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## Iodine-mediated C–N and N–N bond formation: a facile one-pot synthetic approach to 1,2,3-triazoles under metal-free and azide-free conditions†

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A novel strategy towards the synthesis of 1,4-disubstituted 1,2,3-triazoles via C–N and N–N bond formation has been demonstrated under transition metal-free and azide-free conditions. These 1,2,3-triazoles were obtained in a regioselective manner from commercially available anilines, aryl alkenes/aryl alkynes and *N*-tosylhydrazines using I<sub>2</sub> under O<sub>2</sub> atmosphere. Broad substrate scope, milder reaction conditions, good to moderate yields and clean protocol are the notable features of the method. Moreover, this protocol is amenable for the generation of a library of medicinally important key building blocks.

### Introduction

Nitrogen-containing heterocyclics constitute a major class of bioactive organic compounds which are essential for life and widely distributed in natural products and synthetic pharmaceuticals.<sup>1</sup> They form a structural part of vitamins, hormones, *etc* and are fundamental for metabolism in living cells.<sup>2</sup> Their unique ability to serve as biomimetics and reactive pharmacophores has facilitated their use as low molecular weight lead molecules in drug design.<sup>3</sup> Particularly, 1,2,3-triazole contributes a noteworthy role among the pharmaceutically important nitrogen-containing heterocyclic scaffolds due to its broad spectrum of biological activities. Active pharmaceuticals based on 1,2,3-triazoles including *tert*-butyldimethylsilylspiroaminoxathioledioxide (TSAO, non-nucleoside reverse transcriptase inhibitor),<sup>4a</sup> carboxyamidotriazole (CAI, anticancer),<sup>4b</sup> cefatrizine<sup>4c</sup> and tazobactum ( $\beta$ -lactam antibiotic)<sup>4d</sup> are shown in Fig. 1. Over the past few years, our research group has significantly developed many novel 1,2,3-triazole bearing molecules with anticancer activities.<sup>4e–k</sup> Moreover, they are also reported to have anti-inflammatory,<sup>5a</sup> anticonvulsant,<sup>5b</sup> anti-viral,<sup>5c</sup> anti-histaminic,<sup>5d</sup> antileishmanial,<sup>5e</sup> peptidomimetic tyrosinase inhibitory,<sup>5f</sup> hepatitis C virus inhibitory,<sup>5g</sup> neuroleptic<sup>5h</sup> and adenosine receptor inhibitory<sup>5i</sup> properties, as well

as being conditioning agents for plant growth.<sup>5j</sup> Additionally, the 1,2,3-triazole moiety is an ideal linker that has been widely utilized in the recent past to bridge the two components in order to get the synergistic effect of the combined molecules and it is relatively resistant to hydrolysis reactions.<sup>6</sup> Beyond pharmaceutical applications, the structural features of 1,2,3-triazole facilitate to mimic various functional groups justifying its use as a bioisostere in the synthesis of biologically active molecules.<sup>7</sup> Moreover, due to the hydrogen-bonding ability of 1,2,3-triazole connecting to a poorly soluble drug could enhance their solubility aspects and accordingly a better pharmacokinetic profile is achieved.<sup>8</sup> Owing to their utility, a wide range of applications and many novel synthetic protocols have been developed by many researchers for the regioselective formation of this five-membered heterocycle and it is highly exploring motif in organic synthesis.

Numerous methodologies have been reported previously and still, many researchers are working for the development of effective new routes for the synthesis of 1,2,3-triazoles due to their valuable drug-like nature. The classical methods include Huisgen's thermally induced 1,3-dipolar cycloaddition of

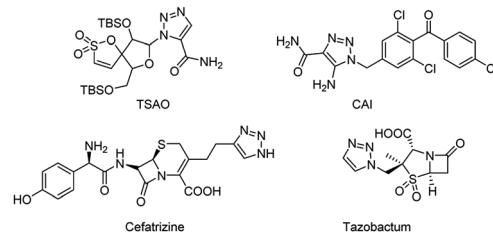


Fig. 1 Representative biologically active molecules containing 1,2,3-triazole.

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alkynes and azides.<sup>9</sup> However, it is well-known that this method suffers from the limited substrate scope and poor regioselectivity. Subsequently, Sharpless and Meldel groups independently proposed a copper-catalyzed azide–alkyne cycloaddition (CuAAC) for the synthesis of 1,2,3-triazoles which is a highly regioselective and straight forward method.<sup>10</sup> This approach made 1,2,3-triazole more accessible in organic synthesis. Later, numerous methods have been developed for the synthesis of 1,2,3-triazoles comprising the use of metal triflates,<sup>11</sup> expensive metal catalyst complexes,<sup>12</sup> organocatalysts,<sup>13</sup> ionic liquids,<sup>14</sup> microwaves,<sup>15</sup> polymers,<sup>16</sup> bases,<sup>17</sup> etc. However, most of these reported methods utilized heavy metals (Cu, Pd, Ru, Ir) which limit their use in the biological, environmental point of views due to their hazardous nature and toxicity profile. Moreover, organic azides are also exploited which are likely to explode and difficult to handle on large scale. Consequently, a great deal of interest was diverted towards the development of simple, metal-free and azide-free approaches for the synthesis of these attractive scaffolds,<sup>18</sup> because metal free approaches are very lucrative on account of being inexpensive and environmentally benign nature. However, regioselective construction of C–N, N–N bonds is quite difficult in the absence of transition metals. In this context, molecular iodine has grabbed much attention of

researchers owing to its advantages *viz.* relatively inexpensive, efficient and a green alternative to transition metals.<sup>19</sup> On the other hand, iodine is also reported to provide a mild and efficient approach involved in numerous oxidative transformations for the formation of C–C, C–N and N–N bonds.<sup>20</sup> As a part of our research program in the development of medicinally active molecules in an eco-friendly manner herein, we developed a novel method for the synthesis of 1,2,3-triazoles regioselectively in a one-pot manner by using I<sub>2</sub>/O<sub>2</sub> and DMSO as a solvent from readily accessible anilines, aryl alkynes or aryl alkenes and *N*-tosylhydrazine as substrates.

## Results and discussion

At the onset to test the feasibility of the reaction, a selected model reaction was performed using 4-methyl aniline (**1p**), phenylacetylene (**2a**) and *N*-tosyl hydrazine (**3a**) in DMSO with iodine (1.0 equiv.) at room temperature for 24 h, resulting in no desired product **4p** was observed (entry 1, Table 1). To our delight, **4p** was obtained in low yield (10%) when we performed the reaction at 100 °C for 12 h (entry 2, Table 1). In order to improve the yield of **4p**, we further screened different oxidants, solvents, catalysts, amount of catalyst as well as reaction

Table 1 Optimisation of the reaction conditions<sup>a</sup>

Entry	Additive (equiv.)	Oxidant (equiv.)	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	I <sub>2</sub> (1.0)	—	DMSO	rt	24	NF
2	I <sub>2</sub> (1.0)	—	DMSO	100	12	10
3	I <sub>2</sub> (1.0)	O <sub>2</sub>	DMSO	100	6	76
4	I <sub>2</sub> (1.0)	TBHP (1)	DMSO	100	6	68
5	I <sub>2</sub> (1.0)	Oxone (1)	DMSO	100	6	56
6	I <sub>2</sub> (1.0)	PhI(OAc) <sub>2</sub> (1)	DMSO	100	6	26
7	I <sub>2</sub> (1.0)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1)	DMSO	100	6	38
8	I <sub>2</sub> (1.0)	O <sub>2</sub>	toluene	100	6	NF
9	I <sub>2</sub> (1.0)	O <sub>2</sub>	DMF	100	6	56
10	I <sub>2</sub> (1.0)	O <sub>2</sub>	1,4-Dioxane	100	6	32
11	I <sub>2</sub> (1.0)	O <sub>2</sub>	CH <sub>3</sub> CN	80	6	12
12	KI (1.0)	O <sub>2</sub>	DMSO	100	6	10
13	NIS (1.0)	O <sub>2</sub>	DMSO	100	6	34
14	TBAI (1.0)	O <sub>2</sub>	DMSO	100	6	28
15	—	O <sub>2</sub>	DMSO	100	24	NF
16	I <sub>2</sub> (1.0)	O <sub>2</sub>	—	100	6	trace
17	I <sub>2</sub> (1.2)	O <sub>2</sub>	DMSO	100	6	82
18	I <sub>2</sub> (1.5)	O <sub>2</sub>	DMSO	100	6	78
19	I <sub>2</sub> (0.8)	O <sub>2</sub>	DMSO	100	6	71
20	I <sub>2</sub> (1.2) <sup>c</sup>	O <sub>2</sub>	DMSO	100	6	86
21	I <sub>2</sub> (1.2) <sup>c</sup>	O <sub>2</sub>	DMSO	120	4	89
22	I <sub>2</sub> (1.2) <sup>c</sup>	O <sub>2</sub>	DMSO	80	12	68
23	I <sub>2</sub> (1.2) <sup>c</sup>	O <sub>2</sub>	DMSO	150	4	87

<sup>a</sup> All reactions were performed with **1p** (1 mmol), **2a** (1.1 mmol), and **3a** (1.5 mmol) in presence of I<sub>2</sub> (1.2 equiv.) and under O<sub>2</sub> at 120 °C for 6 h.

<sup>b</sup> Isolated yields. <sup>c</sup> Iodine was added to a solution of **1p** (1 mmol), **2a** (1.1 mmol) and allowed to stir for 1 h followed by addition of **3a** (1.5 mmol) under O<sub>2</sub> at 120 °C for 4 h. NF – Not Formed. TBHP = *tert*-butyl hydroperoxide (70% in water), DMSO = dimethyl sulfoxide, DMF = dimethyl formamide.

temperature. Interestingly, reaction yield was increased to a greater extent providing the formation of **4p** with 76% yield, when the reaction mixture was heated to 100 °C for 6 h in the presence of oxygen (entry 3, Table 1). Encouraged by the above result, common oxidants namely TBHP, oxone, PhI(OAc)<sub>2</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (entries 4–7, Table 1) were screened and O<sub>2</sub> was found to be a suitable oxidant. DMSO played a crucial role in this reaction and found to be the best solvent when compared to other tested solvents such as DMF, 1,4-dioxane and CH<sub>3</sub>CN found to deliver the required product with inferior yields (entries 9–11, Table 1). In non-polar solvent such as toluene, under optimized reaction conditions, product **4p** was not formed (entry 8, Table 1). Next, we screened various iodine-containing catalysts such as potassium iodide (KI), *N*-iodosuccinimide (NIS) and tetrabutylammonium iodide (TBAI) in DMSO to check the feasibility of the reaction (entry 12–14, Table 1).

However, all the tested iodine sources were found to be ineffective as they deliver the product **4p** with reduced yields. While in the absence of iodine, product **4p** was not produced (entry 15, Table 1). The desired product **4p** was obtained in trace amounts in the absence of solvent (entry 16, Table 1). The reduced yield of **4p** is due to the low solubility of reactants. After establishing a suitable oxidant, solvent, and catalyst for the synthesis of 1,2,3-triazole, we focussed our interest in the quantity of iodine. Interestingly, improvement in the yield of **4p** was observed when the stoichiometric amount of iodine was increased to 1.2 equiv. (entry 17, Table 1). The molecular iodine was revived *in situ* from iodide anions. Hence, the reaction proceeded well only with 1.2 equiv. of iodine. However, a further increase in the amount of iodine (entry 18, Table 1) did not improve the yield. Further, reaction efficiency was improved to a smaller extent providing an increased yield of **4p** with 86%, when iodine (1.2 equiv.) was added to a solution of **1p** (1 mmol), **2a** (1.1 mmol) and stirred at 100 °C for 1 h under oxygen atmosphere followed by addition of **3a** (1.5 mmol) (entry 20, Table 1). To our delight, the yield of **4p** was increased to 89%, when the reaction was performed with 1.2 equiv. of iodine at 120 °C for 4 h (entry 21, Table 1). Further, increase or decrease in the temperature leads to a negative impact on the yield of **4p** (entries 22–23, Table 1). Therefore, systematic screening of the reaction conditions revealed that iodine (1.2 equiv.)/O<sub>2</sub> atmosphere in DMSO at 120 °C is the optimal choice for the formation of 1,2,3-triazoles.

After achieving the optimized conditions, we have explored the generality and substrate scope of the present protocol. Hence, a diverse range of anilines **1a–t** were treated with phenylacetylene (**2a**) and *N*-tosyl hydrazine (**3a**) under optimized reaction conditions to afford the corresponding products **4a–t** in a moderate to good yields (25–89%, Table 2). As shown in Table 2, it was observed that electron with-drawing group bearing anilines including halo groups like fluoro, chloro, bromo, and iodo (**4b–h**) were well tolerated to furnish the desired products with good yields. It was noted that the corresponding products obtained in these reactions act as potential substrates for further functionalizations. Substrates having electron deficient trifluoromethyl (**4i**), nitro (**4j**), and ester (**4k**) groups displayed good tolerance towards the reaction yields

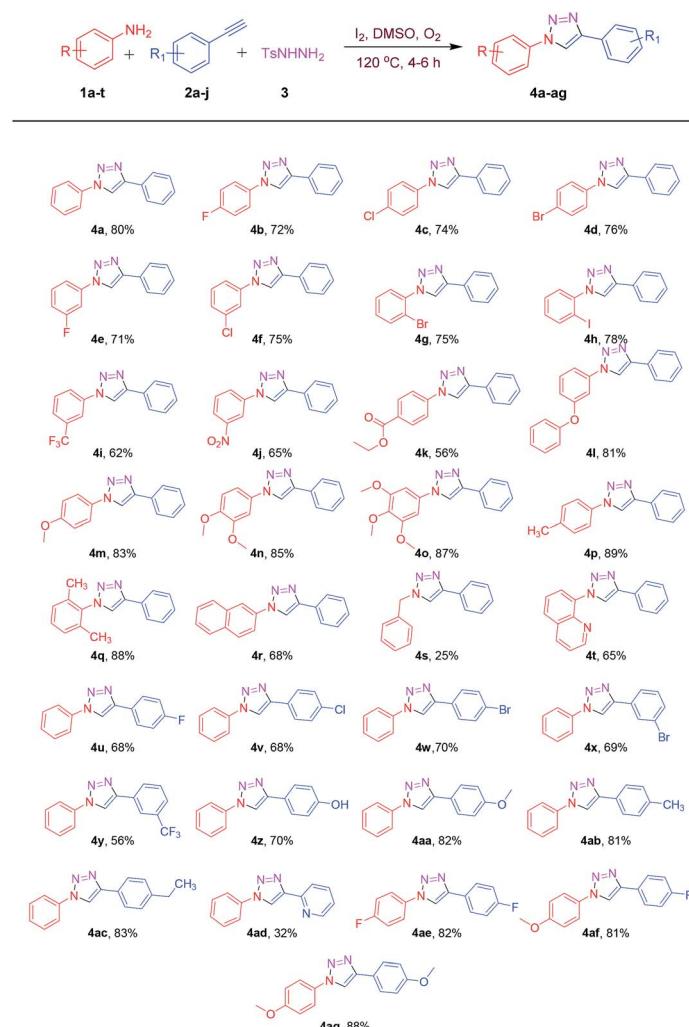
provided 62%, 65%, and 56% respectively. However, an electron donating groups like phenoxy, methyl, and methoxy containing anilines **4l–q** showed high reactivity with excellent yields as shown in Table 2. Moreover, the position of substituents on the aromatic ring of anilines had a little influence on the yield of the products. 2-Naphthylamine (**1r**) was also readily participated in the reaction to afford product **4r** in 68% yield. Interestingly, the reaction proceeded with benzylamine (**4s**) under optimized condition albeit at lower yield (25%). Unluckily, the complex mixture was observed when we attempted this protocol with aliphatic and propargyl amine. Furthermore, heteroaryl aniline such as 8-aminoquinoline (**1t**) was also served well to generate the corresponding product in good yield (**4t**, 65%). In addition, 8-aminoquinoline is a core structure in many antimalarial drugs (primaquine, pamaquine, *etc.*).<sup>21</sup> The antimalarial properties of a molecule can be readily modulated with respect to structure–activity parameters by attaching new fragments on a conventional 8-aminoquinoline pharmacophore, for example, compound **4t**. By applying this efficient method, a tail fragment can be easily incorporated on established pharmacophore in a one-pot manner.

With the consistent results of this protocol, we have also applied this new approach towards a range of aryl alkynes **2a–j** (Table 2). To our delight, aromatic ring of aryl alkyne bearing electron rich and electron deficient groups reacted smoothly under these optimized conditions to furnish the corresponding 1,2,3-triazoles **4u–ad** with moderate to good yields as shown in Table 2. Aryl alkynes substituted with electron donating groups like hydroxyl (**2f**), methoxy (**2g**), methyl (**2h**) and ethyl (**2i**) participated efficiently to offer the corresponding products **4z** (70%), **4aa** (82%), **4ab** (81%), **4ac** (83%) respectively in good yields (Table 2). However, the substrates with electron with-drawing fluoro, chloro, bromo, trifluoromethyl (**2a–e**) groups delivered the corresponding 1,2,3-triazoles with moderate yields and longer reaction times (**4u–y**, Table 2). Investigation with 2-ethynyl pyridine (**2j**) was also found to be fruitful with the current strategy but the reaction proceeded sluggishly to offer the corresponding product **4ad** in low yield *i.e.* 32% (Table 2). However, the extension of the reaction towards aliphatic alkynes and propargyl derivatives were failed to yield the desired products. Subsequently, we performed the reaction with substituted anilines, substituted aryl alkynes, and *N*-tosyl hydrazine. The reaction proceeded efficiently as expected to deliver the corresponding products **4ae–ag** in decent yields (Table 2).

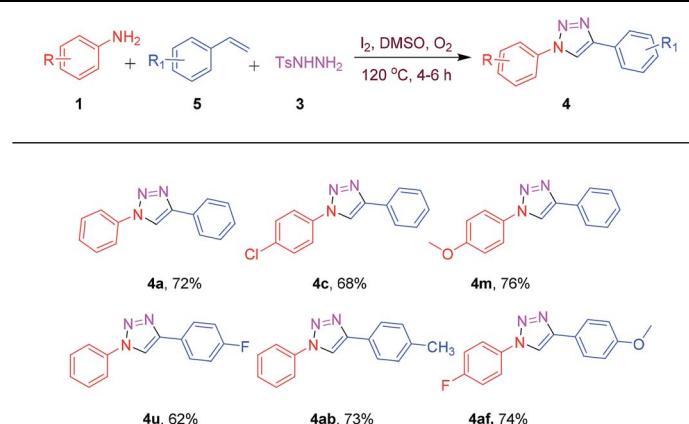
Encouraged by the above results, in order to expand the synthetic applicability of the present protocol, we replaced the terminal aryl alkyne functionality with terminal aryl alkene. To our delight, the reactions proceeded successfully under standard conditions. Aryl alkenes and anilines bearing electron donating and electron withdrawing groups reacted efficiently to deliver a valuable 1,2,3-triazoles **4a**, **4c**, **4m**, **4u**, **4ab** and **4af** as shown in Table 3. Electronic nature of aryl alkenes had a little influence on the reaction efficiency, by affording all the desired products in a moderate to good yields (62–76%).

To further elucidate the synthetic competence of our protocol, a gram scale reaction was performed using **1a** (2 g,



Table 2 Substrate scope for  $I_2$  catalysed synthesis of 1,2,3-triazoles from diverse amines, phenyl acetylene and *N*-tosylhydrazine<sup>a</sup>

<sup>a</sup> All reactions were performed with **1** (1 mmol), **2a** (1.1 mmol), **3** (1.5 mmol) and  $I_2$  (1.2 mmol) in DMSO (3 mL) at 120 °C for 4–6 h.

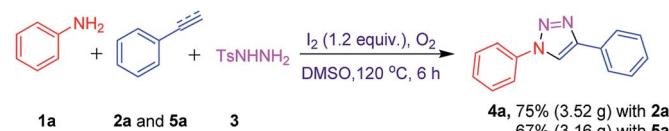
Table 3 Substrate scope for synthesis of 1,2,3-triazoles from diverse anilines, diverse aryl alkenes and *N*-tosylhydrazine<sup>a</sup>

<sup>a</sup> All reactions were performed with **1** (1 mmol), **5** (1.1 mmol), **3** (1.5 mmol) and  $I_2$  (1.2 mmol) in DMSO (3 mL) at 120 °C for 4–6 h.

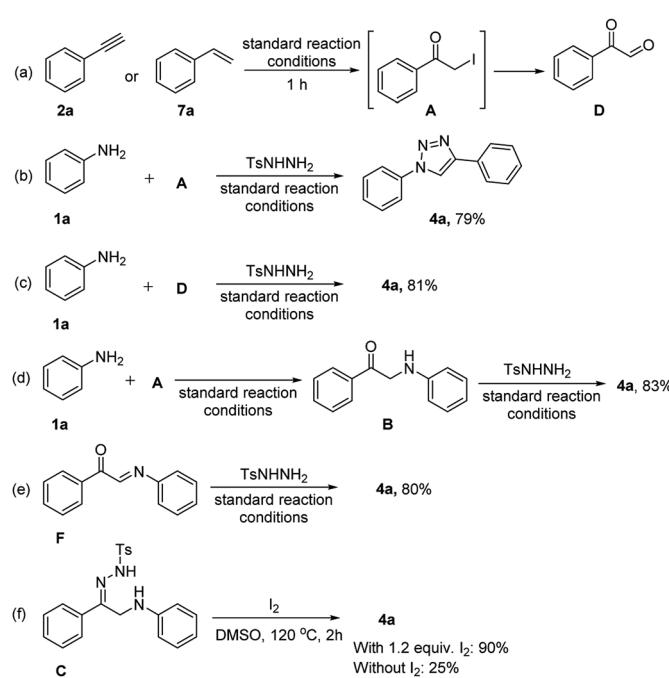


21.27 mmol), 3 (5.93 g, 31.91 mmol) with 2a (2.38 g, 23.40 mmol) and 5a (2.43 g, 23.40 mmol) under standard optimal conditions. To our delight, reaction forwarded smoothly to afford the corresponding product 4a in 75% (3.52 g) and 67% (3.16 g) isolated yields with 2a and 5a respectively (Scheme 1). Scalability of this protocol has the potential for utility in industrial scale-up operations.

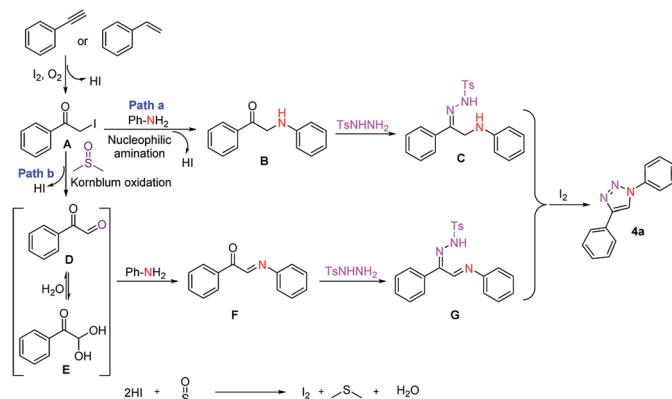
In order to understand the possible reaction mechanism, a series of control experiments were carried out subsequently (Scheme 2). In this context, we performed the reaction with phenylacetylene (2a) or styrene (7a) under optimized reaction conditions in the absence of aniline (1a) and tosyl hydrazine (3) to afford phenylglyoxal (D) in a quantitative yield (Scheme 2a). Assuming that the reaction proceeds through  $\alpha$ -iodo ketone (A) and phenylglyoxal (D) intermediates.<sup>22</sup> Next, they were treated with aniline (1a), N-tosyl hydrazine (3) under standard reaction conditions, which deliver the corresponding product 4a with good yields (Scheme 2b and c). Moreover, aniline (1a) reacted with an  $\alpha$ -iodo ketone (A) under standard optimised conditions to afford a phenylaminoethanone (B) intermediate which was cyclized to afford 4a in the presence of tosyl hydrazine (3) under optimized reaction conditions (Scheme 2d). It was found that phenyl acetylene (2a) or styrene (7a) with molecular iodine and DMSO in the presence of oxygen affords phenylglyoxal (D), subsequent addition of aniline affords a condensed



Scheme 1 Gram scale synthesis of 4a.



Scheme 2 Control experiments (a)–(f).



Scheme 3 Plausible mechanism for the iodine-catalyzed synthesis of 1,2,3-triazoles.

intermediate F. The reaction of intermediate F with N-tosyl hydrazine affords 1,2,3-triazole with 80% yield (Scheme 2e). Furthermore, intermediate C which was synthesized by a literature report,<sup>23</sup> could be smoothly cyclized and aromatized through N–N bond formation to afford the triazole product 4a with a 90% yield in the presence of iodine and 25% in the absence of iodine (Scheme 2f). However, these reactions were proceeded well under optimised reaction temperature and not fruitful when these reactions were performed at lower temperatures *i.e.* at rt and 60 °C.

Based on the control experiments and literature reports, a plausible mechanistic pathway for the formation of 1,4-disubstituted 1,2,3-triazole is depicted in Scheme 3. Initially, phenylacetylene (2a) or styrene (7a) is converted into  $\alpha$ -iodoacetophenone (A) through consequent iodination followed by oxidation with  $I_2/O_2$  system. Next, in the pathway a, intermediate A undergoes nucleophilic amination directly with aniline to give an intermediate B. Subsequently, intermediate B undergoes condensation with N-tosylhydrazine (3) and afforded the intermediate C which upon oxidative cyclization and aromatization in the presence of iodine and molecular oxygen gave the desired triazole 4a. Alternatively, in pathway b,  $\alpha$ -iodoacetophenone (A) converted into phenylglyoxal (D) *via* Kornblum oxidation<sup>24</sup> in DMSO which act as oxygen donor in the reaction process then upon condensation with aniline (1a) provided a C-acylimine intermediate followed by a subsequent condensation with N-tosylhydrazine to afford an intermediate G, which further undergo cyclization and aromatization in the presence of iodine and oxygen to afford the desired triazole 4a. Molecular iodine can be readily regenerated *in situ* by the oxidation of iodide anions with DMSO.

## Conclusion

In summary, we have developed an efficient  $I_2/O_2$  mediated protocol for the synthesis of 1,4-disubstituted 1,2,3-triazoles in a regioselective manner from commercially available anilines, aryl alkynes or aryl alkenes, and N-tosyl hydrazine through C–N, N–N bond formation. Advantages of the presented methodology are broad substrate scope, milder reaction conditions,



operational simplicity and cost-effective. Importantly, gram scale synthesis was also accomplished which makes this protocol for the utilization in the synthesis of biologically important molecules.

## Experimental section

### General information

All the reagents and chemicals were obtained from commercial sources and used without further purification. Analytical thin layer chromatography (TLC) was performed with silica gel MERCK silica gel 60-F254 (0.5 mm) precoated glass plates. TLC plates were visualized by exposure to ultraviolet light. Column chromatography was performed using 100–200 mesh silica gel, and the eluent was as a mixture of ethyl acetate and *n*-hexane. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker 500 MHz NMR instrument in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> with tetramethylsilane (TMS) as an internal standard. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are reported in parts per million (ppm), Hertz (Hz) respectively. The peak patterns are indicated as follows: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *m*, multiplet; *dd*, doublet of doublet; *dt*, doublet of triplet; *td*, triplet of doublet; *ddd*, doublet of doublet of doublet. Melting points were determined using an electrothermal apparatus (Model IA9200) and are uncorrected. High-resolution mass spectra (HRMS) were recorded on LC-QTOF mass spectrometer.

### General procedure for the synthesis of 1,4-disubstituted 1,2,3-triazoles (4a–ag)

In a 25 mL round-bottomed flask, aryl alkyne (1.1 mmol)/aryl alkene (1.1 mmol), arylamine (1 mmol) and iodine (1.2 mmol) in DMSO were refluxed at 120 °C under molecular dioxygen atmosphere for 1 h followed by an addition of *N*-tosyl hydrazine (1.5 mmol), continued to reflux at 120 °C for 3–5 h. After completion of the reaction (monitored with TLC), the reaction mixture was quenched with a saturated solution of sodium thiosulfate and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography using ethyl acetate–hexane as an eluent in increasing polarity to afford the desired 1,4-disubstituted 1,2,3-triazoles 4a–ag.

#### 1,4-Diphenyl-1*H*-1,2,3-triazole (4a)

176 mg (80%) of 4a was obtained as a white solid;  $R_f$  = 0.420 (ethyl acetate/*n*-hexane, 1 : 1); mp. 173–175 °C (lit. 181–183 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.21 (s, 1H), 7.96–7.90 (m, 2H), 7.80 (dd,  $J$  = 8.5, 1.0 Hz, 2H), 7.56 (dd,  $J$  = 10.7, 5.0 Hz, 2H), 7.49–7.44 (m, 3H), 7.38 (t,  $J$  = 7.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  137.09, 130.13, 129.80, 128.94, 128.84, 128.50, 125.92, 120.58, 117.66; HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub> [M + H]<sup>+</sup> 222.1031, found 222.1031.

#### 1-(4-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4b)

172 mg (72%) of 4b was obtained as a white solid;  $R_f$  = 0.587 (ethyl acetate/*n*-hexane, 1 : 1); mp. 203–205 °C (lit. 209–210

°C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.16 (s, 1H), 7.92 (d,  $J$  = 7.5 Hz, 2H), 7.78 (dd,  $J$  = 8.6, 4.5 Hz, 2H), 7.47 (t,  $J$  = 7.4 Hz, 2H), 7.37 (dd,  $J$  = 24.3, 17.0 Hz, 1H), 7.27 (d,  $J$  = 2.8 Hz, 1H), 7.24 (d,  $J$  = 8.2 Hz, 1H); <sup>13</sup>C NMR (125 MHz, DMSO):  $\delta$  162.18 (d,  $J$  = 234.4 Hz), 147.79, 133.71 (d,  $J$  = 2.7 Hz), 130.69, 129.49, 128.75, 125.82, 122.86 (d,  $J$  = 8.8 Hz), 120.39, 117.28 (d,  $J$  = 23.2 Hz), HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>3</sub> [M + H]<sup>+</sup> 240.0937, found 240.0943.

#### 1-(4-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4c)

178 mg (70%) of 4c was obtained as a white solid;  $R_f$  = 0.516 (ethyl acetate/*n*-hexane, 1 : 1); mp. 221–224 °C (lit. 222–224 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  9.35 (s, 1H), 8.05–7.99 (m, 2H), 7.95 (dd,  $J$  = 8.2, 1.2 Hz, 2H), 7.77–7.70 (m, 2H), 7.52 (dd,  $J$  = 10.6, 4.7 Hz, 2H), 7.44–7.37 (m, 1H); <sup>13</sup>C NMR (125 MHz, DMSO):  $\delta$  147.94, 135.93, 133.45, 130.62, 130.42, 129.52, 128.82, 125.84, 122.16, 120.21; HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub> [M + H]<sup>+</sup> 256.0642, found 256.0641.

#### 1-(4-Bromophenyl)-4-phenyl-1*H*-1,2,3-triazole (4d)

227 mg (76%) of 4d was obtained as a white solid;  $R_f$  = 0.586 (ethyl acetate/*n*-hexane, 1 : 1); mp. 222–224 °C (lit. 216–217 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.18 (s, 1H), 7.97–7.85 (m, 2H), 7.75–7.66 (m, 4H), 7.47 (dt,  $J$  = 12.5, 3.2 Hz, 2H), 7.42–7.36 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  141.64, 136.07, 132.97, 130.02, 128.98, 128.61, 125.91, 122.43, 121.91, 117.34; HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub><sup>81</sup>BrN<sub>3</sub> [M + H]<sup>+</sup> 302.0116, found 302.0118.

#### 1-(3-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4e)

169 mg (71%) of 4e was obtained as a solid;  $R_f$  = 0.586 (ethyl acetate/*n*-hexane, 1 : 1); mp. 179–182 °C (lit. 185–187 °C);<sup>25a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (s, 1H), 7.92 (dd,  $J$  = 10.2, 8.9 Hz, 2H), 7.62–7.57 (m, 2H), 7.56–7.50 (m, 1H), 7.47 (t,  $J$  = 7.6 Hz, 2H), 7.38 (td,  $J$  = 7.1, 1.1 Hz, 1H), 7.19–7.14 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  163.15 (d,  $J$  = 252.5 Hz), 148.66, 138.25 (d,  $J$  = 10.3 Hz), 131.23 (d,  $J$  = 9.0 Hz), 129.95, 128.97, 128.63, 125.93, 117.44, 115.81 (d,  $J$  = 3.3 Hz), 115.67 (d,  $J$  = 21.2 Hz), 108.29 (d,  $J$  = 26.2 Hz); HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>3</sub> [M + H]<sup>+</sup> 240.0937, found 240.0941.

#### 1-(3-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (4f)

191 mg (75%) of 4f was obtained as a yellow solid;  $R_f$  = 0.500 (ethyl acetate/*n*-hexane, 1 : 1); mp. 172–174 °C (lit. 167–170 °C);<sup>25a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (s, 1H), 7.93–7.88 (m, 2H), 7.84 (t,  $J$  = 2.0 Hz, 1H), 7.71 (ddd,  $J$  = 8.0, 2.0, 1.1 Hz, 1H), 7.49 (dd,  $J$  = 7.3, 4.8 Hz, 1H), 7.47 (d,  $J$  = 1.7 Hz, 1H), 7.46–7.42 (m, 2H), 7.40–7.36 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  148.70, 137.85, 135.66, 130.87, 129.96, 128.97, 128.82, 128.63, 125.92, 120.75, 118.48, 117.44; HRMS (ESI):  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub> [M + H]<sup>+</sup> 256.0642, found 256.0645.

#### 1-(2-Bromophenyl)-4-phenyl-1*H*-1,2,3-triazole (4g)

224 mg (75%) of 4g was obtained as a solid;  $R_f$  = 0.482 (ethyl acetate/*n*-hexane, 1 : 1); mp. 99–100 °C (100–101 °C);<sup>25b</sup> <sup>1</sup>H NMR



(500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 (s, 1H), 7.95–7.91 (m, 2H), 7.78 (dd,  $J$  = 8.1, 1.3 Hz, 1H), 7.62 (dd,  $J$  = 7.9, 1.6 Hz, 1H), 7.51 (td,  $J$  = 7.7, 1.4 Hz, 1H), 7.49–7.45 (m, 2H), 7.43–7.40 (m, 1H), 7.39–7.35 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.02, 136.93, 132.28, 131.32, 130.51, 129.87, 129.00, 128.83, 124.40, 123.05, 120.59, 118.02; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{BrN}_3$  [M + H]<sup>+</sup> 300.0136, found 300.0099.

### 1-(2-Iodophenyl)-4-phenyl-1*H*-1,2,3-triazole (4h)

269 mg (78%) of **4h** was obtained as a pale yellow solid;  $R_f$  = 0.550 (ethyl acetate/*n*-hexane, 1 : 1); mp. 159–162 °C (lit. 156–158 °C);<sup>25b</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (d,  $J$  = 5.0 Hz, 1H), 8.02 (dd,  $J$  = 8.0, 1.0 Hz, 1H), 7.95–7.91 (m, 2H), 7.55–7.51 (m, 1H), 7.50 (d,  $J$  = 2.0 Hz, 1H), 7.49–7.44 (m, 2H), 7.39–7.35 (m, 1H), 7.28–7.23 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.65, 140.32, 140.10, 131.55, 130.26, 129.33, 128.96, 128.37, 127.88, 125.94, 121.61, 93.91; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{IN}_3$  [M + H]<sup>+</sup> 347.9998, found 348.0010.

### 4-Phenyl-1-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (4i).

179 mg (62%) of **4i** was obtained as a white solid;  $R_f$  = 0.560 (ethyl acetate/*n*-hexane, 1 : 1); mp. 152–154 °C (lit. 144–146 °C);<sup>25c</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26 (s, 1H), 8.08 (s, 1H), 8.04 (d,  $J$  = 7.5 Hz, 1H), 7.92 (d,  $J$  = 7.3 Hz, 2H), 7.71 (m,  $J$  = 7.8 Hz, 2H), 7.47 (t,  $J$  = 7.6 Hz, 2H), 7.39 (t,  $J$  = 7.4 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.43, 132.50 (q,  $J$  = 33.3 Hz), 130.61, 129.87, 129.00, 128.71, 125.94, 125.35 (q,  $J$  = 3.3 Hz), 123.56, 123.38 (q,  $J$  = 272.7 Hz), 117.34 (q,  $J$  = 3.8 Hz), HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_3$  [M + H]<sup>+</sup> 290.0905, found 290.0916.

### 1-(3-Nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (4j)

172 mg (65%) of **4j** was obtained as an yellow solid;  $R_f$  = 0.379 (ethyl acetate/*n*-hexane, 1 : 1); mp. 198–200 °C (198–200 °C);<sup>25b</sup>  $^1\text{H}$  NMR (500 MHz, DMSO):  $\delta$  9.57 (s, 1H), 8.80 (t,  $J$  = 2.1 Hz, 1H), 8.48 (ddd,  $J$  = 8.1, 2.1, 0.7 Hz, 1H), 8.40–8.34 (m, 1H), 7.97 (dt,  $J$  = 14.8, 4.7 Hz, 3H), 7.54 (dd,  $J$  = 10.6, 4.8 Hz, 2H), 7.45–7.39 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz, DMSO):  $\delta$  149.08, 148.09, 137.71, 132.12, 130.40, 129.56, 128.97, 126.44, 125.87, 123.62, 120.53, 115.08; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_4\text{O}_2$  [M + H]<sup>+</sup> 267.0882, found 267.0885.

### Ethyl 4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (4k)

164 mg (56%) of **4k** was obtained as a white solid;  $R_f$  = 0.448 (ethyl acetate/*n*-hexane, 1 : 1); mp. 175–178 °C (lit. 181–183 °C);<sup>18c</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.34–8.17 (m, 3H), 7.92 (dd,  $J$  = 7.6, 6.3 Hz, 4H), 7.48 (t,  $J$  = 7.5 Hz, 2H), 7.39 (t,  $J$  = 7.4 Hz, 1H), 4.43 (q,  $J$  = 7.1 Hz, 2H), 1.44 (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.44, 148.77, 140.04, 131.30, 130.63, 129.92, 129.00, 128.68, 125.96, 119.84, 117.35, 61.35, 14.59; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2$  [M + H]<sup>+</sup> 294.1240, found 294.1243.

### 1-(3-Phenoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (4l)

253 mg (81%) of **4l** was obtained as a white solid;  $R_f$  = 0.519 (ethyl acetate/*n*-hexane, 1 : 1); mp. 137–139 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (s, 1H), 7.90 (d,  $J$  = 7.4 Hz, 2H), 7.53–7.43

(m, 5H), 7.42–7.35 (m, 3H), 7.19 (t,  $J$  = 7.4 Hz, 1H), 7.08 (dd,  $J$  = 10.9, 7.9 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.85, 156.11, 148.40, 138.38, 130.92, 130.09, 128.86, 128.53, 125.93, 124.34, 119.61, 118.33, 117.68, 114.72, 110.62; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$  [M + H]<sup>+</sup> 314.1293, found 314.1300.

### 1-(4-Methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (4m)

208 mg (83%) of **4m** was obtained as a off white solid;  $R_f$  = 0.206 (ethyl acetate/*n*-hexane, 1 : 1); mp. 163–165 °C (lit. 162–164 °C);<sup>23a</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.24 (s, 1H), 7.93 (s, 2H), 7.69 (d,  $J$  = 8.8 Hz, 2H), 7.47 (dd,  $J$  = 16.9, 10.5 Hz, 2H), 7.37 (t,  $J$  = 7.4 Hz, 1H), 7.03 (d,  $J$  = 8.7 Hz, 2H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.96, 130.58, 130.22, 128.94, 128.74, 128.45, 126.70, 125.88, 122.25, 114.87, 55.46; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}$  [M + H]<sup>+</sup> 252.1137, found 252.1137.

### 1-(3,4-Dimethoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (4n)

238 mg (85%) of **4n** was obtained as a pale brown solid;  $R_f$  = 0.160 (ethyl acetate/*n*-hexane, 1 : 1); mp. 147–149 °C (lit. 151–153 °C);<sup>25d</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1H), 7.91 (d,  $J$  = 7.5 Hz, 2H), 7.45 (t,  $J$  = 7.4 Hz, 2H), 7.40 (d,  $J$  = 2.4 Hz, 1H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.21 (dd,  $J$  = 8.6, 2.4 Hz, 1H), 6.96 (d,  $J$  = 8.6 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.66, 163.65, 161.12, 150.17, 143.51, 137.47, 125.86, 125.03, 123.36, 105.05, 55.82; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_2$  [M + H]<sup>+</sup> 282.1243, found 282.1231.

### 4-Phenyl-1-(3,4,5-trimethoxyphenyl)-1*H*-1,2,3-triazole (4o)

270 mg (87%) of **4o** was obtained as pale yellow solid;  $R_f$  = 0.152 (ethyl acetate/*n*-hexane, 1 : 1); mp. 119–122 °C (110–112 °C);<sup>25d</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1H), 7.91 (d,  $J$  = 7.5 Hz, 2H), 7.46 (t,  $J$  = 7.5 Hz, 2H), 7.36 (dd,  $J$  = 18.3, 11.1 Hz, 1H), 7.02 (d,  $J$  = 20.3 Hz, 2H), 3.95 (s, 6H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.96, 138.35, 132.92, 130.16, 128.94, 128.49, 125.86, 118.14, 98.55, 61.06, 56.47; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}_3$  [M + H]<sup>+</sup> 312.1348, found 312.1357.

### 4-Phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (4p)

209 mg (89%) of **4p** was obtained as a white solid;  $R_f$  = 0.580 (ethyl acetate/*n*-hexane, 1 : 1); mp. 173–175 °C (lit. 169–171 °C);<sup>23a</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1H), 7.91 (d,  $J$  = 7.5 Hz, 2H), 7.66 (d,  $J$  = 8.3 Hz, 2H), 7.45 (t,  $J$  = 7.6 Hz, 2H), 7.37 (d,  $J$  = 7.4 Hz, 1H), 7.33 (d,  $J$  = 8.2 Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.12, 138.99, 134.81, 130.29, 130.21, 128.93, 128.43, 125.91, 120.49, 117.91, 21.10; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_3$  [M + H]<sup>+</sup> 236.1188, found 236.1188.

### 1-(2,6-Dimethylphenyl)-4-phenyl-1*H*-1,2,3-triazole (4q)

219 mg (88%) of **4q** was obtained as a pale white solid;  $R_f$  = 0.519 (ethyl acetate/*n*-hexane, 1 : 1); mp. 122–124 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (s, 1H), 7.93–7.90 (m, 2H), 7.45 (t,  $J$  = 7.6 Hz, 2H), 7.36 (dd,  $J$  = 10.9, 3.9 Hz, 1H), 7.28–7.20 (m, 3H), 2.39 (s, 3H), 2.22 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.55, 136.88, 136.33, 131.32, 130.61, 130.47, 130.42, 128.92, 128.29,



126.48, 125.83, 121.12, 20.82, 17.57; HRMS (ESI): *m/z* calcd for  $C_{16}H_{16}N_3 [M + H]^+$  250.1344, found 250.1346.

#### 1-(Naphthalen-2-yl)-4-phenyl-1*H*-1,2,3-triazole (4r)

184 mg (68%) of **4r** was obtained as a white solid;  $R_f = 0.500$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 186–189 °C (lit. 182–184 °C);<sup>25d</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.35 (s, 1H), 8.24 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 8.01–7.91 (m, 5H), 7.64–7.55 (m, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 134.38, 133.26, 133.02, 130.16, 129.87, 129.04, 128.68, 128.37, 128.00, 127.56, 127.12, 126.09, 118.98, 118.58, 118.23; HRMS (ESI): *m/z* calcd for  $C_{18}H_{14}N_3 [M + H]^+$  272.1188, found 272.1194.

#### 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (4s)

58 mg (25%) of **4s** was obtained as a white solid;  $R_f = 0.360$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 132–133 °C (lit. 128–130 °C);<sup>25b</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.81 (t, *J* = 7.2 Hz, 2H), 7.68 (s, 1H), 7.43–7.34 (m, 5H), 7.35–7.27 (m, 3H), 5.56 (t, *J* = 6.1 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 148.15, 134.69, 130.47, 129.16, 128.82, 128.79, 128.22, 128.08, 125.76, 119.69, 54.47; HRMS (ESI): *m/z* calcd for  $C_{15}H_{14}N_3 [M + H]^+$  236.1188, found 236.1197.

#### 8-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)quinoline (4t)

176 mg (65%) of **4t** was obtained as a yellow solid;  $R_f = 0.230$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 120–123 °C (lit. 115–117 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.06 (d, *J* = 43.6 Hz, 2H), 8.35 (d, *J* = 46.8 Hz, 2H), 7.98 (d, *J* = 22.4 Hz, 3H), 7.73 (s, 1H), 7.47 (t, *J* = 46.1 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 150.86, 147.31, 140.30, 136.54, 133.93, 130.89, 129.18, 128.81, 128.05, 126.49, 125.98, 124.51, 123.65, 122.03; HRMS (ESI): *m/z* calcd for  $C_{17}H_{13}N_4 [M + H]^+$  273.1140, found 273.1139.

#### 4-(4-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazole (4u)

162 mg (68%) of **4u** was obtained as white solid;  $R_f = 0.466$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 205–207 °C (lit. 198–200 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.15 (s, 1H), 7.91–7.87 (m, 2H), 7.81–7.77 (m, 2H), 7.58–7.53 (m, 2H), 7.50–7.43 (m, 1H), 7.19–7.13 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 162.91 (d, *J* = 255.5 Hz), 147.53, 137.01, 129.86, 129.01, 127.72 (d, *J* = 8.2 Hz); 126.35 (d, *J* = 3.0 Hz), 120.61, 117.57, 115.99 (d, *J* = 21.8 Hz); HRMS (ESI): *m/z* calcd for  $C_{14}H_{11}FN_3 [M + H]^+$  240.0937, found 240.0943.

#### 4-(4-Chlorophenyl)-1-phenyl-1*H*-1,2,3-triazole (4v)

173 mg (68%) of **4v** was obtained as a white solid;  $R_f = 0.820$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 209–211 °C (lit. 207–209 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, DMSO): δ 9.37 (d, *J* = 11.2 Hz, 1H), 8.03–7.91 (m, 4H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 146.71, 137.02, 133.21, 130.44, 129.66, 129.57, 129.31, 127.51, 120.54, 120.50; HRMS (ESI): *m/z* calcd for  $C_{14}H_{11}ClN_3 [M + H]^+$  256.0642, found 256.0645.

#### 4-(4-Bromophenyl)-1-phenyl-1*H*-1,2,3-triazole (4w)

210 mg of **4w** was obtained as a white solid;  $R_f = 0.630$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 205–208 °C (lit. 212–214 °C);<sup>22a</sup> <sup>1</sup>H NMR (500 MHz, DMSO): δ 9.37 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 146.75, 139.16, 137.05, 132.48, 130.45, 130.01, 129.32, 127.78, 122.36, 121.74, 120.54; HRMS (ESI): *m/z* calcd for  $C_{14}H_{11}BrN_3 [M + H]^+$  300.0136, found 300.0140.

#### 4-(3-Bromophenyl)-1-phenyl-1*H*-1,2,3-triazole (4x)

206 mg (69%) of **4x** was obtained as a white solid;  $R_f = 0.655$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 148–151 °C (lit. 148–150 °C);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.20 (s, 1H), 8.06 (dd, *J* = 5.7, 4.0 Hz, 1H), 7.88–7.84 (m, 1H), 7.81–7.76 (m, 2H), 7.58–7.53 (m, 2H), 7.52–7.45 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 146.99, 136.92, 132.27, 131.36, 130.51, 129.86, 128.99, 128.83, 124.42, 123.04, 120.58, 118.12; HRMS (ESI): *m/z* calcd for  $C_{14}H_{11}BrN_3 [M + H]^+$  300.0136, found 300.0141.

#### 1-Phenyl-4-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (4y)

161 mg (56%) of **4y** was obtained as white solid;  $R_f = 0.519$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 223–225 °C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 9.39 (s, 1H), 8.25–8.10 (m, 2H), 8.02–7.91 (m, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.71–7.57 (m, 2H), 7.50 (ddt, *J* = 11.5, 10.4, 5.2 Hz, 1H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 146.41, 135.88 (q, *J* = 286.7 Hz), 130.47, 129.43, 128.97, 126.51 (q, *J* = 3.3 Hz), 126.42, 126.36; 126.28, 125.80, 121.48, 120.62; HRMS (ESI): *m/z* calcd for  $C_{15}H_{11}F_3N_3 [M + H]^+$  290.0905, found 290.0909.

#### 4-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)phenol (4z)

165 mg (70%) of **4z** was obtained as a pale white solid;  $R_f = 0.137$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 194–196 °C; <sup>1</sup>H NMR (500 MHz, DMSO): δ 9.62 (s, 1H), 9.24 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, DMSO): δ 158.32, 147.92, 137.16, 131.94, 130.49, 130.38, 129.14, 120.48, 119.99, 116.67, 115.77, 112.63; HRMS (ESI): *m/z* calcd for  $C_{14}H_{12}N_3O [M + H]^+$  238.0980, found 238.0987.

#### 4-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (4aa)

205 mg (82%) of **4aa** was obtained as a white solid;  $R_f = 0.206$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 137–139 °C (lit. 142–143);<sup>23a</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.10 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 159.86, 148.28, 137.14, 129.78, 128.70, 127.24, 122.91, 120.44, 116.95, 114.38, 55.47; HRMS: *m/z* calcd for  $C_{15}H_{14}N_3O [M + H]^+$  252.1137, found 252.1106.

#### 1-Phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (4ab)

190 mg (81%) of **4ab** was obtained as a white solid;  $R_f = 0.551$  (ethyl acetate/*n*-hexane, 1 : 1); mp. 148–150 °C (lit. 152–154



$^{\circ}\text{C}$ )<sup>23a</sup>;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (s, 1H), 7.85–7.66 (m, 4H), 7.54–7.42 (m, 2H), 7.38 (t,  $J$  = 7.2 Hz, 1H), 7.20 (d,  $J$  = 5.6 Hz, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.48, 138.41, 137.12, 129.84, 129.68, 128.78, 127.33, 125.92, 120.65, 117.83, 21.46; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_3$  [ $\text{M} + \text{H}]^+$  236.1188, found 236.1184.

#### 4-(4-Ethylphenyl)-1-phenyl-1*H*-1,2,3-triazole (4ac)

206 mg (83%) of **4ac** was obtained as a white solid;  $R_f$  = 0.866 (ethyl acetate/*n*-hexane, 1 : 1); mp. 123–125  $^{\circ}\text{C}$  (128–130  $^{\circ}\text{C}$ )<sup>23a</sup>;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1H), 7.90–7.74 (m, 4H), 7.61–7.50 (m, 2H), 7.48–7.43 (m, 1H), 7.30 (d,  $J$  = 8.3 Hz, 2H), 2.70 (q,  $J$  = 7.6 Hz, 2H), 1.28 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.51, 144.72, 137.12, 129.78, 128.72, 128.45, 127.65, 125.88, 120.51, 117.32, 28.64, 15.52; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_3$  [ $\text{M} + \text{H}]^+$  250.1344, found 250.1353.

#### 2-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (4ad)

71 mg (32%) of **4ad** was obtained as a light yellow solid;  $R_f$  = 0.510 (ethyl acetate/*n*-hexane, 1 : 1); mp. 85–88  $^{\circ}\text{C}$  (lit. 89–92  $^{\circ}\text{C}$ )<sup>25e</sup>;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.71 (s, 1H), 8.64 (t,  $J$  = 10.2 Hz, 1H), 8.29 (d,  $J$  = 7.9 Hz, 1H), 7.91–7.79 (m, 3H), 7.57 (dd,  $J$  = 17.5, 9.9 Hz, 2H), 7.47 (t,  $J$  = 7.4 Hz, 1H), 7.33–7.28 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.63, 148.94, 148.30, 137.58, 136.97, 129.86, 128.95, 123.21, 120.70, 120.49, 120.36; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_4$  [ $\text{M} + \text{H}]^+$  223.0984, found 223.0980.

#### 1,4-Bis(4-fluorophenyl)-1*H*-1,2,3-triazole (4ae)

210 mg (82%) of **4ae** was obtained as a off white solid;  $R_f$  = 0.866 (ethyl acetate/*n*-hexane, 1 : 1); mp. 228–229  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO):  $\delta$  9.28 (s, 1H), 8.07–7.92 (m, 4H), 7.58–7.46 (m, 2H), 7.42–7.29 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$  + DMSO):  $\delta$  162.57 (d,  $J$  = 249.6 Hz), 162.14 (d,  $J$  = 260.0 Hz), 147.03, 133.60 (d,  $J$  = 2.9 Hz), 127.72 (d,  $J$  = 8.2 Hz), 127.15 (d,  $J$  = 3.1 Hz), 122.47 (d,  $J$  = 8.6 Hz), 119.60, 116.94 (d,  $J$  = 23.2 Hz), 116.08 (d,  $J$  = 21.7 Hz); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_2\text{N}_3$  [ $\text{M} + \text{H}]^+$  258.0843, found 258.0850.

#### 4-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1*H*-1,2,3-triazole (4af)

215 mg (81%) of **4af** was obtained as a off white solid;  $R_f$  = 0.666 (ethyl acetate/*n*-hexane, 1 : 1); mp. 178–180  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO):  $\delta$  8.06 (s, 1H), 7.94–7.81 (m, 2H), 7.74–7.62 (m, 2H), 7.20–7.10 (m, 2H), 7.09–6.97 (m, 2H), 3.88 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.63 (d,  $J$  = 239.0 Hz), 159.92, 147.38, 130.51, 127.58 (d,  $J$  = 8.2 Hz), 126.66 (d,  $J$  = 3.3 Hz), 115.90 (d,  $J$  = 21.8 Hz), 114.86, 55.66; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{FN}_3$  [ $\text{M} + \text{H}]^+$  270.0143, found 270.1054.

#### 1,4-Bis(4-methoxyphenyl)-1*H*-1,2,3-triazole (4ag)

247 mg (88%) of **4ag** was obtained as a white solid;  $R_f$  = 0.563 (ethyl acetate/*n*-hexane, 1 : 1); mp. 198–200  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (s, 1H), 7.86–7.80 (m, 2H), 7.70–7.65 (m, 2H), 7.05–7.01 (m, 2H), 7.01–6.96 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.83, 148.13, 130.70,

127.16, 123.16, 122.23, 117.11, 114.81, 114.35, 55.65, 55.35; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_2$  [ $\text{M} + \text{H}]^+$  282.1243, found 282.1255.

## Conflicts of interest

There are no conflicts to declare.

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