m.p. 83-85°C; ^1H NMR (600 MHz, CDCl_3): δ 7.67-7.65 (m, 2H), 7.51 (dd, $J = 3.6$ Hz, 1.8 Hz, 1H), 7.40-7.38 (m, 2H), 7.28-7.22 (m, 6H), 7.09 (dd, $J = 5.4$ Hz, 1.8 Hz, 1H), 7.00 (dd, $J = 5.4$ Hz, 3.6 Hz, 1H), 5.94 (s, 1H), 5.65 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.7, 146.0, 142.6, 138.8, 138.3, 129.7, 128.4, 128.36, 128.3, 128.2, 127.7, 126.8, 126.4, 121.0, 119.2, 115.9; HRMS Calculated for $[\text{C}_{20}\text{H}_{15}\text{N}_3\text{S}+\text{H}]^+$: 330.10594, Found: 330.10602.

4-phenyl-5-(1-phenylvinyl)-2-(thiophen-3-yl)-2H-1,2,3-triazole 1.2.7b: yield 60%; oil; ^1H NMR (600 MHz, CDCl_3): δ 7.73 (dd, $J = 3.0$ Hz, 1.2 Hz, 1H), 7.71 (dd, $J = 4.8$ Hz, 1.2 Hz, 1H), 7.67-7.64 (m, 2H), 7.40-7.37 (m, 2H), 7.34 (dd, $J = 5.4$ Hz, 3.6 Hz, 1H), 7.27-7.19 (m, 6H), 5.92 (s, 1H), 5.62 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.1, 145.4, 139.3, 139.1, 138.4, 130.0, 128.33, 128.27, 128.1, 127.6, 126.8, 126.3, 120.5, 119.0, 112.2; HRMS Calculated for $[\text{C}_{20}\text{H}_{15}\text{N}_3\text{S}+\text{H}]^+$: 330.10594, Found: 330.10600.

2-(benzo[b]thiophen-2-yl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.7c: yield 50%; 259-261°C; ^1H NMR (600 MHz, CDCl_3): δ 7.80 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 7.2$ Hz, 1H), 7.74 (s, 1H), 7.68-7.66 (m, 2H), 7.41-7.32 (m, 4H), 7.29-7.22 (m, 6H), 5.96 (s, 1H), 5.68 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.3, 146.7, 141.6, 138.7, 138.5, 138.2, 136.2, 129.5, 128.6, 128.4, 128.35, 128.26, 127.8, 126.8, 125.1, 124.8, 124.0, 122.3, 119.5, 111.4; HRMS Calculated for $[\text{C}_{24}\text{H}_{17}\text{N}_3\text{S}+\text{H}]^+$: 380.12159, Found: 380.12166.

2-(furan-2-yl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.7d: yield 30%; oil; ^1H NMR (600 MHz, CDCl_3): δ 7.59-7.57 (m, 2H), 7.32-7.28 (m, 3H), 7.20-7.15 (m, 6H), 6.56 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 6.48 (dd, $J = 3.0$ Hz, 1.8 Hz, 1H), 5.87 (s, 1H), 5.58 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.1, 146.4, 139.6, 138.7, 138.3, 132.2, 129.5, 128.6, 128.4, 128.3, 128.2, 127.8, 126.8, 119.4, 111.9, 97.7; HRMS Calculated for $[\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}+\text{H}]^+$: 314.12879, Found: 314.12884.

2-(furan-3-yl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.2.7e: yield 50%; oil; ^1H NMR (600 MHz, CDCl_3): δ 8.06 (s, 1H), 7.64 (dd, $J = 7.8$ Hz, 1.8 Hz, 2H), 7.45 (t, $J = 1.2$ Hz, 1H), 7.40-7.36 (m, 2H), 7.28-7.21 (m, 6H), 7.04 (d, $J = 1.2$ Hz, 1H), 5.92 (s, 1H), 5.62 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 146.3, 145.5, 143.4, 139.0, 138.4, 132.8, 130.1, 129.9, 128.4, 128.3, 128.2, 127.7, 126.8, 119.0, 104.8; HRMS Calculated for $[\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}+\text{H}]^+$: 314.12879, Found: 314.12882.

2-(4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazol-2-yl)phenol 1.2.7f: yield 82%; oil; ^1H NMR (270 MHz, CDCl_3): δ 10.70 (s, 1H), 8.21 (d, $J = 7.6$ Hz, 1H), 7.72-7.65 (m, 2H), 7.44-7.37 (m, 2H), 7.35-7.23 (m, 7H), 7.17 (d, $J = 7.6$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 5.94 (s, 1H), 5.65 (s, 1H); ^{13}C NMR (67.5 MHz, CDCl_3): δ 148.1, 144.8, 143.9, 138.3, 138.0, 129.1, 128.8, 128.7, 128.4, 128.3, 127.7, 126.7, 124.9, 119.9, 119.4, 118.6; HRMS Calculated for $[\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}+\text{H}]^+$: 340.14444, Found: 340.14452.

ORTEP Drawing of the Crystal Structures

Figure S1.2-1. Perspective view of the molecular structures of the two independent molecules of **N-1-1.2.3b** (C₁₄H₉N₅O₄) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 702805

Figure S1.2-2. Perspective view of the molecular structures of the two independent molecules of **1.2.5d** ($\text{C}_{21}\text{H}_{15}\text{N}_3$) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 702800

Figure S1.2-3. Perspective view of the molecular structure of **1.2.5j** (C₂₄H₂₁N₃O) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.
CCDC number: 702801

Figure S1.2-4: Perspective view of the molecular structure of **N-3-1.2.5j** ($\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}$) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 702806.

Figure **S1.2-5**: Perspective view of the molecular structure of **1.2.5q** (C₂₀H₁₄N₄O) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.
CCDC number: 702802

Figure S1.2-6. Perspective view of the molecular structure of **1.2.5u** ($\text{C}_{26}\text{H}_{19}\text{N}_3$) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.
CCDC number: 702804

Figure S1.2-7. Perspective view of the molecular structure of **1.2.5v** ($\text{C}_{38}\text{H}_{28}\text{N}_6$) with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 702803

1.3 Highly efficient synthesis of vinyl substituted triazoles by Au(I) catalyzed alkyne activation

General Methods and materials

Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. ^1H -NMR and ^{13}C -NMR spectra were recorded on Joel 270 and Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) or DMSO (δ 2.49 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) or DMSO (δ 39.5 ppm) for ^{13}C . Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. R_f values were obtained by elution in the stated solvent ratios.

General Procedure for Au(I) catalyzed addition of triazoles to alkynes

To a solution of benzotriazole **1.2.1** (59.5mg, 0.5mmol) in 2.5ml of freshly distilled toluene, was added PP_3AuCl (12.5mg, 0.025mmol), $AgOTf$ (6.5mg, 0.025mmol) and phenylacetylene **1.3.2** (76.5mg, 0.75mmol). The reaction mixture was then heated at $80\text{ }^\circ\text{C}$ for 12 hours. After heating, the reaction mixture was cooled, passed through a short silica plug and concentrated to remove toluene. The crude mixture was then purified by flash silica gel chromatography to give the vinyl triazole **1.3.4** as clear oil in quantitative yield.

Compound Characterization

1-(1-phenylvinyl)-1H-benzo[d][1,2,3]triazole 1.3.3a: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 92%. ^1H -NMR (600 MHz, CDCl_3) δ 8.05-8.09 (m, 1H), 7.30-7.39 (m, 5H), 7.25 (d, J = 7.8 Hz, 2H), 7.00-7.05 (m, 1H), 5.76 (s, 1H), 5.73 (s, 1H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 146.1, 142.6, 134.6, 132.9, 129.72, 128.8, 127.7, 126.8, 124.1, 120.0, 111.1, 111.0; HRMS Calculated for $[\text{C}_{14}\text{H}_{11}\text{N}_3]^+$: 221.2572, Found: 221.0953.

1-(1-p-tolylvinyl)-1H-benzo[d][1,2,3]triazole 1.3.3b: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 94%. ^1H -NMR (600 MHz, CDCl_3) δ 8.08-8.10 (m, 1H), 7.33-7.36 (m, 2H), 7.16 (s, 4H), 7.05-7.08 (m, 1H), 5.73 (s, 1H), 5.70 (s, 1H), 2.37 (s, 3H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 146.4, 142.9, 140.2, 133.2, 132.0, 129.7, 127.9, 127.0, 124.3, 120.3, 111.5, 110.4, 21.5; HRMS Calculated for $[\text{C}_{15}\text{H}_{13}\text{N}_3]^+$: 235.2838, Found: 235.1109.

1.3.3c

1-(1-(4-fluorophenyl)vinyl)-1H-benzo[d][1,2,3]triazole 1.3.3c: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 96%. ^1H -NMR (600 MHz, CDCl_3) δ 8.08 (d, J = 6.6Hz, 1H), 7.34-7.39 (m, 2H), 7.24-7.24 (m, 2H), 7.08 (d, J = 7.2Hz, 1H), 7.04 (t, J = 8.4Hz, 2H), 5.72 (d, J = 4.2Hz, 2H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 164.6, 163.0, 146.3, 141.9, 133.1, 131.1, 129.1, 128.2, 124.5, 120.4, 116.2, 111.3; HRMS Calculated for $[\text{C}_{14}\text{H}_{10}\text{FN}_3]^+$: 239.2477, Found: 239.0859.

1.3.3d

1-(hex-1-en-2-yl)-1H-benzo[d][1,2,3]triazole 1.3.3d: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 90%. ^1H -NMR (600 MHz, CDCl_3) δ 8.05 (d, J = 7.8Hz, 1H), 7.64 (d, J = 8.4Hz, 1H), 7.48 (t, J = 7.2Hz, 1H), 7.36 (t, J = 7.8Hz, 1H), 5.38 (s, 1H), 5.24 (s, 1H), 2.89 (t, J = 7.2Hz, 2H), 1.43-1.48 (m, 2H), 1.32-1.43 (m, 2H), 0.86 (t, J = 7.2Hz, 3H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 146.4, 144.6, 132.5, 128.1, 124.4, 120.3, 111.3, 106.3, 34.31, 29.3, 22.2, 13.9; HRMS Calculated for $[\text{C}_{12}\text{H}_{15}\text{N}_3]^+$: 201.2676, Found: 201.1266.

1.3.3e

(Z)-1-(1,2-diphenylvinyl)-1H-benzo[d][1,2,3]triazole 1.3.3e: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 70%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.14 (d, J = 8.4Hz, 1H), 7.34-7.41 (m, 6H), 7.22 (d, J = 9.0Hz, 2H), 7.06-7.13 (m, 4H), 6.75 (d, J = 7.8Hz, 2H); $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 145.8, 136.6, 133.6, 133.5, 133.1, 129.3, 128.9, 128.6, 128.5, 128.2, 128.0, 127.6, 125.9, 124.2, 120.0, 110.5; HRMS Calculated for $[\text{C}_{20}\text{H}_{15}\text{N}_3]^+$: 297.3532, Found: 297.1266.

1.3.3f

(Z)-1-(oct-4-en-4-yl)-1H-benzo[d][1,2,3]triazole 1.3.3f: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 83%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.04 (d, J = 8.4Hz, 1H), 7.44 (t, J = 7.8Hz, 1H), 7.33 (q, J = 8.4Hz, 16.2Hz, 2H), 5.79 (t, J = 7.2Hz, 1H), 2.55 (t, J = 7.8Hz, 2H), 1.68 (q, J = 7.2Hz, 14.4Hz, 2H), 1.26-1.34 (m, 4H), 0.86(t, J = 7.2Hz, 3H), 0.74 (t, J = 7.8Hz, 3H); $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 145.5, 135.2,

133.5, 129.7, 127.7, 124.0, 120.1, 110.3, 38.4, 29.6, 22.5, 20.5, 13.8, 13.5; HRMS Calculated for $[C_{14}H_{19}N_3]^+$: 229.3208, Found: 229.1579.

1.3.3g

1-(prop-1-en-2-yl)-1H-benzo[d][1,2,3]triazole 1.3.3g: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 82%. 1H -NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4Hz, 1H), 7.72 (d, J = 8.4Hz, 1H), 7.51 (t, J = 7.2Hz, 1H), 7.39 (t, J = 7.8Hz, 1H), 5.44 (s, 1H), 5.21 (s, 1H), 2.55 (s, 3H); ^{13}C -NMR (67.5 MHz, $CDCl_3$) δ 146.6, 140.6, 132.0, 128.2, 124.5, 120.5, 111.6, 105.5, 21.3; HRMS Calculated for $[C_9H_9N_3]^+$: 159.1879, Found: 159.0796.

1.3.3h

1-((Z)-1-phenylprop-1-en-2-yl)-1H-benzo[d][1,2,3]triazole vs 1-((E)-1-phenylprop-1-en-2-yl)-1H-benzo[d][1,2,3]triazole 1.3.3h: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 84%. 1H -NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8Hz, 1H), 8.02 (d, J = 8.4Hz, 1H), 7.36-7.41 (m, 2H), 7.16-7.28 (m, 6H), 7.06-7.08 (m, 2H), 6.97-7.02

(m, 3H), 6.73 (s, 1H), 6.68 (d, J = 7.2Hz, 2H), 6.59 (q, J = 7.2Hz, 13.8Hz, 1H), 2.48 (s, 2H), 1.67(d, J = 7.2Hz, 3H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 145.9, 145.8, 136.2, 135.9, 134.0, 133.8, 131.8, 131.5, 129.0, 129.0, 128.9, 128.6, 128.2, 128.1, 128.0, 127.7, 127.1, 126.1, 126.0, 125.6, 124.3, 124.1, 120.3, 120.0, 110.9, 110.6, 23.8, 14.1; HRMS Calculated for $[\text{C}_{15}\text{H}_{13}\text{N}_3]^+$: 235.2838, Found: 235.1109.

1-((Z)-hex-2-en-2-yl)-1H-benzo[d][1,2,3]Triazole vs **1-((Z)-hex-2-en-3-yl)-1H-benzo[d][1,2,3]triazole** **1.3.3i**: purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 81%. ^1H -NMR (600 MHz, CDCl_3) δ 8.05 (d, J = 9.0Hz, 2H), 7.45 (t, J = 7.8Hz, 2H), 7.32-7.37 (m, 4H), 5.86 (q, J = 7.2Hz, 13.8Hz, 1H), 5.80 (t, J = 7.8Hz, 1H), 2.57 (t, J = 7.2Hz, 2H), 2.23 (s, 3H), 1.71 (q, J = 7.2Hz, 14.4Hz, 2H), 1.40 (d, J = 7.2Hz, 3H), 1.23-1.35 (m, 4H), 0.84 (t, J = 7.2Hz, 3H), 0.74 (t, J = 7.2Hz, 3H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 145.6, 145.5, 136.3, 133.4, 133.0, 131.1, 130.0, 127.8, 127.8, 124.1, 124.0, 123.7, 120.2, 120.1, 110.4, 110.3; HRMS Calculated for $[\text{C}_{12}\text{H}_{15}\text{N}_3]^+$: 201.2676, Found: 201.1266.

1.3.4a(N2)

4-phenyl-2-(1-phenylvinyl)-2H-1,2,3-triazole 1.3.4a(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 91%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.02 (s, 1H), 7.85-7.86 (m, 2H), 7.36-7.48 (m, 8H), 5.97 (s, 1H), 5.41 (s, 1H); $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 148.9, 146.4, 135.0, 132.7, 130.1, 129.5, 129.2, 129.1, 128.6, 128.5, 126.4, 107.6; HRMS Calculated for $[\text{C}_{16}\text{H}_{13}\text{N}_3]^+$: 247.2954, Found: 247.1109.

1.3.4a(N1)

4-phenyl-1-(1-phenylvinyl)-1H-1,2,3-triazole 1.3.4a(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 91%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.83-7.85 (m, 2H), 7.79 (s, 1H), 7.32-7.46 (m, 8H), 5.85 (s, 1H), 5.54 (s, 1H); $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 147.6, 142.9, 134.6, 129.9, 128.9, 128.8, 128.7, 128.3, 127.3, 125.8, 119.8, 109.4; HRMS Calculated for $[\text{C}_{16}\text{H}_{13}\text{N}_3]^+$: 247.2954, Found: 247.1109.

1.3.4b(N2)

2-(1-cyclohexylvinyl)-4-phenyl-2H-1,2,3-triazole 1.3.4b(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 87%. ¹H-NMR (600 MHz, CDCl₃) δ 7.93 (s, 1H), 7.82-7.84 (m, 2H), 7.42-7.44 (m, 2H), 7.34-7.37(m, 1H), 5.83 (s, 1H), 4.90 (s, 1H), 3.07-3.12 (m, 1H), 2.01 (d, *J*=12.0 Hz, 2H) 1.74-1.84 (m, 3H), 1.40-1.47 (m, 2H), 1.22-1.34 (m, 3H), ¹³C-NMR (67.5 MHz, CDCl₃) δ 151.6, 148.2, 131.8, 130.5, 129.0, 128.8, 126.3, 101.1, 39.6, 32.2, 26.7, 26.6; HRMS Calculated for [C₁₆H₁₉N₃]⁺: 253.3422, Found: 253.1579.

1.3.4b(N1)

1-(1-cyclohexylvinyl)-4-phenyl-1H-1,2,3-triazole 1.3.4b(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 87%. ¹H-NMR (600 MHz, CDCl₃) δ 7.90 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.39-7.43 (m, 2H), 7.31-7.34(m, 1H), 5.36 (s, 1H), 5.00 (s, 1H), 2.90 (t, *J*= 9.0, 1H), 1.91 (d, *J* = 12.6 Hz, 2H), 1.80 (d, *J* = 14.4 Hz, 2H), 1.74 (d, *J* = 13.8 Hz, 2H), 1.19-1.41 (m, 4H); ¹³C-NMR (67.5 MHz, CDCl₃) δ 149.7, 131.8, 130.6, 129.0, 128.7, 126.3, 118.4, 104.2, 40.9, 31.6, 26.4, 26.3; HRMS Calculated for [C₁₆H₁₉N₃]⁺: 253.3422, Found: 253.1579.

1.3.4c(N2)

2-((Z)-oct-4-en-4-yl)-4-phenyl-2H-1,2,3-triazole 1.3.4c(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 81%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.93 (s, 1H), 7.82 (d, $J = 7.2\text{Hz}$, 2H), 7.43 (t, $J = 7.2\text{Hz}$, 2H), 7.35 (t, $J = 7.2\text{Hz}$, 1H), 5.49 (t, $J = 7.2\text{Hz}$, 1H), 2.62 (t, $J = 7.2\text{Hz}$, 2H), 2.21 (q, $J = 7.2\text{Hz}$, 9.0Hz, 2H), 1.41-1.47 (m, 4H), 0.89-0.93 (m, 6H), $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 147.5, 138.8, 131.1, 130.7, 129.1, 128.6, 126.2, 125.2, 37.51, 29.7, 22.9, 20.7, 14.0, 13.6; HRMS Calculated for $[\text{C}_{16}\text{H}_{21}\text{N}_3]^+$: 255.3580, Found: 255.1735.

1.3.4c(N1)

1-((Z)-oct-4-en-4-yl)-4-phenyl-1H-1,2,3-triazole 1.3.4c(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 81%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.87 (d, $J = 7.2\text{Hz}$, 2H), 7.73 (s, 1H), 7.42 (t, $J = 7.2\text{Hz}$, 2H), 7.33 (t, $J = 7.8\text{Hz}$, 1H), 5.60 (t, $J = 7.2\text{Hz}$, 1H), 2.52 (t, $J = 7.8\text{Hz}$, 2H), 1.95 (q, $J = 7.2\text{Hz}$, 14.4Hz, 2H), 1.37-1.43 (m, 4H), 0.90-0.93 (m, 3H), 0.85-0.88 (m, 3H); $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 147.1, 136.3, 130.8,

129.1, 128.4, 127.6, 125.9, 120.5, 38.4, 29.4, 22.7, 20.4, 13.9, 13.5; HRMS Calculated for $[C_{16}H_{21}N_3]^+$: 255.3580, Found: 255.1735.

1.3.4d(N2)

4-phenyl-2,5-bis(1-phenylvinyl)-2H-1,2,3-triazole 1.3.4d(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 81%. ^1H -NMR (600 MHz, CDCl_3) δ 7.67-7.69 (m, 2H), 7.56-7.58 (m, 2H), 7.42-7.45 (m, 5H), 7.25-7.30 (m, 6H), 6.04 (s, 1H), 5.95 (s, 1H), 5.66 (s, 1H), 5.46 (s, 1H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 146.7, 146.3, 146.0, 139.4, 138.8, 135.0, 130.3, 129.5, 128.62, 128.61, 128.58, 128.56, 128.52, 128.4, 128.0, 127.1, 119.4, 107.8; HRMS Calculated for $[C_{24}H_{19}N_3]^+$: 349.4728, Found: 349.1579.

1.3.4d(N1)

4-phenyl-1,5-bis(1-phenylvinyl)-1H-1,2,3-triazole 1.3.4d(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 90%. ^1H -NMR (600 MHz, CDCl_3) δ 7.86-7.88 (m, 2H), 7.30-7.33 (m, 2H), 7.24-7.28 (m, 2H), 7.16-7.22 (m, 5H), 7.05-7.09 (m, 4H), 5.82 (s, 1H), 5.64 (s, 1H), 5.41 (s, 1H), 5.29 (s, 1H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 145.3, 143.0, 137.4, 136.4, 135.3, 133.9, 130.9, 129.5, 128.8, 128.7, 128.6, 128.5, 128.2, 127.1, 126.5, 126.4, 121.4, 114.5; HRMS Calculated for $[\text{C}_{24}\text{H}_{19}\text{N}_3]^+$: 349.4728, Found: 349.1579.

1.3.4d(N3)

5-phenyl-1,4-bis(1-phenylvinyl)-1H-1,2,3-triazole 1.3.4d(N3): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 90%. ^1H -NMR (600 MHz, CDCl_3) δ 7.29-7.31 (m, 2H), 7.21-7.25 (m, 3H), 7.14-7.18 (m, 3H), 7.07-7.12 (m, 3H), 7.00-7.05 (m, 4H), 5.82 (s, 1H), 5.64 (s, 1H), 5.63 (s, 1H), 5.55 (s, 1H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 145.0, 143.0, 139.4, 139.3, 135.9, 135.3, 129.5, 129.4, 129.0, 128.8, 128.7, 128.2, 127.9, 127.6, 127.1, 126.1, 118.5, 115.0; HRMS Calculated for $[\text{C}_{24}\text{H}_{19}\text{N}_3]^+$: 349.4728, Found: 349.1579.

1.3.4e(N2)

2-((Z)-oct-4-en-4-yl)-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole 1.3.4e(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 85%. ¹H-NMR (600 MHz, CDCl₃) δ 7.63 (d, *J*= 8.4Hz, 2H), 7.36 (d, *J*= 8.4Hz, 2H), 7.22-7.25 (m, 6H), 5.88 (s, 1H), 5.57 (s, 1H), 5.50 (t, *J*= 7.2Hz, 1H), 2.65 (t, *J*= 7.2Hz, 2H), 2.27 (q, *J*= 7.2Hz, 14.4Hz, 2H), 1.45-1.51 (m, 4H), 0.90-0.96 (m, 6H); ¹³C-NMR (67.5 MHz, CDCl₃) δ 145.1, 144.3, 139.6, 139.1, 138.7, 130.8, 128.6, 128.4, 128.2, 128.1, 127.8, 127.0, 125.0, 118.8, 37.4, 29.9, 22.9, 20.8, 14.1, 13.6; HRMS Calculated for [C₂₄H₂₇N₃]⁺: 357.4913, Found: 357.2205.

1.3.4e(N1)

1-((Z)-oct-4-en-4-yl)-4-phenyl-5-(1-phenylvinyl)-1H-1,2,3-triazole 1.3.4e(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 85%. ¹H-NMR (600 MHz, CDCl₃) δ 7.85 (d, *J*= 7.2Hz, 2H), 7.24-7.31 (m, 8H), 6.01 (s, 1H), 5.51 (t,

$J = 7.2\text{Hz}$, 1H), 5.44 (s, 1H), 2.06 (t, $J = 7.2\text{Hz}$, 2H), 1.69 (q, $J = 7.2\text{Hz}$, 15.0Hz, 2H), 1.23-1.32 (m, 4H), 0.77-0.82 (m, 6H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 144.3, 137.5, 136.7, 135.2, 132.8, 130.8, 130.5, 128.7, 128.6, 128.4, 127.7, 126.6, 126.2, 120.5, 37.5, 29.7, 22.1, 19.8, 13.7, 13.2; HRMS Calculated for $[\text{C}_{24}\text{H}_{27}\text{N}_3]^+$: 357.4913, Found: 357.2205.

1.3.4f(N2)

4-phenyl-5-(1-phenylethyl)-2-(1-phenylvinyl)-2H-1,2,3-triazole 1.3.4f(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 88%. ^1H -NMR (600 MHz, CDCl_3) δ 7.48-7.52 (m, 4H), 7.39-7.42 (m, 3H), 7.27-7.36 (m, 8H), 5.95 (s, 1H), 5.40 (s, 1H), 4.39 (q, $J = 7.2\text{Hz}$, 14.4Hz, 1H), 1.68 (d, $J = 7.2\text{Hz}$, 3H), ; ^{13}C -NMR (67.5 MHz, CDCl_3) δ 149.4, 146.3, 146.2, 144.7, 135.0, 130.6, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 126.4, 106.9, 37.0, 23.1; HRMS Calculated for $[\text{C}_{24}\text{H}_{21}\text{N}_3]^+$: 351.4436, Found: 351.1735.

1.3.4f(N1)

4-phenyl-5-(1-phenylethyl)-1-(1-phenylvinyl)-1H-1,2,3-triazole 1.3.4f(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 88%. ^1H -NMR (600 MHz, CDCl_3) δ 7.34 (d, J = 7.8Hz, 4H), 7.25-7.29 (m, 2H), 7.16-7.24 (m, 7H), 7.04 (d, J = 7.8Hz, 2H), 6.98 (d, J = 7.2Hz, 2H), 5.74 (s, 1H), 5.48 (s, 1H), 4.14 (q, J = 7.2Hz, 14.4Hz, 1H), 1.76 (d, J = 7.2Hz, 3H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 148.5, 145.7, 143.1, 135.4, 134.6, 129.6, 129.4, 129.0, 128.7, 128.6, 128.5, 127.7, 127.5, 126.47, 126.2, 114.5, 36.7, 22.7; HRMS Calculated for $[\text{C}_{24}\text{H}_{21}\text{N}_3]^+$: 351.4436, Found: 351.1735.

1.3.4g(N2)

4-cyclohexenyl-5-phenyl-2-(1-phenylvinyl)-2H-1,2,3-triazole 1.3.4g(N2): was purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 87%. ^1H -NMR (600 MHz, CDCl_3) δ 7.67-7.69 (m, 2H), 7.48-7.50 (m, 2H), 7.38-7.41 (m, 5H), 7.34-7.36 (m, 1H), 6.06-6.09 (m, 1H), 5.90 (s, 1H), 5.36 (s, 1H), 2.32-2.36 (m, 2H), 2.11-2.16 (m, 2H), 1.70-1.76 (m, 2H), 1.63-1.69 (m, 2H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 147.9, 146.2, 145.4,

135.1, 131.6, 130.4, 129.3, 128.7, 128.6, 128.53, 128.50, 128.42, 128.37, 107.1, 27.8, 25.7, 22.8, 22.1; HRMS Calculated for $[C_{22}H_{21}N_3]^+$: 327.4222, Found: 327.1735.

1.3.4g(N1)

5-cyclohexenyl-4-phenyl-1-(1-phenylvinyl)-1H-1,2,3-triazole 1.3.4g(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 87%. ^1H -NMR (600 MHz, CDCl_3) δ 7.18-7.27 (m, 6H), 7.13 (d, J = 7.2Hz, 2H), 7.04 (d, J = 7.8Hz, 2H), 6.05-6.16 (m, 1H), 5.75 (s, 1H), 5.46 (s, 1H), 2.29-2.36 (m, 2H), 2.03-2.10 (m, 2H), 1.65-1.71 (m, 2H), 1.52-1.63 (m, 2H); ^{13}C -NMR (67.5 MHz, CDCl_3) δ 147.7, 146.4, 143.0, 135.7, 133.5, 130.0, 129.4, 129.0, 128.6, 128.4, 128.3, 127.9, 126.1, 114.7, 27.3, 25.7, 22.9, 22.2; HRMS Calculated for $[C_{22}H_{21}N_3]^+$: 327.4222, Found: 327.1735.

1.3.4h(N2)

4-benzyl-2-(1-cyclohexylvinyl)-5-phenyl-2H-1,2,3-triazole 1.3.4h(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 93%. ¹H-NMR (600 MHz, CDCl₃) δ 7.54 (d, *J*= 7.2Hz, 2H), 7.26-7.32 (m, 3H), 7.21 (t, *J*= 7.8Hz, 2H), 7.14 (t, *J*= 7.8Hz, 3H), 5.72 (s, 1H), 4.79 (s, 1H), 4.18 (s, 2H), 3.03(t, *J*= 11.4Hz, 1H), 1.95 (d, *J*= 12.6Hz, 2H), 1.75 (d, *J*= 13.8Hz, 2H), 1.34 (d, *J*= 13.2Hz, 2H), 1.17-1.27 (m, 4H); ¹³C-NMR (67.5 MHz, CDCl₃) δ 151.5, 144.2, 138.8, 131.0, 128.9, 128.8, 128.7, 128.6, 128.4, 127.9, 126.6, 100.6, 39.5, 32.2, 31.8, 26.7, 26.6; HRMS Calculated for [C₂₃H₂₅N₃]⁺: 343.4647, Found: 343.2048.

1.3.4h(N1)

5-benzyl-1-(1-cyclohexylvinyl)-4-phenyl-1H-1,2,3-triazole 1.3.4h(N1): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 93%. ¹H-NMR (600 MHz, CDCl₃) δ 7.73 (d, *J*= 7.8Hz, 2H), 7.37 (t, *J*= 7.2Hz 2H), 7.25-7.32 (m, 3H), 7.21 (t, *J*= 7.2Hz 1H), 7.03 (d, *J*= 7.8Hz, 2H), 5.15(s, 1H), 4.96(s, 1H), 4.24(s, 2H), 2.47 (t, *J*= 10.8Hz 1H), 1.63-1.71 (m, 5H), 1.03-1.17 (m, 5H); ¹³C-NMR (67.5 MHz, CDCl₃) δ 148.7, 145.1, 137.1, 131.2, 131.1, 128.9, 128.7, 127.9, 127.8, 127.0, 126.9, 111.0, 42.7, 30.8, 29.3, 26.0, 25.9; HRMS Calculated for [C₂₃H₂₅N₃]⁺: 343.4647, Found: 343.2048.

1.3.4i(N2)

Phenyl(5-phenyl-2-(1-phenylvinyl)-2H-1,2,3-triazol-4-yl)methanone 1.3.4i(N2): purified by flash chromatography (Hexane-EtOAc, v/v 5/1) as yellow oil with overall isolated yield: 84%. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.09(d, $J= 7.2\text{Hz}$, 2H), 7.84-7.85 (m, 2H), 7.57 (t, $J= 7.2\text{Hz}$, 1H), 7.49-7.51(m, 2H), 7.38-7.46 (m, 8H), 6.06 (s, 1H), 5.54 (s, 1H); $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3) δ 188.0, 150.3, 146.2, 143.1, 137.2, 134.3, 133.7, 130.8, 129.7, 129.5, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 109.5; HRMS Calculated for $[\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}]^+$: 351.4006, Found: 351.1372.

1.4 Iron catalyzed C-O bond activation for the synthesis of propargyl-1,2,3-triazoles and 1,1-bis-triazoles

General Methods and materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. HRMS were recorded on LTQ-FTUHRA spectrometer.

Substrates **1.4.2b**, **1.4.4** were synthesized according to the literatures as below:

1. Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* **2007**, *9*, 2147-2150.
2. Marion, N.; Carlqvist, P.; Gealageas, R.; Fremont, P.; Maseras, F.; Nolan, S. P. *Chem. Eur. J.* **2007**, *13*, 6437-6451.
3. Wang, D.; Ye, X.; Shi, X. *Org. Lett.* **2010**, *12*, 2088-2091.

Representative procedure for the preparation of propargylic acetate 1.4.2a

To a solution of hex-1-yne (39 mmol) in anhydrous THF (50 mL) at $-78\text{ }^{\circ}\text{C}$ under N_2 atmosphere was added $n\text{-BuLi}$ (1.6 M solution in hexanes, 20.6 mL, 33 mmol). The reaction was stirred at this temperature for 20 min then at room temperature for one hour. After cooling to at $-78\text{ }^{\circ}\text{C}$, benzaldehyde (30 mmol) was added to the mixture and was allowed to warm to room temperature gradually and stirred for an additional hour. After addition of acetate anhydrous (60 mmol) at $0\text{ }^{\circ}\text{C}$, the reaction mixture was warmed to room temperature and stirred for 2h before quenched with aqueous NH_4Cl . The mixture was extracted with EtOAc (3 x 20 mL), and the combined organic phases were washed with water and brine, dried with anhydrous MgSO_4 , and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, V/V, 20:1) to produce the desired acetate as yellow oil in quantitative yield.

Representative procedure for the preparation of propargylic alcohol 1.4.4

To a solution of alkyne (39 mmol) in anhydrous THF (50 mL) at $-78\text{ }^{\circ}\text{C}$ under N_2 atmosphere was added $n\text{-BuLi}$ (1.6 M solution in hexanes, 20.6 mL, 33 mmol). The reaction was stirred at this temperature for 20 min then at room temperature for 1h. After cooling to at $-78\text{ }^{\circ}\text{C}$, aldehyde (30 mmol) was added to the mixture and was allowed to warm to room temperature gradually and stirred for an additional hour before quenched with aqueous NH_4Cl . The mixture was extracted with EtOAc (3 x 20 mL), and the combined organic phases were washed with water and brine, dried with anhydrous MgSO_4 , and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, V/V, 15:1) to produce the desired alcohol as yellow oil in quantitative yield.

Representative procedure for propargylation of 1.4.4 with triazoles

A solution of propargylic alcohol **1.4.4** (1 mmol) and triazole (1.2 mmol) with catalyst iron(III) chloride (0.1 mmol) in acetonitrile (10 ml) was stirred at 90 degree in the presence of water condensor for 5h. The reaction mixture was quenched with 10 ml distilled water and then extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with water and brine, dried with anhydrous MgSO₄, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, V/V, 15:1) to produce the desired product as yellow oil except for **1.4.3f**.

Compounds Characterization

1.4.3a (N-1)

1-(1-phenylhept-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3a (N-1)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.54-7.51 (m, 3H), 7.37-7.29 (m, 5H), 7.14 (s, 1H), 2.34 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.56 (quintet, $J = 7.2$ Hz, 2H), 1.42 (hextet, $J = 7.2$ Hz, 2H), 0.90 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.7, 135.9, 131.3, 128.7, 128.6, 127.1, 123.9, 120.0, 111.1, 90.3, 73.6, 55.5, 30.4, 21.9, 18.4, 13.4; HRMS Calculated for $\text{C}_{19}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 290.16572, Found: 290.16517.

1.4.3b (N-1)

4-phenyl-1-(1-phenylhept-2-ynyl)-1H-1,2,3-triazole (1.4.3b (N-1)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.89 (s, 1H), 7.82 (d, $J = 7.8$ Hz, 2H), 7.52 (d, $J = 7.2$ Hz, 2H), 7.41-7.30 (m, 6H), 6.73 (s, 1H), 2.37 (dt, $J = 7.2$ Hz, 1.8 Hz, 2H), 1.60 (quintet, $J = 7.2$ Hz, 2H), 1.47 (hextet, $J = 7.2$ Hz, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.0, 136.7, 130.5, 129.0, 128.8,

128.7, 128.1, 127.1, 125.7, 118.0, 90.1, 74.4, 56.3, 30.4, 22.0, 18.5, 13.5; HRMS Calculated for $C_{21}H_{22}N_3$ $[M+H]^+$: 316.18137, Found: 316.18082.

1.4.3b (N-2)

4-phenyl-2-(1-phenylhept-2-ynyl)-2H-1,2,3-triazole (1.4.3b (N-2)): 1H -NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.81 (d, $J = 7.2$ Hz, 2H), 7.59 (d, $J = 7.2$ Hz, 2H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.39-7.32 (m, 5H), 2.37 (dt, $J = 7.2$ Hz, 1.8 Hz, 2H), 1.59 (quintet, $J = 7.2$ Hz, 2H), 1.47 (hexet, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 147.9, 137.0, 131.7, 130.3, 128.7, 128.6, 128.5, 128.4, 127.4, 126.0, 89.3, 74.7, 60.8, 30.4, 21.9, 18.6, 13.5; HRMS Calculated for $C_{21}H_{22}N_3$ $[M+H]^+$: 316.18137, Found: 316.18082.

1.4.3c (N-1)

phenyl(5-phenyl-1-(1-phenylhept-2-ynyl)-1H-1,2,3-triazol-4-yl)methanone (1.4.3c (N-1)): 1H -NMR (600 MHz, $CDCl_3$) δ 8.26 (d, $J = 7.2$ Hz, 2H), 7.56 (d, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.2$ Hz, 2H), 7.38-7.29 (m, 4H), 7.25-7.23 (m, 4H), 7.05 (dd, $J = 7.2$ Hz, 2.4 Hz, 2H), 6.27 (t, $J = 3.6$

Hz, 1H), 2.71 (dt, $J = 7.2$ Hz, 1.8 Hz, 2H), 1.54 (quintet, $J = 7.2$ Hz, 2H), 1.28 (hextet, $J = 7.2$ Hz, 2H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 186.4, 141.9, 141.5, 137.1, 133.0, 131.9, 130.7, 129.8, 129.6, 128.7, 128.5, 128.4, 128.2, 127.8, 127.4, 126.8, 111.8, 103.4, 32.3, 28.7, 22.0, 13.7; HRMS Calculated for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 420.20759, Found: 420.20704.

1.4.3c (N-2)

phenyl(5-phenyl-2-(1-phenylhept-2-ynyl)-2H-1,2,3-triazol-4-yl)methanone (1.4.3c (N-2)):

^1H -NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 8.4$ Hz, 2H), 7.83 (dd, $J = 7.2$ Hz, 2.4 Hz, 2H), 7.63 (d, $J = 7.2$ Hz, 2H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.41-7.37 (m, 6H), 6.69 (t, $J = 2.4$ Hz, 1H), 2.37 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.60 (quintet, $J = 7.2$ Hz, 2H), 1.48 (hextet, $J = 7.8$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 187.7, 149.9, 142.1, 137.2, 136.4, 133.2, 130.6, 129.7, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.6, 90.0, 74.3, 61.5, 30.4, 21.9, 18.6, 13.5; HRMS Calculated for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 420.20759, Found: 420.20704.

1.4.3d (N-1)

1-(3-cyclopropyl-1-phenylprop-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3d (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.49 (d J = 7.2 Hz, 2H), 7.38-7.29 (m, 5H), 7.10 (s, 1H), 1.40-1.37 (m, 1H), 0.86-0.83 (m, 2H), 0.78-0.75 (m, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 143.4, 136.0, 134.6, 131.8, 128.8, 128.7, 127.2, 127.0, 123.9, 120.0, 111.1, 93.2, 68.7, 55.5, 8.4; HRMS Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 274.13442, Found: 274.13423.

1.4.3e (N-1)

1-(1,3-diphenylprop-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3e (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.08 (d, J = 7.2 Hz, 1H), 7.60-7.64 (m, 3H), 7.52 (d, J = 7.8 Hz, 2H), 7.40-7.33 (m, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.8, 135.4, 131.8, 131.4, 129.2, 128.9, 128.8, 128.4, 127.4, 127.0, 124.0, 121.5, 120.1, 111.0, 89.1, 82.4, 55.7; HRMS Calculated for $\text{C}_{21}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 310.13442, Found: 310.13387.

1.4.3f (N-1)

1-(1,3-diphenylprop-2-ynyl)-4-phenyl-1H-1,2,3-triazole (1.4.3f (N-1)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.96 (s, 1H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 7.2$ Hz, 2H), 7.55 (d, $J = 7.2$ Hz, 2H), 7.44-7.37 (m, 8H), 7.33-7.31 (m, 1H), 6.99 (s, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.3, 136.2, 131.9, 130.5, 129.3, 129.2, 129.1, 128.8, 128.5, 128.2, 127.2, 125.8, 121.4, 118.1, 88.8, 83.1, 56.7; HRMS Calculated for $\text{C}_{23}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 336.15007, Found: 336.14992.

1.4.3f (N-2)

2-(1,3-diphenylprop-2-ynyl)-4-phenyl-2H-1,2,3-triazole (1.4.3f (N-2)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.95 (s, 1H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 2H), 7.59 (dd, $J = 7.2$ Hz, 2.4 Hz, 2H), 7.45 (q, $J = 7.8$ Hz, 4H), 7.40-7.35 (m, 5H), 6.94 (s, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.2, 136.4, 131.9, 131.8, 130.2, 128.9, 128.8, 128.7, 128.5, 128.2, 127.5, 126.0, 122.0, 88.0, 83.7, 61.0; HRMS Calculated for $\text{C}_{23}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 336.15007, Found: 336.14992.

1.4.3g (N-2)

(2-(1,3-diphenylprop-2-ynyl)-5-phenyl-2H-1,2,3-triazol-4-yl)(phenyl)methanone (1.4.3g (N-2)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 7.8$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 2H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 2H), 7.47-7.34 (m, 11H), 6.94 (s, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 187.6, 150.1, 142.3, 137.2, 135.8, 133.3, 131.9, 130.6, 129.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 127.8, 121.8, 88.7, 83.1, 61.8; HRMS Calculated for $\text{C}_{30}\text{H}_{22}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 440.17629, Found: 440.17679.

1.4.3h (N-1)

1-(1-(naphthalen-1-yl)hept-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3h (N-1)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.25 (d, $J = 9.0$ Hz, 1H), 8.19 (d, $J = 7.2$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.82 (d, $J = 9.0$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.48-7.41 (m, 3H), 7.30-7.23 (m, 2H), 2.32 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.54 (quintet, $J = 7.2$ Hz, 2H), 1.39 (hextet, $J = 7.2$ Hz, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.6, 134.0, 131.7, 130.6, 130.5, 130.3, 128.8, 127.1, 127.0, 126.5, 126.1, 124.8, 123.7, 122.9, 120.0, 111.1, 90.5, 74.3, 53.7, 30.4, 21.9, 18.5, 13.5; HRMS Calculated for $\text{C}_{23}\text{H}_{22}\text{N}_3$ $[\text{M}+\text{H}]^+$: 340.18137, Found: 340.18082.

1-(1-(4-fluorophenyl)hept-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3i (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.53-7.49 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.11 (s, 1H), 7.02 (t, J = 8.4 Hz, 2H), 2.34 (dt, J = 7.2 Hz, 2.4 Hz, 2H), 1.56 (quintet, J = 7.2 Hz, 2H), 1.41 (hextet, J = 7.2 Hz, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 163.6, 162.0, 146.8, 131.9, 131.8, 131.2, 129.0, 128.9, 127.2, 124.0, 120.1, 115.8, 115.6, 110.9, 90.6, 73.5, 54.8, 30.3, 21.9, 18.4, 13.4; HRMS Calculated for $\text{C}_{19}\text{H}_{19}\text{FN}_3$ $[\text{M}+\text{H}]^+$: 308.15630, Found: 308.15588.

1-(1-(4-fluorophenyl)hept-2-ynyl)-4-phenyl-1H-1,2,3-triazole (1.4.3j (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 7.89 (s, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.51-7.49 (m, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 7.8 Hz, 2H), 6.68 (s, 1H), 2.35 (dt, J = 7.2 Hz, 2.4 Hz, 2H), 1.58 (quintet, J = 7.2 Hz, 2H), 1.45 (hextet, J = 7.2 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 163.7, 162.1, 148.0, 132.6, 132.5, 130.3, 129.0, 128.9, 128.7, 128.2,

125.7, 117.9, 115.9, 115.7, 90.4, 74.2, 55.7, 30.3, 22.0, 18.4, 13.5; HRMS Calculated for $C_{21}H_{21}FN_3$ $[M+H]^+$: 334.17195, Found: 334.17140.

2-(1-(4-fluorophenyl)hept-2-ynyl)-4-phenyl-2H-1,2,3-triazole (1.4.3j (N-2)): 1H -NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.79 (d, $J = 7.2$ Hz, 2H), 7.57 (q, $J = 4.8$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.36-7.33 (m, 1H), 7.05 (t, $J = 7.8$ Hz, 2H), 6.64 (s, 1H), 2.36 (dt, $J = 7.2$ Hz, 2.4 Hz, 2H), 1.58 (quintet, $J = 7.2$ Hz, 2H), 1.47 (hextet, $J = 7.2$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 163.9, 162.3, 148.3, 133.1, 133.0, 132.0, 130.5, 129.7, 129.6, 129.0, 128.7, 126.3, 115.9, 115.7, 89.9, 74.9, 60.3, 30.7, 22.2, 18.8, 13.8; HRMS Calculated for $C_{21}H_{21}FN_3$ $[M+H]^+$: 334.17195, Found: 334.17140.

4-phenyl-1-(3-phenyl-1-p-tolylprop-2-ynyl)-1H-1,2,3-triazole (1.4.3k (N-1)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.94 (s, 1H), 7.82 (d, $J = 7.2$ Hz, 2H), 7.54 (d, $J = 7.2$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.41-7.36 (m, 5H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 6.94 (s, 1H), 2.37 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.2, 139.3, 133.2, 131.9, 130.5, 129.7, 129.3, 128.7, 128.5, 128.2, 127.2, 125.7, 121.5, 118.1, 88.6, 83.3, 56.5, 21.1; HRMS Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 350.16572, Found: 350.16517.

1.4.3k (N-2)

4-phenyl-2-(3-phenyl-1-p-tolylprop-2-ynyl)-2H-1,2,3-triazole (1.4.3k (N-2)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.92 (s, 1H), 7.83 (d, $J = 7.2$ Hz, 2H), 7.59-7.55 (m, 4H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.37-7.33 (m, 4H), 7.23 (d, $J = 7.8$ Hz, 2H), 6.89 (s, 1H), 2.37 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.1, 138.8, 133.5, 132.0, 131.8, 130.3, 129.4, 128.8, 128.7, 128.4, 128.2, 127.5, 126.0, 122.1, 87.8, 83.9, 60.8, 21.1; HRMS Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 350.16572, Found: 350.16517.

1.4.3l (N-1)

1-(3-phenyl-1-p-tolylprop-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3l (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.51-7.48 (m, 4H), 7.40-7.32 (m, 6H), 7.18 (d, $J = 7.8$ Hz, 2H), 2.33 (s, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.8, 138.9, 132.5, 131.9, 131.4, 129.6, 129.1, 128.4, 127.3, 127.0, 124.0, 121.7, 120.1, 111.1, 88.9, 82.7, 55.6, 21.1; HRMS Calculated for $\text{C}_{22}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 324.15007, Found: 324.14952.

1.4.3m (N-1)

4-phenyl-1-(1-phenyl-3-(trimethylsilyl)prop-2-ynyl)-1H-1,2,3-triazole (1.4.3m (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.42-7.37 (m, 5H), 7.32 (t, $J = 8.4$ Hz, 1H), 6.75 (s, 1H), 0.26 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 148.2, 135.9, 130.5, 129.2, 129.0, 128.8, 128.2, 127.2, 125.7, 118.0, 98.8, 94.8, 56.6, -0.3; HRMS Calculated for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 332.15830, Found: 332.15790.

1.4.3m (N-2)

4-phenyl-2-(1-phenyl-3-(trimethylsilyl)prop-2-ynyl)-2H-1,2,3-triazole (1.4.3m (N-2)): ^1H -NMR (600 MHz, CDCl_3) δ 7.88 (s, 1H), 7.81 (d, $J = 7.2$ Hz, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.43-7.33 (m, 6H), 6.69 (s, 1H), 0.25 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 148.1, 136.1, 131.9, 130.2, 128.8, 128.7, 128.6, 128.5, 127.5, 126.0, 99.1, 93.6, 61.0, -0.3; HRMS Calculated for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 332.15830, Found: 332.15790.

1.4.3n (N-1)

1-(1-phenyl-3-(trimethylsilyl)prop-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3n (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 2H), 7.38-7.28 (m, 5H), 7.17 (s, 1H), 0.23 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.7, 135.1, 131.3, 128.8, 128.7, 127.1, 126.9, 123.9, 120.0, 111.1, 98.0, 95.0, 55.7, -0.4; HRMS Calculated for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 306.14265, Found: 306.14210.

1.4.3o (N-2)

2-(1-(hex-1-ynyl)cyclohex-2-enyl)-4-phenyl-2H-1,2,3-triazole (1.4.3o (N-2)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.83 (s, 1H), 7.79 (d, $J = 7.2$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 1H), 6.14 (s, 1H), 5.31-5.27 (m, 1H), 2.35-2.30 (m, 3H), 2.23-2.14 (m, 3H), 1.99-1.95 (m, 1H), 1.77-1.72 (m, 1H), 1.51 (quintet, $J = 7.2$ Hz, 2H), 1.42 (sextet, $J = 7.2$ Hz, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.7, 131.0, 130.8, 129.3, 129.0, 128.5, 126.2, 126.1, 90.8, 81.1, 61.0, 31.0, 29.7, 29.0, 22.2, 20.1, 19.2, 13.8; HRMS Calculated for $\text{C}_{20}\text{H}_{24}\text{N}_3$ $[\text{M}+\text{H}]^+$: 306.19702, Found: 306.19678.

1.4.3p (N-1)

1-(1-(hex-1-ynyl)cyclohex-2-enyl)-1H-benzo[d][1,2,3]triazole (1.4.3p (N-1)): $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.06 (d, $J = 7.8$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 6.10 (s, 1H), 5.65-5.68 (m, 1H), 2.43-2.37 (m, 1H), 2.32 (t, $J = 7.2$ Hz, 3H), 2.29-2.22 (m, 1H), 2.16-2.08 (m, 1H), 2.00-1.96 (m, 1H), 1.86-1.81 (m, 1H), 1.52 (quintet, $J = 7.2$ Hz, 2H), 1.42 (sextet, $J = 7.2$ Hz, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3)

δ 146.5, 132.1, 128.8, 127.0, 126.9, 123.7, 120.1, 110.4, 91.3, 80.5, 56.4, 30.7, 29.5, 28.9, 21.9, 20.6, 19.0, 13.6; HRMS Calculated for $C_{18}H_{22}N_3$ $[M+H]^+$: 280.18137, Found: 280.18082.

1.4.3p (N-2)

2-(1-(hex-1-ynyl)cyclohex-2-enyl)-2H-benzo[d][1,2,3]triazole (1.4.3p (N-2)): 1H -NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, $J = 6.6$ Hz, 3.0 Hz, 2H), 7.36 (dd, $J = 6.6$ Hz, 3.0 Hz, 2H), , 6.19 (s, 1H), 5.55-5.58 (m, 1H), 2.39-2.21 (m, 6H), 2.02-1.97 (m, 1H), 1.80-1.76 (m, 1H), 1.50 (quintet, $J = 7.2$ Hz, 2H), 1.41 (sextet, $J = 7.2$ Hz, 2H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 144.4, 128.8, 126.7, 126.4, 118.3, 91.3, 81.0, 62.7, 30.9, 29.7, 29.6, 22.1, 20.1, 19.2, 13.8; HRMS Calculated for $C_{18}H_{22}N_3$ $[M+H]^+$: 280.18137, Found: 280.18082.

1.4.3q (N-1)

1-(((trimethylsilyl)ethynyl)cyclohex-2-enyl)-1H-benzo[d][1,2,3]triazole (1.4.3q (N-1)): 1H -NMR (600 MHz, $CDCl_3$) δ 8.05 (d, $J = 7.2$ Hz, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.2$ Hz, 1H), 6.23 (s, 1H), 5.65-5.61 (m, 1H), 2.44-2.37 (m, 1H), 2.33-2.30

(m, 1H), 2.25-2.20 (m, 1H), 2.14-2.08 (m, 1H), 2.01-1.95 (m, 1H), 1.85-1.78 (m, 1H), 0.17 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.4, 132.1, 131.4, 127.1, 126.3, 123.8, 120.1, 110.2, 104.7, 95.0, 56.1, 29.0, 28.7, 20.5, -0.2; HRMS Calculated for $\text{C}_{17}\text{H}_{22}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 290.15830, Found: 290.15786.

1.4.3r (N-1)

(E)-1-(1-phenyl-5-(trimethylsilyl)pent-1-en-4-yn-3-yl)-1H-benzo[d][1,2,3]triazole (1.4.3r (N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.07 (d, $J = 7.8$ Hz, 1H), 7.36-7.32 (m, 5H), 7.27-7.24 (m, 3H), 6.92 (dd, $J = 16.2$ Hz, 6.6 Hz, 1H), 6.63 (d, $J = 7.2$ Hz, 1H), 5.65 (dd, $J = 16.2$ Hz, 1.8 Hz, 1H), 0.18 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.4, 139.0, 136.6, 132.2, 129.0, 128.8, 127.4, 127.3, 124.0, 120.2, 114.8, 110.2, 101.7, 97.8, 64.8, -0.3; HRMS Calculated for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 332.15830, Found: 332.15883.

1.4.3s (N-1)

1-(1-(2-methoxyphenyl)-3-(trimethylsilyl)prop-2-ynyl)-1H-benzo[d][1,2,3]triazole (1.4.3s

(N-1)): ^1H -NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 1H), 7.97 (dd, $J = 7.8$ Hz, 1.8 Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.34-7.28 (m, 3H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 3.66 (s, 3H), 0.19 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 156.8, 146.0, 131.9, 130.6, 129.2, 126.8, 123.5, 123.4, 120.5, 119.8, 110.9, 110.7, 99.1, 93.3, 55.4, 50.3, -0.4; HRMS Calculated for $\text{C}_{19}\text{H}_{22}\text{N}_3\text{OSi}$ $[\text{M}+\text{H}]^+$: 336.15321, Found: 336.15266.

1.4.5a

1-((1-benzyl-1H-1,2,3-triazol-4-yl)(phenyl)methyl)-1H-benzo[d][1,2,3]triazole (1.4.5a): ^1H -NMR (600 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.65 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.45 (s, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.38-7.33 (m, 4H), 7.31-7.28 (m, 3H), 7.25-7.24 (m, 4H), 5.52 (s, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.1, 145.8, 137.3, 134.2, 132.7, 129.2, 128.9, 128.8, 128.6, 128.0, 127.6, 127.2, 124.1, 123.8, 120.0, 110.3, 59.5, 54.4; HRMS Calculated for $\text{C}_{22}\text{H}_{19}\text{N}_6$ $[\text{M}+\text{H}]^+$: 367.16712, Found: 367.16789.

1.4.5b

1-benzyl-4-(phenyl(4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-1H-1,2,3-triazole (1.4.5b): ^1H -NMR (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.74 (d, $J = 7.2$ Hz, 2H), 7.57 (s, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.37-7.24 (m, 12H), 5.53 (s, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 138.1, 134.5, 131.6, 130.2, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.2, 126.0, 123.6, 65.5, 54.3; HRMS Calculated for $\text{C}_{24}\text{H}_{21}\text{N}_6$ $[\text{M}+\text{H}]^+$: 393.18277, Found: 393.18342.

1.4.5c

1-benzyl-4-(phenyl(4-phenyl-2H-1,2,3-triazol-2-yl)methyl)-1H-1,2,3-triazole (1.4.5c): ^1H -NMR (600 MHz, CDCl_3) δ 8.02 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 2H), 7.56 (s, 1H), 7.41-7.27 (m, 13H), 7.17 (s, 1H), 5.53 (s, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 137.3, 134.0, 130.5, 129.3, 129.1, 129.0, 128.8, 128.7, 128.4, 128.2, 127.5, 125.7, 123.4, 119.9, 60.7, 54.5; HRMS Calculated for $\text{C}_{24}\text{H}_{21}\text{N}_6$ $[\text{M}+\text{H}]^+$: 393.18277, Found: 393.18342.

1.4.5d

(E)-1-benzyl-4-(3-phenyl-1-(4-phenyl-2H-1,2,3-triazol-2-yl)allyl)-1H-1,2,3-triazole (1.4.5d):

$^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.78 (d, $J = 7.2$ Hz, 2H), 7.50 (d, $J = 9.0$ Hz, 1H), 7.45 (s, 1H), 7.43-7.39 (m, 4H), 7.37-7.26 (m, 9H), 6.67-6.60 (m, 2H), 5.51 (s, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.6, 139.3, 134.4, 131.1, 130.5, 129.1, 129.0, 128.8, 128.7, 128.6, 128.3, 128.1, 128.0, 127.0, 126.0, 122.8, 119.9, 66.2, 54.1; HRMS Calculated for $\text{C}_{26}\text{H}_{23}\text{N}_6$ $[\text{M}+\text{H}]^+$: 419.19842, Found: 419.19793.

1.4.5e

1-(1-(1-benzyl-1H-1,2,3-triazol-4-yl)cyclohex-2-enyl)-1H-benzo[d][1,2,3]triazole (1.4.5e):

$^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.45 (s, 1H), 7.41-7.32 (m, 5H), 7.28-7.27 (m, 2H), 6.55 (s, 1H), 5.77-5.74 (m, 1H), 5.52 (s, 2H), 2.68-2.66 (m, 2H), 2.34-2.30 (m, 1H), 2.25-2.19 (m, 1H), 2.14-2.08 (m, 1H), 1.97-1.90 (m, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.1, 146.4, 134.5, 132.9, 132.2, 129.1, 128.8, 128.1, 127.0, 123.7, 121.4,

120.1, 119.5, 110.3, 56.3, 54.2, 29.4, 25.9, 20.4; HRMS Calculated for C₂₁H₂₁N₆ [M+H]⁺: 357.18277, Found: 357.18226.

1-((1-benzyl-1H-1,2,3-triazol-4-yl)(2-methoxyphenyl)methyl)-1H-benzo[d][1,2,3]triazole

(1.4.5f): ¹H-NMR (600 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.59 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.36-7.30 (m, 4H), 7.28-7.23 (m, 4H), 6.89-6.85 (m, 2H), 5.50 (s, 2H), 3.74 (s, 3H); ¹³C-NMR (150 MHz, CDCl₃) δ 156.5, 145.9, 145.6, 134.4, 132.9, 133.0, 129.1, 128.8, 128.7, 127.9, 127.2, 125.5, 123.8, 123.7, 120.8, 119.7, 110.8, 110.3, 55.5, 54.2, 53.2; HRMS Calculated for C₂₃H₂₁N₆O [M+H]⁺: 397.17768, Found: 397.17698.

(4-((1H-benzo[d][1,2,3]triazol-1-yl)(2-methoxyphenyl)methyl)-1H-1,2,3-triazol-1-yl)methyl

pivalate (1.4.5g): ¹H-NMR (600 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 2H), 7.49 (d,

$J = 8.4$ Hz, 1H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.31 (quintet, $J = 7.2$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 1H), 6.92-6.89 (m, 2H), 6.22 (s, 2H), 3.78 (s, 3H), 1.17 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 177.5, 156.5, 146.1, 145.8, 133.0, 130.2, 128.6, 127.3, 125.2, 125.1, 123.9, 120.9, 119.9, 110.9, 110.2, 69.8, 55.6, 53.2, 38.8, 26.7; HRMS Calculated for $\text{C}_{22}\text{H}_{25}\text{N}_6\text{O}_3$ $[\text{M}+\text{H}]^+$: 421.19881, Found: 421.19816.

(E)-1-benzyl-4-(3-phenyl-1-(4-phenyl-1H-1,2,3-triazol-1-yl)allyl)-1H-1,2,3-triazole (1.4.5h):

^1H -NMR (600 MHz, CDCl_3) δ 7.89 (s, 1H), 7.79 (d, $J = 7.2$ Hz, 2H), 7.44 (s, 1H), 7.79 (t, $J = 7.8$ Hz, 3H), 7.39-7.30 (m, 9H), 7.25 (d, $J = 5.4$ Hz, 1H), 7.04 (dd, $J = 15.6$ Hz, 5.4 Hz, 1H), 6.54 (d, $J = 15.6$ Hz, 1H), 6.47 (d, $J = 7.2$ Hz, 1H), 5.50 (s, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 147.9, 138.1, 134.4, 131.3, 130.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.4, 126.0, 122.4, 120.7, 70.5, 54.2; HRMS Calculated for $\text{C}_{26}\text{H}_{23}\text{N}_6$ $[\text{M}+\text{H}]^+$: 419.19842, Found: 419.19793

ORTEP Drawing of the Crystal Structures:

Figure S1.4-1. Perspective view of the molecular structure of $C_{22}H_{24}N_6O_3$ (**1.4.3f (N-2)**) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 775267

For details regarding the crystal structure, refer to supporting information for paper: Yan, W.; Wang, Q.; Chen, Y.; Petersen, J. L.; Shi, X. *Org. Lett.* **2010**, *12*, 3308-3311.

Figure S1.4-2. Perspective view of the molecular structure of $C_{22}H_{24}N_6O_3$ (**1.4.5g**) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 775268

1.5 Synthesis of allene triazole through iron catalyzed regioselective addition to propargyl alcohols

General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. Infrared (IR) spectra were obtained on a FT-IR spectrometer. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with *p*-anisaldehyde or potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer. UV-visible spectra were obtained on a Shimadzu UV-2550.

Propargylic alcohols **1.5.3** were synthesized according to the literatures as below:

Yan, W.; Wang, Q.; Chen, Y.; Petersen, J.; Shi, X. *Org. Lett.* **2010**, *12*, 3308-3311.

Representative procedure for propargylation of 1.5.4 with triazoles

A solution of triazole (**1.3** mmol) with catalyst iron(III) chloride (0.1 mmol) in 1,2-dichloroethane(DCE) (5 ml) was stirred at 60 °C for one hour, then propargyl alcohol **1.5.3** (1.0 mmol) was added. The reaction mixture was quenched with 10 ml distilled water and then extracted with EtOAc (3 x 10 mL) after 5 hours. The combined organic phases were washed with water and brine, dried with anhydrous MgSO₄, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, V/V, 20/1) to produce the desired product.

Compounds Characterization

1.5.4a

1-(1-(trimethylsilyl)-3,3-diphenylpropa-1,2-dienyl)-1H-benzo[*d*][1,2,3]triazole (1.5.4a) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. Isolated yield 84%; m. p. 127-129 °C; *R_f*(hexanes/ethyl acetate, V/V, 10/1) = 0.49; UV absorption: 232(0.182), 263(0.134), 295(0.126); IR (neat), 2957, 1598, 1489, 1447, 1285, 1245, 1062, 936, 833, 767, 694; ¹H-NMR (600 MHz, CDCl₃) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.50-7.47 (m, 4H), 7.43-7.38 (m, 5H), 7.37-7.32 (m, 3H), 0.50 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.4 (C), 146.2 (C), 135.8 (C), 132.5 (C), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 124.3 (CH), 118.0 (CH), 115.3 (C), 111.9 (CH), 108.8 (C), -0.5 (CH₃); HRMS Calculated for C₂₄H₂₄N₃Si [M+H]⁺: 382.1734, Found: 382.1735.

1.5.4b

1-(1,1-diphenylhepta-1,2-dien-3-yl)-1H-benzo[*d*][1,2,3]triazole (1.5.4b) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 74%; *R_f*

(hexanes/ethyl acetate, V/V, 10/1) = 0.45; UV absorption: 233(0.160), 259(0.129), 295(0.100); IR (neat), 2935, 1603, 1485, 1447, 1281, 1244, 1056, 957, 785, 744, 691; ^1H -NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 7.8$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.46-7.43 (m, 4H), 7.42-7.30 (m, 8H), 3.22 (t, $J = 7.8$ Hz, 2H), 1.75 (quin, $J = 7.8$ Hz, 2H), 1.47 (sex, $J = 7.8$ Hz, 2H), 0.93 (t, $J = 7.8$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 197.0 (C), 146.3 (C), 135.9 (C), 132.1 (C), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.9 (CH), 124.3 (CH), 120.0 (CH), 119.8 (C), 113.5 (C), 111.6 (CH), 31.2 (CH_2), 29.2 (CH_2), 22.3 (CH_2), 13.8 (CH_3); HRMS Calculated for $\text{C}_{25}\text{H}_{24}\text{N}_3$ $[\text{M}+\text{H}]^+$: 366.1965, Found: 366.1964.

1-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-1*H*-benzo[*d*][1,2,3]triazole (1.5.4c) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 80%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.51; UV absorption: 234(0.301), 263(0.209), 299(0.195); IR (neat), 2930, 1600, 1485, 1449, 1281, 1246, 1068, 935, 838, 764, 693; ^1H -NMR (600 MHz, CDCl_3) δ 8.07 (d, $J = 7.8$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.40-7.36 (m, 4H), 7.35-7.32 (m, 3H), 7.20 (d, $J = 7.8$ Hz, 2H), 2.38 (s, 3H), 0.46 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 200.4 (C), 146.2 (C), 138.0 (C), 136.0 (C), 132.8 (C), 132.5 (C), 129.5 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 124.3 (CH), 120.0 (CH), 115.2 (C), 112.0 (CH), 108.7 (C), 21.2 (CH_3), -0.5 (CH_3); HRMS Calculated for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 396.1887, Found: 396.1883.

1-(1-cyclopropyl-3,3-diphenylpropa-1,2-dienyl)-1H-benzo[d][1,2,3]triazole (1.5.4d) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. Isolated yield 82%; m. p. 107-109 °C; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.48; UV absorption: 229(0.205), 260(0.146), 295(0.102); IR (neat), 3008, 1598, 1490, 1449, 1278, 1161, 1078, 977, 853, 747, 692; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.09-8.07 (m, 1H), 7.54-7.51 (m, 1H), 7.41-7.32 (m, 12H), 2.51-2.45 (m, 1H), 1.13-1.09 (m, 2H), 0.85-0.81 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 196.4 (C), 146.4 (C), 135.7 (C), 132.0 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 127.9 (CH), 124.3 (CH), 120.9 (C), 120.0 (CH), 116.6 (C), 111.4 (CH), 11.8 (CH), 7.7 (CH_2); HRMS Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 350.1652, Found: 350.1653.

1-(4,4-dimethyl-1,1-diphenylpenta-1,2-dien-3-yl)-1H-benzo[d][1,2,3]triazole (1.5.4e) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 91%; m. p. 81-83 °C; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.47; UV absorption: 236(0.193),

265(0.215); IR (neat), 2972, 1589, 1490, 1451, 1274, 1231, 1062, 947, 810, 766, 694; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.06-8.02 (m, 1H), 7.39-7.33 (m, 10H), 7.31-7.28 (m, 2H), 7.18-7.16 (m, 1H), 1.38 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 200.6 (C), 145.0 (C), 135.2 (C), 134.3 (C), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.5 (CH), 123.8 (CH), 119.7 (CH), 119.1 (C), 117.2 (C), 110.6 (CH), 37.2 (C), 29.1 (CH_3); HRMS Calculated for $\text{C}_{25}\text{H}_{24}\text{N}_3$ $[\text{M}+\text{H}]^+$: 366.1965, Found: 366.1966.

1-(4-methyl-1,1-diphenylpenta-1,2,4-trien-3-yl)-1H-benzo[*d*][1,2,3]triazole (1.5.4f) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 86%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.52; UV absorption: 235(0.165), 265(0.096), 297(0.062); IR (neat), 3057, 1597, 1490, 1448, 1278, 1160, 1065, 1002, 908, 743, 695; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.08 (d, $J = 7.8$ Hz, 1H), 7.45-7.34 (m, 12H), 7.29 (d, $J = 7.8$ Hz, 1H), 5.17 (s, 1H), 4.66 (s, 1H), 2.15 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 204.6 (C), 145.4 (C), 136.0 (C), 134.6 (C), 133.7 (C), 128.9 (CH), 128.8 (CH), 128.7 (CH), 127.7 (CH), 124.0 (CH), 120.0 (CH), 118.7 (C), 115.4 (CH), 113.4 (C), 110.4 (CH_2), 20.5 (CH_3); HRMS Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 350.1651, Found: 350.1650.

1.5.4g

1-(3-(2-(4-methoxybenzyloxy)phenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-1H-

benzo[d][1,2,3]triazole (1.5.4g) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 90%; R_f (hexanes/ethyl acetate, V/V, 6/1) = 0.58; UV absorption: 231(0.186), 263(0.145), 299(0.128); IR (neat), 2976, 1583, 1493, 1450, 1286, 1240, 1063, 938, 831, 757, 692; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.42-7.31 (m, 7H), 7.24 (t, J = 8.4 Hz, 1H), 7.07-7.03 (m, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.81 (s, 1H), 6.69 (d, J = 8.4 Hz, 2H), 4.93 (q, J = 11.4 Hz, 2H), 3.78 (s, 3H), 0.5(s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 200.0 (C), 159.0 (C), 156.1 (C), 145.9 (C), 136.4 (C), 132.4 (C), 130.8 (C), 129.5 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 125.0 (CH), 124.1 (CH), 121.0 (CH), 119.4 (CH), 113.5 (CH), 112.8 (CH), 112.3 (CH), 111.8 (C), 108.4 (C), 69.5 (CH_2), 55.2 (CH_3), -0.4 (CH_3); HRMS Calculated for $\text{C}_{32}\text{H}_{32}\text{N}_3\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 517.2179, Found: 517.5180.

1.5.4h

1-(3-(2-methoxyphenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-1H-

benzo[d][1,2,3]triazole (1.5.4h) was purified by flash chromatography (Hexane-EtOAc, v/v

20/1) as white solid. Isolated yield 90%; m. p. 131-133 °C; *R_f*(hexanes/ethyl acetate, V/V, 6/1) = 0.60; UV absorption: 230(0.200), 264(0.210), 295(0.173); IR (neat), 2957, 1599, 1490, 1453, 1286, 1245, 1066, 939, 829, 740, 691; ¹H-NMR (600 MHz, CDCl₃) δ 8.15 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.42-7.32 (m, 8H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 0.51(s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.0 (C), 157.1 (C), 146.1 (C), 136.0 (C), 132.5 (C), 130.8 (CH), 129.5 (CH), 128.5 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 124.5 (CH), 124.2 (CH), 120.8 (CH), 119.6 (CH), 112.7 (C), 111.3 (C), 111.2 (CH), 108.3 (C), 55.1 (CH₃), -0.4 (CH₃); HRMS Calculated for C₂₅H₂₆N₃OSi [M+H]⁺: 412.1840, Found: 412.1841.

1-(3-(4-methoxyphenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-1*H*-

benzo[*d*][1,2,3]triazole (1.5.4i) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 91%; *R_f*(hexanes/ethyl acetate, V/V, 6/1) = 0.64; UV absorption: 231(0.197), 262(0.184), 296(0.155); IR (neat), 2963, 1603, 1498, 1466, 1270, 1235, 1055, 930, 821, 747, 695; ¹H-NMR (600 MHz, CDCl₃) δ 8.08 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.41-7.32 (m, 7H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 0.47 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.6 (C), 159.8 (C), 146.4 (C), 136.3 (C), 132.7 (C), 129.9 (CH), 129.0 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 124.6 (CH), 120.2 (CH),

115.3 (C), 114.5 (CH), 112.2 (CH), 108.9 (C), 55.6 (CH₃), -0.22 (CH₃); HRMS Calculated for C₂₅H₂₆N₃OSi [M+H]⁺: 412.1838, Found: 412.1840.

4-(3-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-(trimethylsilyl)-1-phenylpropa-1,2-dienyl)phenol

(1.5.4j) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 80%; *R_f*(hexanes/ethyl acetate, V/V, 4/1) = 0.44; UV absorption: 233(0.217), 257(0.166), 271(0.187), 300(0.134); IR (neat), 3363, 2988, 1620, 1476, 1433, 1271, 1212, 1055, 938, 811, 745, 698; ¹H-NMR (600 MHz, CDCl₃) δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.41-7.37 (m, 4H), 7.36-7.30 (m, 3H), 6.95 (d, *J* = 7.2 Hz, 2H), 0.45 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.5 (C), 156.4 (C), 145.7 (C), 136.0 (C), 132.5 (C), 129.8 (CH), 128.7 (CH), 128.5 (CH), 128.0 (CH), 127.3 (CH), 124.7 (CH), 119.6 (CH), 115.9 (CH), 115.3 (C), 112.2 (CH), 108.6 (C), -0.51 (CH₃); HRMS Calculated for C₂₄H₂₄N₃OSi [M+H]⁺: 398.1681, Found: 398.1682.

4-(3-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-4,4-dimethyl-1-phenylpenta-1,2-dienyl)phenol (1.5.4k)

was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 83%; *R_f* (hexanes/ethyl acetate, V/V, 4/1) = 0.43; UV absorption: 231(0.233), 270(0.209), 298(0.174); IR (neat), 3345, 2995, 1605, 1455, 1445, 1287, 1225, 1043, 936, 814, 748, 695; ¹H-NMR (600 MHz, CDCl₃) δ 8.06-8.03 (m, 1H), 7.40-7.35 (m, 5H), 7.33-7.30 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.20-7.17 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.4 (C), 156.5 (C), 144.5 (C), 135.5 (C), 134.4 (C), 132.9 (CH), 130.0 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 124.1 (CH), 119.4 (CH), 115.7 (CH), 115.3 (C), 110.8 (C), 37.2 (C), 29.2 (CH₃); HRMS Calculated for C₂₅H₂₄N₃O [M+H]⁺: 382.1912, Found: 382.1910.

1.5.4l

1-(4,4-dimethyl-1-phenyl-1-(thiophen-2-yl)penta-1,2-dien-3-yl)-1*H*-benzo[*d*][1,2,3]triazole

(1.5.4l) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 95%; *R_f* (hexanes/ethyl acetate, V/V, 6/1) = 0.46; UV absorption: 236(0.189), 260(0.237), 289(0.125); IR (neat), 2988, 1621, 1490, 1454, 1268, 1221, 1034, 951, 830, 745, 688; ¹H-NMR (600 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.45-7.36 (m, 5H), 7.34 (dd, *J* = 5.4 Hz, 1.2 Hz, 1H), 7.12 (dd, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.08 (dd, *J* = 5.4 Hz, 3.6 Hz, 1H), 0.50 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 199.9 (C),

146.2 (C), 139.4 (C), 135.5 (C), 132.4 (C), 128.8 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.0 (CH), 126.4 (CH), 124.4 (CH), 120.0 (CH), 111.9 (CH), 110.5 (C), 109.0 (C), -0.57 (CH₃); HRMS Calculated for C₂₃H₂₂N₃S [M+H]⁺: 372.1528, Found: 372.1527.

N-2-1.5.4m

2-(1-(trimethylsilyl)-3,3-diphenylpropa-1,2-dienyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4m)

was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 60%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.62; UV absorption: 237(0.202), 264(0.153), 299(0.135); IR (neat), 2923, 1633, 1487, 1446, 1281, 1243, 1039, 931, 827, 779, 692; ¹H-NMR (600 MHz, CDCl₃) δ 8.01 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.45-7.40 (m, 8H), 7.39-7.36 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 0.47 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 201.3 (C), 147.6 (C), 138.0 (C), 135.2 (C), 129.4 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 127.5 (C), 125.6 (CH), 117.0 (CH), 116.1 (C), 109.3 (C), 21.2 (CH₃), -0.62 (CH₃); HRMS Calculated for C₂₇H₂₈N₃Si [M+H]⁺: 422.2046, Found: 422.2044.

N-1-1.5.4m

1-(1-(trimethylsilyl)-3,3-diphenylpropa-1,2-dienyl)-4-*p*-tolyl-1*H*-1,2,3-triazole (N-1-1.5.4m)

was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 12%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.29; UV absorption: 236(0.179), 265(0.144), 297(0.114); IR (neat), 2928, 1635, 1469, 1433, 1287, 1222, 1032, 930, 816, 770, 694; ¹H-NMR (600 MHz, CDCl₃) δ 7.63 (s, 1H), 7.30-7.27 (m, 6H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.05-7.03 (m, 4H), 6.73 (d, *J* = 7.8 Hz, 2H), 2.14 (s, 3H), 0.32 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 203.8 (C), 138.8 (C), 137.8 (C), 135.0 (C), 133.3 (C), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 124.3 (CH), 114.2 (C), 107.3 (C), 21.2 (CH₃), -0.66 (CH₃); HRMS Calculated for C₂₇H₂₈N₃Si [M+H]⁺: 422.2046, Found: 422.2045.

N-2-1.5.4m'

2-(3-(trimethylsilyl)-1,1-diphenylprop-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4m')

was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 13%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.48; UV absorption: 244(0.408), 255(0.418); IR (neat), 3108, 2960, 1490, 1456, 1354, 1296, 1071, 974, 833, 764, 734, 687; ¹H-NMR (600 MHz, CDCl₃) δ 7.91 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.36-7.33 (m, 6H), 7.32-7.29 (m, 4H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 0.28 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 148.0 (C), 141.2 (C), 138.3 (C), 131.2 (CH), 129.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.5 (C), 126.0 (CH),

104.4 (C), 94.2 (C), 73.8 (C), 21.3 (CH₃), -0.28 (CH₃); HRMS Calculated for C₂₇H₂₈N₃Si [M+H]⁺: 422.2046, Found: 422.2047.

N-1-1.5.4m'

1-(3-(trimethylsilyl)-1,1-diphenylprop-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-1-1.5.4m') was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 5%; R_f(hexanes/ethyl acetate, V/V, 10/1) = 0.24; UV absorption: 243(0.314), 253(0.298); IR (neat), 3083, 2936, 1490, 1456, 1425, 1156, 1073, 976, 833, 751, 730, 686; ¹H-NMR (600 MHz, CDCl₃) δ 7.97 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.37-7.35 (m, 6H), 7.32-7.29 (m, 4H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 0.29 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 146.8 (C), 140.6 (C), 137.9 (C), 129.4 (CH), 128.7 (CH), 128.4 (CH), 128.0 (CH), 127.7 (C), 125.6 (CH), 120.2 (CH), 104.1 (C), 94.9 (C), 70.0 (C), 21.2 (CH₃), -0.37 (CH₃); HRMS Calculated for C₂₇H₂₈N₃Si [M+H]⁺: 422.2046, Found: 422.2049.

N-2-1.5.4n

4-(4-methoxyphenyl)-2-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-2*H*-1,2,3-triazole (N-2-1.5.4n) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. R_f (hexanes/ethyl acetate, V/V, 6/1) = 0.66; Isolated yield 70%; UV absorption: 244(0.223), 271(0.189), 298(0.154); IR (neat), 2987, 1621, 1503, 1454, 1268, 1237, 1067, 941, 832, 754, 687; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.92 (s, 1H), 7.77 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 9.0$ Hz, 4H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 6.94 (d, $J = 9.0$ Hz, 2H), 3.84 (s, 3H), 2.39 (s, 3H), 0.42 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 201.3 (C), 159.7 (C), 147.4 (C), 138.3 (C), 135.4 (C), 132.2 (C), 129.5 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.1 (CH), 123.1 (C), 116.6 (CH), 116.0 (C), 114.2 (CH), 109.2 (C), 55.3 (CH_3), 21.2 (CH_3), -0.59 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{30}\text{N}_3\text{OSi}$ $[\text{M}+\text{H}]^+$: 452.2153, Found: 452.2156.

N-1-1.5.4n

4-(4-methoxyphenyl)-1-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-1*H*-1,2,3-triazole (N-1-1.5.4n) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 14%; R_f (hexanes/ethyl acetate, V/V, 6/1) = 0.30; UV absorption: 244(0.165), 273(0.132), 299(0.103); IR (neat), 2960, 1611, 1494, 1469, 1284, 1232, 1049, 938,

819, 732, 691; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.62 (s, 1H), 7.36-7.33 (m, 2H), 7.20-7.14 (m, 3H), 7.10 (d, $J = 9.0$ Hz, 4H), 7.07-7.05 (m, 2H), 6.46 (d, $J = 7.8$ Hz, 2H), 3.64 (s, 3H), 2.36 (s, 3H), 0.31 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 204.0 (C), 160.2 (C), 142.9 (C), 137.9 (C), 135.4 (C), 132.3 (C), 130.5 (CH), 129.3 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.0 (C), 127.9 (CH), 120.0 (C), 113.9 (CH), 107.4 (C), 55.2 (CH_3), 21.3 (CH_3), -0.45 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{30}\text{N}_3\text{OSi}$ $[\text{M}+\text{H}]^+$: 452.2153, Found: 452.2150.

4-(4-methoxyphenyl)-2-(3-(trimethylsilyl)-1-phenyl-1-*p*-tolylprop-2-ynyl)-2H-1,2,3-triazole (N-2-1.5.4n') was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 10%; R_f (hexanes/ethyl acetate, V/V, 6/1) = 0.51; UV absorption: 256(0.413), 269(0.424); IR (neat), 3096, 2943, 1482, 1423, 1368, 1299, 1065, 975, 830, 751, 724, 689; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.83 (s, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.32-7.29 (m, 2H), 7.25-7.23 (m, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.12 (t, $J = 8.4$ Hz, 3H), 6.91 (t, $J = 8.4$ Hz, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 0.26 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 159.8 (C), 147.7 (C), 141.5 (C), 138.3 (C), 137.4 (C), 130.8 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 123.1 (C), 114.1 (CH), 104.6 (C), 93.9 (C), 73.5 (C), 55.2 (CH_3), 21.1 (CH_3), -0.26 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{30}\text{N}_3\text{OSi}$ $[\text{M}+\text{H}]^+$: 452.2153, Found: 452.2150.

N-1-1.5.4n'

4-(4-methoxyphenyl)-1-(3-(trimethylsilyl)-1-phenyl-1-*p*-tolylprop-2-ynyl)-1*H*-1,2,3-triazole

(**N-1-1.5.4n'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid.

Isolated yield 4%; *R_f* (hexanes/ethyl acetate, V/V, 6/1) = 0.33; UV absorption: 256(0.335),

266(0.356); IR (neat), 3090, 2955, 1498, 1453, 1434, 1149, 1068, 956, 837, 750, 721, 680; ¹H-

NMR (600 MHz, CDCl₃) δ 7.90 (s, 1H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.36-7.34 (m, 3H), 7.29-7.25

(m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H),

2.36 (s, 3H), 0.27 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 159.6 (C), 146.6 (C), 140.8 (C), 138.6

(C), 137.6 (C), 129.0 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.0 (CH), 123.4

(C), 119.7 (CH), 114.2 (CH), 104.3 (C), 94.6 (C), 69.8 (C), 55.3 (CH₃), 21.1 (CH₃), -0.35 (CH₃);

HRMS Calculated for C₂₈H₃₀N₃OSi [M+H]⁺: 452.2153, Found: 452.2151.

N-2-1.5.4o

4-(4-chlorophenyl)-2-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-2*H*-1,2,3-triazole (N-2-1.5.4o) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 57%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.57; UV absorption: 238(0.329), 269(0.254), 301(0.216); IR (neat), 2937, 1623, 1477, 1450, 1276, 1235, 1063, 932, 818, 745, 696; ¹H-NMR (600 MHz, CDCl₃) δ 7.99 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.40-7.38 (m, 5H), 7.37-7.35 (m, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 0.43 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 201.3 (C), 146.5 (C), 138.4 (C), 135.3 (C), 134.0 (C), 132.1 (C), 129.5 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 128.2 (C), 127.0 (CH), 117.5 (CH), 116.2 (C), 109.2 (C), 21.2 (CH₃), -0.62 (CH₃); HRMS Calculated for C₂₇H₂₇ClN₃Si [M+H]⁺: 456.1655, Found: 456.1652.

4-(4-chlorophenyl)-1-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-1*H*-1,2,3-triazole (N-1-1.5.4o) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 15%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.29; UV absorption: 242(0.308), 261(0.249), 300(0.233); IR (neat), 2946, 1589, 1480, 1441, 1292, 1231, 1063, 939, 825, 756, 694; ¹H-NMR (600 MHz, CDCl₃) δ 7.65 (s, 1H), 7.32-7.28 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.05-7.02 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H), 0.34 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 204.0 (C), 138.0 (C), 136.6 (C), 135.0 (C), 134.8 (C), 133.5 (C), 131.6 (C), 129.9 (CH), 129.2 (CH), 128.5 (CH), 128.4

(CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 125.8 (CH), 114.5 (C), 107.2 (C), 21.2 (CH₃), -0.67 (CH₃); HRMS Calculated for C₂₇H₂₇ClN₃Si [M+H]⁺: 456.1655, Found: 456.1654.

4-(4-chlorophenyl)-2-(3-(trimethylsilyl)-1-phenyl-1-*p*-tolylprop-2-ynyl)-2*H*-1,2,3-triazole

(**N-2-1.5.4o'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 19%; *R_f*(hexanes/ethyl acetate, V/V, 10/1) = 0.47; UV absorption: 250(0.378), 265(0.345); IR (neat), 3100, 2947, 1498, 1434, 1367, 1292, 1049, 967, 854, 788, 730, 691; ¹H-NMR (600 MHz, CDCl₃) δ 7.90 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.35-7.33 (m, 3H), 7.27-7.24 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H), 0.27 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 146.9 (C), 141.3 (C), 138.3 (C), 138.1 (C), 134.2 (C), 131.2 (CH), 128.9 (CH), 128.8 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.4 (CH), 104.4 (C), 94.2 (C), 73.8 (C), 21.1 (CH₃), -0.28 (CH₃); HRMS Calculated for C₂₇H₂₇ClN₃Si [M+H]⁺: 456.1655, Found: 456.1654.

4-(4-chlorophenyl)-1-(3-(trimethylsilyl)-1-phenyl-1-*p*-tolylprop-2-ynyl)-2*H*-1,2,3-triazole

(**N-1-1.5.4o'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 5%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.26; UV absorption: 248(0.268), 263(0.247); IR (neat), 3054, 2921, 1495, 1458, 1421, 1150, 1054, 971, 827, 749, 720, 688; ^1H -NMR (600 MHz, CDCl_3) δ 7.95 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.38-7.33 (m, 5H), 7.28-7.25 (m, 2H), 7.18 (d, J = 9.0 Hz, 2H), 7.15 (d, J = 9.0 Hz, 2H), 2.35 (s, 3H), 0.27 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 145.9 (C), 140.8 (C), 139.0 (C), 137.7 (C), 134.0 (C), 129.4 (CH), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 127.2 (CH), 120.8 (CH), 104.3 (C), 95.1 (C), 70.3 (C), 21.3 (CH_3), -0.13 (CH_3); HRMS Calculated for $\text{C}_{27}\text{H}_{27}\text{ClN}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 456.1655, Found: 456.1655.

4-(4-fluorophenyl)-2-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-2*H*-1,2,3-

triazole (N-2-1.5.4p) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow

liquid. Isolated yield 62%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.55; UV absorption: 257(0.405), 263(0.353), 311(0.252); IR (neat), 2966, 1586, 1493, 1444, 1282, 1234, 1039, 933, 854, 756, 682; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.97 (s, 1H), 7.84-7.81 (m, 2H), 7.42-7.40 (m, 4H), 7.38-7.35 (m, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.11 (t, J = 7.8 Hz, 2H), 2.40 (s, 3H), 0.44 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 201.3 (C), 163.5 (C), 161.9 (C), 146.6 (C), 138.4 (C), 135.3 (C), 132.1 (C), 129.5 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.5 (CH), 127.4 (CH), 126.7 (C), 126.6 (C), 117.2 (CH), 116.1 (C), 115.8 (CH), 115.7 (CH), 109.2 (C), 21.2 (CH_3), -0.63 (CH_3); HRMS Calculated for $\text{C}_{27}\text{H}_{27}\text{FN}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 440.1951, Found: 440.1950.

4-(4-fluorophenyl)-1-(1-(trimethylsilyl)-3-phenyl-3-*p*-tolylpropa-1,2-dienyl)-1H-1,2,3-triazole (N-1-1.5.4p) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 14%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.25; UV absorption: 253(0.333), 261(0.279), 313(0.223); IR (neat), 2987, 1618, 1464, 1426, 1289, 1235, 1052, 946, 823, 745, 688; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.64 (s, 1H), 7.31-7.28 (m, 3H), 7.14-7.11 (m, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.06-7.03 (m, 2H), 6.94 (d, J = 7.8 Hz, 2H), 6.59 (t, J = 7.8 Hz, 2H), 2.37 (s, 3H), 0.32 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 203.8 (C), 163.7 (C), 163.0 (C), 162.0 (C), 138.0 (C), 136.8 (C), 134.9 (C), 133.5 (CH), 131.7 (CH), 130.8 (C), 130.7 (C), 129.2 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 123.3 (CH), 115.4 (CH), 115.3 (CH),

114.4 (C), 107.2 (C), 21.2 (CH₃), -0.67 (CH₃); HRMS Calculated for C₂₇H₂₇FN₃Si [M+H]⁺: 440.1951, Found: 440.1954.

4-(4-fluorophenyl)-2-(3-(trimethylsilyl)-1-phenyl-1-*p*-tolylprop-2-ynyl)-2H-1,2,3-triazole

(**N-2-1.5.4p'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 15%; R_f(hexanes/ethyl acetate, V/V, 10/1) = 0.45; UV absorption: 271(0.513), 285(0.446); IR (neat), 3118, 2937, 1476, 1424, 1375, 1299, 1055, 963, 850, 781, 727, 690; ¹H-NMR (600 MHz, CDCl₃) δ 7.87 (s, 1H), 7.77-7.74 (m, 2H), 7.35-7.32 (m, 3H), 7.28-7.24 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H), 0.27 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 163.7 (C), 162.0 (C), 147.0 (C), 141.4 (C), 138.3 (C), 138.2 (C), 131.0 (CH), 128.9 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 126.7 (C), 126.6 (C), 115.8 (CH), 115.6 (CH), 104.4 (C), 94.1 (C), 73.7 (C), 21.1 (CH₃), -0.27 (CH₃); HRMS Calculated for C₂₇H₂₇FN₃Si [M+H]⁺: 440.1951, Found: 440.1948.

4-(4-fluorophenyl)-1-(3-(trimethylsilyl)-1-phenyl-1-*p*-tolylprop-2-ynyl)-2*H*-1,2,3-triazole

(**N-1-1.5.4p'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 4%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.28; UV absorption: 270(0.436), 283(0.389); IR (neat), 3089, 2931, 1488, 1433, 1363, 1281, 1042, 965, 864, 774, 735, 695; ^1H -NMR (600 MHz, CDCl_3) δ 7.94 (s, 1H), 7.81-7.78 (m, 2H), 7.36-7.34 (m, 3H), 7.29-7.27 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.10 (t, J = 8.4 Hz, 2H), 2.36 (s, 3H), 0.28 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 163.5 (C), 161.8 (C), 145.9 (C), 140.6 (C), 138.7 (C), 137.5 (C), 129.1 (CH), 128.7 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 125.9 (C), 125.8 (C), 120.3 (CH), 115.8 (CH), 115.7 (CH), 104.1 (C), 94.8 (C), 70.0 (C), 21.0 (CH_3), -0.36 (CH_3); HRMS Calculated for $\text{C}_{27}\text{H}_{27}\text{FN}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 440.1951, Found: 440.1953.

2-(4,4-dimethyl-1,1-diphenylpenta-1,2-dien-3-yl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4q)

was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 65%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.60; UV absorption: 240(0.214), 258(0.182), 294(0.195); IR (neat), 2956, 1588, 1497, 1441, 1264, 1245, 1072, 958, 815, 760, 675; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.77 (s, 1H), 7.74 (d, $J = 7.8$ Hz, 2H), 7.44-7.39 (m, 8H), 7.38-7.34 (m, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 2.37 (s, 3H), 1.39 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 199.4 (C), 146.8 (C), 138.0 (C), 135.2 (C), 129.4 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 127.6 (C), 125.6 (CH), 121.0 (C), 120.6 (CH), 117.6 (C), 36.3 (C), 29.1 (CH_3), 21.3 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{28}\text{N}_3$ $[\text{M}+\text{H}]^+$: 406.2280, Found: 406.2280.

1-(4,4-dimethyl-1,1-diphenylpenta-1,2-dien-3-yl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-1-1.5.4q)

was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 11%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.28; UV absorption: 243(0.253), 259(0.298), 297(0.203); IR (neat), 2934, 1576, 1501, 1433, 1237, 1216, 1066, 939, 811, 773, 683; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.69 (s, 1H), 7.40-7.33 (m, 10H), 7.02 (d, $J = 7.8$ Hz, 2H), 6.84 (d, $J = 7.8$ Hz, 2H), 2.29 (s, 3H), 1.11 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 202.6 (C), 163.0 (C), 138.9 (C), 134.7 (C), 132.1 (CH), 129.1 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 124.2 (C), 119.1 (C), 117.1 (C), 37.1 (C), 29.1 (CH_3), 21.3 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{28}\text{N}_3$ $[\text{M}+\text{H}]^+$: 406.2280, Found: 406.2285.

N-2-1.5.4q'

2-(4,4-dimethyl-1,1-diphenylpent-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4q') was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 15%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.45; UV absorption: 240(0.267), 253(0.305); IR (neat), 3123, 2956, 1500, 1431, 1362, 1280, 1040, 968, 842, 781, 733, 701; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.88 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.35-7.31 (m, 6H), 7.30-7.27 (m, 4H), 7.20 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H), 1.35 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.7 (C), 142.1 (C), 138.1 (C), 131.0 (CH), 129.4 (CH), 128.1 (CH), 128.1 (CH), 128.0 (CH), 127.7 (C), 126.0 (CH), 97.7 (C), 79.0 (C), 73.4 (C), 30.6 (CH_3), 27.8 (C), 21.3 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{28}\text{N}_3$ $[\text{M}+\text{H}]^+$: 406.2280, Found: 406.2284.

N-1-1.5.4q'

1-(4,4-dimethyl-1,1-diphenylpent-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-1-1.5.4q') was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 4%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.25; UV absorption: 242(0.253), 254(0.236); IR (neat), 3076, 2927, 1463, 1448, 1354, 1290, 1033, 985, 855, 793, 721, 698; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.96 (s, 1H), 7.71 (d, $J = 7.8$ Hz, 2H), 7.36-7.33 (m, 6H), 7.31-7.27 (m, 4H), 7.21 (d, $J = 7.8$ Hz, 2H), 2.37 (s, 3H), 1.35 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 163.0 (C), 146.7 (C), 141.3 (C), 137.9 (C), 129.4 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 125.6 (CH), 120.2 (CH), 98.3 (C), 78.9 (C), 69.7 (C), 30.6 (CH_3), 27.9 (C), 21.3 (CH_3); HRMS Calculated for $\text{C}_{28}\text{H}_{28}\text{N}_3$ $[\text{M}+\text{H}]^+$: 406.2280, Found: 406.2279.

N-2-1.5.4r

2-(4-methyl-1,1-diphenylpenta-1,2,4-trien-3-yl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4r) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 70%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.64; UV absorption: 231(0.405), 263(0.353), 311(0.252); IR (neat), 3033, 1586, 1495, 1438, 1266, 1153, 1071, 992, 903, 734, 694; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.86 (s, 1H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.47-7.45 (m, 4H), 7.43-7.35 (m, 6H), 7.23 (d, $J = 8.4$ Hz, 2H), 5.21 (s, 1H), 4.88 (s, 1H), 2.38 (s, 3H), 2.09 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 203.5 (C), 147.3 (C), 138.1 (C), 136.2 (C), 134.6 (C), 129.5 (CH), 128.9 (CH), 128.7 (CH), 128.7 (CH), 127.5 (C), 125.7 (CH), 120.8 (CH), 119.0 (C), 115.4 (CH_2),

114.8 (C), 21.3 (CH₃), 20.7 (CH₃); HRMS Calculated for C₂₇H₂₄N₃ [M+H]⁺: 390.1960, Found: 390.1962.

2-(4-methyl-1,1-diphenylpent-4-en-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4r') was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 10%; R_f(hexanes/ethyl acetate, V/V, 10/1) = 0.50; UV absorption: 248(0.231), 259(0.210); IR (neat), 3110, 2930, 1471, 1423, 1373, 1297, 1053, 960, 838, 779, 718, 679; ¹H-NMR (600 MHz, CDCl₃) δ 7.91 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.36-7.33 (m, 6H), 7.31-7.28 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.48 (s, 1H), 5.35 (quin, *J* = 1.8 Hz, 1H), 2.37 (s, 3H), 2.01 (s, 3H); ¹³C-NMR (150 MHz, CDCl₃) δ 148.0 (C), 141.5 (C), 138.4 (C), 131.2 (CH), 129.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.5 (C), 126.1 (C), 126.0 (CH), 123.1 (CH₂), 90.2 (C), 88.0 (C), 73.8 (C), 23.2 (CH₃), 21.3 (CH₃); HRMS Calculated for C₂₇H₂₄N₃ [M+H]⁺: 390.1960, Found: 390.1962.

Mixture of **1-(4-methyl-1,1-diphenylpenta-1,2,4-trien-3-yl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4r)** and **1-(4-methyl-1,1-diphenylpent-4-en-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-1-1.5.4r')** couldn't separated by flash chromatography with different developing solvent systems which were Hexane-EtOAc (v/v: 20/1) and Hexane-ethylene chloride (v/v: 5/1) as yellow liquid. R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.29; Isolated yield 11%; UV absorption: 233(0.333), 245(0.200), 261(0.257), 313(0.163); IR (neat), 3066, 2935, 1589, 1477, 1448, 1350, 1284, 1165, 1049, 997, 913, 857 732, 688; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.88 (s, 1.00H), 7.57-7.54 (m, 3.47H), 7.38-7.34 (m, 3.88H), 7.33-7.28 (m, 7.77H), 7.25-7.23 (m, 4.18H), 7.19 (d, $J = 7.8$ Hz, 2.20H), 7.01 (d, $J = 7.8$ Hz, 2.10H), 2.41 (s, 2.62H), 2.34 (s, 3.00H), 2.01 (s, 3.03H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 205.3 (C), 163.0 (C), 143.2 (C), 139.2 (C), 138.8 (C), 137.0 (C), 134.0 (C), 131.7 (C), 129.4 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.3 (CH), 127.9 (CH), 126.0 (CH), 123.7 (CH_2), 118.8 (C), 115.0 (CH_2), 113.9 (C), 92.4 (C), 85.8 (C), 74.5 (C), 32.7 (CH_3), 21.3 (CH_3), 20.2 (CH_3); HRMS Calculated for $\text{C}_{27}\text{H}_{24}\text{N}_3$ $[\text{M}+\text{H}]^+$: 390.1960, Found: 390.1962.

N-2-1.5.4s

2-(1-cyclopropyl-3,3-diphenylpropa-1,2-dienyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-2-1.5.4s) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 87%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.61; UV absorption: 226(0.242), 257(0.166), 299(0.129); IR (neat), 2962, 1583, 1480, 1423, 1262, 1151, 1067, 956, 862, 742, 690; ¹H-NMR (600 MHz, CDCl₃) δ 7.97 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.42-7.36 (m, 10H), 7.23 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 2.29-2.24 (m, 1H), 1.11-1.07 (m, 2H), 0.83-0.79 (m, 2H); ¹³C-NMR (150 MHz, CDCl₃) δ 196.7 (C), 147.8 (C), 138.1 (C), 135.4 (C), 129.5 (CH), 128.7 (CH), 128.6 (CH), 128.6 (CH), 127.6 (C), 125.7 (CH), 121.2 (C), 117.4 (CH), 116.6 (C), 21.3 (CH₃), 10.8 (CH), 7.5 (CH₂); HRMS Calculated for C₂₇H₂₄N₃ [M+H]⁺: 390.1960, Found: 390.1963.

N-1-1.5.4s

1-(1-cyclopropyl-3,3-diphenylpropa-1,2-dienyl)-4-*p*-tolyl-1*H*-1,2,3-triazole (N-1-1.5.4s) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 9%; *R_f* (hexanes/ethyl acetate, V/V, 10/1) = 0.30; UV absorption: 229(0.199), 258(0.113), 298(0.098); IR (neat), 3001, 1597, 1474, 1444, 1273, 1175, 1073, 976, 849, 737, 694; ¹H-NMR (600 MHz, CDCl₃) δ 7.69 (s, 1H), 7.32-7.27 (m, 6H), 7.17-7.13 (m, 6H), 6.88 (d, *J* = 7.8 Hz,

2H), 2.25 (s, 3H), 1.94-1.88 (m, 1H), 0.91-0.86 (m, 2H), 0.69-0.65 (m, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 200.6 (C), 138.9 (C), 137.8 (C), 134.8 (C), 132.8 (CH), 129.2 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 123.9 (C), 119.1 (C), 114.1 (C), 21.3 (CH_3), 13.3 (CH), 7.3 (CH_2); HRMS Calculated for $\text{C}_{27}\text{H}_{24}\text{N}_3$ $[\text{M}+\text{H}]^+$: 390.1960, Found: 390.1959.

1-(1,5-bis(trimethylsilyl)-3-phenylpenta-1,2-dien-4-ynyl)-1H-benzo[d][1,2,3]triazole (1.5.4t) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 76%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.46; UV absorption: 234(0.093), 250(0.077), 296(0.054); IR (neat), 3057, 2950, 1587, 1476, 1418, 1256, 1160, 1079, 987, 813, 710, 685; ^1H -NMR (600 MHz, CDCl_3) δ 8.07 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 8.4 Hz, 1H), 7.39 (t, J = 8.4 Hz, 3H), 7.32 (t, J = 8.4 Hz, 1H), 0.48 (s, 9H), 0.29 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 205.8 (C), 146.0 (C), 132.8 (C), 132.4 (C), 128.8 (CH), 128.4 (CH), 128.2 (CH), 126.3 (CH), 124.6 (CH), 119.9 (CH), 111.8 (CH), 110.2 (C), 102.1 (C), 99.1 (C), 96.9 (C), -0.10 (CH_3), -0.63 (CH_3); HRMS Calculated for $\text{C}_{23}\text{H}_{28}\text{N}_3\text{Si}_2$ $[\text{M}+\text{H}]^+$: 402.1820, Found: 402.1819.

1-(3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-1*H*-benzo[*d*][1,2,3]triazole (1.5.4u) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. *R_f*(hexanes/ethyl acetate, V/V, 2/1) = 0.45; UV absorption: 233(0.081), 253(0.06), 295(0.071); IR (neat), 3150, 3030, 2951, 1448, 1286, 1241, 1108, 1048, 938, 835, 766, 697; Isolated yield 58%; m. p. 155-157 °C; ¹H-NMR (600 MHz, CDCl₃) δ 8.05 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.48 (s, 1H), 7.41-7.29 (m, 10H), 5.57 (s, 2H), 0.44 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.9 (C), 146.1 (C), 143.6 (C), 134.4 (C), 134.3 (C), 132.6 (C), 129.2 (CH), 128.9 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 124.4 (CH), 122.4 (CH), 119.9 (CH), 112.1 (CH), 109.4 (C), 106.0 (C), 54.4 (CH₂), -0.55 (CH₃); HRMS Calculated for C₂₇H₂₇N₆Si [M+H]⁺: 463.2056, Found: 46.04059.

1-(1-(trimethylsilyl)-3-(4-nitrophenyl)-3-phenylpropa-1,2-dienyl)-1H-

benzo[d][1,2,3]triazole (1.5.4v) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 71%; R_f (hexanes/ethyl acetate, V/V, 6/1) = 0.48; UV absorption: 231(0.078), 256(0.059), 299(0.041); IR (neat), 2967, 1634, 1523, 1438, 1299, 1235, 1157, 1045, 933, 847, 722; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.24 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.46-7.38 (m, 7H), 0.48 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 200.9 (C), 147.4 (C), 146.3 (C), 143.0 (C), 134.6 (C), 132.4 (C), 129.2 (CH), 129.0 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 124.6 (CH), 124.1 (CH), 120.3 (CH), 114.0 (C), 111.4 (CH), 109.7 (C), -0.45 (CH_3); HRMS Calculated for $\text{C}_{24}\text{H}_{23}\text{N}_4\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 427.1593, Found: 427.1590.

1-(3-(4-fluorophenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-1H-

benzo[d][1,2,3]triazole (1.5.4w) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. Isolated yield 88%; m. p. 114-116 °C; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.46; UV absorption: 234(0.203), 262(0.160), 300(0.141); IR (neat), 2955, 1603, 1504, 1447, 1285, 1248, 1155, 1066, 936, 833, 744, 692; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.08 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 7.2 Hz, 1H), 7.46-7.34 (m, 9H), 7.12-7.06 (m, 2H), 0.47 (s, 9H); $^{13}\text{C-NMR}$ (150

MHz, CDCl₃) δ 200.2 (C), 163.4 (C), 161.7 (C), 146.2 (C), 135.7 (C), 132.4 (C), 131.82 (C), 131.80 (C), 130.1 (CH), 130.0 (CH), 128.8 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 124.4 (CH), 120.0 (CH), 115.9 (CH), 115.7 (CH), 114.5 (C), 111.8 (C), 109.0 (CH), -0.49 (CH₃); HRMS Calculated for C₂₄H₂₃FN₃Si [M+H]⁺: 400.1655, Found: 400.1658.

1-(3-(4-chlorophenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-1H-

benzo[d][1,2,3]triazole (1.5.4x) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. Isolated yield 72%; m. p. 139-141 °C; R_f(hexanes/ethyl acetate, V/V, 10/1) = 0.47; UV absorption: 238(0.229), 264(0.167), 299(0.156); IR (neat), 2957, 1485, 1448, 1285, 1248, 1156, 1069, 937, 876, 831, 743, 692; ¹H-NMR (600 MHz, CDCl₃) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.46-7.35 (m, 11H), 0.49 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 200.2 (C), 146.2 (C), 135.4 (C), 134.4 (C), 134.0 (C), 132.4 (C), 129.6 (CH), 129.0 (CH), 128.9 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 124.4 (CH), 120.0 (CH), 114.4 (C), 111.7 (CH), 109.1 (C), -0.49 (CH₃); HRMS Calculated for C₂₄H₂₃ClN₃Si [M+H]⁺: 416.1344, Found: 416.1346.

1.5.4y

1-(3,3-bis(4-fluorophenyl)-1-(trimethylsilyl)propa-1,2-dienyl)-1H-benzo[d][1,2,3]triazole

(**1.5.4y**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. Isolated yield 84%; m. p. 118-120 °C; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.43; UV absorption: 235(0.175), 261(0.151), 299(0.127); IR (neat), 2964, 1602, 1504, 1450, 1282, 1223, 1157, 1069, 937, 836, 752; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.08 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.45-7.40 (m, 5H), 7.38 (t, J = 7.8 Hz, 1H), 7.13-7.08 (m, 4H), 0.48 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 200.0 (C), 163.4 (C), 161.7 (C), 146.2 (C), 132.4 (C), 131.7 (C), 131.6 (C), 130.0 (CH), 129.9 (CH), 128.0 (CH), 124.4 (CH), 120.1 (CH), 116.0 (CH), 115.8 (CH), 113.6 (C), 111.6 (CH), 109.1 (C), -0.53 (CH_3); HRMS Calculated for $\text{C}_{24}\text{H}_{22}\text{F}_2\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 418.1546, Found: 418.1550.

N-2-1.5.4z

2-(3-(4-chlorophenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-4-p-tolyl-2H-1,2,3-

triazole (N-2-1.5.4z) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow

liquid. Isolated yield 59%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.60; UV absorption: 243(0.318), 270(0.267), 295(0.116); IR (neat), 2917, 1613, 1457, 1443, 1278, 1233, 1073, 929, 816, 738, 699; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.94 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 7.39-7.36 (m, 5H), 7.34 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.16 (s, 3H), 0.43 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 201.2 (C), 147.7 (C), 138.2 (C), 134.8 (C), 134.3 (C), 133.8 (C), 129.6 (CH), 129.5 (CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 127.4 (CH), 125.7 (CH), 117.0 (C), 115.2 (CH), 109.7 (C), 21.3 (CH_3), -0.60 (CH_3); HRMS Calculated for $\text{C}_{27}\text{H}_{27}\text{ClN}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 456.1655, Found: 456.1652.

N-1-1.5.4z

1-(3-(4-chlorophenyl)-1-(trimethylsilyl)-3-phenylpropa-1,2-dienyl)-4-*p*-tolyl-2*H*-1,2,3-triazole (N-1-1.5.4z) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 15%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.33; UV absorption: 244(0.295), 264(0.244), 299(0.138); IR (neat), 2936, 1588, 1477, 1422, 1278, 1213, 1034, 932, 843, 771, 687; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.63 (s, 1H), 7.30-7.28 (m, 3H), 7.24 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 7.03-7.01 (m, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 7.8 Hz, 2H), 2.16 (s, 3H), 0.32 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 203.6 (C), 138.9 (C), 137.8 (C), 134.6 (C), 133.7 (C), 133.6 (C), 133.4 (C), 129.6 (CH), 129.0 (CH), 128.7 (CH), 128.5

(CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 124.3 (C), 113.2 (CH), 107.6 (C), 21.2 (CH₃), -0.68 (CH₃); HRMS Calculated for C₂₇H₂₇ClN₃Si [M+H]⁺: 456.1655, Found: 456.1659.

2-(1-(4-chlorophenyl)-3-(trimethylsilyl)-1-phenylprop-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole

(**N-2-1.5.4z'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 15%; *R_f*(hexanes/ethyl acetate, V/V, 10/1) = 0.49; UV absorption: 256(0.408), 271(0.393); IR (neat), 3077, 2934, 1483, 1446, 1343, 1297, 1041, 961, 852, 777, 739, 695; ¹H-NMR (600 MHz, CDCl₃) δ 7.91 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.37-7.34 (m, 3H), 7.33-7.31 (m, 2H), 7.29-7.26 (m, 4H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 0.29 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 148.1 (C), 140.9 (C), 139.8 (C), 138.5 (C), 134.4 (C), 131.3 (CH), 129.8 (CH), 129.4 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.4 (C), 126.0 (CH), 103.8 (C), 94.8 (C), 73.2 (C), 21.3 (CH₃), -0.32 (CH₃); HRMS Calculated for C₂₇H₂₇ClN₃Si [M+H]⁺: 456.1655, Found: 456.1652.

1-(1-(4-chlorophenyl)-3-(trimethylsilyl)-1-phenylprop-2-ynyl)-4-*p*-tolyl-2*H*-1,2,3-triazole

(**N-1-1.5.4z'**) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Isolated yield 4%; R_f (hexanes/ethyl acetate, V/V, 10/1) = 0.30; UV absorption: 255(0.358), 273(0.367); IR (neat), 3089, 2928, 1487, 1455, 1433, 1148, 1052, 989, 820, 734, 709, 679; ^1H -NMR (600 MHz, CDCl_3) δ 8.01 (s, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.39-7.35 (m, 3H), 7.33 (d, J = 8.4 Hz, 2H), 7.29-7.27 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H), 0.29 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 147.0 (C), 140.2 (C), 139.1 (C), 138.0 (C), 134.8 (C), 129.6 (CH), 129.5 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.6 (C), 125.6 (CH), 120.1 (CH), 103.5 (C), 95.6 (C), 69.5 (C), 21.3 (CH_3), -0.41 (CH_3); HRMS Calculated for $\text{C}_{27}\text{H}_{27}\text{ClN}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 456.1655, Found: 456.1650.

1-(3-(2-methoxyphenyl)-3-phenylpropa-1,2-dienyl)-1*H*-benzo[*d*][1,2,3]triazole (1.5.7a) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as white solid. Isolated yield 98%;

m. p. 173-175 °C; *R_f* (hexanes/ethyl acetate, V/V, 6/1) = 0.42; UV absorption: 235(0.327), 299(0.206); IR (neat), 3056, 1596, 1491, 1443, 1278, 1172, 1061, 741, 694; ¹H-NMR (600 MHz, CDCl₃) δ 8.26 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.44-7.27 (m, 9H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H); ¹³C-NMR (150 MHz, CDCl₃) δ 196.6 (C), 157.0 (C), 146.6 (C), 135.3 (C), 131.4 (C), 130.9 (CH), 130.0 (CH), 128.5 (CH), 128.4 (CH), 127.9 (CH), 127.6 (CH), 124.5 (CH), 124.1 (CH), 120.8 (CH), 119.9 (CH), 117.8 (C), 111.9 (CH), 111.3 (C), 99.4 (CH), 55.3 (CH₃); HRMS Calculated for C₂₂H₁₈N₃O [M+H]⁺: 340.1458, Found: 340.1455.

ORTEP Drawing of the Crystal Structure

Figure S1.5-1. Perspective view of the molecular structure of **1.5.4a** (C₂₄H₂₃N₃Si) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 851290.

Figure S1.5-2. Perspective view of the molecular structure of **1.5.4g** ($\text{C}_{25}\text{H}_{25}\text{N}_3\text{SiO}$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 851291.

Figure S1.5-3. Perspective view of the molecular structure of **1.5.4u** (C₂₇H₂₆N₆Si) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 851293.

Figure S1.5-4. Perspective view of the molecular structure of **1.5.4y** ($\text{C}_{24}\text{H}_{21}\text{F}_2\text{N}_3\text{Si}$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 851294.

Figure S1.5-5. Perspective view of the molecular structure of **1.5.7a** ($C_{22}H_{17}N_3O$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 851292.

1.6 Mitsunobu reaction of 1,2,3-*NH*-triazoles: regio- and stereo-selective synthesis of triazole derivatives

General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer. Optical rotations were measured with a digital polarimeter in the solvent specified. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. The configuration of products was determined by comparison of rotation sign with the literature data or by analogue.

Substrates **1.6.4g**, **1.6.4h**, **1.6.4i**, **1.6.4m** were reported the literature as below:

Chen, Y.; Liu, Y.; Petersen, J. L.; Shi, X. *Chem. Commun.* **2008**, 3254-3256.

General Procedure for Mitsunobu reaction of 1,2,3-NH-triazole with alcohol.

A 25 mL round-bottomed flask is equipped with a stirring bar, nitrogen inlet, rubber septum. The flask is charged with alcohol (3.0 mmol), NH-triazole (3.6 mmol), triphenylphosphine (PPh₃) (3.6 mmol), and 12 mL of distilled tetrahydrofuran (THF). The flask is immersed in an ice bath, and diisopropyl azodicarboxylate (3.6 mmol) is added dropwise at a rate such that the temperature of the reaction mixture is maintained below 10 °C. Upon completion of the addition, the flask is removed from the ice bath and the solution is allowed to stir at room temperature for 3 hours, and monitored by TLC. After the reaction is completed, 30 ml of water is added to quench the reaction. The mixture is extracted three times with 20 mL portions of ethyl acetate. The combined organic layers are washed with 20 ml brine twice and dried over anhydrous sodium sulfate (Na₂SO₄). Excess solvent and other volatile reaction components are completely removed under reduced pressure initially on a rotary evaporator. The residue is applied to a flash silica gel chromatography column (hexane/ethyl acetate = 10:1) to give the products.

Compounds Characterization

N-2-1.6.3a

2-benzyl-2H-benzo[d][1,2,3]triazole (N-2-1.6.3a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.87-7.85 (m, 2H), 7.42-7.40 (m, 2H), 7.37-7.30 (m, 5H), 5.87 (s, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.9, 134.9, 129.1, 128.8, 128.6, 126.6, 118.4, 60.6; HRMS Calculated for $\text{C}_{13}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 210.1031, Found: 210.1025.

N-1-1.6.3a

1-benzyl-1H-benzo[d][1,2,3]triazole (N-1-1.6.3a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.05-8.03 (m, 1H), 7.39-7.23 (m, 8H), 5.82 (s, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.6, 135.0, 133.0, 129.2, 128.7, 127.8, 127.6, 124.1, 120.3, 109.9, 52.4; HRMS Calculated for $\text{C}_{13}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 210.1031, Found: 210.1036.

N-2-1.6.3b

2-allyl-2H-benzo[d][1,2,3]triazole (N-2-1.6.3b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.87-7.84 (m, 2H), 7.38-7.34 (m, 2H), 6.23-6.15 (m, 1H), 5.38 (d, $J = 10.8$ Hz, 1H), 7.37-7.35 (m, 1H), 5.32 (d, $J = 6.6$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.7, 131.3, 126.6, 120.4, 118.2, 59.1; HRMS Calculated for $\text{C}_9\text{H}_{10}\text{N}_3$ $[\text{M}+\text{H}]^+$: 160.0875, Found: 160.0870.

N-1-1.6.3b

1-allyl-1H-benzo[d][1,2,3]triazole (N-1-1.6.3b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.50-7.48 (m, 1H), 7.46-7.42 (m, 1H), 7.35-7.32 (m, 1H), 6.07-6.00 (m, 1H), 5.29 (d, $J = 10.2$ Hz, 1H), 5.26-5.21 (m, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.4, 133.1, 131.4, 127.5, 124.1, 120.2, 119.4, 109.9, 51.0; HRMS Calculated for $\text{C}_9\text{H}_{10}\text{N}_3$ $[\text{M}+\text{H}]^+$: 160.0875, Found: 160.0879.

N-2-1.6.3c

2-(prop-2-ynyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3c) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.89-7.86 (m, 2H), 7.40-7.37 (m, 2H), 5.52 (d, $J = 3.0$ Hz, 2H), 2.61 (t, $J = 3.0$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.9, 127.0, 118.4, 75.9, 75.4, 46.2; HRMS Calculated for $\text{C}_9\text{H}_8\text{N}_3$ $[\text{M}+\text{H}]^+$: 158.0718, Found: 158.0711.

1-(prop-2-ynyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3c) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.36 (t, $J = 7.8$ Hz, 1H), 5.42 (d, $J = 2.4$ Hz, 2H), 2.48 (t, $J = 2.4$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.5, 132.7, 128.0, 124.4, 120.3, 110.0, 75.5, 75.3, 38.2; HRMS Calculated for $\text{C}_9\text{H}_8\text{N}_3$ $[\text{M}+\text{H}]^+$: 158.0718, Found: 158.0725.

2-(2-chloroethyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3d) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ

7.86-7.83 (m, 2H), 7.36-7.33 (m, 2H), 4.99 (t, $J = 6.0$ Hz, 2H), 4.11 (t, $J = 6.0$ Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 144.3, 126.5, 117.9, 57.3, 41.4; HRMS Calculated for $\text{C}_8\text{H}_9\text{ClN}_3$ $[\text{M}+\text{H}]^+$: 182.0485, Found: 182.0480.

1-(2-chloroethyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3d) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 4.96 (t, $J = 6.0$ Hz, 2H), 4.05 (t, $J = 6.0$ Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 145.8, 133.5, 127.7, 124.1, 120.1, 109.3, 49.4, 42.2; HRMS Calculated for $\text{C}_8\text{H}_9\text{ClN}_3$ $[\text{M}+\text{H}]^+$: 182.0485, Found: 182.0492.

2-(2-ethoxyethyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3e) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.85-7.82 (m, 2H), 7.35-7.32 (m, 2H), 4.86 (t, $J = 6.0$ Hz, 2H), 4.05 (t, $J = 6.0$ Hz, 2H), 3.46 (q, J

= 7.2 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 144.3, 126.1, 117.9, 68.3, 66.5, 56.1, 14.8; HRMS Calculated for $\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 192.1137, Found: 192.1126.

1-(2-ethoxyethyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3e) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.01 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 4.78 (t, J = 6.0 Hz, 2H), 3.88 (t, J = 6.0 Hz, 2H), 3.40 (q, J = 7.2 Hz, 2H), 1.06 (t, J = 7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 145.8, 133.5, 127.7, 124.1, 120.1, 109.3, 49.4, 42.2; HRMS Calculated for $\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 192.1137, Found: 192.1131.

(E)-2-(pent-2-en-4-ynyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3f) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.87-7.83 (m, 2H), 7.40-7.36 (m, 2H), 6.52 (dt, J = 15.6 Hz, 6.0 Hz, 1H), 5.76 (dq, J = 15.6 Hz, 1.8 Hz, 1H), 5.36 (dd, J = 6.6 Hz, 1.2 Hz, 2H), 2.95 (d, J = 1.2 Hz, 1H); ^{13}C -NMR (150 MHz,

CDCl₃) δ 144.5, 136.7, 126.5, 118.0, 114.1, 80.4, 79.5, 57.5; HRMS Calculated for C₁₁H₁₀N₃ [M+H]⁺: 184.0875, Found: 184.0868.

N-1-1.6.3f

(E)-1-(pent-2-en-4-ynyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3f) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ¹H-NMR (600 MHz, CDCl₃) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.46-7.41 (m, 2H), 7.34-7.31 (m, 1H), 6.35 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 5.59 (dq, *J* = 15.6 Hz, 1.8 Hz, 1H), 5.28 (dd, *J* = 6.6 Hz, 1.2 Hz, 2H), 2.91 (d, *J* = 1.2 Hz, 1H); ¹³C-NMR (150 MHz, CDCl₃) δ 145.9, 137.0, 132.6, 127.5, 123.9, 119.9, 113.0, 109.3, 80.1, 79.5, 49.3; HRMS Calculated for C₁₁H₁₀N₃ [M+H]⁺: 184.0875, Found: 184.0882.

N-2-1.6.3g

(E)-2-(pent-2-en-4-ynyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3g) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ¹H-NMR (600 MHz, CDCl₃) δ 7.89-7.83 (m, 2H), 7.37-7.32 (m, 2H), 7.30 (dt, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.11 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 2H), 5.94 (s, 2H), 3.85 (s, 3H); ¹³C-NMR (150 MHz, CDCl₃) δ

157.3, 144.7, 130.1, 129.9, 126.4, 123.4, 121.0, 118.4, 111.0, 55.8, 55.2; HRMS Calculated for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.1137, Found: 240.1127.

(E)-1-(pent-2-en-4-ynyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3g) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. 1H -NMR (600 MHz, $CDCl_3$) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.88 (t, $J = 7.2$ Hz, 1H), 5.86 (s, 2H), 3.88 (s, 3H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 156.9, 146.1, 133.1, 129.8, 129.4, 127.1, 123.7, 123.2, 120.9, 119.9, 110.6, 110.0, 55.4, 46.8; HRMS Calculated for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.1137, Found: 240.1135.

2-(1-phenylallyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3h) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. 1H -NMR (600 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.40-7.36 (m, 4H), 7.31-7.27 (m, 2H), 7.25-7.21 (m, 1H), 6.76 (d, $J = 15.6$ Hz, 1H), 6.53 (dt, $J = 15.6$ Hz, 6.6 Hz, 1H), 5.47 (d, $J = 6.6$ Hz, 2H); ^{13}C -NMR (150 MHz,

CDCl_3) δ 144.8, 136.0, 135.5, 128.8, 128.5, 127.0, 126.6, 122.2, 118.3, 58.8; HRMS Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 236.1188, Found: 236.1180.

1-(1-phenylallyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3h) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.37-7.32 (m, 3H), 7.31-7.27 (m, 2H), 7.26-7.22 (m, 1H), 6.66 (d, $J = 8.4$ Hz, 1H), 6.38 (dt, $J = 15.6$ Hz, 6.0 Hz, 1H), 5.42 (dd, $J = 15.6$ Hz, 6.0 Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.5, 135.8, 134.7, 133.1, 128.9, 128.6, 127.6, 126.9, 124.2, 122.4, 120.3, 110.0, 50.8; HRMS Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 236.1188, Found: 236.1178.

(E)-2-(pent-3-en-2-yl)-2H-benzo[d][1,2,3]triazole (N-2-3i) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.90-7.85 (m, 2H), 7.40-7.35 (m, 2H), 5.90 (qq, $J = 7.2$ Hz, 1.2 Hz, 1H), 5.80 (dq, $J = 15.6$ Hz, 7.2 Hz, 1.2 Hz, 1H), 5.50 (quin, $J = 7.2$ Hz, 1H), 1.81 (d, $J = 7.2$ Hz, 3H), 1.73 (dq, $J = 7.2$ Hz,

1.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 144.3, 130.4, 129.4, 126.3, 118.3, 64.9, 21.3, 17.9; HRMS Calculated for $\text{C}_{11}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 188.118, Found: 188.1183.

(E)-1-(pent-3-en-2-yl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3i) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.42 (t, $J = 7.2$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 5.81 (qq, $J = 7.2$ Hz, 1.2 Hz, 1H), 5.71 (dq, $J = 15.6$ Hz, 7.2 Hz, 1.2 Hz, 1H), 5.47 (quin, $J = 7.2$ Hz, 1H), 1.81 (d, $J = 7.2$ Hz, 3H), 1.70 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.6, 132.4, 130.2, 128.8, 127.0, 123.9, 120.2, 110.4, 57.6, 20.3, 17.8; HRMS Calculated for $\text{C}_{11}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 188.118, Found: 188.1189.

2-(2,3-dihydro-1H-inden-2-yl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3j) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.87-7.83 (m, 2H), 7.37-7.32 (m, 3H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.21-7.15 (m, 2H), 6.47 (t, $J = 7.2$ Hz, 1H), 3.47-3.41 (m, 1H), 3.13-3.07 (m, 1H), 2.90-2.82 (m, 2H); ^{13}C -NMR (150 MHz, CDCl_3)

δ 144.6, 144.2, 140.7, 129.3, 127.2, 126.4, 125.4, 125.0, 118.4, 71.5, 33.0, 31.2; HRMS Calculated for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.1344, Found: 250.1349.

N-1-1.6.3j

2-(2,3-dihydro-1H-inden-2-yl)-2H-benzo[d][1,2,3]triazole (N-1-1.6.3j) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. 1H -NMR (600 MHz, $CDCl_3$) δ 8.04 (d, $J = 7.2$ Hz, 1H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.31-7.24 (m, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.98 (d, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 7.2$ Hz, 1H), 6.63 (t, $J = 7.2$ Hz, 1H), 3.31 (ddd, $J = 15.6$ Hz, 9.0 Hz, 4.2 Hz, 1H), 3.13 (quin, $J = 7.2$ Hz, 1H), 2.89-2.82 (m, 1H), 2.56-2.49 (m, 1H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 147.0, 143.7, 139.5, 131.9, 129.3, 127.4, 127.2, 125.5, 125.0, 124.0, 120.4, 110.6, 65.1, 32.8, 31.0; HRMS Calculated for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.1344, Found: 250.1343.

N-2-1.6.3k

2-(2,3-dihydro-1H-inden-2-yl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3k) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. 1H -NMR (600 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.40-7.35 (m, 2H), 7.32-7.29 (m, 2H), 7.27-7.23 (m, 2H), 5.80 (tt, $J = 8.4$ Hz,

6.6 Hz, 1H), 3.84 (d, $J = 6.6$ Hz, 1H), 3.82 (d, $J = 6.6$ Hz, 1H), 3.71 (d, $J = 8.4$ Hz, 1H), 3.68 (d, $J = 8.4$ Hz, 1H); ^{13}C -NMR (150 MHz, CDCl_3) δ 144.1, 139.8, 127.2, 126.2, 124.5, 118.0, 66.2, 39.9; HRMS Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 250.1344, Found: 250.1351.

N-1-1.6.3k

2-(2,3-dihydro-1H-inden-2-yl)-2H-benzo[d][1,2,3]triazole (N-1-1.6.3k) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.42-7.38 (m, 1H), 7.37-7.27 (m, 6H), 5.82 (quin, $J = 7.2$ Hz, 1H), 3.69 (s, 2H), 3.67 (s, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.6, 139.9, 132.0, 127.4, 127.1, 124.6, 123.8, 120.2, 109.9, 59.4, 38.9; HRMS Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 250.1344, Found: 250.1353.

N-2-1.6.3l

2-(1-phenylethyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3l) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.88-7.82 (m, 2H), 7.40-7.38 (m, 2H), 7.37-7.25 (m, 5H), 6.14 (q, $J = 7.2$ Hz, 1H), 2.13 (d, $J =$

7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 144.4, 140.4, 129.0, 128.5, 126.8, 126.4, 118.4, 66.4, 21.6; HRMS Calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 224.1188, Found: 224.1189.

N-1-1.6.3l

1-(1-phenylethyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.3l) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.03 (d, $J = 7.2$ Hz, 1H), 7.33-7.22 (m, 8H), 6.02 (q, $J = 7.2$ Hz, 1H), 2.16 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.4, 140.1, 132.4, 128.9, 128.2, 127.0, 126.2, 123.8, 119.9, 110.1, 59.0, 21.1; HRMS Calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 224.1188, Found: 224.1191.

N-2-1.6.3m

2-(2,2-dimethyl-1-phenylpropyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.3m) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.91-7.86 (m, 2H), 7.77-7.73 (m, 2H), 7.38-7.28 (m, 5H), 5.82 (s, 1H), 1.11 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 143.7, 135.8, 129.6, 128.0, 127.8, 126.0, 118.2, 80.5, 36.9, 27.1; HRMS Calculated for $\text{C}_{17}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 266.1657, Found: 266.1663.

N-1-1.6.3m

2-(2,2-dimethyl-1-phenylpropyl)-2H-benzo[d][1,2,3]triazole (N-1-1.6.3m) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.64-7.61 (m, 2H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.32-7.23 (m, 4H), 5.43 (s, 1H), 1.13 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.7, 136.4, 134.3, 129.4, 127.9, 127.0, 123.7, 119.8, 109.4, 72.5, 37.2, 27.6; HRMS Calculated for $\text{C}_{17}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 266.1657, Found: 266.1648.

N-2-1.6.4a

2-benzyl-4-phenyl-2H-1,2,3-triazole (N-2-1.6.4a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.93 (s, 1H), 7.87-7.84 (m, 2H), 7.46 (t, $J = 8.4$ Hz, 2H), 7.43-7.33 (m, 6H), 5.67 (s, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.9, 135.2, 131.3, 130.2, 128.7, 128.6, 128.3, 128.1, 127.8, 125.8, 58.5; HRMS Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 236.1188, Found: 236.1178.

N-1-1.6.4a

1-benzyl-4-phenyl-1H-1,2,3-triazole (N-1-1.6.4a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.81-7.79 (m, 2H), 7.66 (s, 1H), 7.41-7.35 (m, 5H), 7.33-7.29 (m, 3H), 5.57 (s, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.2, 134.7, 130.5, 129.1, 128.8, 128.1, 128.0, 125.7, 119.4, 54.2; HRMS Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 236.1188, Found: 236.1178.

N-2-1.6.4b

2-allyl-4-phenyl-2H-1,2,3-triazole (N-2-1.6.4b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.86 (s, 1H), 7.81-7.78 (m, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.34-7.30 (m, 1H), 6.15-6.07 (m, 1H), 5.31-5.26 (m, 2H), 5.05 (dt, $J = 6.0$ Hz, 1.2 Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.6, 131.5, 130.9, 130.1, 128.6, 128.1, 125.6, 118.9, 57.1; HRMS Calculated for $\text{C}_{11}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 186.1031, Found: 186.1032.

1-allyl-4-phenyl-1H-1,2,3-triazole (N-1-1.6.4b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.84-7.82 (m, 2H), 7.76 (s, 1H), 7.44-7.40 (m, 2H), 7.35-7.31 (m, 1H), 6.10-6.03 (m, 1H), 5.40-5.36 (m, 1H), 5.34-5.33 (m, 1H), 5.03 (dt, $J = 6.0$ Hz, 1.2 Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.0, 131.3, 130.6, 128.8, 128.1, 125.7, 120.2, 119.4, 93.0, 52.8; HRMS Calculated for $\text{C}_{11}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 186.1031, Found: 186.1043.

4-phenyl-2-(prop-2-ynyl)-2H-1,2,3-triazole (N-2-1.6.4c) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.89 (s, 1H), 7.80-7.78 (m, 2H), 7.44-7.40 (m, 2H), 7.37-7.33 (m, 1H), 5.25 (d, $J = 2.4$ Hz, 2H), 2.54 (t, $J = 2.4$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.5, 131.7, 129.9, 128.8, 128.5, 125.9, 75.7, 74.8, 44.4; HRMS Calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3$ $[\text{M}+\text{H}]^+$: 184.0875, Found: 184.0879.

4-phenyl-1-(prop-2-ynyl)-1H-1,2,3-triazole (N-1-1.6.4c) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.97 (s, 1H), 7.83-7.81 (m, 2H), 7.42-7.39 (m, 2H), 7.34-7.30 (m, 1H), 5.18 (d, $J = 2.4$ Hz, 2H), 2.59 (t, $J = 2.4$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.0, 130.2, 128.7, 128.2, 125.6, 119.3, 75.7, 75.1, 39.7; HRMS Calculated for $\text{C}_{11}\text{H}_{10}\text{N}_3$ $[\text{M}+\text{H}]^+$: 184.0875, Found: 184.0885.

4-phenyl-2-(1-phenylethyl)-2H-1,2,3-triazole (N-2-1.6.4d) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.82-7.80 (m, 2H), 7.44-7.41 (m, 2H), 7.37-7.32 (m, 5H), 7.31-7.27 (m, 1H), 5.89 (q, $J = 7.2$ Hz, 1H), 2.04 (d, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.4, 140.9, 130.9, 130.6, 128.8, 128.6, 128.3, 128.0, 126.4, 125.9, 64.5, 21.3; HRMS Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 250.1344, Found: 250.1343.

N-1-1.6.4d

4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole (N-1-1.6.4d) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.82-7.79 (m, 2H), 7.66 (s, 1H), 7.41-7.28 (m, 8H), 5.86 (q, $J = 7.2$ Hz, 1H), 2.02 (d, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.7, 139.9, 130.6, 129.0, 128.7, 128.5, 128.0, 126.4, 125.6, 118.3, 60.2, 21.2; HRMS Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 250.1344, Found: 250.1352.

N-2-1.6.4e

2-(2,2-dimethyl-1-phenylpropyl)-4-phenyl-2H-1,2,3-triazole (N-2-1.6.4e) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.85 (s, 1H), 7.84-7.82 (m, 2H), 7.70-7.67 (m, 2H), 7.45-7.41 (m, 2H), 7.36-7.27 (m, 4H), 5.55 (s, 1H), 1.08 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.9, 136.3, 130.7, 130.1, 129.5, 128.8, 128.2, 127.7, 125.9, 78.8, 36.8, 27.1; HRMS Calculated for $\text{C}_{19}\text{H}_{22}\text{N}_3$ $[\text{M}+\text{H}]^+$: 292.1814, Found: 292.1810.

2-(2,2-dimethyl-1-phenylpropyl)-4-phenyl-2H-1,2,3-triazole (N-1-1.6.4e) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.85 (s, 1H), 7.84-7.82 (m, 2H), 7.60-7.57 (m, 2H), 7.41 (t, $J = 7.8$ Hz, 2H), 7.37-7.31 (m, 4H), 5.30 (s, 1H), 1.11 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 136.3, 130.7, 129.3, 128.8, 128.1, 128.0, 125.6, 120.6, 75.8, 36.6, 27.5; HRMS Calculated for $\text{C}_{19}\text{H}_{22}\text{N}_3$ $[\text{M}+\text{H}]^+$: 292.1814, Found: 292.1810.

2-(2,3-dihydro-1H-inden-1-yl)-4-phenyl-2H-1,2,3-triazole (N-2-1.6.4f) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.86 (s, 1H), 7.79 (d, $J = 7.8$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.35-7.32 (m, 2H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 6.22 (t, $J = 7.8$ Hz, 1H), 3.39-3.33 (m, 1H), 3.08-3.02 (m, 1H), 2.82-2.72 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.5, 143.7, 140.7, 131.0, 130.5, 128.7, 128.2, 126.8, 125.9, 125.0, 124.7, 69.6, 32.2, 30.7; HRMS Calculated for $\text{C}_{18}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 276.1501, Found: 276.1498.

N-1-1.6.4f

1-(2,3-dihydro-1H-inden-1-yl)-4-phenyl-1H-1,2,3-triazole (N-1-1.6.4f) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.80-7.77 (m, 2H), 7.48 (s, 1H), 7.40-7.35 (m, 4H), 7.32-7.28 (m, 2H), 7.28-7.21 (m, 1H), 6.31-6.28 (m, 1H), 3.25-3.19 (m, 1H), 3.10-3.04 (m, 1H), 2.90-2.83 (m, 1H), 2.45-2.39 (m, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 147.9, 143.9, 139.8, 130.7, 129.4, 128.7, 128.1, 127.4, 125.7, 125.3, 124.9, 117.6, 65.5, 34.2, 30.4; HRMS Calculated for $\text{C}_{18}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 276.1501, Found: 276.1495.

N-2-1.6.4j

2-benzyl-4-cyclohexenyl-5-phenyl-2H-1,2,3-triazole (N-2-1.6.4j) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.71-7.68 (m, 2H), 7.43-7.40 (m, 4H), 7.38-7.35 (m, 3H), 7.34-7.30 (m, 1H), 6.07 (sep, $J = 1.8$ Hz, 1H), 5.59 (s, 2H), 7.38-7.34 (m, 2H), 2.18-2.14 (m, 2H), 1.79-1.73 (m, 2H), 1.72-1.67 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.6, 144.0, 135.4, 131.6, 129.2, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 58.3, 27.6, 25.3, 22.6, 21.8; HRMS Calculated for $\text{C}_{21}\text{H}_{22}\text{N}_3$ $[\text{M}+\text{H}]^+$: 316.1814, Found: 316.1821.

N-2-1.6.4k

2-allyl-4-cyclohexenyl-5-phenyl-2H-1,2,3-triazole (N-2-1.6.4k) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.66-7.64 (m, 2H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.34-7.30 (m, 1H), 6.16-6.08 (m, 1H), 6.03 (sep, $J = 1.8$ Hz, 1H), 5.33-5.28 (m, 2H), 5.01 (d, $J = 7.2$ Hz, 2H), 2.34-2.30 (m, 2H), 2.15-2.11 (m, 2H), 1.75-1.70 (m, 2H), 1.68-1.63 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.5, 143.9, 131.7, 131.6, 129.2, 128.5, 128.3, 127.8, 119.0, 57.1, 27.5, 25.3, 22.5, 21.8; HRMS Calculated for $\text{C}_{17}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 266.1657, Found: 266.1650.

N-2-1.6.4l

4-cyclohexenyl-5-phenyl-2-(1-phenylethyl)-2H-1,2,3-triazole (N-2-1.6.4l) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.78-7.76 (m, 2H), 7.45 (t, $J = 7.2$ Hz, 4H), 7.40-7.36 (m, 3H), 7.32 (tt, $J = 7.2$ Hz, 1.2 Hz, 1H), 6.13 (sep, $J = 1.8$ Hz, 1H), 5.91 (q, $J = 7.2$ Hz, 1H), 2.46-2.41 (m, 2H), 2.22-2.18 (m, 2H), 2.07 (d, $J = 7.2$ Hz, 3H), 1.83-1.78 (m, 2H), 1.76-1.71 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ

145.9, 143.4, 141.0, 131.8, 128.9, 128.7, 128.4, 128.2, 127.8, 127.7, 127.6, 126.3, 64.1, 27.5, 25.3, 22.5, 21.7, 21.3; HRMS Calculated for $C_{22}H_{24}N_3$ $[M+H]^+$: 330.1970, Found: 330.1965.

1,6-di(2H-benzo[d][1,2,3]triazol-2-yl)hexane (1.6.5a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. 1H -NMR (600 MHz, $CDCl_3$) δ 7.86-7.82 (m, 4H), 7.39-7.35 (m, 4H), 4.71 (t, $J = 7.2$ Hz, 4H), 2.14-2.09 (m, 4H), 1.43-1.40 (m, 4H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 144.3, 126.2, 117.9, 56.3, 29.8, 26.0; HRMS Calculated for $C_{18}H_{21}N_6$ $[M+H]^+$: 321.1828, Found: 321.1820.

1,6-bis(4-phenyl-2H-1,2,3-triazol-2-yl)hexane (1.6.5b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. 1H -NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.78-7.76 (m, 4H), 7.42 (t, $J = 7.2$ Hz, 4H), 7.34 (tt, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 4H), 2.03-1.98 (m, 4H), 1.42-1.39 (m, 4H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 147.7, 130.6, 130.5, 128.8, 128.3, 125.8, 54.8, 29.5, 26.0; HRMS Calculated for $C_{22}H_{25}N_6$ $[M+H]^+$: 373.2141, Found: 373.2150.

(Z)-1,4-bis(4-phenyl-2H-1,2,3-triazol-2-yl)but-2-ene (1.6.5c) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.88-7.85 (m, 4H), 7.40-7.36 (m, 4H), 6.27 (t, $J = 6.0$ Hz, 2H), 5.62 (d, $J = 6.0$ Hz, 4H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.6, 127.8, 126.5, 118.0, 52.9; HRMS Calculated for $\text{C}_{16}\text{H}_{15}\text{N}_6$ $[\text{M}+\text{H}]^+$: 291.1358, Found: 291.1350.

(Z)-1,4-bis(4-p-tolyl-2H-1,2,3-triazol-2-yl)but-2-ene (1.6.5d) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.83 (s, 2H), 7.68 (d, $J = 7.8$ Hz, 4H), 7.23 (d, $J = 7.8$ Hz, 4H), 6.13 (t, $J = 4.8$ Hz, 2H), 5.29 (d, $J = 4.8$ Hz, 4H), 2.39 (s, 6H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.2, 138.3, 131.0, 129.5, 127.6, 127.4, 125.8, 51.5, 21.2; HRMS Calculated for $\text{C}_{22}\text{H}_{23}\text{N}_6$ $[\text{M}+\text{H}]^+$: 371.1984, Found: 371.1989.

1,4-bis((2H-benzo[d][1,2,3]triazol-2-yl)methyl)benzene (1.6.5e) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.85-7.82 (m, 4H), 7.41 (s, 4H), 7.37-7.34 (m, 4H), 5.84 (s, 4H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.6, 135.1, 128.9, 126.4, 118.1, 59.9; HRMS Calculated for $\text{C}_{20}\text{H}_{17}\text{N}_6$ $[\text{M}+\text{H}]^+$: 341.1515, Found: 341.1519.

1,4-bis((4-p-tolyl-2H-1,2,3-triazol-2-yl)methyl)benzene (1.6.5f) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.79 (s, 2H), 7.63 (d, $J = 7.8$ Hz, 4H), 7.31 (s, 4H), 7.20 (d, $J = 7.8$ Hz, 4H), 5.57 (s, 4H), 2.36 (s, 6H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.2, 138.3, 135.5, 131.3, 129.5, 128.4, 127.4, 125.8, 58.2, 21.3; HRMS Calculated for $\text{C}_{26}\text{H}_{25}\text{N}_6$ $[\text{M}+\text{H}]^+$: 421.2141, Found: 421.2137.

cis-2-(2-methylcyclohexyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.6a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.89-7.85 (m, 2H), 7.37-7.33 (m, 2H), 4.97 (quin, $J = 4.8$ Hz, 1H), 2.58-2.53 (m, 1H), 2.44-2.36 (m, 1H), 2.17-2.03 (m, 2H), 1.89-1.83 (m, 1H), 1.76-1.64 (m, 2H), 1.55-1.46 (m, 2H), 0.70 (d, J

= 7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 143.7, 125.8, 118.0, 67.9, 34.8, 30.8, 26.7, 24.1, 21.2, 13.5; HRMS Calculated for $\text{C}_{13}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 216.1501, Found: 216.1498.

N-1-1.6.6a

cis-1-(2-methylcyclohexyl)-1H-benzo[d][1,2,3]triazole (**N-1-1.6.6a**) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.06 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 8.4 Hz, 1H), 7.34 (t, J = 8.4 Hz, 1H), 4.82 (quin, J = 4.8 Hz, 1H), 2.55-2.48 (m, 1H), 2.43-2.36 (m, 1H), 2.12-2.04 (m, 2H), 1.92-1.88 (m, 1H), 1.78-1.69 (m, 2H), 1.59-1.50 (m, 2H), 0.72 (d, J = 7.2 Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 145.7, 133.2, 126.7, 123.6, 120.1, 109.7, 60.8, 34.2, 30.9, 27.0, 24.4, 21.4, 14.0; HRMS Calculated for $\text{C}_{13}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 216.1501, Found: 216.1495.

N-2-1.6.6b

cis-2-(2-methylcyclohexyl)-4-phenyl-2H-1,2,3-triazole (**N-2-1.6.6b**) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.83 (s, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.33 (tt, J = 7.2 Hz, 1.2 Hz, 1H), 4.71

(quin, $J = 4.8$ Hz, 1H), 2.46-2.39 (m, 1H), 2.31-2.23 (m, 1H), 2.06-1.99 (m, 2H), 1.86-1.78 (m, 1H), 1.71-1.62 (m, 2H), 1.52-1.44 (m, 2H), 0.75 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.7, 130.9, 129.9, 128.7, 128.0, 125.8, 66.1, 34.5, 30.5, 26.8, 23.8, 21.5, 13.9; HRMS Calculated for $\text{C}_{15}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 242.1657, Found: 242.1655.

cis-1-(2-methylcyclohexyl)-4-phenyl-1H-1,2,3-triazole (**N-1-1.6.6b**) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 7.2$ Hz, 2H), 7.75 (s, 1H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.32 (tt, $J = 7.2$ Hz, 1.2 Hz, 1H), 4.82 (dt, $J = 10.8$ Hz, 4.8 Hz, 1H), 2.47-2.43 (m, 1H), 2.17-2.09 (m, 1H), 2.04-1.95 (m, 2H), 1.75-1.69 (m, 2H), 1.68-1.57 (m, 1H), 1.56-1.48 (m, 2H), 0.78 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 130.9, 128.8, 127.9, 125.6, 118.5, 62.4, 34.2, 30.8, 26.5, 24.6, 20.7, 13.1; HRMS Calculated for $\text{C}_{15}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}]^+$: 242.1657, Found: 242.1655.

***cis*-2-(2-methylcyclopentyl)-2H-benzo[d][1,2,3]triazole (N-2-1.6.6c)** was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.88-7.84 (m, 2H), 7.34-7.31 (m, 2H), 5.31-5.27 (m, 1H), 2.62-2.55 (m, 1H), 2.48-2.33 (m, 2H), 2.23-2.16 (m, 1H), 1.93-1.87 (m, 1H), 1.81-1.71 (m, 2H), 0.55 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 143.8, 125.8, 117.9, 70.8, 40.5, 32.5, 31.5, 23.6, 13.8; HRMS Calculated for $\text{C}_{12}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 202.1344, Found: 202.1340.

N-1-1.6.6c

***cis*-1-(2-methylcyclopentyl)-1H-benzo[d][1,2,3]triazole (N-1-1.6.6c)** was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 8.06 (d, $J = 7.2$ Hz, 1H), 7.53 (d, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.2$ Hz, 1H), 5.11-5.07 (m, 1H), 2.68-2.63 (m, 1H), 2.51-2.45 (m, 1H), 2.44-2.37 (m, 1H), 2.25-2.19 (m, 1H), 1.99-1.94 (m, 1H), 1.84-1.73 (m, 2H), 0.53 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 145.4, 134.0, 126.8, 123.6, 119.9, 109.6, 62.9, 39.8, 32.6, 31.0, 23.3, 14.3; HRMS Calculated for $\text{C}_{12}\text{H}_{16}\text{N}_3$ $[\text{M}+\text{H}]^+$: 202.1344, Found: 202.1337.

N-2-1.6.6d

***cis*-2-(2-methylcyclopentyl)-4-phenyl-2H-1,2,3-triazole (N-2-1.6.6d)** was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.82 (s, 1H), 7.81 (d, $J = 7.2$ Hz, 2H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.33 (tt, $J = 7.2$ Hz, 1.2 Hz, 1H), 5.06-5.02 (m, 1H), 2.49-2.43 (m, 1H), 2.39-2.26 (m, 2H), 2.17-2.11 (m, 1H), 1.92-1.86 (m, 1H), 1.74-1.67 (m, 2H), 0.65 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 146.8, 130.9, 130.0, 128.7, 128.1, 125.8, 69.2, 40.3, 32.4, 31.1, 23.5, 14.0; HRMS Calculated for $\text{C}_{14}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 228.1501, Found: 228.1496.

***cis*-1-(2-methylcyclopentyl)-4-phenyl-1H-1,2,3-triazole (N-1-1.6.6d)** was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 7.2$ Hz, 2H), 7.68 (s, 1H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 1H), 4.98-4.94 (m, 1H), 2.42-2.33 (m, 2H), 2.32-2.26 (m, 1H), 2.14-2.08 (m, 1H), 2.00-1.93 (m, 1H), 1.84-1.77 (m, 1H), 1.61-1.54 (m, 1H), 0.70 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 147.1, 130.9, 128.8, 127.9, 125.6, 119.3, 65.3, 39.4, 32.1, 31.2, 22.9, 14.2; HRMS Calculated for $\text{C}_{14}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+$: 228.1501, Found: 228.1506.

(R)-N-2-1.6.7a

(R)-2-(1-phenylethyl)-2H-benzo[d][1,2,3]triazole ((R)-N-2-1.6.7a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.91-7.87 (m, 2H), 7.43-7.40 (m, 2H), 7.39-7.32 (m, 4H), 7.29 (tt, $J = 7.2$ Hz, 1.2 Hz, 1H), 6.16 (q, $J = 7.2$ Hz, 1H), 2.16 (d, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 144.1, 140.2, 128.7, 128.3, 126.5, 126.2, 118.1, 66.1, 21.3; HRMS Calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 224.1188, Found: 224.1179. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column; $\lambda = 254$ nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 1.0 mL/min; $t_R = 6.8$ min, $t_R = 11.4$ min; 87% ee.

(R)-N-1-1.6.7a

(R)-1-(1-phenylethyl)-1H-benzo[d][1,2,3]triazole ((R)-N-1-1.6.7a) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.02 (d, $J = 7.2$ Hz, 1H), 7.32-7.22 (m, 8H), 6.02 (q, $J = 7.2$ Hz, 1H), 2.15 (d, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.7, 140.4, 132.7, 129.1, 128.4, 127.2, 126.5, 124.0, 120.1, 110.4, 59.3, 21.4; HRMS Calculated for $\text{C}_{14}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 224.1188, Found: 224.1190. Enantiomeric

excess was determined by HPLC with a Chiralcel OD-H column; $\lambda = 254$ nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 1.0 mL/min; $t_R = 6.8$ min, $t_R = 11.4$ min; 87% ee.

N-2-1.6.7b

(2*S*,4*S*,7*R*)-2-((*S*)-(2*H*-benzo[*d*][1,2,3]triazol-2-yl)(6-methoxyquinolin-4-yl)methyl)-7-

vinylquinuclidine (N-2-1.6.7b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as white solid. $[\alpha]_D^{25} = -243.20$ (CH₂Cl₂, *c* 1.0); ¹H-NMR (600 MHz, CDCl₃) δ 8.83 (d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 4.2 Hz, 1H), 7.83-7.79 (m, 2H), 7.77 (s, 1H), 7.36 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.31-7.27 (m, 2H), 6.74 (d, *J* = 11.4 Hz, 1H), 5.99-5.92 (m, 1H), 5.12-5.10 (m, 1H), 5.08 (s, 1H), 4.45 (q, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 3.57-3.51 (m, 1H), 3.14 (dd, *J* = 13.8 Hz, 10.2 Hz, 1H), 2.84 (d, *J* = 14.4 Hz, 1H), 2.79-2.73 (m, 1H), 2.31 (s, 1H), 1.90 (t, *J* = 12.0 Hz, 1H), 1.76 (sex, *J* = 3.0 Hz, 1H), 1.69-1.57 (m, 2H), 0.93 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H); ¹³C-NMR (150 MHz, CDCl₃) δ 158.4, 148.1, 147.6, 147.0, 144.9, 144.1, 141.4, 139.0, 128.3, 126.2, 122.0, 118.3, 118.1, 114.7, 101.1, 58.6, 55.8, 55.7, 41.1, 39.3, 27.8, 27.7, 26.8; HRMS Calculated for C₂₆H₂₈N₅O [M+H]⁺: 426.2294, Found: 426.2290.

N-1-1.6.7b

(2*S*,4*S*,7*R*)-2-((*S*)-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(6-methoxyquinolin-4-yl)methyl)-7-

vinylquinuclidine (N-1-1.6.7b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as white solid. $[\alpha]_D^{25} = -96.20$ (CH₂Cl₂, *c* 1.0); ¹H-NMR (600 MHz, CDCl₃) δ 8.84 (d, *J* = 4.8 Hz, 1H), 7.98 (dd, *J* = 11.4 Hz, 9.0 Hz, 2H), 7.72 (d, *J* = 4.2 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.33 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 7.30 (tt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.23 (tt, *J* = 7.8 Hz, 1.2 Hz, 1H), 6.70 (d, *J* = 11.4 Hz, 1H), 5.99-5.93 (m, 1H), 5.10 (tt, *J* = 9.0 Hz, 1.2 Hz, 2H), 4.39 (s, 1H), 3.95 (s, 3H), 3.51-3.45 (m, 1H), 3.07 (dd, *J* = 13.8 Hz, 9.0 Hz, 1H), 2.73 (d, *J* = 12.6 Hz, 1H), 2.70-2.65 (m, 1H), 2.31 (s, 1H), 2.07-2.02 (m, 1H), 1.81 (sex, *J* = 3.0 Hz, 1H), 1.70-1.64 (m, 1H), 1.61-1.55 (m, 1H), 1.04 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H); ¹³C-NMR (150 MHz, CDCl₃) δ 158.5, 147.1, 146.3, 145.1, 141.5, 138.2, 132.2, 132.0, 128.4, 127.2, 123.6, 122.2, 120.4, 114.7, 109.7, 101.0, 56.4, 55.9, 55.8, 41.0, 39.2, 27.8, 27.7; HRMS Calculated for C₂₆H₂₈N₅O [M+H]⁺: 426.2294, Found: 426.2302.

III. ORTEP Drawing of the Crystal Structure

Figure S1.6-1. Perspective view of the molecular structure of **1.6.5a** ($C_{18}H_{20}N_6$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

CCDC number: 775283

Figure S1.6-2. Perspective view of the molecular structure of **N-2-1.6.7b** (C₂₆H₂₇N₅O) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 775283

Chapter Two: 1,2,3-triazoles applied as ligands in transition metal catalysis

2.2 Synthesis of $[\text{Ir}(\text{L}^{\wedge}\text{X})(\text{ArTriaz})_2]$ and $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$ complexes and their application in photoredox catalysis

General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

Procedure for preparation of 2-Phenyl-1,2,3-triazole (2.2.1)

To a 40% aqueous solution of glyoxal (50 mmol) was added phenylhydrazine (100 mmol) with stirring. Immediately a yellow solid was formed. To the reaction solution was added methanol (150 mL), and the yellow suspension was stirred for 0.5 h at room temperature and filtered to yield the resulting products Glyoxalbis(*N*-phenyl)osazone which was pure enough for running the next step.

A mixture of glyoxal phenylosazone from previous step and Cu(OTf)₂ (0.2 equiv.) was heated in water to reflux at 100 °C for 2 hours. The reaction mixture then purified by vacuum distillation to give the mixture products 2-phenyl-1,2,3-triazole and aniline at 120°C. For the isolation of the target product, 100 ml of ether have been added in the distillate. The solution then was treated in succession with 1 N HCl (3×10 ml) until PH = 6. The extract was dried with potassium carbonate, followed by the removal of ether to give the final products **2.2.1** as yellow liquid (60% yield in two steps).

General procedure for preparation of N-2-aryl-1,2,3-triazole-Ir(III) complex

[(ArTriaz)₂Ir(μ-Cl)]₂: IrCl₃ · H₂O (1 mmol) and N-2-aryl-1,2,3-triazole (4 mmol) were dissolved in 40 mL mixed solution of 2-EtOEtOH and H₂O (V/V: 3/1), and refluxed at 140 °C for 24 hours. After cooling, yellow precipitate was filtered and washed with 40 mL water. The washed product was dried in air to give yellow-green solids.

[Ir(L^X)(ArTriaz)₂]: [(ArTriaz)₂Ir(μ-Cl)]₂ complex (1 mmol), sodium carbonate (10 mmol) and ancillary ligand (2.5 mmol) were dissolved in 80 mL of 2-EtOEtOH under the nitrogen environment. The reaction mixture was heated up to 140 °C and stirred for 12 hours. Then cooled reaction mixture was poured to ethyl acetate (200 mL) and washed with water to remove 2-EtOEtOH. Silica column purification with dichloromethane gave the pure products.

General procedure for 1,2,3,4-tetrahydroisoquinoline substrates

Copper(I) iodide (0.1 mmol) and potassium phosphate (2.0 mmol) were put into a 100 mL round-bottom flask. The flask was evacuated and refilled with nitrogen. 2-Propanol (10 mL), ethylene glycol (2.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (1.0 mmol) and iodobenzene (1.2 mmol) were added successively using a syringe at room temperature. The reaction mixture was heated at 90 °C and kept for 24 h and then allowed to cool down to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted by diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (hexane/ethyl acetate=20:1) to give the desired product **2.2.5**.

General procedure for reaction of photoredox catalysis

To a 20 mL white cap vial equipped with a magnetic stir bar were added $[\text{Ir}(\text{bbpy})(\text{ArTriaz})_2]\text{Cl}$ (0.005 mmol), a 1,2,3,4-tetrahydroisoquinoline derivative (0.5 mmol), and nitromethane (2.0 mL). The reaction stirred open to air at room temperature at a distance of ~10 cm from a blue LED light. After the reaction completed (monitored by TLC analysis), the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate=10:1) to yield pure 2-aryl-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline **2.2.6**.

Compounds Characterization

2-Phenyl-1,2,3-triazole (2.2.1) was purified by flash chromatography as yellow liquid. Isolated yield 60%; ^1H NMR (CDCl_3 , 600 MHz) δ 8.12-8.08 (m, 2H), 7.79 (s, 2H), 7.48-7.44 (m, 2H), 7.35-7.31 (m, 1H); ^{13}C -NMR (150 MHz, CDCl_3) δ 139.8, 135.4, 129.2, 127.4, 118.8.

1,2,3,4-Tetrahydro-2-phenylisoquinoline (2.2.5a) was purified by flash chromatography as brown solid. ^1H NMR (CDCl_3 , 600 MHz) δ 7.36-7.33 (m, 2H), 7.25-7.19 (m, 4H), 7.04(d, J = 7.8 Hz, 2H), 6.89 (dd, J = 7.2, 7.2 Hz, 1H), 4.46 (s, 2H), 3.61 (dd, J = 6.0, 6.0 Hz, 2H), 3.04 (dd, J = 6.0, 6.0 Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 150.5, 134.8, 134.4, 129.1, 128.5, 126.5, 126.3, 126.0, 118.6, 115.1, 50.7, 46.5, 29.1.

1,2,3,4-Tetrahydro-2-(4-methoxyphenyl)isoquinoline (2.2.5b) was purified by flash chromatography as brown solid. ^1H NMR (CDCl_3 , 600 MHz) δ 7.19-7.12 (m, 4H), 6.99 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 4.31 (s, 2H), 3.79 (s, 3H), 3.46 (dd, J = 6.0, 6.0 Hz, 2H), 3.00 (dd, J = 6.0, 6.0 Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 153.5, 145.4, 134.6, 134.5, 128.7, 126.5, 126.2, 125.9, 118.0, 114.6, 55.6, 52.7, 48.4, 29.1.

2.2.5c

1,2,3,4-Tetrahydro-2-(4-fluorophenyl)isoquinoline (2.2.5c) was purified by flash chromatography as brown solid. ^1H NMR (CDCl_3 , 600 MHz) δ 7.21-7.14 (m, 4H), 7.02-6.98 (m, 2H), 6.98-6.94 (m, 2H), 4.35 (s, 2H), 3.79 (s, 3H), 3.50 (dd, J = 6.0, 6.0 Hz, 2H), 3.00 (dd, J = 6.0, 6.0 Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 157.5, 155.9, 147.3, 134.5, 134.2, 128.6, 126.5, 126.4, 126.0, 117.2, 117.1, 115.6, 115.5, 51.9, 47.8, 29.0.

2.2.6a

1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2.2.6a) purified by flash chromatography as yellow liquid. Reaction time about 12 h; Isolated yield 75%; ^1H NMR

(CDCl₃, 600 MHz) δ 7.28-7.22 (m, 3H), 7.21-7.17 (m, 2 H), 7.12 (d, J = 7.8 Hz, 1 H), 6.97 (d, J = 8.4 Hz, 2 H), 6.84 (t, J = 7.2 Hz, 1 H), 5.54 (d, J = 7.2 Hz, 1 H), 4.86 (dd, J = 12.6, 7.8 Hz, 1 H), 4.41 (dd, J = 12.0, 6.6 Hz, 1 H), 3.68-3.58 (m, 2 H), 3.08 (ddd, J = 16.0, 8.4, 6.0 Hz, 1 H), 2.78 (dt, J = 16.8, 5.1, 4.8 Hz, 1 H); ¹³C-NMR (150 MHz, CDCl₃) δ 148.4, 135.3, 133.0, 129.5, 129.2, 128.1, 127.0, 126.7, 119.5, 115.1, 78.8, 58.2, 42.1, 26.5.

2.2.3e

[Ir(Flrpic)(PhTriaz)₂] (**2.2.3e**) was purified by flash chromatography as yellow solid. ¹H NMR (CDCl₃, 600 MHz) δ 8.22 (d, J = 7.2 Hz, 1 H), 7.92 (d, J = 4.8 Hz, 2 H), 7.85 (t, J = 7.8 Hz, 1 H), 7.82 (d, J = 4.8 Hz, 1 H), 7.79 (s, 1H), 7.64 (d, J = 7.8 Hz, 1 H), 7.54 (d, J = 7.8 Hz, 1 H), 7.27 (d, J = 6.0 Hz, 1 H), 6.97 (t, J = 7.2 Hz, 2 H), 6.87 (t, J = 7.2 Hz, 1 H), 6.80 (t, J = 7.2 Hz, 1 H), 6.73 (t, J = 7.2 Hz, 1 H), 6.28 (d, J = 7.8 Hz, 1 H), 6.15 (d, J = 7.8 Hz, 1 H); ¹³C-NMR (150 MHz, CDCl₃) δ 172.9, 151.7, 148.8, 141.6, 141.5, 138.5, 135.1, 135.0, 133.0, 132.9, 132.6, 131.9, 127.94, 127.92, 127.87, 127.49, 127.33, 125.1, 122.9, 114.2, 113.9.

2.2.3f

[Ir(Flrpca)(PhTriaz)₂] (2.2.3f) was purified by flash chromatography as yellow solid. ¹H NMR (CDCl₃, 600 MHz) δ 8.24 (d, *J* = 7.2 Hz, 1 H), 7.92 (d, *J* = 16.8 Hz, 2 H), 7.89 (d, *J* = 6.0 Hz, 2 H), 7.87 (t, *J* = 6.0 Hz, 1 H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 7.25 (t, *J* = 6.6 Hz, 2 H), 7.04 (t, *J* = 7.2 Hz, 1 H), 6.99 (s, 1H), 6.97 (t, *J* = 7.2 Hz, 1 H), 6.80 (t, *J* = 7.2 Hz, 1 H), 6.44 (t, *J* = 7.2 Hz, 1 H), 6.21 (d, *J* = 7.8 Hz, 1 H), 5.89 (br, 1 H); ¹³C-NMR (150 MHz, CDCl₃) δ 173.8, 156.3, 149.7, 142.1, 141.2, 138.1, 135.18, 135.09, 135.00, 133.3, 133.2, 132.7, 131.7, 128.3, 128.1, 127.6, 126.9, 126.4, 122.8, 122.5, 114.3, 114.1.

ORTEP Drawing of the Crystal Structure

Figure S2.2-1. Perspective view of the molecular structure of **2.2.3b** (C₃₄H₂₅IrN₈O) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

Figure S2.2-2. Perspective view of the molecular structure of **2.2.3c** ($C_{34}H_{22}F_2IrN_7O_2$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

Figure S2.2-3. Perspective view of the molecular structure of **2.2.3d** ($\text{C}_{34}\text{H}_{23}\text{F}_2\text{IrN}_8\text{O}$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

2.3 1,2,3-Triazole as Unique Ligand in Promoting Iron Catalyzed Propargyl Alcohol Dehydration for the Synthesis of Conjugated Enynes

General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

Propargylic alcohols **2.3.1** were synthesized according to the literatures as below:

Yan, W.; Wang, Q.; Chen, Y.; Petersen, J.; Shi, X. *Org. Lett.* **2010**, *12*, 3308-3311.

Representative procedure for propargyl alcohol dehydration reaction

A 20 mL screw-cap vial was charged with the catalyst FeCl_3 (16.2 mg, 0.1 mmol) and the ligand 2-(1H-benzo[d][1,2,3]triazol-1-yl)ethanol **L10** (32.4 mg, 0.2 mmol) in 5 mL MeCN. The vial was placed in a preheated metal block at 60°C for 15 mins, and then propargyl alcohol (1 mmol) was added. The reaction mixture was stirred at 60°C and monitored by TLC. After the reaction was completed (about 2-7 h), the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1:40, V/V) to give desired enyne product as yellow oil.

General procedure for NBS promoted enyne activation reaction.

The enynyl acid (1 mmol), NBS (230 mg, 1.2 mmol), DABCO (2 mg, 0.02 mmol) and 5 mL chloroform CHCl_3 were combined in a 20 mL vial. The reaction mixture was stirred at rt until all the enynyl acid consumed as indicated by TLC. The reaction mixture was concentrated under reduced pressure and directly purified by flash chromatography on silica gel (ethyl acetate/hexane = 1:20, V/V) to give product as yellow oil.

Optimization of solvents^a

	catalyst	loading (%)	solv.	temp (°C)	time (h)	conv. (%) ^b	yield (%) ^c
18	FeCl ₃	10	MeCN	60	7	95	29
19	FeCl ₃	10	Acetone	60	7	66	13
20	FeCl ₃	10	THF	60	7	73	20
21	FeCl ₃	10	Toluene	60	7	35	<5
22	FeCl ₃	10	MeOH	60	7	65	<5
23	FeCl ₃	10	MeNO ₂	60	7	70	18
24	FeCl ₃	10	DMSO	60	7	<5	<5
25	FeCl ₃	10	DMF	60	7	<5	<5
26	FeCl ₃	10	CHCl ₃	60	7	80	17
27	FeCl ₃	10	EtOAc	60	7	78	15
28	FeCl ₃	10	DCE	60	7	81	24

^a General reaction conditions: 1a (0.25 mmol, 1.0 equiv.) and FeCl₃ (10 mol%) in solvent (5 mL); ^b Conversions were determined based on the consumption of propargyl alcohol; ^c NMR yields of 2a with 1,3,5-trimethoxybenzene as internal standard.

Compounds Characterization

2.3.2a

Oct-1-en-3-yn-2-ylbenzene (2.3.2a) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 91%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.67-7.64 (m, 2H), 7.37-7.33 (m, 2H), 7.31-7.28 (m, 1H), 5.84 (s, 1H), 5.58 (s, 1H), 2.42 (t, $J = 7.2$ Hz, 2H), 1.61 (quin, $J = 7.2$ Hz, 2H), 1.49 (sex, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 137.8, 131.0, 128.2, 128.0, 126.0, 119.3, 92.0, 79.7, 30.8, 22.0, 19.0, 13.6; HRMS Calculated for $\text{C}_{14}\text{H}_{17} [\text{M}+\text{H}]^+$: 185.1330, Found: 185.1333.

2.3.2b

(Z)-dec-3-en-5-yn-4-ylbenzene (2.3.2b) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 2 h; Isolated yield 95%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.61-7.59 (m, 2H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 1H), 6.33 (t, $J = 7.2$ Hz, 1H), 2.49 (quin, $J = 7.2$ Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.62 (quin, $J = 7.2$ Hz, 2H), 1.51 (sex, $J = 7.2$ Hz, 2H), 1.11 (t, $J = 7.2$ Hz, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 138.9,

138.7, 128.2, 127.1, 125.9, 123.2, 96.2, 77.6, 31.0, 24.5, 22.0, 19.3, 13.6, 13.5; HRMS Calculated for C₁₆H₂₁ [M+H]⁺: 213.1643, Found: 213.1640.

2.3.2c

Trimethyl(3-phenylbut-3-en-1-ynyl)silane (2.3.2c) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 81%; ¹H-NMR (600 MHz, CDCl₃) δ 7.67-7.64 (m, 2H), 7.38-7.35 (m, 2H), 7.33-7.30 (m, 1H), 5.94 (s, 1H), 5.72 (s, 1H), 0.27 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃) δ 136.9, 130.6, 128.3, 128.2, 126.0, 121.4, 104.1, 95.9, -0.1; HRMS Calculated for C₁₃H₁₇Si [M+H]⁺: 201.1100, Found: 201.1093.

2.3.2d

(5-methylhexa-1,5-dien-3-yn-2-yl)benzene (2.3.2d) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 90%; ¹H-NMR (600 MHz, CDCl₃) δ 7.67-7.64 (m, 2H), 7.38-7.34 (m, 2H), 7.33-7.29 (m, 1H), 5.92 (s, 1H), 5.66 (s, 1H), 5.40 (q, *J* = 1.2 Hz, 1H), 5.31 (quin, *J* = 1.2 Hz, 1H), 1.99 (t, *J* = 1.2 Hz, 3H); ¹³C-NMR (150 MHz, CDCl₃) δ 137.3, 130.6, 128.3, 128.2, 126.7, 126.0, 122.2, 120.5, 92.0, 87.5, 23.4; HRMS Calculated for C₁₃H₁₃ [M+H]⁺: 169.1017, Found: 169.1006.

2.3.2e

But-3-en-1-yne-1,3-diyl dibenzene (2.3.2e) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 88%; ^1H -NMR (600 MHz, CDCl_3) δ 7.74-7.72 (m, 2H), 7.55-7.53 (m, 2H), 7.41-7.36 (m, 2H), 7.35-7.33 (m, 4H), 5.98 (s, 1H), 5.76 (s, 1H); ^{13}C -NMR (150 MHz, CDCl_3) δ 137.3, 131.7, 130.6, 128.4, 128.3, 126.1, 123.1, 120.7, 90.7, 88.5; HRMS Calculated for $\text{C}_{16}\text{H}_{13}$ $[\text{M}+\text{H}]^+$: 205.1017, Found: 205.1013.

2.3.2f

(4-cyclohexylbut-1-en-3-yn-2-yl)benzene (2.3.2f) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 85%; ^1H -NMR (600 MHz, CDCl_3) δ 7.68-7.66 (m, 2H), 7.37-7.33 (m, 2H), 7.31-7.28 (m, 1H), 5.84 (s, 1H), 5.59 (s, 1H), 2.64-2.59 (m, 1H), 1.91-1.88 (m, 2H), 1.79-1.74 (m, 2H), 1.56-1.54 (m, 2H), 1.40-1.34 (m, 4H); ^{13}C -NMR (150 MHz, CDCl_3) δ 137.8, 130.9, 128.2, 128.0, 126.0, 119.1, 96.0, 79.0, 32.7, 29.7, 25.9, 24.9; HRMS Calculated for $\text{C}_{16}\text{H}_{19}$ $[\text{M}+\text{H}]^+$: 211.1487, Found: 211.1480.

2.3.2g

(4-cyclopropylbut-1-en-3-yn-2-yl)benzene (2.3.2g) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 85%; ^1H -NMR (600 MHz, CDCl_3) δ 7.63-7.61 (m, 2H), 7.36-7.32 (m, 2H), 7.31-7.27 (m, 1H), 5.82 (s, 1H), 5.56 (s, 1H), 1.48-1.43 (m, 1H), 0.89-0.85 (m, 2H), 0.82-0.79 (m, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ ,137.8, 130.8, 128.2, 128.1, 126.0, 119.4, 95.0, 75.0, 8.6, 0.2; HRMS Calculated for $\text{C}_{13}\text{H}_{13}$ $[\text{M}+\text{H}]^+$: 169.1017, Found: 169.1000.

2.3.2h

(Z)-trimethyl(3-phenylpent-3-en-1-ynyl)silane (2.3.2h) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 2 h; Isolated yield 70%; ^1H -NMR (600 MHz, CDCl_3) δ 7.60-7.58 (m, 2H), 7.36-7.32 (m, 2H), 7.28-7.25 (m, 1H), 6.52 (q, J = 7.2 Hz, 1H), 2.10 (d, J = 7.2 Hz, 3H), 0.29 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 138.0, 134.2, 128.3, 127.3, 125.8, 124.6, 102.2, 100.7, 17.0, 0.12; HRMS Calculated for $\text{C}_{14}\text{H}_{19}\text{Si}$ $[\text{M}+\text{H}]^+$: 215.1256, Found: 215.1250.

2.3.2i

(Cyclohexenylethynyl)trimethylsilane (2.3.2i) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 46% (conv. 50%); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 6.19-6.17 (m, 1H), 2.15-2.11 (m, 2H), 2.10-2.06 (m, 2H), 1.64-1.60 (m, 2H), 1.58-1.54 (m, 2H), 0.18 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 136.2, 120.8, 107.3, 90.8, 29.0, 25.6, 22.2, 21.4, 0.14; HRMS Calculated for $\text{C}_{11}\text{H}_{19}\text{Si}$ $[\text{M}+\text{H}]^+$: 179.1256, Found: 179.1262.

2.3.2j

1-(4-cyclohexylbut-1-en-3-yn-2-yl)-4-methoxybenzene (2.3.2j) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 81%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.60 (d, $J = 9.0$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 5.73 (s, 1H), 5.48 (s, 1H), 2.63-2.59 (m, 1H), 1.91-1.88 (m, 2H), 1.79-1.73 (m, 2H), 1.59-1.53 (m, 2H), 1.40-1.32 (m, 4H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 159.8, 130.7, 130.4, 127.5, 117.5, 113.7, 96.0, 80.0, 55.5, 32.9, 29.9, 26.1, 25.1; HRMS Calculated for $\text{C}_{17}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$: 241.1592, Found: 241.1590.

2.3.2k

1-methoxy-4-(4-phenylbut-1-en-3-yn-2-yl)benzene (2.3.2k) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 10 h; Isolated yield 75%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.67 (d, $J = 9.0$ Hz, 2H), 7.55-7.52 (m, 2H), 7.38-7.33 (m, 3H), 6.91 (d, $J = 9.0$ Hz, 2H), 5.88 (s, 1H), 5.66 (s, 1H), 3.84 (s, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 159.8, 131.6, 129.9, 128.3, 127.3, 123.2, 118.7, 113.7, 102.8, 90.5, 88.8, 55.3; HRMS Calculated for $\text{C}_{17}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$: 235.1123, Found: 235.1122.

2.3.2l

((1H-inden-3-yl)ethynyl)trimethylsilane (2.3.2l) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 2 h; Isolated yield 80%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.53 (d, $J = 7.8$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 7.2$ Hz, 1H), 6.79 (t, $J = 2.4$ Hz, 1H), 3.46 (d, $J = 2.4$ Hz, 2H), 0.29 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 145.9, 137.0, 132.6, 127.5, 123.9, 119.9, 113.0, 109.3, 80.1, 79.5, 49.3; HRMS Calculated for $\text{C}_{14}\text{H}_{17}\text{Si}$ $[\text{M}+\text{H}]^+$: 213.1100, Found: 213.1113.

2.3.2m

(Z)-3-(2-methoxyphenyl)hept-3-en-1-ynyltrimethylsilane (2.3.2m) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 2 h; Isolated yield 85%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.39 (dd, $J = 7.2$ Hz, 1.8 Hz, 1H), 7.23 (dt, $J = 7.2$ Hz, 1.8 Hz, 1H), 6.94 (dt, $J = 7.2$ Hz, 1.2 Hz, 1H), 6.90 (dd, $J = 7.2$ Hz, 1.2 Hz, 1H), 6.39 (t, $J = 7.8$ Hz, 1H), 3.84 (s, 3H), 2.47 (q, $J = 7.8$ Hz, 2H), 1.54 (sex, $J = 7.8$ Hz, 2H), 0.99 (t, $J = 7.8$ Hz, 3H), 0.22 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 156.8, 144.2, 130.1, 128.4, 128.3, 120.6, 120.5, 111.6, 103.4, 98.1, 55.6, 33.3, 22.2, 13.9, 0.1, 55.2; HRMS Calculated for $\text{C}_{17}\text{H}_{25}\text{OSi}$ $[\text{M}+\text{H}]^+$: 273.1675, Found: 273.1671.

2.3.2n

(Z)-5,7-diphenylhept-4-en-6-ynoic acid (2.3.2n) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as white solid. Reaction time about 0.5 h; Isolated yield 91%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.68-7.65 (m, 2H), 7.56-7.53 (m, 2H), 7.39-7.34 (m, 5H), 7.32-7.29 (m, 1H), 6.48 (t, $J = 7.2$ Hz, 1H), 2.91 (q, $J = 7.2$ Hz, 2H), 2.64 (t, $J = 7.2$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 179.0, 137.6, 135.2, 131.6, 128.40, 128.38, 128.35, 127.8, 126.1, 125.1,

123.2, 96.1, 86.1, 33.3, 26.3; HRMS Calculated for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1229, Found: 277.1230.

2.3.2o

(Z)-5-phenylundec-4-en-6-ynoic acid (2.3.2o) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 89%; 1H -NMR (600 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.24 (m, 1H), 6.34 (t, $J = 7.2$ Hz, 1H), 2.79 (q, $J = 7.2$ Hz, 2H), 2.57 (t, $J = 7.2$ Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.62 (quin, $J = 7.2$ Hz, 2H), 1.50 (sex, $J = 7.2$ Hz, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, $CDCl_3$) δ 178.9, 138.4, 133.6, 128.2, 127.5, 126.0, 125.5, 97.4, 33.3, 30.9, 26.0, 22.0, 19.3, 13.6; HRMS Calculated for $C_{17}H_{21}O_2$ $[M+H]^+$: 257.1542, Found: 257.1536.

2.3.2p

(Z)-6,8-diphenyloct-5-en-7-ynoic acid (2.3.2p) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 92%; 1H -NMR (600 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.54-7.51 (m, 2H), 7.38-7.32 (m, 5H), 7.31-7.27 (m, 1H),

6.43 (t, $J = 7.2$ Hz, 1H), 2.65 (q, $J = 7.2$ Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.91 (quin, $J = 7.2$ Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 179.0, 137.9, 136.7, 131.5, 128.4, 128.3, 128.2, 127.7, 126.0, 124.8, 123.3, 95.5, 86.5, 33.2, 30.5, 24.0; HRMS Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 236.1188, Found: 236.1178.

2.3.2q

(Z)-6-phenyldodec-5-en-7-ynoic acid (2.3.2q) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 88%; ^1H -NMR (600 MHz, CDCl_3) δ 7.60-7.57 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 1H), 6.29 (t, $J = 7.2$ Hz, 1H), 2.54 (q, $J = 7.2$ Hz, 2H), 2.46 (t, $J = 7.2$ Hz, 2H), 2.44 (t, $J = 7.2$ Hz, 2H), 1.86 (quin, $J = 7.2$ Hz, 2H), 1.61 (quin, $J = 7.2$ Hz, 2H), 1.49 (sex, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 179.8, 138.6, 135.1, 128.2, 127.4, 125.9, 125.1, 96.7, 77.5, 33.4, 30.9, 30.3, 24.0, 22.0, 19.2, 13.6; HRMS Calculated for $\text{C}_{18}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$: 271.1698, Found: 271.1704.

2.3.2r

(E)-5-phenylhept-4-en-6-ynoic acid (2.3.2r) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 85%; ^1H -NMR (600 MHz, CDCl_3) δ 7.60-7.58 (m, 2H), 7.36-7.32 (m, 2H), 7.29-7.27 (m, 1H), 7.32-7.29 (m, 1H), 6.50 (t, $J = 7.2$ Hz, 1H), 3.38 (s, 1H), 2.83 (q, $J = 7.2$ Hz, 2H), 2.59 (t, $J = 7.2$ Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 178.5, 137.2, 136.8, 128.4, 127.9, 125.9, 124.2, 83.9, 80.3, 33.0, 26.1; HRMS Calculated for $\text{C}_{13}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 201.0916, Found: 201.0912.

2.3.2s

(E)-5-(4-fluorophenyl)hept-4-en-6-ynoic acid (2.3.2s) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 92%; ^1H -NMR (600 MHz, CDCl_3) δ 7.63-7.60 (m, 2H), 7.54-7.51 (m, 2H), 7.37-7.34 (m, 3H), 7.06-7.03 (m, 2H), 6.40 (t, $J = 7.2$ Hz, 1H), 2.88 (q, $J = 7.2$ Hz, 2H), 2.63 (t, $J = 7.2$ Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 178.4, 163.3, 161.7, 134.9, 133.9, 133.8, 131.6, 128.5, 128.4, 127.7, 127.6, 124.1, 123.0, 115.3, 115.2, 96.3, 85.8, 33.2, 26.3; HRMS Calculated for $\text{C}_{13}\text{H}_{12}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 219.0821, Found: 219.0815.

2.3.2t

(Z)-5-(4-fluorophenyl)-7-(trimethylsilyl)hept-4-en-6-ynoic acid (2.3.2t) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 88%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.55-7.52 (m, 2H), 7.03-7.00 (m, 2H), 6.38 (t, $J = 7.2$ Hz, 1H), 2.80 (q, $J = 7.2$ Hz, 2H), 2.59 (t, $J = 7.2$ Hz, 2H), 0.26 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 178.9, 163.3, 161.7, 135.9, 133.5, 133.4, 127.6, 127.5, 124.2, 115.2, 115.1, 101.9, 101.3, 33.0, 26.2, -0.05; HRMS Calculated for $\text{C}_{16}\text{H}_{20}\text{FO}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 291.1217, Found: 291.1200.

2.3.2u

(Z)-5-(4-fluorophenyl)undec-4-en-6-ynoic acid (2.3.2u) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 83%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.56-7.53 (m, 2H), 7.02-6.99 (m, 2H), 6.26 (t, $J = 7.2$ Hz, 1H), 2.77 (q, $J = 7.2$ Hz, 2H), 2.57 (t, $J = 7.2$ Hz, 2H), 2.46 (t, $J = 7.2$ Hz, 2H), 1.61 (quin, $J = 7.2$ Hz, 2H),

1.48 (sex, $J = 7.2$ Hz, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 178.9, 163.2, 161.6, 134.5, 134.4, 133.3, 127.6, 127.5, 124.5, 115.1, 115.0, 97.7, 33.2, 30.9, 26.0, 22.0, 19.2, 13.6; HRMS Calculated for $\text{C}_{17}\text{H}_{20}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 275.1447, Found: 275.1441.

2.3.2v

(3-(propan-2-ylidene)penta-1,4-diyne-1,5-diyl)dibenzene (2.3.2v) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 7 h; Isolated yield 87%; ^1H -NMR (600 MHz, CDCl_3) δ 7.53-7.50 (m, 4H), 7.36-7.31 (m, 6H), 2.18 (s, 6H); ^{13}C -NMR (150 MHz, CDCl_3) δ 154.2, 131.4, 128.2, 128.0, 123.4, 101.3, 91.1, 86.4, 22.8; HRMS Calculated for $\text{C}_{20}\text{H}_{17}$ $[\text{M}+\text{H}]^+$: 257.1330, Found: 257.1333.

2.3.2w

Trimethyl(4-methyl-3-(phenylethynyl)pent-3-en-1-ynyl)silane (2.3.2w) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 7 h; Isolated yield 90%; ^1H -NMR (600 MHz, CDCl_3) δ 7.48-7.45 (m, 2H), 7.33-7.28 (m, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 0.23 (s, 9H); ^{13}C -NMR (150 MHz, CDCl_3) δ 155.6, 131.4, 128.2, 128.0, 123.4,

101.6, 101.5, 96.1, 91.3, 86.1, 22.8, 22.7, -0.03; HRMS Calculated for C₁₇H₂₁Si [M+H]⁺: 253.1413, Found: 253.1420.

2.3.2x

(3-(propan-2-ylidene)nona-1,4-diynyl)benzene (2.3.2x) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. Reaction time about 7 h; Isolated yield 79%; ¹H-NMR (600 MHz, CDCl₃) δ 7.47-7.45 (m, 2H), 7.32-7.27 (m, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 1.57 (quin, *J* = 7.2 Hz, 2H), 1.47 (sex, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ¹³C-NMR (150 MHz, CDCl₃) δ 152.4, 131.4, 128.1, 127.9, 123.6, 101.4, 92.3, 90.5, 87.1, 77.4, 30.9, 22.6, 22.5, 22.0, 19.2, 13.6; HRMS Calculated for C₁₈H₂₁ [M+H]⁺: 237.1643, Found: 237.1635.

2.3.2y

Methyl 7-phenyl-5-(phenylethynyl)hept-4-en-6-ynoate (2.3.2y) was purified by flash chromatography (Hexane-EtOAc, v/v 30/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 93%; ¹H-NMR (600 MHz, CDCl₃) δ 7.53-7.51 (m, 2H), 7.50-7.48 (m, 2H), 7.35-7.33 (m,

3H), 7.33-7.31 (m, 3H), 6.46 (t, $J = 7.2$ Hz, 1H), 3.71 (s, 3H), 2.81 (q, $J = 7.2$ Hz, 2H), 2.53 (t, $J = 7.2$ Hz, 2H); ^{13}C -NMR (150 MHz, CDCl_3) δ 172.9, 164.2, 131.7, 131.6, 128.6, 128.4, 128.3, 128.2, 122.8, 122.7, 107.1, 93.6, 87.2, 87.0, 84.3, 51.7, 32.8, 26.2; HRMS Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 315.1385, Found: 315.1392.

Methyl 5-(hex-1-ynyl)undec-4-en-6-ynoate (2.3.2z) was purified by flash chromatography (Hexane-EtOAc, v/v 30/1) as yellow liquid. Reaction time about 0.5 h; Isolated yield 90%; ^1H -NMR (600 MHz, CDCl_3) δ 6.11 (t, $J = 7.2$ Hz, 1H), 3.67 (s, 3H), 2.60 (q, $J = 7.2$ Hz, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 2.35 (t, $J = 7.2$ Hz, 2H), 2.28 (t, $J = 7.2$ Hz, 2H), 1.53 (quin, $J = 7.2$ Hz, 2H), 1.50 (quin, $J = 7.2$ Hz, 2H), 1.42 (sex, $J = 7.2$ Hz, 2H), 1.39 (sex, $J = 7.2$ Hz, 2H), 0.91 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 173.1, 143.4, 107.3, 94.5, 87.6, 78.8, 76.2, 51.6, 32.9, 30.6, 25.7, 22.0, 21.9, 19.1, 18.9, 13.6, 13.5; HRMS Calculated for $\text{C}_{18}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$: 275.2011, Found: 275.2023.

Syn-1-(2-bromo-1-(hex-1-ynyl)cyclohexyl)-4-fluorobenzene (2.3.3e) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Check ^1H , ^{13}C -NMR data in section (Full NMR characterizations of 3e, 3f, 3g); HRMS Calculated for $\text{C}_{18}\text{H}_{23}\text{BrF}$ $[\text{M}+\text{H}]^+$: 337.0967, Found: 337.0960.

Syn-5-(3-bromo-1-(4-fluorophenyl)-3-(trimethylsilyl)propa-1,2-dienyl)dihydrofuran-2(3H)-one (2.3.3f) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Check ^1H , ^{13}C -NMR data in section (Full NMR characterizations of 3e, 3f, 3g); HRMS Calculated for $\text{C}_{16}\text{H}_{19}\text{BrFO}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 369.0322, Found: 369.0315.

Syn-5-(3-bromo-1-(4-fluorophenyl)hepta-1,2-dienyl)dihydrofuran-2(3H)-one (2.3.3g) was purified by flash chromatography (Hexane-EtOAc, v/v 20/1) as yellow liquid. Check ^1H , ^{13}C -NMR data in section (**Full NMR characterizations of 3e, 3f, 3g**); HRMS Calculated for $\text{C}_{17}\text{H}_{19}\text{BrFO}_2$ $[\text{M}+\text{H}]^+$: 353.0552, Found: 353.0556.

2.3.5a

(Z)-(1-chlorodec-3-en-5-yn-4-yl)benzene (2.3.5a) was purified by flash chromatography (Hexane-EtOAc, v/v 40/1) as yellow liquid. ^1H -NMR (600 MHz, CDCl_3) δ 7.62-7.59 (m, 2H), 7.35-7.32 (m, 2H), 7.29-7.25 (m, 1H), 6.36 (t, $J = 7.2$ Hz, 1H), 3.66 (t, $J = 7.2$ Hz, 2H), 2.94 (q, $J = 7.2$ Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.62 (quin, $J = 7.2$ Hz, 2H), 1.50 (sex, $J = 7.2$ Hz, 2H), 0.97 (t, $J = 7.2$ Hz, 3H); ^{13}C -NMR (150 MHz, CDCl_3) δ 138.2, 131.3, 128.3, 127.8, 126.6, 126.0, 97.5, 77.3, 43.6, 34.2, 30.9, 22.0, 19.3, 13.6; HRMS Calculated for $\text{C}_{16}\text{H}_{20}\text{Cl}$ $[\text{M}+\text{H}]^+$: 247.1254, Found: 247.1250.

2.3.5b

(Z)-1-(4-phenyldec-3-en-5-ynyl)-1H-benzo[d][1,2,3]triazole (2.3.5b) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as yellow liquid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.50-7.48 (m, 2H), 7.46 (t, $J = 7.8$ Hz, 1H), 7.36 (t, $J = 7.8$ Hz, 1H), 7.32-7.28 (m, 2H), 7.27-7.23 (m, 1H), 6.26 (t, $J = 7.2$ Hz, 1H), 4.81 (t, $J = 7.2$ Hz, 2H), 3.15 (q, $J = 7.2$ Hz, 2H), 2.41 (t, $J = 7.2$ Hz, 2H), 1.57 (quin, $J = 7.2$ Hz, 2H), 1.45 (sex, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.0, 138.0, 133.0, 130.0, 128.3, 127.8, 127.4, 127.1, 126.0, 123.7, 120.0, 109.4, 97.8, 76.8, 47.3, 31.4, 30.8, 22.1, 19.2, 13.6; HRMS Calculated for $\text{C}_{22}\text{H}_{24}\text{N}_3$ $[\text{M}+\text{H}]^+$: 330.1970, Found: 330.1977.

2.3.5c

(Z)-1-(4-phenyl-6-(trimethylsilyl)hex-3-en-5-ynyl)-1H-benzo[d][1,2,3]triazole (2.3.5c) was purified by flash chromatography (Hexane-EtOAc, v/v 10/1) as white solid. Isolated yield 75%; $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.51-7.48 (m, 2H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.33-7.29 (m, 2H), 7.28-7.25 (m, 1H), 6.38 (t, $J = 7.2$ Hz, 1H), 4.82 (t, $J = 7.2$ Hz, 2H), 3.18 (q, $J = 7.2$ Hz, 2H), 0.26 (s, 9H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 146.0, 137.0, 133.0, 132.4, 128.3, 128.0, 127.1, 127.0, 126.0, 123.8, 120.0, 109.3, 102.0, 101.2, 47.1, 31.6, -0.06; HRMS Calculated for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 346.1739, Found: 346.1745.

ORTEP Drawing of the Crystal Structure

Figure S2.3-1. Perspective view of the molecular structure of **2.3.2n** (C₁₉H₁₆O₂) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 861258.

Figure S2.3-2. Perspective view of the molecular structure of **2.3.5b** ($\text{C}_{21}\text{H}_{23}\text{N}_3\text{Si}$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 861257.

Full NMR characterizations of 2.3.3e, 2.3.3f, 2.3.3g

^1H NMR spectrum of 2.3.3e in CDCl_3

Virtual coupling of tetrahydropyrane-2-one protons in the ^1H NMR spectrum of **2.3.3e** in CDCl_3

Experimental (a) and calculated (b) ^1H NMR spectrum

Chemical shifts (δ/ppm) Coupling constants (in Hz)

H2	4.3446	$J(\text{H2-H3a}) = 4.87$
H3a	2.5251	$J(\text{H2-H3b}) = 11.04$
H3b	2.8087	$J(\text{H3a-H3b}) = -13.98$
H4a	3.0344	$J(\text{H3a-H4a}) = 3.72$
H4b	2.8152	$J(\text{H3a-H4b}) = 8.38$
		$J(\text{H3b-H4a}) = 8.68$
		$J(\text{H3b-H4b}) = 8.60$
		$J(\text{H4a-H4b}) = -18.51$

Expansion of splitting patterns

Expanded regions of the ^1H NMR spectrum of **2.3.3e** in CDCl_3 (a) and **Toluene- d_8** (b)

Experimental (a) and calculated (b) multiplicity patterns of Phenyl- and p-Fluoro-phenyl ring protons

X part of ABX spin system

(A = H3a, B = H3b, X = H2)

800 MHz calculated ^1H NMR spectrum in CDCl_3

Strongly coupled splitting patterns

^1H NMR spectrum of **2.3.3e** in Toluene- d_8

1D TOCSY spectrum (b); Control ^1H NMR spectrum (a).

Selective excitation of H3a (mix = 250 ms)

DPFGSNOE spectra (b-c); Control ^1H NMR spectrum (a)

Experiemntal (a) and calculated (b) multiplicity patterns of Phenyl- and p-Fluoro-phenyl ring protons

A	7.67
A'	7.67
B	7.11
B'	7.11

J(A,A')	2.52
J(A,B)	8.51
J(A,B')	0.22
J(A,X)	5.15
J(A',B)	0.72
J(A',B')	8.51
J(A',X)	5.15
J(B,B')	2.89
J(B,X)	8.71
J(B',C)	8.71

AA'BB'X spin system

A	7.2677
A'	7.2677
B	6.9309
B'	6.9309
C	6.9699

J(A,A')	1.71
J(A,B)	7.71
J(A,B')	0.61
J(A,C)	1.32
J(A',B)	0.61
J(A',B')	7.73
J(A',C)	1.30
J(B,B')	1.47
J(B,C)	7.54
J(B',C)	7.54

AA'BB'C spin system

• residual protons peaks from toluene- d_8

Experiemntal (a) and calculated (b) multiplicity patterns of Phenyl ring protons

Expanded regions of the experimental (a) and calculated (b) ^1H NMR spectrum of **2.3.3e** in *Toluene- d_8*

¹³C NMR chemical shifts (δ/ppm)

gHMBC spectrum of 2.3.3e

Portion of the gHMBC spectrum of 2.3.3e

NMR spectral parameters of 2.3.3f

¹H and ¹³C NMR chemical shifts (δ/ppm) and coupling constants (J/Hz)

	δ _H /ppm		J/Hz		δ _C /ppm
H1	5.52	H1----H2a	7.24	C1	76.47
H2a	2.50	H1----H2b	5.62	C2	26.28
H2b	2.31	H2a----H2b	12.82	C3	28.08
H3a	2.67	H2a----H3a	7.24	C4	176.03
H3b	2.59	H2a----H3b	9.14	C5	108.13
H9/H13	7.40	H2b----H3a	9.55	C6	202.45 (d, J _{CF} = 1.87 Hz)
H10/H12	7.06	H2b----H3b	6.46	C7	92.41
CH ₃ (TMS)	0.25	H3a----H3b	17.63	C8	128.24 (d, J _{CF} = 3.48 Hz)
		H9----F	5.22	C9/C13	128.74 (d, J _{CF} = 8.3 Hz)
		H13----F	5.22	C10/C12	115.92 (d, J _{CF} = 21.95)
		H10----F	8.90	C11	162.57 (d, J _{CF} = 249.23 Hz)
		H12----F	8.90	CH ₃	-1.71
		H9---H10	8.50		
		H12---H13	8.50		
		H9-----H13	2.52		
		H10-----H12	2.87		
		H9-----H12	0.34		
		H10-----H13	0.34

Coupling constants (J/Hz)

Experimental (a) and calculated (b) ^1H NMR spectrum

Experimental (a) and calculated (b) ^1H NMR spectrum

Experimental (a) and calculated (b) ^1H NMR spectrum

1D NOESY

spectrum

Selective excitation of H1

1D NOESY

Splitting diagram
(tree) for H3a and H3b

Splitting diagram (tree) for H2a

Splitting diagram

(tree) for H2b

dddd

H2b

COSY

COSY correlations
between protons for the
5-membered ring

expansion

^{13}C NMR spectrum of 2.3.3f in CDCl_3

gHMQC

One-bond correlations

gHMBC

Long-range correlations

gHMBC Long-range correlations

gHMBC

Long-range correlations

^1H and ^{13}C NMR chemical shifts (δ/ppm) and coupling constants (J/Hz)

$\delta_{\text{H}}/\text{ppm}$		J/Hz	
H1	5.52	H1----H2a	7.19
H2a	2.51	H1----H2b	5.48
H2b	2.35	H2a----H2b	12.82
H3a	2.67	H2a----H3a	7.35
H3b	2.59	H2a----H3b	9.14
H9/H13	7.42	H2b----H3a	9.57
H10/H12	7.07	H2b----H3b	6.18
14-CH ₂	2.54	H3a----H3b	17.47
15-CH ₂	1.54	H9----F	5.07
16-CH ₂	1.37	H13----F	5.07
16-CH ₃	0.91	H10----F	8.86
		H12----F	8.86
		H9----H10	8.41
		H12----H13	8.41
		H9----H13	2.45
		H10----H12	2.95
		H9----H12	0.24
		H10----H13	0.24
		H15----H16	7.46
		H16----H17	7.46

$\delta_{\text{C}}/\text{ppm}$

C1	76.62
C2	26.02
C3	26.88
C4	176.09
C5	110.31
C6	197.90 (d, $J_{\text{CF}} = 2.14 \text{ Hz}$)
C7	98.66
C8	128.58 (d, $J_{\text{CF}} = 3.48 \text{ Hz}$)
C9/C13	129.14 (d, $J_{\text{CF}} = 8.3 \text{ Hz}$)
C10/C12	115.68 (d, $J_{\text{CF}} = 21.68$)
C11	162.75 (d, $J_{\text{CF}} = 249.23 \text{ Hz}$)
C14	37.65
C15	30.12
C16	21.80
C17	13.70

^1H NMR spectrum of 2.3.3g in CDCl_3

^{13}C NMR spectrum of 2.3.3g in CDCl_3

Experimental (a) and calculated (b) ^1H NMR spectra for the 5-membered ring protons

gHMBC spectrum of 2.3.3g

Chapter Three: N-2-aryl-1,2,3-triazoles: a new class of UV-Blue emitting fluorophores through Planar-Intramolecular-Charge-Transfer (PICT)

General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer. UV-visible spectra were obtained on a Shimadzu UV-2500. Fluorescence spectra for emission and excitation were obtained on a Hitachi 7000.

All N-H triazoles were synthesized according to the literatures as below:

1. Quiclet-Sire, B.; Zard, S. Z.; *Synthesis* **2005**, 19, 3319.
2. Sengupta, S.; Duan, H.; Lu, W.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008**, 10, 1493.

General Procedure for preparation of N-2-aryl-1,2,3-triazoles.

To a 25 mL round-bottom bottle was successively added N-H triazole (1 mmol), potassium carbonate (345 mg, 2.5 mmol), L-proline (23 mg, 0.2 mmol), copper (I) chloride (10 mg, 0.1 mmol) and iodo-substituted benzene (1.2 mmol) in 10 mL DMSO under N₂ protection. The reaction mixture was stirred and heated up to 85 °C for 4 hours, and monitored by TLC. After the reaction was completed, water (20 mL) was added. The mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic phases were washed with brine and dried with anhydrous Na₂SO₄. The solvent was removed under reduced pressure to get a residue, the residue was purified by flash silica gel chromatography (hexane/ethyl acetate = 20:1) to give the product. All yields were about 60% - 75% (N-2 isomer).

Procedure for the synthesis of N^ε-(1,1-dimethylethoxycarbonyl)-L-lysine-methyl ester(3.5)

The N^ε-*t*Boc-N^ε-(carbobenzyloxy)-L-lysine **3.4** (1.14 g, 3 mmol), 4-dimethyl-aminopyridine (DMAP, 225 mg, 1.83 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC, 1.15 g, 6 mmol) were added in dry CH₂Cl₂ (4 ml), and then dry MeOH (2 ml, 33 mmol) was injected by syringe under N₂ protection. After the reaction mixture was stirred at room temperature for 20 h, 20 ml CH₂Cl₂ was added. The mixture was washed with water and brine, dried with anhydrous Na₂SO₄ and concentrated under reduced pressure to give a yellow residue. The crude residue was purified by flash silica gel chromatography to produce the N^ε-*t*Boc-N^ε-(carbobenzyloxy)-L-lysine-methyl ester as yellow oil.

The N^ε-*t*Boc-N^ε-(carbobenzyloxy)-L-lysine-methyl ester from last step was dissolved in 10 ml of MeOH-CH₂Cl₂ (1:1) with the addition of palladium-activated carbon (0.157 g, 1.5 mmol). The mixture was stirred under high pressure hydrogen gas for 30 min, and filtered by vacuum filtration to remove the palladium-activated carbon catalyst. The solvent was removed under reduced pressure to get a residue, the residue was purified by flash silica gel chromatography to afford product **3.5** (0.663 g, 85%).

Procedure for the synthesis of methyl 2-(tert-butoxycarbonylamino)-6-(2-(4-iodophenyl)acetamido)hexanoate(3.7)

To a solution of 2-(4-iodophenyl)acetic acid **3.6** (1.44, 5.5 mmol) and N[□]-(1,1-dimethylethoxycarbonyl)-L-lysine-methyl ester **3.5** (1.3, 5 mmol) were dissolved in 20 mL CH₂Cl₂ was added 4-dimethyl-aminopyridine (DMAP, 62 mg, 0.5 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC, 1.15 g, 6 mmol). The reaction mixture was stirred under N₂ protection for 12 h at room temperature, washed with water and brine, dried with anhydrous Na₂SO₄ and concentrated under reduced pressure to give the residue. , the residue was purified by flash silica gel chromatography to give product **3.7** (2.02 g, 80%).

UV absorption spectra:

Absorption spectra were recorded on a Shimadzu UV-2500 spectrophotometer in 1 cm-length quartz cell with a resolution of 0.2 nm. All samples were measured from the 10^{-5} M solution of N-2-aryl-1,2,3-triazole in MeOH with the wavelength range between 200 nm and 800 nm.

Fluorescence excitation and emission spectra:

Fluorescence excitation and emission spectra were measured on a Hitachi 7000 fluorophotometer with a slit width of 2.5 nm. The photomultiplier voltage was 400 V and the scanning speed was 240 nm/min. The emission spectra were obtained from the 10^{-5} M solution of N-2-aryl-1,2,3-triazole in MeOH with an excitation wavelength at 254 nm or 310 nm and the excitation spectra were recorded with the emission wavelength λ_{max} which depended on different triazoles.

Quantum yield:

Quantum yields were determined by using an integrated emission area and comparing that value to the area measured for the standard quinine sulfate dihydrate when excited at 365 nm ($\Phi_{\text{reference}} = 0.564$) in water. Quantum yields were calculated by using the following equation, where Φ is the quantum yield, Int is the area of emission peak, A represents absorbance at the excitation wavelength and n is reflective index of the solvent. The subscript reference is the respective values of the standard quinine sulfate dihydrate.

$$\Phi = \Phi_{\text{reference}} \times \frac{Int \times A_{\text{reference}} \times n^2}{Int_{\text{reference}} \times A \times n_{\text{reference}}^2}$$

Compounds Characterization

3.1e

2,4-diphenyl-2H-1,2,3-triazole (3.1e) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.15 (d, $J = 7.8$ Hz, 2H), 8.06 (m, 1H), 7.91 (d, $J = 6.6$ Hz, 2H), 7.52-7.46 (m, 4H), 7.42-7.35 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.9, 139.9, 132.5, 130.1, 129.3, 128.9, 128.8, 127.4, 126.1, 118.8; HRMS Calculated for $\text{C}_{14}\text{H}_{11}\text{N}_3$ $[\text{M}+\text{H}]^+$: 222.1032, Found: 222.1025.

3.2a

4-(4-phenyl-2H-1,2,3-triazol-2-yl)benzonitrile (3.2a) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.28 (d, $J = 9.0$ Hz, 2H), 8.12 (s, 1H), 7.90 (d, $J = 7.2$ Hz, 2H), 7.80 (d, $J = 9.0$ Hz, 2H), 7.50-7.48 (m, 2H), 7.45-7.42 (m, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 150.1, 142.4, 133.9, 133.5, 129.4, 129.3, 129.1, 126.3, 119.0, 118.3, 110.7; HRMS Calculated for $\text{C}_{15}\text{H}_{10}\text{N}_4$ $[\text{M}+\text{H}]^+$: 247.0984, Found: 247.0978.

3.2b

2-(4-fluorophenyl)-4-phenyl-2H-1,2,3-triazole (3.2b) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.13-8.11 (m, 2H), 8.04 (s, 1H), 7.89 (d, $J = 7.2$ Hz, 2H), 7.48 (t, $J = 7.8$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.19 (t, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 162.6, 161.0, 149.0, 136.2, 132.6, 130.0, 129.0, 128.9, 126.1, 120.6, 120.5, 116.2, 116.0; HRMS Calculated for $\text{C}_{14}\text{H}_{10}\text{FN}_3$ $[\text{M}+\text{H}]^+$: 240.0938, Found: 240.0931.

3.2c

2-(4-chlorophenyl)-4-phenyl-2H-1,2,3-triazole (3.2c) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.09 (d, $J = 9.0$ Hz, 2H), 8.05 (s, 1H), 7.89 (d, $J = 7.8$ Hz, 2H), 7.48 (t, $J = 8.4$ Hz, 4H), 7.41 (t, $J = 7.2$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 149.2, 138.4, 133.0, 132.8, 129.8, 129.4, 129.0, 126.2, 120.0; HRMS Calculated for $\text{C}_{14}\text{H}_{10}\text{ClN}_3$ $[\text{M}+\text{H}]^+$: 256.0642, Found: 256.0636.

3.2d

2-(4-methoxyphenyl)-4-phenyl-2H-1,2,3-triazole (3.2d) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.05 (d, $J = 9.0$ Hz, 2H), 8.02 (s, 1H), 7.89 (d, $J = 6.6$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.40-7.37 (m, 1H), 7.01 (t, $J = 9.0$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 159.2, 148.7, 134.0, 132.3, 130.4, 129.1, 128.9, 126.3, 120.5, 114.6, 55.8; HRMS Calculated for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 252.1138, Found: 252.1170.

3.2e

2-(4-nitrophenyl)-4-phenyl-2H-1,2,3-triazole (3.2e) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as yellow solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.38 (d, $J = 9.0$ Hz, 2H), 8.32 (d, $J = 9.0$ Hz, 2H), 8.15 (s, 1H), 7.92-7.88 (m, 2H), 7.52-7.48 (m, 2H), 7.46-7.43 (m, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 150.4, 146.3, 143.7, 134.3, 129.5, 129.2, 129.1, 126.3, 125.2, 118.8; HRMS Calculated for $\text{C}_{14}\text{H}_{11}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 267.0804, Found: 267.0836.

3.2f

phenyl(4-(4-phenyl-2H-1,2,3-triazol-2-yl)phenyl)methanone (3.2f) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.27 (d, $J = 9.0$ Hz, 2H), 8.12 (s, 1H), 7.97 (d, $J = 9.0$ Hz, 2H), 7.93-7.91 (m, 2H), 7.84-7.82 (m, 2H), 7.64-7.60 (m, 1H), 7.53-7.47 (m, 4H), 7.44-7.40 (m, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 195.5, 149.7, 142.4, 137.5, 136.1, 133.5, 132.5, 131.5, 129.9, 129.6, 129.1, 129.0, 128.4, 126.2, 118.3; HRMS Calculated for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 326.1215, Found: 326.1220.

3.2g

4-(4-phenyl-2H-1,2,3-triazol-2-yl)pyridine (3.2g) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.72 (d, $J = 6.0$ Hz, 2H), 8.13 (s, 1H), 8.05 (d, $J = 6.0$ Hz, 2H), 7.89 (d, $J = 7.2$ Hz, 2H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.43 (t, $J = 7.8$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 151.0, 150.2, 145.7, 134.2, 129.5, 129.2, 129.1, 126.3, 112.6; HRMS Calculated for $\text{C}_{13}\text{H}_{11}\text{N}_4$ $[\text{M}+\text{H}]^+$: 223.0905, Found: 223.0930.

3.2h

2-(4-phenyl-2H-1,2,3-triazol-2-yl)pyridine (3.2h) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.81 (s, 1H), 8.52 (d, J = 4.2 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.96-7.91 (m, 3H), 7.47 (t, J = 7.2 Hz, 2H), 7.39-7.34 (m, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 149.2, 148.5, 148.0, 139.1, 130.2, 128.9, 128.4, 125.9, 123.5, 116.8, 113.8; HRMS Calculated for $\text{C}_{13}\text{H}_{11}\text{N}_4$ $[\text{M}+\text{H}]^+$: 223.0905, Found: 223.0930.

3.2i

2-(naphthalen-1-yl)-4-phenyl-2H-1,2,3-triazole (3.2i) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.29-8.26 (m, 1H), 8.21 (s, 1H), 7.99-7.93 (m, 4H), 7.87 (d, J = 7.2 Hz, 1H), 7.61-7.56 (m, 3H), 7.49 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.9, 136.9, 134.4, 132.5, 130.1, 129.6, 129.0, 128.8, 128.2, 127.6, 127.4, 126.6, 126.2, 125.0, 123.6, 122.8; HRMS Calculated for $\text{C}_{18}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+$: 272.1109, Found: 272.1125.

4-(4-fluorophenyl)-2-phenyl-2H-1,2,3-triazole (3.3a) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 2H), 8.01 (s, 1H), 7.88 (dd, $J = 8.4$ Hz, 5.4 Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.16 (t, $J = 9.0$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 164.1, 162.5, 148.2, 140.0, 132.5, 129.5, 128.2, 128.1, 127.7, 126.5, 119.0, 116.3, 116.1; HRMS Calculated for $\text{C}_{14}\text{H}_{10}\text{FN}_3$ $[\text{M}+\text{H}]^+$: 240.0938, Found: 240.0931.

4-(4-(4-fluorophenyl)-2H-1,2,3-triazol-2-yl)benzonitrile (3.3b) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.26 (d, $J = 8.4$ Hz, 2H), 8.07 (s, 1H), 7.88-7.86 (m, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.17 (t, $J = 9.0$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 149.2, 142.4, 133.7, 133.5, 128.2, 128.1, 125.5, 119.0, 118.3, 116.3, 116.1, 110.8, 29.7; HRMS Calculated for $\text{C}_{15}\text{H}_9\text{FN}_4$ $[\text{M}+\text{H}]^+$: 265.0890, Found: 265.0884.

2,4-bis(4-fluorophenyl)-2H-1,2,3-triazole (3.3c) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.10 (q, $J = 4.8$ Hz, 2H), 7.99 (s, 1H), 7.86 (dd, $J = 8.4$ Hz, 5.4 Hz, 2H), 7.20-7.15 (m, 4H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 164.0, 162.7, 162.3, 161.0, 148.1, 136.2, 132.3, 128.0, 127.9, 126.2, 120.6, 120.5, 116.2, 116.1, 116.0, 115.9; HRMS Calculated for $\text{C}_{14}\text{H}_9\text{F}_2\text{N}_3$ $[\text{M}+\text{H}]^+$: 258.0843, Found: 258.0837.

2-(4-chlorophenyl)-4-(4-fluorophenyl)-2H-1,2,3-triazole (3.3d) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 2H), 8.00 (s, 1H), 7.86 (dd, $J = 5.4$ Hz, 8.4 Hz, 2H), 7.47 (d, $J = 9.0$ Hz, 2H), 7.16 (t, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 164.0, 162.4, 148.3, 138.3, 133.1, 132.6, 129.4, 128.0, 127.9, 126.0, 120.0, 116.1, 116.0; HRMS Calculated for $\text{C}_{14}\text{H}_9\text{ClFN}_3$ $[\text{M}+\text{H}]^+$: 274.0548, Found: 274.0541.

4-(4-fluorophenyl)-2-(4-methoxyphenyl)-2H-1,2,3-triazole (3.3e) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.96 (s, 1H), 7.86 (dd, $J = 8.4$ Hz, 5.4 Hz, 2H), 7.15 (t, $J = 8.4$ Hz, 2H), 7.10 (d, $J = 9.0$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 163.8, 162.2, 159.0, 147.6, 133.7, 131.8, 127.9, 127.8, 126.4, 120.3, 116.0, 115.9, 114.4, 55.6; HRMS Calculated for $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$: 270.1043, Found: 270.1037.

4-(4-methoxyphenyl)-2-phenyl-2H-1,2,3-triazole (3.3f) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.13 (d, $J = 7.2$ Hz, 2H), 7.99 (s, 1H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 160.2, 148.7, 139.9, 132.1, 129.2, 127.5, 127.2, 122.7, 118.7, 114.4, 55.4; HRMS Calculated for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 252.1138, Found: 252.1131.

4-(4-(4-methoxyphenyl)-2H-1,2,3-triazol-2-yl)benzonitrile (3.3g) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.24 (d, $J = 8.4$ Hz, 2H), 8.04 (s, 1H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 9.0$ Hz, 2H), 6.51 (d, $J = 9.0$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 160.6, 149.9, 142.4, 133.5, 133.4, 127.6, 121.9, 118.9, 118.4, 114.5, 110.4, 55.4; HRMS Calculated for $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$: 277.1090, Found: 277.1083.

2-(4-fluorophenyl)-4-(4-methoxyphenyl)-2H-1,2,3-triazole (3.3h) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.08 (q, $J = 4.8$ Hz, 2H), 7.95 (s, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.16 (t, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 136.3, 132.1, 127.4, 122.5, 120.4, 120.3, 116.1, 116.0, 114.4, 55.3; HRMS Calculated for $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$: 270.1043, Found: 270.1037.

2-(4-chlorophenyl)-4-(4-methoxyphenyl)-2H-1,2,3-triazole (3.3i) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 9.0$ Hz, 2H), 7.97 (s, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 160.3, 149.0, 138.4, 132.8, 132.4, 129.3, 127.5, 122.4, 119.8, 114.4, 55.3; HRMS Calculated for $\text{C}_{15}\text{H}_{13}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$: 286.0748, Found: 286.0776.

2,4-bis(4-methoxyphenyl)-2H-1,2,3-triazole (3.3j) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.94 (s, 1H), 7.81 (d, $J = 9.0$ Hz, 2H), 7.00 (dd, $J = 7.8$ Hz, 1.8 Hz, 4H), 3.86 (d, $J = 1.8$ Hz, 6H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 160.0, 158.8, 148.3, 133.8, 131.5, 127.4, 122.9, 120.2, 114.3, 55.6, 55.3; HRMS Calculated for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 282.1243, Found: 282.1237.

4-(4-chlorophenyl)-2-phenyl-2H-1,2,3-triazole (3.3k) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 2H), 8.02 (s, 1H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.34 (t, $J = 7.8$ Hz, 1H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.0, 140.0, 134.9, 132.7, 129.5, 129.4, 128.8, 127.8, 127.6, 119.0; HRMS Calculated for $\text{C}_{14}\text{H}_{10}\text{ClN}_3$ $[\text{M}+\text{H}]^+$: 256.0642, Found: 256.0636.

4-(4-(4-chlorophenyl)-2H-1,2,3-triazol-2-yl)benzonitrile (3.3l) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.27 (d, $J = 9.0$ Hz, 2H), 8.10 (s, 1H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 149.0, 142.3, 135.4, 133.8, 133.5, 129.3, 127.8, 127.5, 119.1, 118.3, 111.0; HRMS Calculated for $\text{C}_{15}\text{H}_9\text{ClN}_4$ $[\text{M}+\text{H}]^+$: 281.0595, Found: 281.0588.

4-(4-chlorophenyl)-2-(4-fluorophenyl)-2H-1,2,3-triazole (3.3m) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.10 (q, $J = 4.8$ Hz, 2H), 8.01 (s, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 162.7, 161.0, 147.9, 136.1, 134.7, 132.5, 129.2, 128.4, 127.3, 120.6, 120.5, 116.2, 116.1; HRMS Calculated for $\text{C}_{14}\text{H}_9\text{ClFN}_3$ $[\text{M}+\text{H}]^+$: 274.0548, Found: 274.0541.

2,4-bis(4-chlorophenyl)-2H-1,2,3-triazole (3.3n) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 2H), 8.02 (s, 1H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.45 (dd, $J = 14.4$ Hz, 9.0 Hz, 4H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 148.1, 138.3, 134.9, 133.2, 132.7, 129.4, 129.2, 128.3, 127.4, 120.0; HRMS Calculated for $\text{C}_{14}\text{H}_9\text{Cl}_2\text{N}_3$ $[\text{M}+\text{H}]^+$: 290.0252, Found: 290.0246.

3.3o

4-(4-chlorophenyl)-2-(4-methoxyphenyl)-2H-1,2,3-triazole (3.3o) was purified by flash chromatography (Hexane- EtOAc, v/v 10/1) as white solid. $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.99 (s, 1H), 7.82 (d, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H); $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ 159.1, 147.4, 134.5, 133.6, 132.0, 129.1, 128.7, 127.3, 120.3, 114.4, 55.6; HRMS Calculated for $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$: 286.0748, Found: 286.0741.

3.5

N-(1,1-dimethylethoxycarbonyl)-L-lysine-methyl ester (3.5). $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 5.18 (br, 1H), 4.23 (br, 1H), 3.68 (s, 3H), 1.81-1.70 (m, 1H), 1.62-1.56 (m, 1H), 1.49-1.40 (m, 1H), 1.38 (s, 9H), 1.37–1.30 (m, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 173.5, 155.6, 79.9, 53.5, 52.4, 41.7, 32.6, 28.5, 22.8. HRMS Calculated for $\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 261.1736, Found: 261.1773.

3.7

Methyl 2-(tert-butoxycarbonylamino)-6-(2-(4-iodophenyl)acetamido)hexanoate (3.7). ^1H NMR (600 MHz, CDCl_3): δ 7.58 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 5.98 (s, 1H), 5.16 (br, 1H), 4.18 (br, 1H), 3.66 (s, 3H), 3.39 (s, 2H), 3.15-3.10 (m, 2H), 1.72-1.69 (m, 1H), 1.59-1.54 (m, 1H), 1.43-1.40 (m, 2H), 1.38 (s, 9H), 1.30-1.23 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 173.0, 170.2, 155.4, 137.6, 134.7, 131.1, 92.4, 79.7, 53.0, 52.1, 42.8, 39.1, 32.0, 28.7, 28.2, 22.4. HRMS Calculated for $\text{C}_{20}\text{H}_{30}\text{IN}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 505.1121, Found: 505.1153.

3.4b

Methyl 2-(tert-butoxycarbonylamino)-6-(2-(4-(4-phenyl-2H-1,2,3-triazol-2-yl)phenyl)acetamido)hexanoate (3.4b) was prepared from 4-phenyl-2H-1,2,3-triazole and iodo-substituted benzene by using the previously reported procedure of arylation. ^1H NMR (600 MHz,

CDCl₃): δ 8.13 (d, *J* = 8.4 Hz, 2H), 8.05 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.49-7.45 (m, 2H), 7.41-7.38 (m, 3H), 5.55 (br, 1H), 5.06 (br, 1H), 4.26 (br, 1H), 3.72 (s, 3H), 3.62 (s, 2H), 3.25-3.20 (m, 2H), 1.84-1.72 (m, 2H), 1.65-1.58 (m, 1H), 1.51-1.45 (m, 2H), 1.43 (s, 9H), 1.36-1.28 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 187.1, 173.1, 170.5, 149.0, 139.1, 134.2, 132.7, 130.3, 129.9, 129.0, 128.9, 126.1, 119.3, 79.9, 53.1, 52.3, 43.3, 39.3, 32.4, 28.9, 28.3, 22.5. HRMS Calculated for C₂₈H₃₆N₅O₅ [M+H]⁺: 522.2638, Found: 522.2680.

ORTEP Drawing of the Crystal Structure

Figure S3-1. Perspective view of the molecular structure of **3.2h** ($C_{13}H_{10}N_4$) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

CCDC number: 775283.

Reported crystal structures

Compound #	CCDC
3.1b	702800
3.1c	702801
3.2g	702802
3.4a	702803

The Data of Fluorophores with Emission Spectra

Sample preparation: To a 20 ml white cap vial was added the N-2-aryl-1,2,3-triazoles (0.01 mmol) in 10 ml MeOH. The solution was shook several times. After triazoles was absolutely dissolved, the 100 μ l triazole solution has been transferred to another new 20 ml white cap vial by using Socorex wheaton single-channel pipetter (50-200 μ l), and was then diluted with additional 9.9 ml MeOH.

Integrated emission area: All the areas were integrated from the original spectra by FL Solution 2.0 software at the wavelength range which was 260 nm to 500 nm with an excitation wavelength at 254 nm or 320 nm to 500 nm with an excitation wavelength at 310 nm.

Quantum yield determination: All the quantum yields of samples were determined based on 1.0×10^{-5} mol/L Quinine sulfate dihydrate in H_2O ($\Phi = 0.564$).

Figure S3-2. Photoemission of N-2-aryl-1,2,3-triazole: sample preparation: 1.0×10^{-5} mol/L in MeOH, excitation at 254 nm with 5 nm slit, quantum yield of **3.1a** $\Phi = 0.154$, quantum yield of **3.1a'** $\Phi = 0.009$.

	Absorption(nm)	Excitation ($\lambda_{\max}$)	Emission ($\lambda_{\max}$)	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.1a	222 (0.127), 305 (0.222)	305	362	57	0.15	19576.0
3.1a'	222(0.108), 292(0.116)	n.d.	343	n.d.	0.01	1444.8

Figure S3-3. Photoemission of N-2-aryl-1,2,3-triazole: sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

	Absorption(nm)	Excitation ($\lambda_{\max}$)	Emission ($\lambda_{\max}$)	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.1a	222 (0.127), 305 (0.222)	305	362	57	0.15	19576.0
3.1b	206 (0.128), 263 (0.250)	n.d.	316	n.d.	0.02	4662.9
3.1c	227 (0.257), 292 (0.268)	n.d.	380, 400	n.d.	0.06	10822.5
3.1d	220 (0.146), 296 (0.276)	n.d.	348	n.d.	0.09	23036.8
3.1e	220 (0.118), 294 (0.263)	298	347	49	0.35	48541.7
3.1f	220 (0.111), 290 (0.253)	284	342	58	0.45	56612.5
3.1g	221 (0.128), 285 (0.265)	285	342	57	0.30	52417.0
STD-1*	207 (0.452), 234 (0.228), 349 (0.710)	361	402, 422	41, 61	0.23	63090.6
STD-2	234 (0.423), 334 (0.068)	n.d.	365	n.d.	0.56	42012.4

* **STD-1** = Disodium 4,4'-bis(2-sulfostyryl)biphenyl (DSBP). **STD-2** = Quinine sulfate dihydrate.

Figure S3-4. Photoemission of N-2-aryl-1,2,3-triazole: sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

	Absorption(nm)	Excitation ($\lambda_{\max}$)	Emission ($\lambda_{\max}$)	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.1e	220(0.118), 294(0.263)	298	347	49	0.35	46309.1
3.2a	224 (0.154), 309 (0.397)	312	350	38	0.31	137679.5
3.2b	240 (0.056), 294 (0.212)	298	343	45	0.34	34963.0
3.2c	298 (0.274)	292	344	52	0.35	72108.9
3.2d	245 (0.041), 298 (0.226)	304	374	70	0.31	61629.7
3.2e	225 (0.181), 336 (0.205)	n.d.	342	n.d.	0.003	443.5
3.2f	228 (0.135), 250 (0.14), 317 (0.365)	n.d.	343	n.d.	0.001	269.2
3.2g	220.5 (0.133), 300 (0.242)	302	341	39	0.28	52195.1
3.2h	238 (0.156), 276 (0.093)	301	341	40	0.15	1684.2
3.2i	222 (0.482), 260 (0.115), 296 (0.127)	289	375	86	0.27	29619.9

Figure S3-5-1. Photoemission of N-2-aryl-1,2,3-triazole: sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

	Absorption(nm)	Excitation (λ _{max})	Emission (λ _{max})	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.1e	220(0.118), 294(0.263)	298	347	49	0.344	46309.1
3.2a	224 (0.154), 309 (0.397)	312	350	38	0.311	137679.5
3.2b	240 (0.056), 294 (0.212)	298	343	45	0.335	34963.0
3.2c	298 (0.274)	292	344	52	0.346	72108.9
3.2d	245 (0.041), 298 (0.226)	304	374	70	0.311	61629.7

Figure S3-5-2. Photoemission of N-2-aryl-1,2,3-triazole: sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

	Absorption(nm)	Excitation (λ _{max})	Emission (λ _{max})	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.3a	279 (0.147), 295 (0.152)	278	343	65	0.393	35187.2
3.3b	310 (0.173)	305	351	46	0.511	99110.2
3.3c	279 (0.203), 295 (0.202)	277	343	66	0.398	45465.3
3.3d	281 (0.328), 299 (0.399)	279	343	64	0.254	79606.4
3.3e	300 (0.319)	280	373	93	0.325	96251.2

Figure S3-5-3. Photoemission of N-2-aryl-1,2,3-triazole: sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

	Absorption(nm)	Excitation (λ _{max})	Emission (λ _{max})	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.3f	245 (0.067), 287 (0.213), 305 (0.198)	284	360	76	0.388	82234.7
3.3g	250 (0.162), 322 (0.388)	318	401	83	0.317	111193.8
3.3h	245 (0.086), 287 (0.241), 305 (0.221)	283	360	77	0.337	78555.8
3.3i	245 (0.096), 289 (0.208), 309 (0.236)	287	364	77	0.341	89760.8
3.3j	255 (0.105), 289 (0.292), 308 (0.299)	284	369	85	0.344	114055.5

Figure S3-5-4. Photoemission of N-2-aryl-1,2,3-triazole: sample information: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm with 2.5 nm slit.

	Absorption(nm)	Excitation (λ _{max})	Emission (λ _{max})	Stoke Shift(nm)	Φ	Fluorescence Intensity
3.3k	284 (0.539), 298 (0.532)	280	341	61	0.345	133654.1
3.3l	211 (0.086), 245 (0.075), 311 (0.350)	306	352	46	0.446	173975.0
3.3m	283 (0.275)	281	343	62	0.406	77275.4
3.3n	245 (0.059), 301 (0.298)	283	345	62	0.361	99041.4
3.3o	303 (0.281)	285	376	91	0.349	100999.4

Figure S3-6. Comparison of photoluminescent spectra of 3.1e and 3.4b

Sample preparation: 1.0×10^{-5} mol/L in MeOH, excitation at 310 nm, quantum yields of **1e** $\Phi = 0.344$, and **4b** $\Phi = 0.346$.

Solvent Screening Data

R	Solvent	Excitation ($\lambda_{\max}$)	Emission ($\lambda_{\max}$)	Stoke Shift	A_{310}	Fluorescence Intensity	n	Φ
CN	MeOH	312	350	38	0.395	137679.5	1.3314	0.311
H	MeOH	298	347	49	0.12	46309.1	1.3314	0.344
F	MeOH	298	343	45	0.093	34963.0	1.3314	0.335
OMe	MeOH	304	374	70	0.177	61629.7	1.3314	0.311
CN	DCM	313	351	38	0.276	101203.8	1.4242	0.374
H	DCM	298	345	47	0.118	41036.9	1.4242	0.355
F	DCM	298	345	47	0.089	29776.1	1.4242	0.342
OMe	DCM	305	367	62	0.182	53109.8	1.4242	0.298
CN	MeCN	311	350	39	0.281	103597.2	1.3460	0.336
H	MeCN	297	346	49	0.112	40844.0	1.3460	0.333
F	MeCN	296	346	50	0.076	28906.5	1.3460	0.347
OMe	MeCN	304	369	65	0.158	51515.4	1.3460	0.297
CN	DCE	314	352	38	0.363	96899.2	1.4448	0.281
H	DCE	298	346	48	0.157	38441.3	1.4448	0.257
F	DCE	299	346	47	0.124	27725.3	1.4448	0.235
OMe	DCE	308	368	60	0.211	51679.6	1.4448	0.257
CN	EtOAc	312	348	36	0.306	118760.7	1.3720	0.368
H	EtOAc	297	344	47	0.097	43464.0	1.3720	0.425
F	EtOAc	297	343	46	0.081	39862.7	1.3720	0.466
OMe	EtOAc	305	365	60	0.214	66321.1	1.3720	0.294
CN	THF	313	349	36	0.27	93017.5	1.4070	0.343
H	THF	300	344	44	0.134	51646.0	1.4070	0.384
F	THF	302	343	41	0.154	54748.2	1.4070	0.354
OMe	THF	306	364	58	0.219	69518.7	1.4070	0.316

Figure S3-7-1. Photoluminescent spectra of 2a in different solvents

Figure S3-7-2. Photoluminescent spectra of 1e in different solvents

Figure S3-7-3. Photoluminescent spectra of 2b in different solvents

Figure S3-7-4. Photoluminescent spectra of 2d in different solvents

Calculated HUMO-LUMO energy gaps

Figure S3-8. HOMO and LUMO orbitals of compounds 3.2d, 3.3g and N-1-3.1e'

Calculated HOMO and LUMO energy gaps of 3.1e to 3.3o

	excitation (λ_{max})	emission (λ_{max})	Φ	Fluorescence Intensity ($\times 10^3$)	Stoke shift (nm)	Eg (eV)	LUMO- HOMO (eV)
3.1e	298	347	0.34	46.3	49	4.16	3.95
3.2a	312	350	0.31	138	38	3.97	3.6
3.2b	298	343	0.34	35	45	4.16	4.06
3.2c	292	344	0.35	72.1	52	4.25	4.06
3.2d	304	374	0.31	61.6	70	4.08	3.94
3.3a	278	343	0.39	35.2	65	4.46	4.29
3.3b	305	351	0.51	99.1	46	4.07	3.94
3.3c	277	343	0.4	45.5	66	4.48	4.78
3.3d	279	343	0.25	79.6	64	4.44	4.77
3.3e	280	373	0.33	96.3	93	4.43	4.21
3.3f	284	360	0.39	82.2	76	4.37	4.34
3.3g	318	401	0.32	111	83	3.9	3.73
3.3h	283	360	0.34	78.6	77	4.38	4.51
3.3i	287	364	0.34	89.8	77	4.32	4.51
3.3j	284	369	0.34	114	85	4.37	3.72
3.3k	280	341	0.35	134	61	4.43	4.27
3.3l	306	352	0.45	174	46	4.05	3.9
3.3m	281	343	0.41	77.3	62	4.41	4.04
3.3n	283	345	0.36	99	62	4.38	4.03
3.3o	285	376	0.35	101	91	4.35	4.16

1.2. NMR Spectra Data

¹H 600MHz NMR
1.2.3a

^{13}C 150MHz NMR
1.2.3a

¹H 600MHz NMR
N-1-1.2.3a

¹H 600MHz NMR
1.2.3b

^{13}C 150MHz NMR
1.2.3b

¹H 600MHz NMR
N-1-1.2.3b

¹H 600MHz NMR
1.2.3c

^{13}C 150MHz NMR
1.2.3c

^{13}C 150MHz NMR
1.2.3d

¹H 600MHz NMR
1.2.3e

^{13}C 150MHz NMR
1.2.3e

¹³C 150MHz NMR
1.2.5a

¹H 600MHz NMR
1.2.5b

^{13}C 150MHz NMR
1.2.5b

¹H 600MHz NMR
N-1-1.2.5b

^{13}C 150MHz NMR
N-1-1.2.5b

¹H 600MHz NMR
N-1-1.2.5c

¹H 600MHz NMR
1.2.5e

^{13}C 150MHz NMR
1.2.5e

¹H 600MHz NMR
1.2.5g

¹³C 150MHz NMR
1.2.5g

¹H 600MHz NMR
1.2.5h

^{13}C 150MHz NMR
1.2.5h

¹H 600MHz NMR
1.2.5i

^{13}C 150MHz NMR
1.2.5i

^{13}C 150MHz NMR
1.2.5j

¹H 600MHz NMR
N-3-1.2.5j

^{13}C 150MHz NMR
N-3-1.2.5j

¹H 600MHz NMR
1.2.5k

¹H 600MHz NMR
1.2.5I

¹H 600MHz NMR
1.2.5m

^{13}C 150MHz NMR
1.2.5n

¹H 600MHz NMR
1.2.5o

¹H 600MHz NMR
1.2.5p

**¹H 600MHz NMR
1.2.5s**

^{13}C 150MHz NMR
1.2.5s

¹H 600MHz NMR
1.2.5t

^{13}C 150MHz NMR
1.2.5t

¹H 600MHz NMR
1.2.5u

¹H 600MHz NMR
1.2.5v

^{13}C 150MHz NMR
1.2.5v

¹H 600MHz NMR
1.2.7a

^{13}C 150MHz NMR
1.2.7a

¹H 600MHz NMR
1.2.7b

^{13}C 150MHz NMR
1.2.7b

¹H 600MHz NMR
1.2.7c

^{13}C 150MHz NMR
1.2.7c

¹H 600MHz NMR
1.2.7d

^{13}C 150MHz NMR
1.2.7d

¹H 600MHz NMR
1.2.7e

^{13}C 150MHz NMR
1.2.7e

¹H 600MHz NMR
1.2.7f

^{13}C 150MHz NMR
1.2.7f

1.3. NMR Spectra Data

¹H 600 MHz NMR
1.3.3a

^{13}C 150 MHz NMR
1.3.3a

**¹H 600 MHz NMR
1.3.3b**

^{13}C 150 MHz NMR
1.3.3b

¹H 600 MHz NMR
1.3.3c

¹³C 150 MHz NMR
1.3.3c

¹H 600 MHz NMR
1.3.3d

^{13}C 150 MHz NMR
1.3.3d

¹H 600 MHz NMR
1.3.3e

^{13}C 150 MHz NMR
1.3.3e

¹H 600 MHz NMR
1.3.3f

¹³C 150 MHz NMR
1.3.3f

^1H 600 MHz NMR
1.3.3g

^{13}C 150 MHz NMR
1.3.3g

**¹H 600 MHz NMR
1.3.4a(N2)**

^{13}C 150 MHz NMR
1.3.4a(N2)

**¹H 600 MHz NMR
1.3.4a(N1)**

**¹³C 150 MHz NMR
1.3.4a(N1)**

**¹H 600 MHz NMR
1.3.4b(N2)**

**^{13}C 150 MHz NMR
1.3.4b(N2)**

**¹H 600 MHz NMR
1.3.4b(N1)**

**^{13}C 150 MHz NMR
1.3.4b(N1)**

**¹H 600 MHz NMR
1.3.4c(N2)**

**¹³C 150 MHz NMR
1.3.4c(N2)**

**¹H 600 MHz NMR
1.3.4c(N1)**

^{13}C 150 MHz NMR
1.3.4c(N1)

**¹H 600 MHz NMR
1.3.4d(N2)**

**^{13}C 150 MHz NMR
1.3.4d(N2)**

**¹H 600 MHz NMR
1.3.4d(N1)**

11
10
9
8
7
6
5
4
3
2
1
-0
ppm

200
180
160
140
120
100
80
60
40
20
0
ppm

**¹³C 150 MHz NMR
1.3.4d(N1)**

¹H 600 MHz NMR
1.3.4d(N3)

¹³C 150 MHz NMR
1.3.4d(N3)

**¹H 600 MHz NMR
1.3.4e(N2)**

^{13}C 150 MHz NMR
1.3.4e(N2)

**¹H 600 MHz NMR
1.3.4e(N1)**

^{13}C 150 MHz NMR
1.3.4e(N1)

¹H 600 MHz NMR
1.3.4f(N2)

¹H 600 MHz NMR
1.3.4g(N2)

^{13}C 150 MHz NMR
1.3.4g(N2)

¹H 600 MHz NMR
1.3.4g(N1)

^{13}C 150 MHz NMR
1.3.4g(N1)

**¹H 600 MHz NMR
1.3.4h(N2)**

^{13}C 150 MHz NMR
1.3.4h(N2)

**¹H 600 MHz NMR
1.3.4h(N1)**

**¹³C 150 MHz NMR
1.3.4h(N1)**

**^1H 600 MHz NMR
1.3.4i(N2)**

^{13}C 150 MHz NMR
1.3.4i(N2)

1.4. NMR Spectra Data

1.4.3a (N-1)
600MHz ^1H NMR

1.4.3a (N-1)
150MHz ^{13}C NMR

1.4.3b (N-1)
600MHz ^1H NMR

1.4.3b (N-1)
150MHz ^{13}C NMR

1.4.3b (N-2)
600MHz ^1H NMR

1.4.3b (N-2)
150MHz ^{13}C NMR

1.4.3c (N-1)
600MHz ^1H NMR

1.4.3c (N-1)
150MHz ^{13}C NMR

1.4.3c (N-2)
600MHz ^1H NMR

1.4.3c (N-2)
150MHz ^{13}C NMR

1.4.3d (N-1)
600MHz ^1H NMR

1.4.3d (N-1)
150MHz ^{13}C NMR

1.4.3e (N-1)
600MHz ^1H NMR

1.4.3e (N-1)
150MHz ^{13}C NMR

1.4.3f (N-1)
600MHz ^1H NMR

1.4.3f (N-1)
150MHz ^{13}C NMR

1.4.3f (N-2)
600MHz ^1H NMR

1.4.3f (N-2)
150MHz ^{13}C NMR

1.4.3g (N-2)
600MHz ^1H NMR

1.4.3g (N-2)
150MHz ^{13}C NMR

1.4.3h (N-1)
600MHz ^1H NMR

1.4.3h (N-1)
150MHz ^{13}C NMR

1.4.3i (N-1)
600MHz ^1H NMR

1.4.3i (N-1)
150MHz ^{13}C NMR

3j (N-1)
150MHz ¹³C NMR

1.4.3j (N-2)
600MHz ^1H NMR

1.4.3j (N-2)
150MHz ^{13}C NMR

1.4.3k (N-1)
600MHz ^1H NMR

1.4.3k (N-1)
150MHz ^{13}C NMR

1.4.3k (N-2)
600MHz ^1H NMR

1.4.3k (N-2)
150MHz ^{13}C NMR

1.4.3I (N-1)
600MHz ^1H NMR

1.4.3I (N-1)
150MHz ^{13}C NMR

1.4.3m (N-1)
600MHz ^1H NMR

1.4.3m (N-1)
150MHz ^{13}C NMR

1.4.3m (N-2)
600MHz ^1H NMR

1.4.3m (N-2)
150MHz ^{13}C NMR

1.4.3n (N-1)
600MHz ^1H NMR

1.4.3n (N-1)
150MHz ^{13}C NMR

1.4.3o (N-2)
600MHz ^1H NMR

1.4.3o (N-2)
150MHz ^{13}C NMR

1.4.3p (N-1)
600MHz ^1H NMR

1.4.3p (N-1)
150MHz ^{13}C NMR

1.4.3p (N-2)
600MHz ^1H NMR

1.4.3p (N-2)
150MHz ¹³C NMR

1.4.3q (N-1)
600MHz ^1H NMR

1.4.3q (N-1)
150MHz ^{13}C NMR

1.4.3r (N-1)
600MHz ^1H NMR

1.4.3r (N-1)
150MHz ^{13}C NMR

1.4.3s (N-1)
150MHz ^{13}C NMR

1.4.5a
600MHz ^1H NMR

1.4.5a
150MHz ¹³C NMR

1.4.5b
600MHz ^1H NMR

1.4.5b
150MHz ^{13}C NMR

1.4.5c
150MHz ^{13}C NMR

1.4.5d
600MHz ^1H NMR

1.4.5d
150MHz ¹³C NMR

1.4.5e
600MHz ^1H NMR

1.4.5e
150MHz ^{13}C NMR

1.4.5f
600MHz ^1H NMR

1.4.5g
600MHz ^1H NMR

1.4.5g
150MHz ^{13}C NMR

1.4.5h
600MHz ^1H NMR

1.4.5h
150MHz ^{13}C NMR

1.5. NMR Spectra Data

^{13}C 150 MHz NMR
1.5.4a

¹H 600 MHz NMR
1.5.4b

¹H 600 MHz NMR
1.5.4c

¹H 600 MHz NMR
1.5.4d

^{13}C 150 MHz NMR
1.5.4d

¹H 600 MHz NMR
1.5.4e

^{13}C 150 MHz NMR
1.5.4e

¹H 600 MHz NMR
1.5.4f

^{13}C 150 MHz NMR
1.5.4f

¹H 600 MHz NMR
1.5.4g

^{13}C 150 MHz NMR
1.5.4g

¹H 600 MHz NMR
1.5.4h

^{13}C 150 MHz NMR
1.5.4h

¹H 600 MHz NMR
1.5.4I

^{13}C 150 MHz NMR
1.5.4I

¹H 600 MHz NMR
N-2-1.5.4m

^{13}C 150 MHz NMR
N-2-1.5.4m

¹H 600 MHz NMR
N-1-1.5.4m

^{13}C 150 MHz NMR
N-1-1.5.4m

¹H 600 MHz NMR
N-2-1.5.4m'

^{13}C 150 MHz NMR
N-2-1.5.4m'

**¹H 600 MHz NMR
N-1-1.5.4m'**

¹³C 150 MHz NMR
N-1-1.5.4m'

¹H 600 MHz NMR
N-2-1.5.4n

^{13}C 150 MHz NMR
N-2-1.5.4n

¹H 600 MHz NMR
N-1-1.5.4n

^{13}C 150 MHz NMR
N-1-1.5.4n

¹H 600 MHz NMR
N-2-1.5.4o

^{13}C 150 MHz NMR
N-2-1.5.4o

¹H 600 MHz NMR
N-1-1.5.4o

^{13}C 150 MHz NMR
N-1-1.5.4o

¹H 600 MHz NMR
N-2-1.5.4o'

^{13}C 150 MHz NMR
N-2-1.5.4o'

¹H 600 MHz NMR
N-1-1.5.4o'

¹³C 150 MHz NMR
N-1-1.5.4o'

¹H 600 MHz NMR
N-2-1.5.4p

^{13}C 150 MHz NMR
N-2-1.5.4p

¹H 600 MHz NMR
N-1-1.5.4p

^{13}C 150 MHz NMR
N-1-1.5.4p

¹H 600 MHz NMR
N-2-1.5.4p'

^{13}C 150 MHz NMR
N-2-1.5.4p'

¹H 600 MHz NMR
N-1-1.5.4p'

¹H 600 MHz NMR
N-2-1.5.4q

^{13}C 150 MHz NMR
N-2-1.5.4q

¹H 600 MHz NMR
N-1-1.5.4q

¹³C 150 MHz NMR
N-1-1.5.4q

¹H 600 MHz NMR
N-2-1.5.4q'

^{13}C 150 MHz NMR
N-2-1.5.4q'

¹H 600 MHz NMR
N-1-1.5.4q'

^{13}C 150 MHz NMR
N-1-1.5.4q'

^{13}C 150 MHz NMR
N-2-1.5.4r

¹H 600 MHz NMR
N-2-1.5.4r'

^{13}C 150 MHz NMR
N-2-1.5.4r'

¹H 600 MHz NMR
N-2-1.5.4s

^{13}C 150 MHz NMR
N-2-1.5.4s

¹H 600 MHz NMR
N-1-1.5.4s

^{13}C 150 MHz NMR
N-1-1.5.4s

¹H 600 MHz NMR
1.5.4t

^1H 600 MHz NMR
1.5.4u

^1H 600 MHz NMR
1.5.4v

^{13}C 150 MHz NMR
1.5.4v

¹H 600 MHz NMR
1.5.4w

^{13}C 150 MHz NMR
1.5.4w

¹H 600 MHz NMR
1.5.4x

¹³C 150 MHz NMR
1.5.4x

^1H 600 MHz NMR
1.5.4y

^{13}C 150 MHz NMR
1.5.4y

¹H 600 MHz NMR
N-2-1.5.4z

^{13}C 150 MHz NMR
N-2-1.5.4z

¹H 600 MHz NMR
N-1-1.5.4z

^{13}C 150 MHz NMR
N-1-1.5.4z

^{13}C 150 MHz NMR
N-2-1.5.4z'

¹H 600 MHz NMR
N-1-1.5.4z'

^{13}C 150 MHz NMR
N-1-1.5.4z'

¹H 600 MHz NMR
1.5.7a

^{13}C 150 MHz NMR
1.5.7a

1.6. HPLC Data and NMR Spectra Data

(R)-N-1-1.6.7a

1: 254 nm, 4 nm Results

Retention Time	Area	Area %
12.996	207380294	44.04
18.532	263554817	55.96
Totals	470935111	100.00

1: 254 nm, 4 nm Results

Retention Time	Area	Area %
14.080	1202352	2.17
19.856	54129512	97.83
Totals	55331864	100.00

¹H 600MHz NMR
N-2-1.6.3a

^{13}C 150MHz NMR
N-2-1.6.3a

¹H 600MHz NMR
N-1-1.6.3a

^{13}C 150MHz NMR
N-1-1.6.3a

¹H 600MHz NMR
N-2-1.6.3b

^{13}C 150MHz NMR
N-2-1.6.3b

¹H 600MHz NMR
N-1-1.6.3b

^{13}C 150MHz NMR
N-1-1.6.3b

¹H 600MHz NMR
N-2-1.6.3c

^{13}C 150MHz NMR
N-2-1.6.3c

¹H 600MHz NMR
N-1-1.6.3c

^{13}C 150MHz NMR
N-1-1.6.3c

¹H 600 MHz NMR
N-2-1.6.3d

^{13}C 150 MHz NMR
N-2-1.6.3d

¹H 600 MHz NMR
N-1-1.6.3d

^{13}C 150 MHz NMR
N-1-1.6.3d

¹H 600 MHz NMR
N-2-1.6.3e

^{13}C 150 MHz NMR
N-2-1.6.3e

¹H 600 MHz NMR
N-1-1.6.3e

^{13}C 150 MHz NMR
N-1-1.6.3e

¹H 600 MHz NMR
N-2-1.6.3f

^{13}C 150 MHz NMR
N-2-1.6.3f

¹H 600 MHz NMR
N-1-1.6.3f

^{13}C 150 MHz NMR
N-1-1.6.3f

¹H 600 MHz NMR
N-2-1.6.3g

^{13}C 150 MHz NMR
N-2-1.6.3g

¹H 600 MHz NMR
N-1-1.6.3g

^{13}C 150 MHz NMR
N-1-1.6.3g

¹H 600 MHz NMR
N-2-1.6.3h

^{13}C 150 MHz NMR
N-2-1.6.3h

^1H 600 MHz NMR
N-1-1.6.3h

^{13}C 150 MHz NMR
N-1-1.6.3h

^1H 600 MHz NMR
N-2-1.6.3i

^{13}C 150 MHz NMR
N-2-1.6.3i

¹H 600 MHz NMR
N-1-1.6.3i

^{13}C 150 MHz NMR
N-1-1.6.3i

¹H 600 MHz NMR
N-2-1.6.3j

^{13}C 150 MHz NMR
N-2-1.6.3j

¹H 600 MHz NMR
N-1-1.6.3j

^{13}C 150 MHz NMR
N-1-1.6.3j

¹H 600 MHz NMR
N-2-1.6.3k

^{13}C 150 MHz NMR
N-2-1.6.3k

¹H 600 MHz NMR
N-1-1.6.3k

^{13}C 150 MHz NMR
N-1-1.6.3k

¹H 600 MHz NMR
N-2-1.6.3I

^{13}C 150 MHz NMR
N-2-1.6.3I

¹H 600 MHz NMR
N-1-1.6.3I

^{13}C 150 MHz NMR
N-1-1.6.3I

¹H 600 MHz NMR
N-2-1.6.3m

¹³C 150 MHz NMR
N-2-1.6.3m

¹H 600 MHz NMR
N-1-1.6.3m

^{13}C 150 MHz NMR
N-1-1.6.3m

^1H 600 MHz NMR
N-2-1.6.4a

^{13}C 150 MHz NMR
N-2-1.6.4a

^{13}C 150 MHz NMR
N-1-1.6.4a

¹H 600 MHz NMR
N-2-1.6.4b

^{13}C 150 MHz NMR
N-2-1.6.4b

¹H 600 MHz NMR
N-1-1.6.4b

^{13}C 150 MHz NMR
N-1-1.6.4b

¹H 600 MHz NMR
N-2-1.6.4c

^{13}C 150 MHz NMR
N-2-1.6.4c

¹H 600 MHz NMR
N-1-1.6.4c

^{13}C 150 MHz NMR
N-1-1.6.4c

¹H 600 MHz NMR
N-2-1.6.4d

^{13}C 150 MHz NMR
N-2-1.6.4d

¹H 600 MHz NMR
N-1-1.6.4d

^{13}C 150 MHz NMR
N-1-1.6.4d

¹H 600 MHz NMR
N-2-1.6.4e

^{13}C 150 MHz NMR
N-2-1.6.4e

¹H 600 MHz NMR
N-1-1.6.4e

^{13}C 150 MHz NMR
N-1-1.6.4e

¹H 600 MHz NMR
N-2-1.6.4f

^{13}C 150 MHz NMR
N-2-1.6.4f

^{13}C 150 MHz NMR
N-1-1.6.4f

^{13}C 150 MHz NMR
N-2-1.6.4j

^{13}C 150 MHz NMR
N-2-1.6.4k

^{13}C 150 MHz NMR
N-2-1.6.4I

¹H 600 MHz NMR
1.6.5a

^{13}C 150 MHz NMR
1.6.5a

¹H 600 MHz NMR
1.6.5b

^{13}C 150 MHz NMR
1.6.5b

¹H 600 MHz NMR
1.6.5c

^{13}C 150 MHz NMR
1.6.5c

¹H 600 MHz NMR
1.6.5d

^{13}C 150 MHz NMR
1.6.5d

¹H 600 MHz NMR
1.6.5e

^{13}C 150 MHz NMR
1.6.5e

¹H 600 MHz NMR
1.6.5f

¹H 600 MHz NMR
N-2-1.6.6a

^{13}C 150 MHz NMR
N-2-1.6.6a

¹H 600 MHz NMR
N-1-1.6.6a

^{13}C 150 MHz NMR
N-1-1.6.6a

¹H 600 MHz NMR
N-2-1.6.6b

¹³C 150 MHz NMR
N-2-1.6.6b

¹H 600 MHz NMR
N-1-1.6.6b

^{13}C 150 MHz NMR
N-1-1.6.6b

¹H 600 MHz NMR
N-2-1.6.6c

^{13}C 150 MHz NMR
N-2-1.6.6c

^1H 600 MHz NMR
N-1-1.6.6c

^{13}C 150 MHz NMR
N-1-1.6.6c

¹H 600 MHz NMR
N-2-1.6.6d

^{13}C 150 MHz NMR
N-2-1.6.6d

¹H 600 MHz NMR
N-1-1.6.6d

^{13}C 150 MHz NMR
N-1-1.6.6d

¹H 600 MHz NMR
(*R*)-N-2-1.6.7a

^{13}C 150 MHz NMR
(*R*)-N-2-1.6.7a

¹H 600 MHz NMR
(*R*)-N-1-1.6.7a

^{13}C 150 MHz NMR
(*R*)-N-1-1.6.7a

¹H 600 MHz NMR
N-2-1.6.7b

¹³C 150 MHz NMR
N-2-1.6.7b

¹H 600 MHz NMR
N-1-1.6.7b

^{13}C 150 MHz NMR
N-1-1.6.7b

2.2. NMR Spectra Data

^1H 600 MHz NMR
2.2.1

^{13}C 150 MHz NMR
2.2.1

^1H 600 MHz NMR
2.2.3e

^{13}C 150 MHz NMR
2.2.3e

^1H 600 MHz NMR
2.2.3f

^{13}C 150 MHz NMR
2.2.3f

¹H 600 MHz NMR
[Ir(bbpy)(ArTriaz)₂]Cl 2.2.4

^{13}C 150 MHz NMR
[Ir(bbp)(ArTriaz)₂]Cl 2.2.4

^1H 600 MHz NMR
2.2.5a

^{13}C 150 MHz NMR
2.2.5a

^1H 600 MHz NMR
2.2.5b

^{13}C 150 MHz NMR
2.2.5b

¹H 600 MHz NMR
2.2.5c

^{13}C 150 MHz NMR
2.2.5c

¹H 600 MHz NMR
2.2.6a

^{13}C 150 MHz NMR
2.2.6a

2.3. NMR Spectra Data

^1H 600 MHz NMR
2.3.2a

^{13}C 150 MHz NMR
2.3.2a

¹H 600 MHz NMR
2.3.2b

^{13}C 150 MHz NMR
2.3.2b

¹H 600 MHz NMR
2.3.2c

¹³C 150 MHz NMR
2.3.2c

¹H 600 MHz NMR
2.3.2d

^{13}C 150 MHz NMR
2.3.2d

^1H 600 MHz NMR
2.3.2e

^{13}C 150 MHz NMR
2.3.2e

^1H 600 MHz NMR
2.3.2f

^{13}C 150 MHz NMR
2.3.2f

¹H 600 MHz NMR
2.3.2g

^{13}C 150 MHz NMR
2.3.2g

¹H 600 MHz NMR
2.3.2h

^{13}C 150 MHz NMR
2.3.2h

^1H 600 MHz NMR
2.3.2i

S883

^{13}C 150 MHz NMR
2.3.2i

¹H 600 MHz NMR
2.3.2j

^{13}C 150 MHz NMR
2.3.2j

^1H 600 MHz NMR
2.3.2k

¹³C 150 MHz NMR
2.3.2k

¹H 600 MHz NMR
2.3.2I

^{13}C 150 MHz NMR
2.3.2I

¹H 600 MHz NMR
2.3.2m

^{13}C 150 MHz NMR
2.3.2m

¹H 600 MHz NMR
2.3.2n

^{13}C 150 MHz NMR
2.3.2n

¹H 600 MHz NMR
2.3.2o

¹³C 150 MHz NMR
2.3.2o

¹H 600 MHz NMR
2.3.2p

^{13}C 150 MHz NMR
2.3.2p

¹H 600 MHz NMR
2.3.2q

^{13}C 150 MHz NMR
2.3.2q

¹H 600 MHz NMR
2.3.2r

^{13}C 150 MHz NMR
2.3.2r

¹H 600 MHz NMR
2.3.2s

^{13}C 150 MHz NMR
2.3.2s

¹H 600 MHz NMR
2.3.2t

¹H 600 MHz NMR
2.3.2u

^{13}C 150 MHz NMR
2.3.2u

^1H 600 MHz NMR
2.3.2v

^{13}C 150 MHz NMR
2.3.2v

^1H 600 MHz NMR
2.3.2w

^{13}C 150 MHz NMR
2.3.2w

¹H 600 MHz NMR
2.3.2x

^{13}C 150 MHz NMR
2.3.2x

^{13}C 150 MHz NMR
2.3.2y

^1H 600 MHz NMR
2.3.2z

^{13}C 150 MHz NMR
2.3.2z

¹H 600 MHz NMR
2.3.3a

^1H 600 MHz NMR
2.3.3b

^{13}C 150 MHz NMR
2.3.3b

^{13}C 150 MHz NMR
2.3.3c

¹H 600 MHz NMR
2.3.5a

^{13}C 150 MHz NMR
2.3.5a

¹H 600 MHz NMR
2.3.5b

^{13}C 150 MHz NMR
2.3.5b

¹H 600 MHz NMR
2.3.5c

^{13}C 150 MHz NMR
2.3.5c

3. NMR Spectra Data

^1H 600MHz NMR
3.1e

^{13}C 150MHz NMR
3.1e

¹H 600MHz NMR
3.2a

^{13}C 150MHz NMR
3.2a

¹H 600MHz NMR
3.2b

¹³C 150MHz NMR
3.2b

¹H 600MHz NMR
3.2c

¹³C 150MHz NMR
3.2c

¹H 600MHz NMR
3.2d

¹³C 150MHz NMR
3.2d

¹H 600MHz NMR
3.2e

^{13}C 150MHz NMR
3.2e

¹H 600MHz NMR
3.2f

^{13}C 150MHz NMR
3.2f

^1H 600MHz NMR
3.2g

¹³C 150MHz NMR
3.2g

¹H 600MHz NMR
3.2h

^{13}C 150MHz NMR
3.2h

¹H 600MHz NMR
3.2i

^{13}C 150MHz NMR
3.2i

¹H 600MHz NMR
3.3a

^{13}C 150MHz NMR
3.3a

¹H 600MHz NMR
3.3b

¹³C 150MHz NMR
3.3b

¹H 600MHz NMR
3.3c

^{13}C 150MHz NMR
3.3c

¹H 600MHz NMR

3.3d

¹³C 150MHz NMR
3.3d

¹H 600MHz NMR
3.3e

^{13}C 150MHz NMR
3.3e

¹H 600MHz NMR

3.3f

^{13}C 150MHz NMR
3.3f

¹H 600MHz NMR

3.3g

^{13}C 150MHz NMR
3.3g

^1H 600MHz NMR
3.3h

^{13}C 150MHz NMR
3.3h

¹H 600MHz NMR
3.3i

^{13}C 150MHz NMR
3.3i

¹H 600MHz NMR
3.3j

^{13}C 150MHz NMR
3.3j

¹H 600MHz NMR
3.3k

^{13}C 150MHz NMR
3.3k

¹H 600MHz NMR
3.3I

^{13}C 150MHz NMR
3.3I

¹H 600MHz NMR
3.3m

^{13}C 150MHz NMR
3.3m

¹H 600MHz NMR
3.3n

^{13}C 150MHz NMR
3.3n

¹H 600MHz NMR
3.3o

¹³C 150MHz NMR
3.3o

¹H 600MHz NMR
3.5

^{13}C 150MHz NMR
3.5

¹H 600MHz NMR
3.7

^{13}C 150MHz NMR
3.7

¹H 600MHz NMR
3.4b

^{13}C 150MHz NMR
3.4b