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Arylation of Click Triazoles with Diaryliodonium Salts

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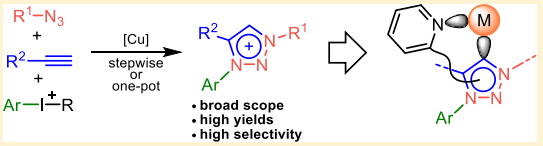
Supporting Information

ABSTRACT: A robust, selective, and highly efficient method for the preparation of 1,3,4-triaryl 1,2,3-triazolium salts has been developed. It features arylation of a click triazole with a diaryliodonium salt in the presence of a copper catalyst under neat conditions. The presence of pyridine functionality is tolerated, enabling the first access to key precursors of pyridyl-mesoionic carbene ligands. The method has been integrated into a one-pot protocol with terminal alkyne, sodium azide, and diaryliodonium salt as starting compounds.



INTRODUCTION

1,3,4-Trisubstituted-1*H*-1,2,3-triazolium salts **I** and **II** (Figure 1; R^1, R^2 = alkyl, aryl, and heteroaryl) upon deprotonation

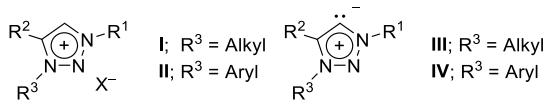


Figure 1. Triazolium salts (left) and triazolylidene ligands (right).

yield 1*H*-1,2,3-triazol-5-ylidenes **III** and **IV**, a class of N-heterocyclic carbenes (NHCs)[1] that belong to the family of mesoionic carbenes (MICs). Because of unique electronic properties,[2] triazolylidene MICs stood out from NHCs, as well as many other ligand classes, not only in the preparation of efficient catalysts and photosensitizers,[3] but also in other chemical and material fields of science.[4]

In a highly modular approach that includes copper-catalyzed azide−alkyne cycloaddition (CuAAC) reaction with subsequent N3 alkylation of the resulting 1,2,3-triazole, 3-alkyltriazolium salts **I** are easily accessed almost at will.[4d] This strategy is even applicable for triazoles having tethered a competing nucleophilic pyridyl moiety R^1 or R^2.[5] In contrast, the synthesis of 1,3-diaryl counterparts **II** is limited to a single protocol that was discovered by Wirschun and Jochims[6] and subsequently greatly developed by Bertrand et al.[7] It is a formal 1,3-dipolar cycloaddition of an alkyne with a 1,3-diaza-2-azoniaallene salt that is formed from 1,3-diaryltriazene (Figure 2a). The cycloaddition is carried out as a one-pot operation by the addition of *tert*-butyl hypochlorite to a solution of 1,3-diaryltriazene, potassium hexafluorophosphate, and alkyne in dichloromethane as a reaction solvent, at −78 °C. Although showing a broad scope in alkyne partners, from the selectivity reasons, the method is limited to symmetrical 1,3-diaryltriazene substrates. Low reaction temperatures can cause some solubility issues, and to the best of our knowledge, it has not been used to access N1/N3-heteroary-functionalized counterparts.

An approach that may potentially address the above limitations is N3 arylation of 1-aryl-1*H*-1,2,3-triazole derivatives. Whereas examples of arylation with a (hetero)aryl halogenide are scarce, limited to the reaction of 1,5-diphenyl-1*H*-1,2,3-triazole with 2-bromopyridine (Figure 2b),[8] the use of a diaryliodonium salt is sought as an attractive alternative. Discovered in the 1890's by Willgerodt,[9] and owing to the group of Olofsson[10] and others[11] who have made this hypervalent iodine reagents readily accessible, diaryliodonium salts found many synthetic applications. These include N-arylation[12] of nitrogen-containing heterocycles like pyridine,[13] imidazole,[14] benzimidazole,[15] and 1,2,4-triazole.[16] The potential breadth of arylation of 1,2,3-triazole with a diaryliodonium salt was first demonstrated by Gao et al. in 2013 (Figure 2c).[14] Although a few related examples have emerged in the literature since then,[17] the method remained undeveloped.

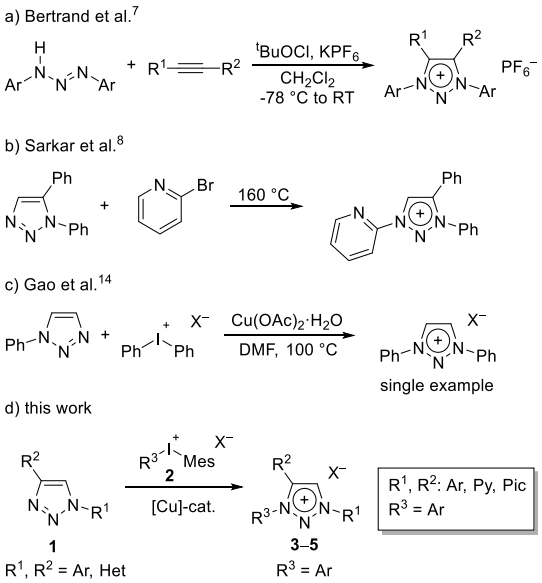


Figure 2. Synthetic approaches toward 1,3-diaryltriazolium salts.

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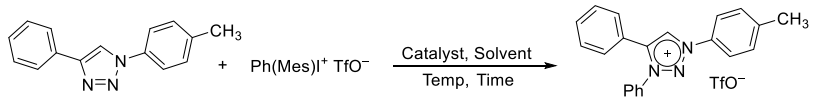
Table 1. Optimization of the Reaction Conditions for Arylation of 1[a]

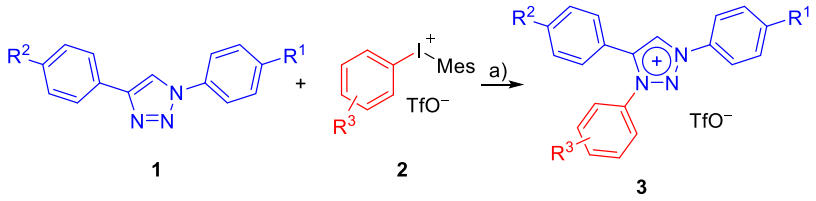


1b 2a 3b

entry	2a (equiv)	solvent	catalyst (mol %)	temp (°C)	time (h)	conversion (yield)[b]
1	1.8	DMF	none	100	4	0
2	1.8	DMF	$CuSO_4$ (10)	rt	17	0
3	1.5	DMF	$CuSO_4$ (10)	100	4	16
4[c]	1.5[d]	DMF	$CuSO_4$ (5)	100	40	(91)[e]
5	1.3	DMF	$CuSO_4$ (10)	130	17	51
6	1.8	DMF	$CuSO_4$ (10)	130	5	53
7	1.8	DMF	$CuSO_4$ (10)	130	17	100 (86)
8	1.3[d]	THF	$CuSO_4$ (10)	100	17	82[f]
9	1.8[d]	THF	$CuSO_4$ (10)	100	17	100[f]
10	1.8	neat	$CuSO_4$ (10)	130	17	100 (97)

[a]Reaction conditions: **1b** (0.2 mmol, 1 equiv), **2a** (0.36 mmol, 1.8 equiv), $CuSO_4$ (0.02 mmol, 0.1 equiv), *V*(solvent) = 0.5 mL. [b]Isolated yield (%). [c]For comparison reasons, the data are adopted from Gao et al.[14a] who arylated monosubstituted 1-phenyl-*1H*-1,2,3-triazole. [d]**2b** was used instead of **2a**. [e]Corresponds to 1,3-diphenyl-*1H*-1,2,3-triazol-3-ium tetrafluoroborate. [f]As tetrafluoroborate salt.

Table 2. Scope of Arylation of 1,4-Diaryl-1*H*-1,2,3-triazoles 1 into 3[a]



1 2 3

1	R^1	R^2	2	R^3	product	yield[b]
1a	H	H	**2a**	H	**3a**	97
1b	CH_3	H	**2a**	H	**3b**	97 (94)[c]
1b	CH_3	H	**2c**	4-CF_3	**3c**	88
1b	CH_3	H	**2d**	4-CH_3	**3d**	92
1b	CH_3	H	**2e**[d]	4-OMe	**3e**[e]	99
1b	CH_3	H	**2f**	4-NO_2	**3f**	61
1b	CH_3	H	**2g**	3-CF_3	**3g**	71
1c	OMe	H	**2a**	H	**3h**	95
1d	NO_2	H	**2a**	H	**3i**	94
1d	NO_2	H	**2h**	4-NMe_2	**3j**	32
1d	NO_2	H	**2e**[d]	4-OMe	**3k**[e]	93
1d	NO_2	H	**2d**	4-CH_3	**3l**	98
1d	NO_2	H	**2f**	4-NO_2	**3m**	95
1e	OMe	NO_2	**2e**[d]	4-OMe	**3n**[e]	88
1f	NO_2	OMe	**2e**[d]	4-OMe	**3o**[e]	84

[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.36 mmol, 1.8 equiv), $CuSO_4$ (0.02 mmol, 0.1 equiv), 130 °C, 17 h. [b]Isolated yield (%). [c]2 mmol scale of **1b**. [d]**2e** refers to (4-MeO-C_6H_4)$_2$$I^+BF_4^-$. [e]As tetrafluoroborate salt.

The motivation to develop a reliable and robust method for the synthesis of 1,3-diaryl-1*H*-1,2,3-triazol-5-ylidene precursors, **II**, stems from the fact that these MICs, **IV**, exhibit enhanced stability in comparison to their alkylated counterparts **III**.[4d,7] To get the desired ligand properties and architecture, access to differently N1 and N3 diaryl- and heteroaryl-substituted 1,2,3-triazolium salts is sought. In this respect, pyridine may be considered as one of the highly desired substituents giving rise to the emerging class of hemilabile/bifunctional pyridyl-MIC ligands of intriguing overall donor capacities to the metal.[2,4g] Herein, we report on the arylation of pyridyl- and picolyl-1*H*-1,2,3-triazoles **1** with diaryliodonium salts **2** (Figure 2d) as easy access to pyridyl-MIC precursors (**IV**, Figure 1).

RESULTS AND DISCUSSION

To assess preliminary parameters for the arylation of triazoles **1**, we conducted a series of test experiments in which 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**; R^1 = *p*-tolyl, R^2 = Ph, Figure 2d) was reacted with diaryliodonium salts (**2**) under different reaction conditions. For example, mesityl(phenyl)iodonium triflate (**2a**) and diphenyliodonium tetrafluoroborate (**2b**) were used as reagents in solvents like dimethylformamide (DMF) and tetrahydrofuran (THF), with or without the addition of $CuSO_4$. Unsymmetrical mesityl(aryl)iodonium triflates were selected out of the iodonium salts because of well-documented selective transfer of the aryl group in the metal-catalyzed arylations[18] and their easy access from aryl

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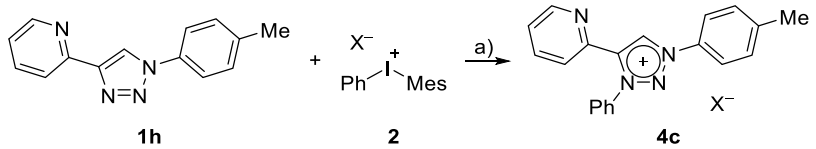
Table 3. Test Arylation of 1h with Phenyl(mesityl)iodonium Salts 2a,m−q[a]



1h **2** **4c**

iodonium salt	anion (X^-)	% conversion to **4c** (X)
2a	TfO^-	74
2m	TsO^-	68
2n	BF_4^-	61
2o	ClO_4^-	59
2p	HSO_4^-	60
2q	PF_6^-	64

[a]Reaction conditions: **1h** (0.2 mmol, 1 equiv), **2** (0.36 mmol, 1.8 equiv), $CuSO_4$ (0.02 mmol, 0.1 equiv), 130 °C, 17 h.

iodides, mesitylene, and triflic acid.[11a,19] In addition, to demonstrate that symmetrical diaryliodonium salts can also be employed, bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**) was selected in all subsequent experiments for the introduction of 4-methoxyphenyl group to triazole. The reactions were monitored by ^{1}H NMR spectroscopy of aliquots taken from the reaction mixtures. The formation of triazolium salt **3** was indicated by the appearance of a characteristic H-5 resonance, shifted ca. 1 ppm downfield as compared to the starting triazole **1**, similar to the N-3 alkylated triazolium salts.[5,20]

The results of optimization of the reaction conditions are presented in Table 1 and can be summarized as follows. Copper salts and elevated temperatures are typically required in arylations of heterocycles with the diaryliodonium salt,[12−16] which is also the case in arylation of triazoles **1**. As is evident from Table 1, stirring the solution of 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**) and **2a** in DMF at 100 °C in the absence of the copper salt (entry 1) or at room temperature in the presence of 10 mol % of $CuSO_4$ (entry 2) returned unreacted starting reagents. The formation of product **3b** (16%) could only be seen by applying 10 mol % of $CuSO_4$ at 100 °C (entry 3). In comparison to the report of Gao et al.[14a] who arylated monosubstituted 1-phenyl-*1H*-1,2,3-triazole under similar reaction conditions (entry 4), the initial result on arylation of **3b** is modest. However, an additional optimization of the reaction from entry 3 in terms of temperature, time, and loading of iodonium salt (entries 5−7) finally furnished complete conversion into **3b** (86% isolated yield, entry 7). Higher loadings of iodonium salts proved beneficial, probably due to its decomposition at higher temperatures (see below). Triazole **1b** also readily reacted with **2b** in THF as a reaction solvent (entries 8 and 9). In addition to the above experiments, the test reaction was also run neat, which gave the same result in terms of the reaction time and conversion to product **3**, yet being the most economic from the solvent cost and isolation perspective (entry 10). As indicated above, thermal stability of iodonium salts was tested under neat conditions. Heating **2a** at 130 °C for 17 h led to decomposition with the formation of mesityl iodide along with other unidentified products.

As a result of the above test experiments, the optimal reaction conditions for arylation employed heating a mixture of triazole **1** (0.2 mmol, 1.0 equiv), diaryliodonium salt **2** (0.36 mmol, 1.8 equiv), and anhydrous $CuSO_4$ (0.02 mmol, 0.1 equiv) neat in a sealed glass vial at 130 °C overnight (17 h). Analytically pure triazolium salts **3** were isolated by column chromatography. Having established the general reaction conditions, we investigated the scope of the arylation of 1,4-diaryl-1*H*-1,2,3-triazoles **1** (Table 2). Phenyl groups having strongly electron-withdrawing and electron-releasing substituents were successfully introduced affording triazolium salts **3**(**c**,**f**,**g**,**m**) and **3**(**e**,**j**,**k**,**n**,**o**), respectively, regardless of the electronic effects in the starting triazoles **1**. Functional groups present in reagents **1** and **2** were found to be compatible, including methyl, trifluoromethyl, methoxy, and nitro, and the yields of the products were generally excellent. The exception was the coupling of **1d** with **2h** where the low yield of dimethylamino-functionalized compound **3j** was a result of undesired arylation at the NMe_2 nucleophilic center. Synthesis of **3b** from **1b** and **2a** was also conducted on a larger (10×) scale also with an excellent result, demonstrating the preparative applicability of the method.

To highlight the real utility of this protocol, aimed at the synthesis of hemilabile/bifunctional NHC ligands,[4g] we moved to the arylation of 4-pyridyl triazoles. Because the introduction of pyridine functionality into the triazole molecule could potentially introduce incompatibility with the copper catalyst as well as some selectivity issues, the effect of a broader selection of copper additives and anions of iodonium salt was re-examined. For this, 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)-pyridine (**1h**) was selected as a model compound. As a result, some minor effects on selectivity were observed in the case of iodonium salts with different anions as shown in Table 3, and some differences could also be noticed in conversions with different copper catalysts as well (Table 4). Although $CuBr_2$ performed better in arylation of **1h** with **2a** (compare entries 6 and 13 in Table 4), its catalytic activity was somehow diminished in arylations of other tested triazoles as compared to $CuSO_4$ (Table 5, compare entry 10 with 11, and entry 13 with 14). As a result, in analogy to the above findings for diaryl triazole **1b**, $CuSO_4$, and $CuBr_2$ as well as iodonium salts having triflate anions proved superior for the arylation of pyridyl triazole **1h** in terms of the yield of triazolium salt (**4c**).

With these results in hand, the scope of the arylation of 4-pyridyl triazoles **1g−l** with mesityl(aryl)iodonium triflates **2a**,**c**,**d**,**i−k**, diphenyliodonium tetrafluoroborate (**2b**), and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**) was investigated as shown in Table 5. With some exceptions (see below), triazolium salts **4a−n** having pyridine substituents at C-4 were obtained in good yields. Somewhat lower yields of the products from Table 5 as compared to those from Table 2 were likely due to the formation of N^{Py}-arylated side products and the need for chromatographic purification. In one instance, that of the arylation of triazole **1j** with iodonium salt **2d**, the

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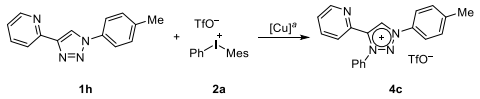
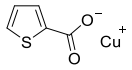
Table 4. Test Arylations of 1h with Different Copper Salts[a]



1h 2a 4c

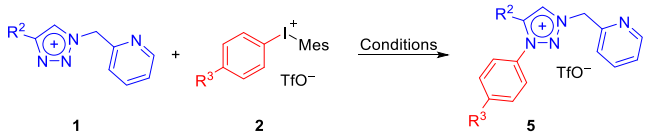
Entry	[Cu]	%Conversion to **4c**
1	CuI	74
2	$Cu(PPh_3)_3Br$	64
3	$CuCl_2$	59
4	$Cu(OAc)_2 \cdot H_2O$	60
5	$Cu(OTf)_2$	56
6	$CuBr_2$	78
7	$Cu(NO_3)_2 \cdot 3\ H_2O$	66
8	CuBr	70
9	Cu(OAc)	59
10		65
11	CuCN	66
12	CuCl	63
13	$CuSO_4$	73

[a]Reaction conditions: **1h** (0.2 mmol, 1 equiv), **2a** (0.36 mmol, 1.8 equiv), [Cu] (0.02 mmol, 0.1 equiv), 130 °C, 17 h.

undesired pyridine monoarylated side product (2-(1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)-1-(*p*-tolyl)pyridine-1-ium triflate, **4k′**) could be isolated and fully characterized by NMR and high-resolution mass spectrometry (HRMS). Nevertheless, the protocol enabled acceptable yields of pyridyl-triazolium salts **4**, having both the electron-withdrawing and electron-releasing substituents, with no need for the pyridine nitrogen atom protection as it was in the case of alkylation.[5] Arylation of 2-(1-ethyl-1*H*-1,2,3-triazol-4-yl)pyridine (**1l**) with **2e** also worked well with **4n** being isolated in 65% yield. In contrast to the above, an attempt to introduce a bulky mesityl group was less successful, yielding in the reaction of **1h** with dimesityliodonium triflate (**2k**) the corresponding triazolium salt **4h** in only 17% yield (Table 5). Interestingly, the reaction of **1h** with mesityl(2-(trifluoromethyl)phenyl)iodonium triflate (**2j**) resulted in a complex mixture of products, from which unreacted **1h** (79%), **4g** (3%), and **4h** (5%) could be identified by ^{1}H NMR spectral analysis and comparison with the spectra of the corresponding authentic samples.

The scope of arylation of 4-aryl-1-picolyl triazoles **1m−o** was also briefly investigated as shown in Table 6. An introduction of a CH_2 bridge between the pyridine and MIC dents should drastically influence electronic effects, bite angle, and conformational mobility of the chelating ligand as

Table 6. Scope of Arylation of 1-Picolyl-1*H*-1,2,3-triazoles[a]

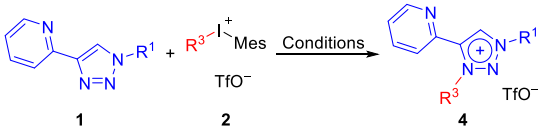


1 2 5

triazole	R^2	2	R^3	product	yield[b]
1m	Ph	**2a**	H	**5a**	94
1n	4-CH_3-C_6H_4	**2a**	H	**5b**	98
1o	4-MeO-C_6H_4	**2a**	H	**5c**	88
1o	4-MeO-C_6H_4	**2e**[c]	OMe	**5d**[d]	91
1p	2-Py	**2a**	H	**5e**	43

[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.36 mmol, 1.8 equiv), $CuSO_4$ (0.02 mmol, 0.1 equiv), 130 °C, 17 h. [b]Isolated yield (%). [c]**2e** refers to $(4\text{-MeO-}C_6H_4)_2I^+BF_4^-$. [d]As tetrafluoroborate salt.

Table 5. Scope of Arylation of 1-Aryl-4-pyridyl-1*H*-1,2,3-triazoles 1 into 4[a]



1 2 4

entry	triazole	R^1	2	R^3	product	conversion (yield)[b]
1	**1g**	Ph	**2a**	Ph	**4a**	71 (63)
2	**1g**	Ph	**2e**[c]	4-MeO-C_6H_4	**4b**[e]	77 (70)
3	**1h**	4-CH_3-C_6H_4	**2a**	Ph	**4c**	73 (69)
4	**1h**	4-CH_3-C_6H_4	**2b**	Ph	**4c**[e]	(51)
5	**1h**	4-CH_3-C_6H_4	**2c**	4-CF_3-C_6H_4	**4d**	(63)
6	**1h**	4-CH_3-C_6H_4	**2e**[c]	4-MeO-C_6H_4	**4e**[e]	72 (59)
7	**1h**	4-CH_3-C_6H_4	**2i**	4-Cl-C_6H_4	**4f**	57 (44)
8	**1h**	4-CH_3-C_6H_4	**2j**	2-CF_3-C_6H_4	**4g**	[d]
9	**1h**	4-CH_3-C_6H_4	**2k**	Mes	**4h**	21 (17)
10	**1i**	4-MeO-C_6H_4	**2a**	Ph	**4i**	70 (58)
11	**1i**	4-MeO-C_6H_4	**2a**	Ph	**4i**	62[f]
12	**1i**	4-MeO-C_6H_4	**2e**[c]	4-MeO-C_6H_4	**4j**[e]	78 (64)
13	**1j**	4-NO_2-C_6H_4	**2d**	4-CH_3-C_6H_4	**4k**	71 (60)
14	**1j**	4-NO_2-C_6H_4	**2d**	4-CH_3-C_6H_4	**4k**	48[f]
15	**1j**	4-NO_2-C_6H_4	**2e**[c]	4-MeO-C_6H_4	**4l**[e]	68 (57)
16	**1k**	4-NMe_2-C_6H_4	**2a**	Ph	**4m**	73 (62)
17	**1l**	Et	**2e**[c]	4-MeO-C_6H_4	**4n**[e]	80 (65)

[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **2** (0.36 mmol, 1.8 equiv), $CuSO_4$ (0.02 mmol, 0.1 equiv), 130 °C, 17 h. [b]Isolated yield (%). [c]**2e** refers to $(4\text{-MeO-}C_6H_4)_2I^+BF_4^-$. [d]Complex mixture of products (see text). [e]As tetrafluoroborate salt. [f]$CuBr_2$ was used instead of $CuSO_4$.

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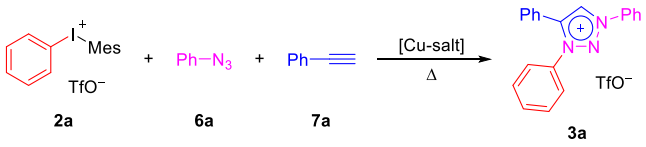
compared to the Py-MIC (**4a–n**).[4d,g,21] By using the same reaction conditions as above (Table 5), the corresponding products **5a–d** were obtained in excellent 88–98% yields (Table 6). Surprisingly, undesired pyridine arylation was not observed in these experiments. 1-Picolyl-4-pyridyl-1*H*-1,2,3-triazole (**1p**), an interesting ligand that has been used to achieve multimetallic coordination architectures,[22] has also been arylated with iodonium salt **2a** to give triazolium salt **5e**, albeit in a modest 43% yield (Table 6). A lower yield is somehow consistent with the results on the arylation of 4-pyridyl triazoles from Table 5.

One-Pot CuAAC-Arylation. The fact that both, the 1,4-disubstituted triazole forming CuAAC reaction, and the above-developed arylation procedure require Cu-catalysts, prompted us to test whether the triazolium salt could be prepared in a one-pot procedure starting from an organic azide, terminal acetylene, and iodonium salt. For this purpose, $Cu(PPh_3)_3Br$ (5 mol %) was selected as a precatalyst. This temperature and oxidation-resistant Cu(I) salt already efficiently promoted demanding CuAAC reactions[20a] as well as arylation of triazoles with iodonium salts.[23] In contrast to $Cu(PPh_3)_3Br$ (Table 7, entry 1), attempts to use other copper salts for this process, that is, $CuSO_4$, $Cu(OAc)_2{\cdot}H_2O$, and CuI, proved unsuccessful (entries 2–4). The result of a brief substrate scope screening to produce triazolium salts (**3–5**)**a**, one from each of the product classes presented in Tables 2, 5, and 6, are shown in Table 8, and demonstrate a remarkable utility of the method.

Table 7. Copper-Catalyst for One-Pot CuAAC-Arylation[a]

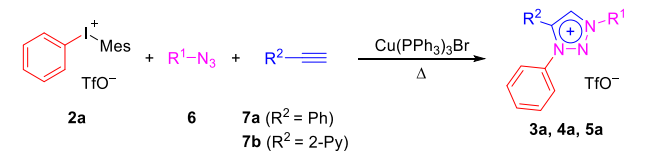


2a **6a** **7a** **3a**

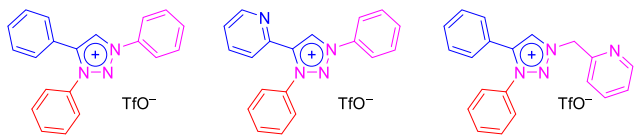
entry	copper salt	% conversion to **4a** (yield)[b]
1	$Cu(PPh_3)_3Br$	100 (92)
2	$CuSO_4$	<10
3	$Cu(OAc)_2{\cdot}H_2O$	<10
4	CuI	<10

[a]Reaction conditions: **2a** (1.6 mmol, 1.6 equiv), **6a** (1 mmol, 1 equiv), **7a** (1.2 mmol, 1.2 equiv), copper salt (0.05 mmol, 0.05 equiv), 130 °C, 3 h. [b]Refers to conversion (isolated % yield).

Table 8. One-Pot CuAAC-Arylation[a]



2a **6** **7a** (R^2 = Ph), **7b** (R^2 = 2-Py) **3a, 4a, 5a**



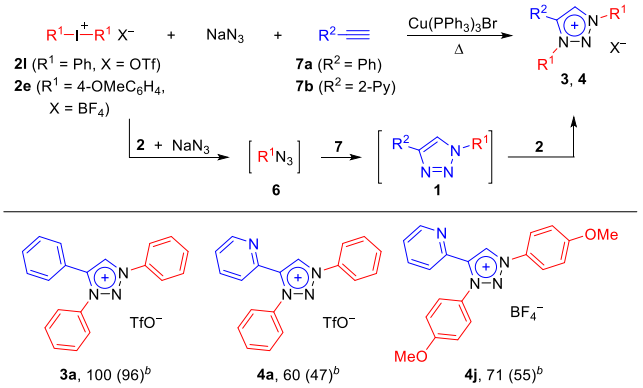
3a, 100 (92)[b,c] **4a**, 60 (48)[b] **5a**, 100 (94)[b]

[a]Reaction conditions: **2a** (1.6 mmol, 1.6 equiv), **6** (1 mmol, 1 equiv), **7** (1.2 mmol, 1.2 equiv), $Cu(PPh_3)_3Br$ (0.05 mmol, 0.05 equiv), 130 °C, 3 h. [b]Refers to conversion (isolated % yield). [c]For comparison reasons, the result is taken from Table 7, entry 1.

Although by conducting reactions on a 2 mmol scale in sealed ACE glass reaction tubes, we have not observed any uncontrollable behavior, the reactions with the azides should be done with caution and on small scales because of their potentially explosive character.

Finally, we decided to extend the two-step one-pot protocol from Table 8 by including an in situ generation of the organic azide (Table 9). Namely, it has been documented that

Table 9. One-Pot Azide-Formation-CuAAC-Arylation[a]



3a, 100 (96)[b] **4a**, 60 (47)[b] **4j**, 71 (55)[b]

[a]Reaction conditions: **2** (0.936 mmol, 2.6 equiv), **7** (0.36 mmol, 1 equiv), NaN_3 (0.36 mmol, 1 equiv), $Cu(PPh_3)_3Br$ (0.018 mmol, 0.05 equiv), 130 °C, 3 h. [b]Refers to conversion (isolated % yield).

iodonium salts readily undergo nucleophilic displacement with sodium azide into aryl azides.[24] Thus, heating the mixture of phenylacetylene **7a**, diphenyliodonium triflate **2l**, and sodium azide in the presence $Cu(PPh_3)_3Br$ (5 mol %) resulted in quantitative formation of **3a**. Similarly, products **4a** and **4j** were obtained from 2-ethynylpiridine **7b** and the corresponding iodonium salts **2l** and **2e**. Although this method enables access to N1/N3 identically substituted molecules, just like in the case of 1,3-dipolar cycloaddition of alkynes with diaryltriazene products (1,3-diaza-2-azoniaallene salts, Figure 2a),[7] the scope can be easily expanded to the preparation of heteroaromatic derivatives like **4a** and **4j**. In contrast, attempts to react diphenyltriazene with 2-ethynylpyridine (**7b**) through the reaction from Figure 2a failed to provide 1,3-diphenyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazolium salt returning an unidentified polymeric material instead.

It is noteworthy that the above-developed one-pot protocols may be suitable for small-scale high-throughput combinatorial screening experiments, aimed at identifying hit compounds, having desired coordination properties or biological activity, for example. Once the hit compound is identified, its synthesis on the preparative scale can easily be conducted through the protocols from Tables 2, 5, and 6.

CONCLUSIONS

In summary, we have developed a robust and highly efficient method for N-3 arylation of click triazoles with diaryliodonium salts. Great functional group tolerance enables the preparation of products with strongly electron-withdrawing or electron-donating characteristics and those possessing a push–pull effect. In contrast to the method that employs 1,3-diaryltriazenes as the starting compounds, this protocol allows for the preparation of N1/N3 differently substituted products as well as those having pyridyl and picolyl moieties, which are inaccessible through other methods. All these features will be

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of prime importance in future designs of organometallic compounds with bifunctional mesoionic-carbene ligands and their application in catalysis. This is the first method for the synthesis of N3-arylated 1-picolyl and/or 4-pyridyl functionalized 1,2,3-triazolium salts.

EXPERIMENTAL SECTION

General Considerations. The reagents and solvents in general procedures were used as obtained from the commercial sources (Merck, Fluorochem), unless indicated otherwise. Dichloromethane used for the syntheses was dried over sodium and distilled prior to use. THF used for the syntheses was dried over sodium and distilled prior to use. Anhydrous DMF (99.8%) used in reactions was purchased at Merck and stored under Sure/Seal and an argon atmosphere. Silica gel column chromatography was carried out on silica gel 60N. Analytical thin-layer chromatography (TLC) was carried out on Fluka Silica Gel TLC cards, visualized with a UV lamp (254 nm and/or 366 nm).

Melting points were determined on a Kofler micro hot-stage microscope and are uncorrected. The reactions were monitored by TLC on TLC-CARDS Silica Gel, 220−440 mesh. IR spectra were obtained with a PerkinElmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. HRMS were recorded with an Agilent 6224 time-of-flight mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an HPLC instrument.

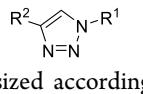
NMR spectra were recorded with a Bruker Avance III 500 MHz NMR instrument operating at 500 MHz (^{1}H), 471 MHz (^{19}F), 126 MHz (^{13}C), and 51 MHz (^{15}N) at 296 K in DMSO-d_6. Proton and carbon spectra are referenced to the residual solvent shifts of δ 2.50 and δ39.52 ppm, respectively.[25] ^{19}F spectra were referenced to CCl_3F as external standards at δ 0 ppm. ^{15}N chemical shifts were extracted from ^{1}H−^{15}N gs-HMBC spectra (with 4.5 Hz digital resolution in the indirect dimension and the parameters adjusted for a long-range ^{1}H−^{15}N coupling constant of 5 Hz), determined with respect to external nitromethane and corrected to external ammonia by addition of 380.5 ppm.

Assignments of proton, carbon, and nitrogen resonances were performed by 2D NMR techniques (^{1}−^{1}H gs-COSY, ^{1}H−^{13}C gs-HSQC, ^{1}H−^{13}C gs-HMBC and ^{1}H−^{15}N gs-HMBC). Coupling constants (J) are given in hertz. Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Resonances of NMe_2 carbon atoms were superimposed with that for the DMSO-d_6 solvent and were identified through the assistance of ^{1}H−^{13}C HSQC spectra.

Starting triazoles **1**,[20] diaryliodonium salts **2**,[26] aromatic and benzyl azides (**6**),[20a] and $Cu(PPh_3)_3Br$[27] were prepared according to the known literature procedures.

Caution! The handling of azides is dangerous because of their explosive character and all reactions should be carried out on a small scale.[28]

Preparation of Triazoles 1.



Triazoles **1** were synthesized according to a slightly modified literature procedure[20a] as follows. A mixture of organic azide **6** (1 mmol, 1 equiv), acetylene **7** (1 mmol, 1 equiv), and $Cu(PPh_3)_3Br$ (0.01 mmol, 9 mg, 1 mol %) was stirred at room temperature overnight. The reaction mixture was dissolved in hot ethyl acetate and the product was precipitated by the addition of light petroleum with cooling, filtered, and dried. ^{1}H NMR data of the isolated products were in agreement with the literature reports.[20,22]

*1,4-Diphenyl-1H-1,2,3-triazole (**1a**, $R^1 = R^2 =$ Ph).* Following the general procedure employing azidobenzene (119 mg, 1 mmol) and phenylacetylene (**7a**, 102 mg, 1 mmol). The product was obtained as an off-white solid (137 mg, 0.620 mmol, 62%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.31 (s, 1H), 8.00−7.90 (m, 4H), 7.68−7.60 (m, 2H), 7.56−7.47 (m, 3H), 7.42−7.35 (m, 1H). Spectral data are in agreement with the literature.[20b,c]

*4-Phenyl-1-(p-tolyl)-1H-1,2,3-triazole (**1b**, R^1 = 4-CH_3-C_6H_4, R^2 = Ph).* Following the general procedure employing azidotoluene (133 mg, 1 mmol) and phenylacetylene (**7a**, 102 mg, 1 mmol). The product was obtained as an off-white solid (199 mg, 0.846 mmol, 85%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.26 (s, 1H), 7.97−7.92 (m, 2H), 7.86−7.81 (m, 2H), 7.53−7.47 (m, 2H), 7.46−7.42 (m, 2H), 7.41−7.36 (m, 1H), 2.40 (s, 3H). Spectral data are in agreement with the literature.[20c]

*1-(4-Methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (**1c**, R^1 = 4-MeO-C_6H_4, R^2 = Ph).* Following the general procedure employing 1-azido-4-methoxybenzene (149 mg, 1 mmol) and phenylacetylene (**7a**, 102 mg, 1 mmol). The product was obtained as a brown solid (216 mg, 0.864 mmol, 86%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.20 (s, 1H), 7.96−7.91 (m, 2H), 7.88−7.83 (m, 2H), 7.52−7.47 (m, 2H), 7.40−7.35 (m, 1H), 7.21−7.15 (m, 2H), 3.85 (s, 3H). Spectral data are in agreement with the literature.[20d]

*1-(4-Nitrophenyl)-4-phenyl-1H-1,2,3-triazole (**1d**, R^1 = 4-NO_2-C_6H_4, R^2 = Ph).* Following the general procedure employing 1-azido-4-nitrobenzene (164 mg, 1 mmol) and phenylacetylene (**7a**, 102 mg, 1 mmol). The product was obtained as a yellow solid (169 mg, 0.635 mmol, 64%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.54 (s, 1H), 8.56−8.46 (m, 2H), 8.30−8.25 (m, 2H), 8.05−7.89 (m, 2H), 7.59−7.47 (m, 2H), 7.46−7.36 (m, 1H). Spectral data are in agreement with the literature.[20b]

*1-(4-Methoxyphenyl)-4-(4-nitrophenyl)-1H-1,2,3-triazole (**1e**, R^1 = 4-MeO-C_6H_4, R^2 = 4-NO_2-C_6H_4).* Following the general procedure employing 1-azido-4-methoxybenzene (149 mg, 1 mmol) and 1-ethynyl-4-nitrobenzene (147 mg, 1 mmol). The product was obtained as an off-white solid (266 mg, 0.897 mmol, 90%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.46 (s, 1H), 8.40−8.35 (m, 2H), 8.22−8.17 (m, 2H), 7.90−7.84 (m, 2H), 7.22−7.16 (m, 2H), 3.85 (s, 3H). Spectral data are in agreement with the literature.[20e]

*4-(4-Methoxyphenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**1f**, R^1 = 4-NO_2-C_6H_4, R^2 = 4-MeO-C_6H_4).* Following the general procedure employing 1-azido-4-nitrobenzene (164 mg, 1 mmol) and 1-ethynyl-4-methoxybenzene (132 mg, 1 mmol). The product was obtained as a yellow solid (262 mg, 0.884 mmol, 88%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.43 (s, 1H), 8.58−8.44 (m, 2H), 8.30−8.23 (m, 2H), 7.93−7.84 (m, 2H), 7.17−7.04 (m, 2H), 3.82 (s, 3H). Spectral data are in agreement with the literature.[20f]

*2-(1-Phenyl-1H-1,2,3-triazol-4-yl)pyridine (**1g**, R^1 = Ph, R^2 = 2-Py).* Following the general procedure employing azidobenzene (119 mg, 1 mmol) and 2-ethynylpyridine (**7b**, 103 mg, 1 mmol). The product was obtained as an off-white solid (186 mg, 0.837 mmol, 84%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (s, 1H), 8.66 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.13 (dt, J = 7.9, 1.1 Hz, 1H), 8.06−8.01 (m, 2H), 7.95 (td, J = 7.7, 1.8 Hz, 1H), 7.67−7.59 (m, 2H), 7.56−7.49 (m, 1H), 7.41 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H). Spectral data are in agreement with the literature.[20a]

*2-(1-(p-Tolyl)-1H-1,2,3-triazol-4-yl)pyridine (**1h**, R^1 = 4-CH_3-C_6H_4, R^2 = 2-Py).* Following the general procedure employing 4-azidotoluene (133 mg, 1 mmol) and 2-ethynylpyridine (**7b**, 103 mg, 1 mmol). The product was obtained as an off-white solid (220 mg, 0.931 mmol, 93%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.27 (s, 1H), 8.66 (ddd, J = 4.9, 1.7, 0.9 Hz, 1H), 8.14−8.10 (m, 1H), 7.95 (td, J = 7.7, 1.8 Hz, 1H), 7.93−7.88 (m, 2H), 7.46−7.36 (m, 4H), 2.40 (s, 3H). Spectral data are in agreement with the literature.[20a]

*2-(1-(4-Methoxyphenyl)-1H-1,2,3-triazol-4-yl)pyridine (**1i**, R^1 = 4-MeO-C_6H_4, R^2 = 2-Py).* Following the general procedure employing 1-azido-4-methoxybenzene (149 mg, 1 mmol) and 2-ethynylpyridine (**7b**, 103 mg, 1 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.23 (s, 1H), 8.65 (d, J = 4.6 Hz, 1H), 8.13−8.08 (m, 1H), 7.97−7.91 (m, 3H), 7.40 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.18−7.13 (m, 2H), 3.84 (s, 3H). The product was obtained as an off-white solid (239 mg, 0.947 mmol, 95%). Spectral data are in agreement with the literature.[20a]

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*2-(1-(4-Nitrophenyl)-1H-1,2,3-triazol-4-yl)pyridine (**1j**, R^1 = 4-NO_2-C_6H_4, R^2 = 2-Py).* Following the general procedure employing 1-azido-4-nitrobenzene (164 mg, 1 mmol) and 2-ethynylpyridine (**7b**, 103 mg, 1 mmol). The product was obtained as an off-white solid (252 mg, 0.943 mmol, 94%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.57 (d, J = 2.4 Hz, 1H), 8.70−8.65 (m, 1H), 8.50−8.45 (m, 2H), 8.40−8.33 (m, 2H), 8.14 (dt, J = 8.0, 1.1 Hz, 1H), 7.97 (td, J = 7.7, 1.8 Hz, 1H), 7.44 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H). Spectral data are in agreement with the literature.[20a]

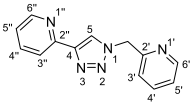
*N,N-Dimethyl-4-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)aniline (**1k**, R^1 = 4-NMe_2-C_6H_4, R^2 = 2-Py).* Following the general procedure employing 4-azido-*N*,*N*-dimethylaniline (162 mg, 1 mmol) and 2-ethynylpyridine (**7b**, 103 mg, 1 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.12 (s, 1H), 8.69−8.57 (m, 1H), 8.10 (d, J = 7.9 Hz, 1H), 7.97−7.88 (m, 1H), 7.83−7.75 (m, 2H), 7.43−7.35 (m, 1H), 6.90−6.84 (m, 2H), 2.98 (s, 6H). The product was obtained as an off-white solid (123 mg, 0.462 mmol, 46%). Spectral data are in agreement with the literature.[20a]

*2-(1-Ethyl-1H-1,2,3-triazol-4-yl)pyridine (**1l**, R^1 = Et, R^2 = 2-Py).* Following a slightly modified literature procedure,[20g] ethyl iodide (702 mg, 4.5 mmol, 1 equiv) and sodium azide (878 mg, 13.5 mmol, 3 equiv) were stirred in 35 mL of THF/water/*tert*-butanol mixture (2:2:1 v/v/v) at room temperature for 1 h. Afterward, $Cu(PPh_3)_3Br$ (52 mg, 55 μmol, 1 mol %) was added followed by addition of 2-ethynylpyridine (**7b**, 284 mg, 2.75 mmol, 0.6 equiv). The reaction mixture was stirred at 70 °C for 20 h. Products were extracted with dichloromethane and washed with brine and saturated water solution of ammonium chloride. The organic layers were dried over sodium sulfate and evaporated. Crude product was purified with column chromatography on silica (dichloromethane/acetone = 50:1 → 5:1). Brown oil (340 mg, 1.95 mmol, 71% relative to 2-ethynylpyridine). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.63 (s, 1H), 8.59 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.02 (dt, J = 7.8, 1.1 Hz, 1H), 7.89 (td, J = 7.7, 1.8 Hz, 1H), 7.34 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 4.45 (q, J = 7.3 Hz, 2H), 1.48 (t, J = 7.3 Hz, 3H). Spectral data are in agreement with the literature.[20g]

*2-((4-Phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridine (**1m**, R^1 = 2-Pic, R^2 = Ph).* Following the general procedure employing 2-(azidomethyl)pyridine (134 mg, 1 mmol) and phenylacetylene (**7a**, 102 mg, 1 mmol). The product was obtained as a white solid (193 mg, 0.817 mmol, 82%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.66 (s, 1H), 8.55 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.89−7.81 (m, 3H), 7.47−7.42 (m, 2H), 7.39−7.31 (m, 4H), 5.76 (s, 2H). Spectral data are in agreement with the literature.[20a]

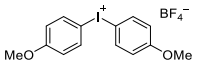
*2-((4-(p-Tolyl)-1H-1,2,3-triazol-1-yl)methyl)pyridine (**1n**, R^1 = 2-Pic, R^2 = 4-CH_3-C_6H_4).* Following the general procedure employing 2-(azidomethyl)pyridine (134 mg, 1 mmol) and 1-azido-4-methylbenzene (133 mg, 1 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.59 (s, 1H), 8.55 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H), 7.84 (td, J = 7.7, 1.8 Hz, 1H), 7.77−7.72 (m, 2H), 7.36 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 7.34−7.30 (m, 1H), 7.27−7.22 (m, 2H), 5.74 (s, 2H), 2.32 (s, 3H). The product was obtained as a white solid (200 mg, 0.799 mmol, 80%). Spectral data are in agreement with the literature.[20a]

*2-((4-(p-Tolyl)-1H-1,2,3-triazol-1-yl)methyl)pyridine (**1o**, R^1 = 2-Pic, R^2 = 4-MeO-C_6H_4).* Following the general procedure employing 2-(azidomethyl)pyridine (134 mg, 1 mmol) and 1-azido-4-methoxylbenzene (149 mg, 1 mmol). The product was obtained as an white solid (219 mg, 0.822 mmol, 82%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.55 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 8.54 (s, 1H), 7.83 (td, J = 7.7, 1.8 Hz, 1H), 7.81−7.76 (m, 2H), 7.36 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 7.34−7.30 (m, 1H), 7.05−6.97 (m, 2H), 5.73 (s, 2H), 3.78 (s, 3H). Spectral data are in agreement with the literature.[20a]

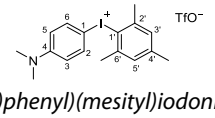


*2-((4-(Pyridin-2-yl)-1H-1,2,3-triazol-1-yl)methyl)pyridine (**1p**).* Following the general procedure employing 2-(azidomethyl)pyridine (134 mg, 1 mmol) and 2-ethynylpyridine (**7b**, 103 mg, 1 mmol). The product was obtained as an off-white solid (136 mg, 0.573 mmol, 57%). mp 76.4−77.3 °C. IR: 3424, 3149, 3056, 2997, 2958, 1593, 1475, 1440, 1420, 1228, 1195, 1149, 1090, 784, 728 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.68 (s, 1H, H-5), 8.60 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H, H-6″), 8.55 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H, H-6′), 8.04 (dt, J = 7.9, 1.1 Hz, 1H, H-3″), 7.89 (td, J = 7.7, 1.8 Hz, 1H, H-4″), 7.83 (td, J = 7.7, 1.8 Hz, 1H, H-4′), 7.39−7.31 (m, 3H, H-5′, H-5″, H-3′), 5.80 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 154.9 (C-2′), 149.9 (C-2″), 149.7 (C-6″), 149.5 (C-6′), 147.4 (C-4), 137.5 (C-4′), 137.3 (C-4″), 124.2 (C-5), 123.3 (C-5″), 123.1 (C-5′), 122.2 (C-3′), 119.5 (C-3″), 54.5 (CH_2). ^{15}N NMR (DMSO-d_6): δ 365 (N-3), 349 (N-2), 313 (N-1′), 306 (N-1″), 248 (N-1). HRMS (ESI$^+$): calcd for $C_{13}H_{12}N_5^+$ [M + H]$^+$ 238.1087; found, 238.1085. Spectral and analytical data are in agreement with those reported in the literature.[22]

Preparation of Diaryliodonium Salts 2. *General Experimental Procedure for the Preparation of Diaryliodonium Triflates **2a**, **2c**, **2d**, **2f**, **2g**, and **2i**−**k** (Adopted from Ref 26a).* Aryl iodide (20 mmol, 1 equiv) and mesitylene (3.13 g, 26 mmol, 1.3 equiv) were dissolved in dry dichloromethane (80 mL) in an oven-dried round-bottomed flask. mCPBA (5.40 g, ∼22 mmol, ∼1.1 equiv, ∼70 wt %) was added to the stirred solution followed by dropwise addition of triflic acid (6.0 g, 40 mmol, 3.5 mL, 2 equiv). The reaction mixture was stirred at room temperature overnight (16 h), concentrated under reduced pressure, and then triturated with diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to obtain pure iodonium salt **2** as a white to off-white solid. ^{1}H NMR data were in agreement with those reported in the literature.[19,26a]



*Bis(4-methoxyphenyl)iodonium Tetrafluoroborate (**2e**).* An oven-dried glass flask was equipped with a magnetic stirring bar followed by the addition of mCPBA (7.40 g, ∼30 mmol, ∼1.5 equiv, ∼70 wt %) and dry dichloromethane (100 mL). 4-Iodoanisole (4.68 g, 20 mmol, 1 equiv), anisole (2.60 g, 24 mmol, 1.2 equiv), and *p*-toluenesulfonic acid monohydrate (4.57 g, 24 mmol, 1.2 equiv) were added. The reaction mixture was stirred at reflux for 2 h. After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure and triturated with diethyl ether. After resting in a fridge (−20 °C) overnight, the precipitate was collected by filtration. The filtrate was dissolved in methanol (200 mL), followed by the addition of water−methanol (300 mL, 1:1, v/v) suspension of KBF_4 (200 mmol). After 30 min of stirring, the precipitate was collected by filtration, washed with water (6 × 250 mL), and dried to give pure iodonium salt **2e** (7.83 g, 18.3 mmol, 91%). NMR data were in agreement with those reported in the literature.[29] ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.16−8.09 (m, 2H), 7.09−7.02 (m, 2H), 3.79 (s, 3H). ^{19}F{^{1}H}NMR (471 MHz, DMSO-d_6): δ −148.3 (d, J = 26 Hz, BF_4).



*(4-(Dimethylamino)phenyl)(mesityl)iodonium Triflate (**2h**).* This compound was prepared by a slightly modified procedure of Bielawski et al.,[26b] to avoid potential N-oxidation at the amine nitrogen atom, as follows. 4-Iodo-*N*,*N*-dimethylaniline (12.35 g, 50 mmol) was dissolved in 200 mL of dry dichloromethane and TfOH (15.5 mL, 175 mmol, 3.5 equiv) was added dropwise while stirring on an ice bath (the reaction is exothermic). The stirring was continued for 15 min at room temperature, followed by the addition of mesitylene (7.81 g, 65 mmol, 1.3 equiv). mCPBA (15.41 g, ∼62.5 mmol, ∼1.25 equiv, ∼70 wt %) was added portionwise and the resulting reaction mixture was refluxed for 1 h. After cooling down to room temperature, the reaction mixture was filtered through a pad of basic Al_2O_3 and eluted with a sufficient amount of a mixture of MeOH/dichloromethane 1:1 (v/v) to isolate all products from the pad (TLC monitoring). The eluate was concentrated under reduced pressure and diethyl ether was added to precipitate pure product **2h** as a white solid, which was isolated by filtration (19.7 g, 38.2 mmol,

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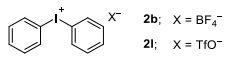
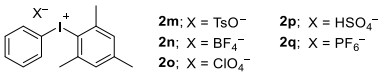
76%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.80−7.70 (m, 2H, H-2, H-6), 7.16 (s, 2H, H-3′, H-5′), 6.72−6.64 (m, 2H, H-3, H-5), 2.93 (s, 6H, NMe_2), 2.60 (s, 6H, *o*-CH_3), 2.27 (s, 3H, *p*-CH_3). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 151.9 (C-4), 142.6 (C-4′), 141.2 (C-2′, C-6′), 136.3 (C-2, C-6), 129.6 (C-3′, C-5′), 123.4 (C-1′), 114.4 (C-3, C-5), 96.1 (C-1), 39.6 (NMe_2) 26.3 (CH_3-2′, CH_3-6′), 20.5 (CH_3-4′). ^{15}N NMR (DMSO-d_6): δ 57 (NMe_2). ^{19}F{^{1}H} NMR (471 MHz, DMSO-d_6): δ −77.73 (TfO). HRMS (ESI$^+$): calcd for $C_{17}H_{21}IN^+$ [M]$^+$, 366.0713; found, 366.0714.



Diphenyliodonium Salts ***2b*** *and* ***2l****.* A mixture of iodobenzene (4.08 g, 20 mmol, 1 equiv) and benzene (2.03 g, 26 mmol, 1.3 equiv) was dissolved in dry dichloromethane (80 mL) in an oven-dried round-bottomed flask. mCPBA (5.40 g, ∼22 mmol, ∼1.1 equiv, ∼70 wt %) was added to the solution followed by dropwise addition of boron trifluoride etherate (9.8 mL, 78 mmol, 3 equiv; for the preparation of **2b**) or triflic acid (6.0 g, 40 mmol, 3.5 mL, 2 equiv; for the preparation of **2l**). The reaction mixture was stirred overnight (16 h) and concentrated under reduced pressure. Diethyl ether was added and the precipitate was collected by filtration and washed with diethyl ether to obtain pure iodonium salt **2b** (5.09 g, 13.8 mmol, 69%) or **2l** (6.12 g, 14.2 mmol, 71%) as a white solid. ^{1}H and ^{19}F NMR data were in agreement with those reported in the literature.[19,26a]

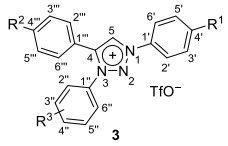
General Procedure for the Preparation of Diaryliodonium Salts ***2m−q****.*



A mixture of aryl iodide (20 mmol) and mesitylene (3.13 g, 26 mmol, 1.3 equiv) was dissolved in dry dichloromethane (80 mL) in an oven-dried round-bottomed flask. mCPBA (5.40 g, ∼22 mmol, ∼1.1 equiv, ∼70 wt %) was added, followed by the addition of 40 mmol (2 equiv) of selected acid ($TsOH·H_2O$ for **2m**; BF_3OEt_2 for **2n**; $HClO_4$ for **2o**; H_2SO_4 for **2p**; 55% water solution of HPF_6 for **2q**). The reaction mixture was stirred overnight (16 h) and then concentrated under reduced pressure. After the addition of diethyl ether the precipitate was formed, which was collected by filtration and washed with diethyl ether to obtain pure iodonium salts **2m−q** as white to off-white solids. ^{1}H NMR data were in agreement with those reported in the literature.[19,26a]

General Procedure for Arylation of Triazoles (Tables 2, 5, and 6). An ACE glass reaction tube equipped with a magnetic stirring bar, predried in an oven at 130 °C and cooled in a stream of nitrogen gas, was charged with the corresponding triazole **1** (0.2 mmol, 1 equiv), diaryliodonium salt **2** (0.36 mmol, 1.8 equiv), and anhydrous $CuSO_4$ (3 mg, 0.02 mmol, 10 mol %). The reaction mixture was flushed with nitrogen gas, sealed, and placed into a preheated metal block at 130 °C. The reaction mixture was stirred overnight (17 h) at 130 °C to obtain tar-like crude product. After cooling down to ambient temperature, the crude product was dissolved in acetone and triturated with light petroleum to obtain triazolium salt **3−5**. Analytically pure triazolium salts **3−5** were obtained by using column chromatography on silica (MeOH/dichloromethane = 1:30 → 1:10, v/v).

Triazolium Salts 3a−o (Table 2).



3

*1,3,4-Triphenyl-1H-1,2,3-triazol-3-ium Triflate (****3a****,* $R^1 = R^2 = R^3 =$ *H).* Following the general procedure employing 1,4-diphenyl-1*H*-1,2,3-triazole (**1a**, 44 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). Analytically pure samples were obtained using column chromatography on silica (MeOH/dichloromethane = 1:10, v/v). The product was obtained as an off-white solid (87 mg, 0.194 mmol, 97%). mp 106−108 °C. IR: 3106, 3067, 1604, 1491, 1255, 1230, 1169, 1157, 1079, 763, 695, 634 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.07 (s, 1H, H-5), 8.20−8.14 (m, 2H, H-2′, H-6′), 7.86−7.79 (m, 3H, H-3′, H-5′, and H-4′), 7.77−7.72 (m, 3H, H-2″, H-6″, and H-4″), 7.69 (ddd, J = 7.6, 4.5, 1.8 Hz, 2H, H-3″, H-5″), 7.62−7.58 (m, 1H, H-4‴), 7.58−7.53 (m, 2H, H-3‴, H-5‴), 7.49−7.45 (m, 2H, H-2‴, H-6‴). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 143.4 (C-4), 134.8 (C-1′), 133.9 (C-1″), 132.32 (C-4″), 132.26 (C-4′), 131.7 (C-4‴), 130.7 (C-3′, C-5′), 130.2 (C-3″, C-5″), 129.4 (C-3‴, C-5‴), 129.3 (C-2‴, C-6‴), 127.7 (C-5), 126.3 (C-2″, C-6″), 122.5 (C-1‴), 121.7 (C-2′, C-6′). ^{15}N NMR (DMSO-d_6): δ 254 (N-1), 249 (N-3). ^{19}F{^{1}H} NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI$^+$): calcd for $C_{20}H_{16}N_3^+$ [M$^+$], 298.1339; found, 298.1349. HRMS (ESI): calcd for $CF_3O_3S^-$ [M$^-$] 148.9526; found, 148.9530.

*3,4-Diphenyl-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (****3b****,* $R^1 = CH_3$, $R^2 = R^3 =$ *H).* Following the general procedure employing 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 47 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). Analytically pure samples were obtained using column chromatography on silica (MeOH/dichloromethane = 1:10, v/v). The product was obtained as an off-white solid (90 mg, 0.194 mmol, 97%). mp 125−128 °C. IR: 3099, 3074, 1610, 1566, 1512, 1490, 1455, 1282, 1255, 1222, 1168, 1149, 1029, 820, 766, 694 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.03 (s, 1H, H-5), 8.09−8.04 (m, 2H, H-2′, H-6′), 7.76−7.73 (m, 3H, H-2″, H-6″ and H-4″), 7.69 (ddt, J = 8.8, 5.7, 1.5 Hz, 2H, H-3″, H-5″), 7.64−7.61 (m, 2H, H-3′, H-5′), 7.61−7.58 (m, 1H, H-4‴), 7.55 (ddd, J = 8.5, 7.1, 1.0 Hz, 2H, H-3‴, H-5‴), 7.49−7.45 (m, 2H, H-2‴, H-6‴), 2.48 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 143.3 (C-4), 142.5 (C-4′), 134.0 (C-1″), 132.5 (C-1′), 132.2 (C-4″), 131.6 (C-4‴), 131.0 (C-3′, C-5′), 130.2 (C-3″, C-5″), 129.33 (C-3‴, C-5‴), 129.30 (C-2‴, C-6‴), 127.4 (C-5), 126.3 (C-2″, C-6″), 122.6 (C-1‴), 121.4 (C-2′, C-6′), 20.8 (CH_3). ^{15}N NMR (DMSO-d_6): δ 255 (N-1), 249 (N-3). ^{19}F{^{1}H} NMR (471 MHz, DMSO-d_6): δ −77.75 (TfO). HRMS (ESI$^+$): calcd for $C_{21}H_{18}N_3^+$ [M$^+$], 312.1495; found, 312.1497. HRMS (ESI): calcd for $CF_3O_3S^-$ [M$^-$] 148.9526; found, 148.9521.

The synthesis of triazolium salt **3b** (871 mg, 1.89 mmol, 94%) was also conducted on a larger scale by the general procedure described above with 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 471 mg, 2 mmol), phenyl(mesityl)iodonium triflate (**2a**, 1700 mg, 3.6 mmol, 1.8 equiv), and anhydrous $CuSO_4$ (32 mg, 0.2 mmol, 10 mol %).

*4-Phenyl-1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-3-ium Triflate (****3c****,* $R^1 = CH_3$, $R^2 =$ H, $R^3 =$ 4-CF_3*).* Following the general procedure employing 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 47 mg, 0.2 mmol) and mesityl(4-(trifluoromethyl)phenyl)-iodonium triflate (**2c**, 194 mg, 0.36 mmol). Analytically pure samples were obtained using column chromatography on silica (MeOH/dichloromethane = 1:10, v/v). The product was obtained as an off-white solid (93 mg, 0.176 mmol, 88%). mp 69−72 °C. IR: 3084, 1611, 1566, 1513, 1490, 1323, 1256, 1224, 1129, 1064, 1029, 853, 818, 765, 695, 636 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.06 (s, 1H, H-5), 8.13 (d, J = 8.5 Hz, 2H, H-3″, H-5″), 8.08 (d, J = 8.5 Hz, 2H, H-2′, H-6′), 7.98 (d, J = 8.4 Hz, 2H, H-2″, H-6″), 7.66−7.56 (m, 5H, H-3′, H-5′, H-4‴, H-3‴, H-5‴), 7.49 (d, J = 7.1 Hz, 2H, H-2‴, H-6‴), 2.48 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6): δ 143.6 (C-4), 142.7 (C-4′), 137.1 (C-1″), 132.4 (C-1′), 131.8 (C-4‴), 131.0 (C-3′, C-5′), 129.5 (C-3‴, C-5‴), 129.4 (C-2‴, C-6‴), 127.5 (m, C-5, C-3″, C-5″), 122.2 (C-1′), 121.4 (C-2′, C-6′), 20.9 (CH_3). Quartet signals for C-4″ and CF_3 carbon atom could not be located in the spectrum. ^{15}N NMR (DMSO-d_6): δ 256 (N-1), 246 (N-3). ^{19}F{^{1}H} NMR (471 MHz, DMSO-d_6): δ −61.43 (CF_3), −77.75 (TfO). HRMS (ESI$^+$): calcd for $C_{22}H_{17}F_3N_3^+$ [M$^+$], 380.1369; found, 380.1377.

*4-Phenyl-1,3-di(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (****3d****,* $R^1 = CH_3$, $R^2 =$ H, $R^3 =$ 4-CH_3*).* Following the general procedure employing 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 47 mg, 0.2 mmol) and mesityl(*p*-tolyl)iodonium triflate (**2d**, 175 mg, 0.36 mmol). Analyti-

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cally pure samples were obtained using column chromatography on silica (MeOH/dichloromethane = 1:10, v/v). The product was obtained as an off-white solid (87 mg, 0.184 mmol, 92%). mp 77−78 °C. IR: 3077, 1707, 1610, 1567, 1510, 1252, 1223, 1154, 1028, 819, 765, 696, 635 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.00 (s, 1H, H-5), 8.05 (d, J = 8.6 Hz, 2H, H-2′, H-6′), 7.64−7.57 (m, 5H, H-2″, H-6″ and H-3′, H-5′ and H-4‴), 7.57−7.51 (m, 2H, H-3‴, H-5‴), 7.50−7.45 (m, 4H, H-3″, H-5″ and H-2‴, H-6‴), 2.47 (s, 3H, CH_3′), 2.42 (s, 3H, CH_3″). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 143.2 (C-4), 142.4 (C-4′), 142.3 (C-4″), 132.4 (C-1′), 131.50 (C-4‴/C-1″), 131.43 (C-1″/C-4‴), 130.9 (C-3′, C-5′), 130.5 (C-3″, C-5″), 129.27 (C-3‴, C-5‴), 129.21 (C-2‴, C-6‴), 127.3 (C-5), 125.9 (C-2″, C-6″), 122.6 (C-1‴), 121.2 (C-2′, C-6′), 20.84 (CH_3″), 20.77 (CH_3′). ^{15}N NMR (DMSO-d_6): δ 254 (N-1), 249 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{22}H_{20}N_3^+$ [M^+], 326.1652; found, 326.1651.

*3-(4-Methoxyphenyl)-4-phenyl-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**3e**, R^1 = CH_3, R^2 = H, R^3 = 4-OMe).* Following the general procedure employing 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 47 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (85 mg, 0.199 mmol, 99%). mp 202−206 °C. IR: 3116, 1605, 1509,1218, 1174, 1049, 1019, 837, 817, 964, 694, 641 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.98 (s, 1H, H-5), 8.09−8.01 (m, 2H, H-2′, H-6′), 7.67−7.63 (m, 2H, H-2″, H-6″), 7.63−7.60 (m, 2H, H-3′, H-5′) 7.60−7.53 (m, 3H, H-3‴, H-5‴ and H-4‴), 7.50−7.44 (m, 2H, H-2‴, H-6‴), 7.22−7.18 (m, 2H, H-3″, H-5″), 3.85 (s, 3H, OCH_3), 2.47 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.6 (OCH_3), 143.3 (C-4), 142.5 (C-4′), 132.5 (C-1′), 131.6 (C-4‴), 131.0 (C-3′, C-5′), 129.36 (H-2‴, H-6‴/H-3‴, H-5‴), 129.27 (H-2‴, H-6‴/H-3‴, H-5‴), 127.8 (C-2″, C-6″), 127.2 (C-5), 126.5 (C-1″), 122.7 (C-1‴), 121.3 (C-2′, C-6′), 115.2 (C-3″, C-5″), 55.9 (OCH_3), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 254 (N-1), 248 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.27 (d, J = 27 Hz, BF_4). HRMS (ESI^+): calcd for $C_{22}H_{20}N_3O^+$ [M^+], 342.1601; found, 342.1604.

*3-(4-Nitrophenyl)-4-phenyl-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**3f**, R^1 = CH_3, R^2 = H, R^3 = 4-NO_2).* Following the general procedure employing 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 47 mg, 0.2 mmol) and mesityl(4-nitrophenyl)iodonium triflate (**2f**, 186 mg, 0.36 mmol). Analytically pure samples were obtained using column chromatography on silica (MeOH/dichloromethane = 1:10, v/v). The product was obtained as an off-white solid (62 mg, 0.122 mmol, 61%). mp 88−92 °C. IR: 3087, 1531, 1491, 1382, 1254, 1223, 1151, 1028, 854, 818, 766, 737, 694 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.07 (s, 1H, H-5), 8.56−8.52 (m, 2H, H-3″, H-5″), 8.10−8.06 (m, 2H, H-2′, H-6′), 8.04−7.99 (m, 2H, H-2″, H-6″), 7.66−7.63 (m, 2H, H-3′, H-5′), 7.62−7.53 (m, 3H, H-3‴, H-5‴ and H-4‴), 7.52−7.47 (m, 2H, H-2‴, H-6‴), 2.49 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 149.3 (C-4″), 143.7 (C-4), 142.8 (C-4′), 138.3 (C-1″), 132.4 (C-1′), 131.9 (C-4‴), 131.1 (C-3′, C-5′), 129.55 (H-2‴, H-6‴/H-3‴, H-5‴), 129.43 (H-2‴, H-6‴/H-3‴, H-5‴), 128.0 (C-2″, C-6″), 127.63 (C-5), 125.6 (C-3″, C-5″), 122.1 (C-1‴), 121.4 (C-2′, C-6′), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 368 (NO_2), 256 (N-1), 245 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{21}H_{17}N_4O_2^+$ [M^+], 357.1346; found, 357.1340.

*4-(Phenyl)-1-(p-tolyl)-3-(3-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-3-ium Triflate (**3g**, R^1 = CH_3, R^2 = H, R^3 = 3-CF_3).* Following the general procedure employing 4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1b**, 47 mg, 0.2 mmol) and mesityl(3-(trifluoromethyl)phenyl)-iodonium triflate (**2g**, 194 mg, 0.36 mmol). The product was obtained as a brown solid (75 mg, 0.142 mmol, 71%). mp 177−179 °C. IR: 3067, 1462, 1341, 1317, 1260, 1223, 1181,1161, 1120, 1070, 1029, 816, 765 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.06 (s, 1H, H-5), 8.21 (d, J = 1.9 Hz, 1H, H-2″), 8.17 (dd, J = 8.2, 1.7 Hz, 1H, H-4″), 8.13−8.07 (m, 2H, H-2′, H-6′), 8.04 (dt, J = 8.3, 1.4 Hz, 1H, H-6″), 7.94 (t, J = 8.0 Hz, 1H, H-5″), 7.68−7.60 (m, 3H, H-3′, H-5′ and H-4‴), 7.60−7.55 (m, 2H, H-3‴, H-5‴), 7.47 (dt, J = 7.0, 1.4 Hz, 2H, H-2‴, H-6‴), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 143.8 (C-4), 142.8 (C-4′), 134.4 (C-1″), 132.4 (C-1′), 131.8 (C-5″), 131.7 (C-4‴), 131.0 (C-3′, C-5′), 130.55 (C-6″), 130.54 (q, J = 33.2 Hz, C-3″), 129.44 (C-2‴, C-6‴/C-3‴, C-5‴), 129.41 (C-2‴, C-6‴/C-3‴, C-5‴), 129.1 (q, J = 3.3 Hz, C-4″), 127.4 (C-5), 123.6 (q, J = 3.6 Hz, C-2″), 123.1 (q, J = 272.9 Hz, CF_3), 122.1 (C-1‴), 121.4 (C-2′, C-6′), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 255 (N-1), 246 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −61.45 (CF_3), −77.77 (TfO). HRMS (ESI^+): calcd for $C_{22}H_{17}F_3N_3^+$ [M^+], 380.1369; found, 380.1363.

*1-(4-Methoxyphenyl)-3,4-diphenyl-1H-1,2,3-triazol-3-ium Triflate (**3h**, R^1 = OMe, R^2 = R^3 = H).* Following the general procedure employing 1-(4-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (**1c**, 50 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as an off-white solid (91 mg, 0.191 mmol, 95%). mp 89−91 °C. IR: 3096, 1606, 1594, 1570, 1515, 1492, 1459, 1440, 1250, 1153, 1027, 832, 762, 690, 635 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.98 (s, 1H, H-5), 8.14−8.07 (m, 2H, H-2′, H-6′), 7.77−7.71 (m, 3H, H-2″, H-6″ and H-4″), 7.68 (ddd, J = 7.5, 4.6, 1.8 Hz, 2H, H-3″, H-5″), 7.63−7.57 (m, 1H, H-4‴), 7.57−7.51 (m, 2H, H-3‴, H-5‴), 7.46 (dd, J = 5.3, 3.3 Hz, 2H, H-2‴, H-6‴), 7.38−7.31 (m, 2H, H-3′, H-5′), 3.91 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.8 (C-4′), 143.2 (C-4), 134.0 (C-1″), 132.2 (C-4″), 131.6 (C-4‴), 130.2 (C-3″, C-5″), 129.33 (H-2‴, H-6‴/H-3‴, H-5‴), 129.27 (H-2‴, H-6‴/H-3‴, H-5‴), 127.8 (C-1′), 127.2 (C-5), 126.3 (C-2″, C-6″), 123.2 (C-2′, C-6′), 122.6 (C-1‴), 115.6 (C-3′, C-5′), 56.0 (OCH_3). ^{15}N NMR (DMSO-d_6): δ 256 (N-1), 248 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.73 (TfO). HRMS (ESI^+): calcd for $C_{21}H_{18}N_3O^+$ [M^+], 328.1444; found, 328.1436.

*1-(4-Nitrophenyl)-3,4-diphenyl-1H-1,2,3-triazol-3-ium Triflate (**3i**, R^1 = NO_2, R^2 = R^3 = H).* Following the general procedure employing 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (**1d**, 53 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as an off-white solid (93 mg, 0.189 mmol, 94%). mp 141−145 °C. IR: 3108, 3082, 1594, 1531, 1488, 1337, 1253, 1224, 1156, 1026, 852, 767, 749, 692, 603 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.23 (s, 1H, H-5), 8.71−8.64 (m, 2H, H-3′, H-5′), 8.50−8.44 (m, 2H, H-2′, H-6′), 7.81−7.69 (m, 5H, H-2″, H-6″ and H-3″, H-5″ and H-4″), 7.66−7.60 (m, 1H, H-4‴), 7.60−7.54 (m, 2H, H-3‴, H-5‴), 7.51−7.44 (m, 2H, H-2‴, H-6‴). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 149.2 (C-4′), 143.6 (C-4), 138.7 (C-1′), 133.8 (C-1″), 132.5 (C-4″), 131.8 (C-4‴), 130.3 (C-3″, C-5″), 129.4 (C-3‴, C-5‴), 129.2 (C-2‴, C-6‴), 128.4 (C-5), 126.14 (C-3′, C-5′ and C-2″, C-6″), 126.10 (C-3′, C-5′ and C-2″, C-6″), 123.1 (C-2′, C-6′), 122.2 (C-1‴). ^{15}N NMR (DMSO-d_6): δ 367 (NO_2), 251 (N-1, N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{20}H_{15}N_4O_2^+$ [M^+], 343.1190; found, 343.1195.

*3-(4-(Dimethylamino)phenyl)-1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazol-3-ium Triflate (**3j**, R^1 = NO_2, R^2 = H, R^3 = 4-NMe_2).* Following the general procedure employing 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (**1d**, 53 mg, 0.2 mmol) and (4-(dimethylamino)phenyl) (mesityl)iodonium triflate (**2h**, 186 mg, 0.36 mmol). Column chromatography on silica (MeOH/dichloromethane = 1:30 → 1:10, v/v). The product was obtained as a dark yellow solid (34 mg, 0.0635 mmol, 32%). mp 115−118 °C. IR: 3072, 3044, 1682, 1607, 1595, 1524, 1340, 1190, 993, 854, 819, 764, 748, 718, 687, 638 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.13 (s, 1H, H-5), 8.70−8.58 (m, 2H, H-3′, H-5′), 8.43 (d, J = 9.1 Hz, 2H, H-2′, H-6′), 7.68−7.55 (m, 3H, H-3‴, H-5‴ and H-4‴), 7.49 (dd, J = 8.1, 1.6 Hz, 2H, H-2‴, H-6‴), 7.47−7.42 (m, 2H, H-2″, H-6″), 6.85 (d, J = 9.2 Hz, 2H, H-3″, H-5″), 3.01 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 152.0 (C-4″), 149.0 (C-4′), 142.9 (C-4), 138.8 (C-1′), 131.6 (C-4‴), 129.4 (C-3‴, C-5‴), 129.2 (C-2‴, C-6‴), 128.2 (C-5), 126.5 (C-2″, C-6″), 126.1 (C-3′, C-5′), 123.0 (C-2′, C-6′), 122.8 (C-1‴), 121.3 (C-1″), 111.7 (C-3″, C-5″), 39.8 (NMe_2). ^{15}N NMR (DMSO-d_6): δ 368 (NO_2), 253 (N-3), 249 (N-1), 56 (NMe_2). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{22}H_{20}N_5O_2^+$ [M^+], 386.1612; found, 386.1604.

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*3-(4-Methoxyphenyl)-1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**3k**, R^1 = NO_2, R^2 = H, R^3 = 4-OMe).* Following the general procedure employing 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (**1d**, 53 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (86 mg, 0.185 mmol, 93%). mp 232−236 °C. IR: 3083, 1594, 1529, 1511, 1305, 1218, 1054, 1019, 845, 770, 749, 710, 697 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.18 (s, 1H, H-5), 8.66 (d, *J* = 9.1 Hz, 2H, H-3′, H-5′), 8.45 (d, *J* = 9.1 Hz, 2H, H-2′, H-6′), 7.66 (d, *J* = 9.0 Hz, 2H, H-2″, H-6″), 7.65−7.55 (m, 3H, H-3‴, H-5‴ and H-4‴), 7.48 (d, *J* = 7.1 Hz, 2H, H-2‴, H-6‴), 7.22 (d, *J* = 9.0 Hz, 2H, H-3″, H-5″), 3.86 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.8 (C-4″), 149.2 (C-4′), 143.5 (C-4), 138.7 (C-1′), 131.7 (C-4‴), 129.5 (C-3‴, C-5‴), 129.2 (C-2‴, C-6‴), 128.2 (C-5), 127.7 (C-2″, C-6″), 126.3 (C-1″), 126.1 (C-3′, C-5′), 123.1 (C-2′, C-6′), 122.4 (C-1‴), 115.3 (C-3″, C-5″), 55.9 (OCH_3). ^{15}N NMR (DMSO-d_6): δ 368 (NO_2), 250 (N-1, N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.26 (d, *J* = 26 Hz, BF_4). HRMS (ESI^+): calcd for $C_{21}H_{17}N_4O_3^+$ $[M^+]$, 373.1295; found, 373.1301.

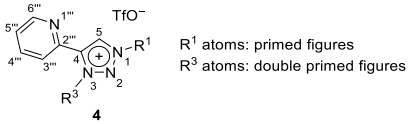
*1-(4-Nitrophenyl)-4-phenyl-3-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**3l**, R^1 = NO_2, R^2 = H, R^3 = 4-CH_3).* Following the general procedure employing 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (**1d**, 53 mg, 0.2 mmol) and mesityl(*p*-tolyl)iodonium triflate (**2d**, 175 mg, 0.36 mmol). The product was obtained as an off-white solid (99 mg, 0.195 mmol, 98%). mp 176−178 °C. IR: 3084, 1596, 1527, 1492, 1341, 1261, 1224, 1152, 1028, 853, 823, 762, 750, 689, 635 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.20 (s, 1H, H-5), 8.71−8.62 (m, 2H, H-3′, H-5′), 8.48−8.42 (m, 2H, H-2′, H-6′), 7.67−7.60 (m, 3H, H-3″, H-6″ and H-4‴), 7.60−7.55 (m, 2H, H-3‴, H-5‴), 7.50 (d, *J* = 8.3 Hz, 2H, H-3″, H-5″), 7.49−7.44 (m, 2H, H-2‴, H-6‴), 2.43 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 149.2 (C-4′) 143.5 (C-4), 142.7 (C-4″), 138.7 (C-1′), 131.7 (C-1″), 131.3 (C-4‴), 130.6 (C-3″, C-5″), 129.44 (C-3‴, C-5‴), 129.21 (C-2‴, C-6‴), 128.4 (C-5), 126.1 (C-3′, C-5′), 125.8 (c-2″, C-6″), 123.1 (C-2′, C-6′), 122.3 (C-1‴), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 368 (NO_2), 252 (N-1), 250 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −73.01 (TfO). HRMS (ESI^+): calcd for $C_{21}H_{17}N_4O_2^+$ $[M^+]$, 357.1346; found, 357.1340.

*1,3-Bis(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazol-3-ium Triflate (**3m**, R^1 = NO_2, R^2 = H, R^3 = 4-NO_2).* Following the general procedure employing 1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (**1d**, 53 mg, 0.2 mmol) and mesityl(4-nitrophenyl)iodonium triflate (**2f**, 186 mg, 0.36 mmol). The product was obtained as an off-white solid (102 mg, 0.190 mmol, 95%). mp 181−186 °C. IR: 3087, 1595, 1529, 1491, 1348, 1337, 1256, 1154, 1029, 853, 748, 694, 682, 637 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.27 (s, 1H, H-5), 8.72−8.66 (m, 2H, H-3′, H-5′), 8.58−8.53 (m, 2H, H-3″, H-5″), 8.52−8.45 (m, 2H, H-2′, H-6′), 8.06−8.01 (m, 2H, H-2″, H-6″), 7.69−7.63 (m, 1H, H-4‴), 7.63−7.57 (m, 2H, H-3‴, H-5‴), 7.50 (dd, *J* = 5.3, 3.4 Hz, 2H, H-2‴, H-6‴). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 149.5 (C-4′), 149.4 (C-4″), 144.0 (C-4), 138.5 (C-1′), 138.1 (C-1″), 132.1 (C-4‴), 129.7 (C-3‴, C-5‴), 129.4 (C-2‴, C-6‴), 128.7 (C-5), 128.0 (C-2″, C-6″), 126.2 (C-3′, C-5′), 125.7 (C-3″, C-5″), 123.2 (C-2′, C-6′), 121.8 (C-1‴). ^{15}N NMR (DMSO-d_6): δ 368 (NO_2' and NO_2''), 252 (N-1), 248 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −73.02 (TfO). HRMS (ESI^+): calcd for $C_{20}H_{14}N_5O_4^+$ $[M^+]$, 388.1040; found, 388.1032.

*1,3-Bis(4-methoxyphenyl)-4-(4-nitrophenyl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**3n**, R^1 = OMe, R^2 = NO_2, R^3 = 4-OMe).* Following the general procedure employing 1-(4-methoxyphenyl)-4-(4-nitrophenyl)-1*H*-1,2,3-triazole (**1e**, 59 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (86 mg, 0.175 mmol, 88%). mp 253−257 °C. IR: 3117, 2940, 2844, 1604, 1509, 1466, 1347, 1262, 1176, 1084, 1055, 837, 691, 652, 638 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.09 (s, 1H, H-5), 8.50−8.35 (m, 2H, H-3‴, H-5‴), 8.14−8.06 (m, 2H, H-2′, H-6′), 7.76−7.71 (m, 2H, H-2‴, H-6‴), 7.69−7.63 (m, 2H, H-2″, H-6″), 7.37−7.32 (m, 2H, H-3′, H-5′), 7.24−7.17 (m, 2H, H-3″, H-5″), 3.91 (s, 3H, OCH_3'), 3.85 (s, 3H, OCH_3''). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.87 (C-4′), 161.77 (C-4″), 149.0 (C-4‴), 141.3 (C-4), 131.0 (C-2‴, C-6‴), 128.8 (C-1‴), 128.1 (C-5), 127.77 (C-2″, C-6″), 127.70 (C-1′), 126.1 (C-1″), 124.5 (C-3‴, C-5‴), 123.2 (C-2′, C-6′), 115.7 (C-3′, C-5′), 115.4 (C-3″, C-5″), 56.06 (OCH_3'), 55.92 (OCH_3''). ^{15}N NMR (DMSO-d_6): δ 369 (NO_2), 254 (N-1), 249 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.25 (d, *J* = 26 Hz, BF_4). HRMS (ESI^+): calcd for $C_{22}H_{19}N_4O_4^+$ $[M + H]^+$, 403.1401; found, 403.1388.

*3,4-Bis(4-methoxyphenyl)-1-(4-nitrophenyl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**3o**, R^1 = NO_2, R^2 = OMe, R^3 = 4-OMe).* Following the general procedure employing 4-(4-methoxyphenyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazole (**1f**, 59 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). Analytically pure samples were obtained using column chromatography on silica (MeOH/dichloromethane = 1:10, v/v). The product was obtained as an off-white solid (82 mg, 0.168 mmol, 84%). mp 219−222 °C. IR: 3140, 2922, 2849, 1612, 1531, 1507, 1350, 1255, 1187, 1060, 1013, 845, 748, 636 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.14 (s, 1H, H-5), 8.65 (d, *J* = 9.2 Hz, 2H, H-3′, H-5′), 8.44 (d, *J* = 9.1 Hz, 2H, H-2′, H-6′), 7.76−7.60 (m, 2H, H-2″, H-6″), 7.40 (d, *J* = 8.8 Hz, 2H, H-2‴, H-6‴), 7.29−7.20 (m, 2H, H-3″, H-5″), 7.13 (d, *J* = 8.9 Hz, 2H, H-3‴, H-5‴), 3.87 (s, 3H, OCH_3''), 3.81 (s, 3H, OCH_3''). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.75 (C-4″), 161.66 (C-4‴), 149.2 (C-4′), 143.6 (C-4), 138.8 (C-1′), 130.8 (C-2‴, C-6‴), 127.7 (C-2″, C-6″), 127.6 (C-5), 126.5 (C-1″), 126.1 (C-3′, C-5′), 123.0 (C-2′, C-6′), 115.4 (C-3″, C-5″), 115.0 (C-3‴, C-5‴), 114.3 (C-1‴), 55.9 (OCH_3''), 55.60 (OCH_3'''). ^{15}N NMR (DMSO-d_6): δ 367 (NO_2), 250 (N-1, N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.26 (d, *J* = 26 Hz, BF_4). HRMS (ESI^+): calcd for $C_{22}H_{19}N_4O_4^+$ $[M^+]$, 403.1401; found, 403.1386.

Triazolium Salts 4a−n (Table 5).



4

*1,3-Diphenyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Triflate (**4a**, R^1 = R^3 = Ph).* Following the general procedure employing 2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (**1g**, 44 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as an off-white solid (57 mg, 0.126 mmol, 63%). mp 103−107 °C. IR: 3083, 1572, 1495, 1461, 1257, 1224, 1149, 1030, 1004, 762, 685 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.29 (s, 1H, H-5′), 8.64 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H, H-6‴), 8.21−8.16 (m, 2H, H-2′, H-6′), 8.08 (td, *J* = 7.8, 1.7 Hz, 1H, H-4‴), 7.85−7.80 (m, 3H, H-3′, H-5′, H-4′), 7.79−7.67 (m, 6H, 3H, H-2″, H-6″, H-4″, H-3″, H-5″, H-3‴), 7.61 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H, H-5‴). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 150.4 (C-6‴), 142.3 (C-2‴), 142.1 (C-4), 138.1 (C-4‴), 134.84 (C-1′/C-1″), 134.79 (C-1′/C-1″), 132.3 (C-4′), 132.1 (C-4″), 130.6 (C-3′, C-5′), 130.0 (C-3″, C-5″), 128.6 (C-5), 126.2 (C-5‴), 126.1 (C-2″, C-6″), 124.9 (C-3‴), 121.8 (C-2′, C-6′). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 254 (N-1), 249 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{19}H_{15}N_4^+$ $[M^+]$, 299.1291; found, 299.1293.

*3-(4-Methoxyphenyl)-1-phenyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**4b**, R^1 = Ph, R^3 = 4-MeO-C_6H_4).* Following the general procedure employing 2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (**1g**, 44 mg, 0.2 mmol) and bis(4-methoxyphenyl)-iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (59 mg, 0.141 mmol, 70%). mp 84−86 °C. IR: 3112, 1624, 1603, 1508, 1467, 1306, 1174, 1067, 977, 879, 837, 761, 732 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.24 (s, 1H, H-5), 8.69 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H, H-6‴), 8.19−8.14 (m, 2H, H-2′, H-6′), 8.06 (td, *J* = 7.8, 1.8 Hz, 1H, H-4‴), 7.85−7.77 (m, 3H, H-3′, H-5′, H-4′), 7.71−7.68 (m, 2H, H-2″, H-6″), 7.67 (dt, *J* = 7.9, 1.0 Hz, 1H, H-3‴), 7.62 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H, H-5‴), 7.25−7.18 (m, 2H, H-3″, H-5″), 3.87 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.6 (C-4″), 150.5 (C-6‴), 142.4 (C-2‴), 142.1 (C-4), 138.1 (C-4‴), 134.8 (C-1′), 132.2 (C-4′), 130.6 (C-3′, C-5′), 128.5 (C-5), 127.7 (C-2″, C-6″), 127.3 (C-1″), 126.2 (C-5‴),

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124.8 (C-3‴), 121.8 (C-2′, C-6′), 115.0 (C-3″, C-5″), 55.9 (OCH_3). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 254 (N-1), 248 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.27 (d, J = 25 Hz, BF_4). HRMS (ESI^+): calcd for $C_{20}H_{17}N_4O^+$ [M^+], 329.1397; found, 329.1394.

*3-Phenyl-4-(pyridin-2-yl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**4c**, R^1 = 4-CH_3-C_6H_4, R^3 = Ph).* Following the general procedure employing 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1h**, 47 mg, 0.2 mmol) and phenyl(mesityl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as an off-white solid (65 mg, 0.138 mmol, 69%). ^1H NMR (500 MHz, DMSO-d_6): δ 10.24 (s, 1H), 8.64 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H), 8.10−8.05 (m, 3H), 7.79−7.67 (m, 6H), 7.65−7.58 (m, 3H), 2.48 (s, 3H). The spectrum is consistent with the ^1H NMR spectrum of **4c**(BF_4) (see below).

For detailed characterization and analyses, **4c**(BF_4) was prepared according to the general procedure, employing 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1h**, 47 mg, 0.2 mmol) and diphenyliodonium tetrafluoroborate (**2b**, 132 mg, 0.36 mmol) to afford 3-phenyl-4-(pyridin-2-yl)-1-(*p*-tolyl)-1*H*-1,2,3-triazol-3-ium tetrafluoroborate (**4c**(BF_4)) after isolation as a white solid (41 mg, 0.102 mmol, 51%). mp 205−208 °C. IR: 3118, 1492, 1471, 1443, 1340, 1218, 1048, 1037, 815, 774, 740, 693 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.24 (s, 1H, H-5), 8.64 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H, H-6‴), 8.10−8.05 (m, 3H, H-4‴, H-2′, H-6′), 7.79−7.67 (m, 6H, H-2″, H-6″, H-4‴, H-3″, H-5″, H-3‴), 7.65−7.58 (m, 3H, H-3′, H-5′, H-5‴), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 150.4 (C-6‴), 142.6 (C-4′), 142.3 (C-2‴), 142.0 (C-4), 138.1 (C-4‴), 134.9 (C-1″), 132.5 (C-1′), 132.1 (C-4″), 130.9 (C-3′, C-5′), 129.9 (C-3″, C-5″), 128.3 (C-5), 126.20 (C-5‴), 126.15 (C-2″, C-6″), 124.9 (C-3‴), 121.5 (C-2′, C-6′), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 254 (N-1), 248 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.29 (d, J = 27 Hz, BF_4). HRMS (ESI^+): calcd for $C_{20}H_{17}N_4^+$ [M^+], 313.1448; found, 313.1451.

*4-(Pyridin-2-yl)-1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-3-ium Triflate (**4d**, R^1 = 4-CH_3-C_6H_4, R^3 = 4-CF_3-C_6H_4).* Following the general procedure employing 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1h**, 47 mg, 0.2 mmol) and mesityl(4-(trifluoromethyl)phenyl)iodonium triflate (**2c**, 194 mg, 0.36 mmol). The product was obtained as an off-white solid (68 mg, 0.126 mmol, 63%). mp 87−90 °C. IR: 2925, 1685, 1593, 1397, 1322, 1237, 1163, 1129, 1065, 1025, 1002, 823, 772, 636 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.31 (s, 1H, H-5), 8.59 (d, J = 4.7 Hz, 1H, H-6‴), 8.16−8.04 (m, 5H, H-4‴ and H-2′, H-6′, H-3″, H-5″), 8.01 (d, J = 8.3 Hz, 2H, H-2″, H-6″), 7.92 (d, J = 7.9 Hz, 1H, H-3‴), 7.62 (dd, J = 12.3, 7.8 Hz, 3H, H-5‴, H-3′, H-5′), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 150.3 (C-6‴), 142.8 (C-4′), 142.08 (C-4/C-2‴), 142.05 (C-4/C-2‴), 138.4 (C-4‴/C-1″), 138.3 (C-4‴/C-1″), 132.4 (C-1′), 131.0 (C-3′, C-5′), 128.4 (C-5), 127.5 (C-2″, C-6″), 127.1 (q, J = 4.0 Hz, 2d, C-3″, C-5″), 126.4 (C-5‴), 125.1 (C-3‴), 121.5 (C-2′, C-6′), 20.9 (CH_3). Quartet signals for C-4″ and CF_3 carbon atom could not be located in the spectrum. ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 256 (N-1), 245 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ 61.33 (CF_3) −77.78 (TfO). HRMS (ESI^+): calcd for $C_{21}H_{16}F_3N_4^+$ [M^+], 381.1322; found, 381.1326.

*3-(4-Methoxyphenyl)-4-(pyridin-2-yl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**4e**, R^1 = 4-CH_3-C_6H_4, R^3 = 4-MeO-C_6H_4).* Following the general procedure employing 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1h**, 47 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (52 mg, 0.119 mmol, 59%). mp 75−79 °C. IR: 2923, 2852, 1605, 1509, 1484, 1306, 1175, 1018, 836, 818, 783 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.20 (s, 1H, H-5), 8.69 (dt, J = 4.8, 1.4 Hz, 1H, H-6‴), 8.06 (dq, J = 7.7, 2.2, 1.7 Hz, 3H, H-2′, H-6′, H-4‴), 7.69 (d, J = 9.0 Hz, 2H, H-2″, H-6″), 7.65 (dt, J = 7.9, 1.1 Hz, 1H, H-3‴), 7.64−7.59 (m, 3H, H-3′, H-5′, H-5‴), 7.24−7.18 (m, 2H, H-3″, H-5″), 3.87 (s, 3H, OCH_3), 2.47 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.6 (C-4″), 150.4 (C-6‴), 142.47 (C-2‴/C-4′), 142.45 (C-2‴/C-4′), 142.1 (C-4), 138.1 (C-4‴), 132.5 (C-1′), 130.9 (C-3′, C-5′), 128.2 (C-5), 127.7 (C-2″, C-6″), 127.3 (C-1″), 126.1 (C-5‴), 124.7 (C-3‴), 121.5 (C-2′, C-6′), 115.0 (C-3″, C-5″), 55.9 (OCH_3), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 254 (N-1), 248 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.27 (d, J = 27 Hz, BF_4). HRMS (ESI^+): calcd for $C_{21}H_{19}N_4O^+$ [M^+], 343.1553; found, 343.1556.

*3-(4-Chlorophenyl)-4-(pyridin-2-yl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**4f**, R^1 = 4-CH_3-C_6H_4, R^3 = 4-Cl-C_6H_4).* Following the general procedure employing 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)-pyridine (**1h**, 47 mg, 0.2 mmol) and (4-chlorophenyl) (mesityl)-iodonium triflate (**2i**, 182 mg, 0.36 mmol). The product was obtained as a brown solid (43 mg, 0.087 mmol, 44%). mp 64−67 °C. IR: 3080, 1572, 1467, 1444, 1254, 1223, 1150, 1091, 1028, 1001, 818 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.27 (s, 1H, H-5), 8.63 (d, J = 4.6 Hz, 4.4H, H-6‴), 8.11 (td, J = 7.8, 1.8 Hz, 1H, H-4‴), 8.06 (d, J = 1.9 Hz, 2H, H-2′, H-6′), 7.86−7.77 (m, 5H, H-3‴, H-2″, H-3″, H-5″, H-6″), 7.66−7.59 (m, 3H, H-5‴, H-3′, H-5′), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 150.3 (C-6‴), 142.7 (C-4′), 142.2 (C-4), 142.1 (C-2‴), 138.2 (C-4‴), 136.7 (C-1″/C-4″), 133.8 (C-1″/C-4″), 132.4 (C-1′), 130.9 (C-3′, C-5′), 129.9 (C-2″, C-6″/C-3″, C-5″), 128.3 (C-5), 128.1 (C-2″, C-6″/C-3″, C-5″), 126.3 (C-5‴), 124.9 (C-3‴), 121.5 (C-2′, C-6′), 20.9 (CH_3). ^{15}N NMR (DMSO-d_6): δ 313 (N-1‴), 255 (N-1), 246 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.77 (TfO). HRMS (ESI^+): calcd for $C_{20}H_{16}ClN_4^+$ [M^+], 347.1058; found, 347.1055.

*3-Mesityl-4-(pyridin-2-yl)-1-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**4h**, R^1 = 4-CH_3-C_6H_4, R^3 = Mes).* Following the general procedure employing 2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1h**, 47 mg, 0.2 mmol) and dimesityliodonium triflate (**2k**, 185 mg, 0.36 mmol). The product was obtained as a brown solid (17 mg, 0.034 mmol, 17%). mp 67−69 °C. IR: 1573, 1513, 1254, 1222, 1149, 1028, 1001, 818, 785 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.43 (s, 1H, H-5), 8.59 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H, H-6‴), 8.12−8.05 (m, 3H, H-4‴, H-2′, H-6′), 7.75 (dt, J = 7.8, 1.1 Hz, 1H, H-3‴), 7.64−7.56 (m, 3H, H-5‴, H-3′, H-5′), 7.19 (s, 2H, H-3″, H-5″), 2.47 (s, 3H, CH_3-4′), 2.37 (s, 3H, CH_3-4″), 2.01 (s, 6H, CH_3-2″, CH_3-6″). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 150.6 (C-6‴), 142.5 (C-4′), 142.13 (C-4/C-2‴), 142.08 (C-4/C-2‴), 141.8 (C-4″), 138.3 (C-4‴), 134.7 (C-2″, C-6″), 132.7 (C-1′), 131.1 (C-1″), 130.6 (C-3′, C-5′), 129.5 (C-3″, C-5″), 129.0 (C-5), 126.3 (C-5‴), 123.7 (C-3‴), 121.6 (C-2′, C-6′), 20.82 (CH_3-4′/CH_3-4″), 20.76 (CH_3-4′/CH_3-4″), 16.9 (CH_3-2″, CH_3-6″). ^{15}N NMR (DMSO-d_6): δ 311 (N-1‴), 257 (N-1), 243 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.77 (TfO). HRMS (ESI^+): calcd for $C_{23}H_{23}N_4^+$ [M^+], 355.1917; found, 355.1915.

*1-(4-Methoxyphenyl)-3-phenyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Triflate (**4i**, R^1 = 4-MeO-C_6H_4, R^3 = Ph).* Following the general procedure employing 2-(1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-pyridine (**1i**, 50 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as an off-white solid (55 mg, 0.116 mmol, 58%). mp 96−99 °C. IR: 1606, 1593, 1243, 1223, 1157, 1025, 836, 768 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.19 (s, 1H, H-5), 8.64 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H, H-6‴), 8.14−8.09 (m, 2H, H-2′, H-6′), 8.07 (td, J = 7.8, 1.8 Hz, 1H, H-4‴), 7.77−7.73 (m, 3H, H-2‴, H-6‴, H-4‴), 7.72−7.66 (m, 3H, H-3‴, H-3″, H-5″), 7.60 (ddd, J = 7.7, 4.8, 1.1 Hz, 1H, H-5‴), 7.36−7.31 (m, 2H, H-3′, H-5′), 3.91 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.8 (C-4′), 150.4 (C-6‴), 142.4 (C-2‴), 141.9 (C-4), 138.1 (C-4‴), 134.8 (C-1″), 132.0 (C-4″), 129.9 (C-3″, C-5″), 128.2 (C-5), 127.8 (C-1′), 126.18 (C-5‴), 126.15 (C-2″, C-6″), 124.8 (C-3‴), 123.4 (C-2′, C-6′), 115.6 (C-3′, C-5′), 56.0 (OCH_3). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 256 (N-1), 245 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{20}H_{17}N_4O^+$ [M^+], 329.1397; found, 329.1399.

*1,3-Bis(4-methoxyphenyl)-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**4j**, R^1 = R^3 = 4-MeO-C_6H_4).* Following the general procedure employing 2-(1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-pyridine (**1i**, 50 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (64 mg, 0.127 mmol, 64%). mp 218−225 °C. IR: 1605, 1509, 1466, 1439, 1307, 1257, 1174, 1111, 1022, 828 cm^{-1}. ^1H

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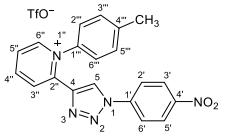
NMR (500 MHz, DMSO-d_6): δ 10.15 (s, 1H, H-5), 8.69 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H, H-6‴), 8.13−8.08 (m, 2H, H-2′, H-6′), 8.06 (td, J = 7.8, 1.7 Hz, 1H, H-4‴), 7.71−7.66 (m, 2H, H-2″, H-6″), 7.64 (dt, J = 7.8, 1.1 Hz, 1H, H-3‴), 7.61 (ddd, J = 7.7, 4.8, 1.1 Hz, 1H, H-5‴), 7.36−7.31 (m, 2H, H-3′, H-5′), 7.24−7.19 (m, 2H, H-3″, H-5″), 3.91 (s, 3H, OCH_3′), 3.87 (s, 3H, OCH_3″). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.8 (C-4′), 161.5 (C-4″), 150.4 (C-6‴), 142.5 (C-2‴), 142.0 (C-4), 138.0 (C-4‴), 128.1 (C-5), 127.79 (C-1′), 127.66 (C-2″, C-6″), 127.3 (C-1″), 126.1 (C-5‴), 124.7 (C-3‴), 123.4 (C-2′, C-6′), 115.5 (C-3′, C-5′), 115.0 (C-3″, C-5″), 56.0 (OCH3′), 55.9 (OCH_3″). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 254 (N-1), 247 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.48 (d, J = 25 Hz, BF_4). HRMS (ESI^+): calcd for $C_{21}H_{19}N_4O_2^+$ [M^+], 359.1503; found, 359.1494.

*1-(4-Nitrophenyl)-4-(pyridin-2-yl)-3-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**4k**, R^1 = 4-NO_2-C_6H_4, R^3 = 4-CH_3-C_6H_4).* Following the general procedure employing 2-(1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1j**, 53 mg, 0.2 mmol) and mesityl(*p*-tolyl)iodonium triflate (**2d**, 175 mg, 0.36 mmol). The product was obtained as an off-white solid (61 mg, 0.121 mmol, 60%). mp 122−124 °C. IR: 3058, 1237, 1221, 1151, 1026, 853, 751 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.42 (s, 1H, H-5), 8.69 (ddd, J = 4.9, 1.7, 1.0 Hz, 1H, H-6‴), 8.68−8.64 (m, 2H, H-3′, H-5′), 8.49−8.44 (m, 2H, H-2′, H-6′), 8.09 (td, J = 7.8, 1.8 Hz, 1H, H-4‴), 7.70 (dt, J = 7.9, 1.0 Hz, 1H, H-3‴), 7.67−7.61 (m, 3H, H-5‴ and H-2″, H-6″), 7.51 (d, J = 8.3 Hz, 2H, H-3″, H-5″), 2.45 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 150.5 (C-6‴), 149.2 (C-4′), 142.5 (C-4″), 142.21 (C-4), 142.16 (C-2‴), 138.8 (C-1′), 138.2 (C-4‴), 132.2 (C-1″), 130.4 (C-3″, C-5″), 129.5 (C-5), 126.4 (C-5‴), 126.0 (C-3′, C-5′), 125.8 (C-2″, C-6″), 124.9 (C-3‴), 123.3 (C-2′, C-6′), 21.0 (CH_3). ^{15}N NMR (DMSO-d_6): δ 367 (NO_2), 314 (N-1‴), 250 (N-1, N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.77 (TfO). HRMS (ESI^+): calcd for $C_{20}H_{16}N_5O_2^+$ [M + H]$^+$, 358.1304; found, 358.1303.

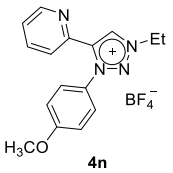
A side product was also isolated in pure form from the column, which was identified as 2-(1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)-1-(*p*-tolyl)pyridine-1-ium triflate (**4k′**, 7 mg, 7%):



^1H NMR (500 MHz, DMSO-d_6): δ 9.18 (dd, J = 6.2, 1.4 Hz, 1H, H-6″), 8.88 (td, J = 8.0, 1.4 Hz, 1H, H-4″), 8.69 (dd, J = 8.2, 1.4 Hz, 1H, H-3″), 8.64 (s, 1H, H-5), 8.49−8.43 (m, 2H, H-3′, H-5′), 8.27 (ddd, J = 7.7, 6.1, 1.5 Hz, 1H, H-5″), 8.08−8.01 (m, 2H, H-2′, H-6′), 7.62−7.56 (m, 2H, H-2‴, H-6‴), 7.45 (d, J = 8.2 Hz, 2H, H-3‴, H-5‴), 2.42 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 148.1 (C-6″), 147.7 (C-4′), 147.4 (C-4″), 144.9 (C-2″), 141.7 (C-4‴), 140.1 (C-4), 140.0 (C-1′), 139.7 (C-1‴), 130.7 (C-3‴, C-5‴), 129.1 (C-3″), 127.4 (C-5″), 126.5 (C-5), 126.1 (C-2‴, C-6‴), 126.0 (C-5′, C-3′), 121.6 (C-2′, C-6′), 21.1 (CH_3). ^{15}N NMR (DMSO-d_6): δ 368 (NO_2), 359 (N-3), 255 (N-1), 210 (N-1″).

*3-(4-Methoxyphenyl)-1-(4-nitrophenyl)-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**4l**, R^1 = 4-NO_2-C_6H_4, R^3 = 4-OMe).* Following the general procedure employing 2-(1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**1j**, 53 mg, 0.2 mmol), and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as an off-white solid (53 mg, 0.115 mmol, 57%). mp 211−218 °C. IR: 3127, 1608, 1511, 1343, 1257, 1055, 1023, 841, 784, 751, 682 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.41 (s, 1H, H-5), 8.71 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H, H-6‴), 8.67−8.64 (m, 2H, H-3′, H-5′), 8.49−8.44 (m, 2H, H-2′, H-6′), 8.08 (td, J = 7.8, 1.7 Hz, 1H, H-4‴), 7.73−7.69 (m, 2H, H-2″, H-6″), 7.67 (dt, J = 7.9, 1.1 Hz, 1H, H-3‴), 7.64 (ddd, J = 7.7, 4.8, 1.1 Hz, 1H, H-5‴), 7.25−7.21 (m, 2H, H-3″, H-5″), 3.88 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.7 (C-4″), 150.5 (C-6‴), 149.2 (C-4′), 142.28 (C-4), 142.19 (C-2‴), 138.7 (C-1′), 138.2 (C-4‴), 129.3 (C-5), 127.6 (C-2″, C-6″), 127.1 (C-1″), 126.3 (C-5‴), 126.0 (C-3′, C-5′), 124.8 (C-3‴), 123.2 (C-2′, C-6′), 115.1 (C-3″, C-5″), 55.9 (OCH_3). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 254 (N-1), 247 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −143.49 (d, J = 27 Hz, BF_4). HRMS (ESI^+): calcd for $C_{20}H_{16}N_5O_3^+$ [M^+], 374.1248; found, 374.1239.

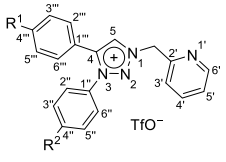
*1-(4-(Dimethylamino)phenyl)-3-phenyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Triflate (**4m**, R^1 = 4-NMe_2-C_6H_4, R^3 = Ph).* Following the general procedure employing *N*,*N*-dimethyl-4-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)aniline (**1k**, 53 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as an off-white solid (61 mg, 0.124 mmol, 62%). mp 91−95 °C. IR: 2923, 1677, 1603, 1522, 1494, 1461, 1439, 1253, 1149, 1027, 816, 770 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.10 (s, 1H, H-5), 8.63 (d, J = 4.4 Hz, 1H, H-6‴), 8.05 (td, J = 7.8, 1.4 Hz, 1H, H-4‴), 7.96 (d, J = 9.2 Hz, 2H, H-2′, H-6′), 7.78−7.64 (m, J = 19.1, 14.7, 8.0 Hz, 6H, H-2″, H-6″, H-4″, H-3″, H-5″, H-3‴), 7.59 (dd, J = 7.2, 4.9 Hz, 1H, H-5‴), 6.97 (d, J = 9.2 Hz, 2H, H-3′, H-5′), 3.07 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 152.1 (C-4), 150.3 (C-6‴), 142.5 (C-2‴), 141.7 (C-4), 138.0 (C-4‴), 134.9 (C-1″), 131.9 (C-4″), 129.9 (C-3″, C-5″), 126.9 (C-5), 126.2 (C-2″, C-6″), 126.1 (C-5‴), 124.8 (C-3‴), 123.0 (C-1′), 122.3 (C-2′, C-6′), 112.0 (C-3′, C-5′), 39.91 (NMe_2). ^{15}N NMR (DMSO-d_6): δ 314 (N-1‴), 256 (N-1), 245 (N-3), 57 (NMe_2). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI^+): calcd for $C_{21}H_{20}N_5^+$ [M^+], 342.1713; found, 342.1702.



4n

*1-Ethyl-3-(4-methoxyphenyl)-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**4n**).* Following the general procedure employing 2-(1-ethyl-1*H*-1,2,3-triazol-4-yl)pyridine (**1l**, 35 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as a brown solid (55 mg, 0.13 mmol, 65%). mp 109−111 °C. IR: 1605, 1512, 1741, 1257, 1179, 1032, 843, 786, 793 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.59 (s, 1H, H-5), 8.66 (dt, J = 4.6, 1.4 Hz, 1H, H-6‴), 8.00 (td, J = 7.8, 1.7 Hz, 1H, H-4‴), 7.63−7.59 (m, 2H, H-3″, H-5″), 7.57 (ddd, J = 7.8, 4.8, 1.1 Hz, 1H, H-5‴), 7.50 (dt, J = 8.0, 1.1 Hz, 1H, H-3‴), 7.21−7.15 (m, 2H, H-2″, H-6″), 4.80 (q, J = 7.3 Hz, 2H, CH_2), 3.86 (s, 3H, OCH_3), 1.67 (t, J = 7.3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.4 (C-4″), 150.4 (C-6‴), 142.6 (C-2‴), 141.5 (C-4), 137.9 (C-4‴), 129.8 (C-5), 127.6 (C-2″, C-6″), 127.3 (C-1″), 126.0 (C-5‴), 124.4 (C-3‴), 115.0 (C-3″, C-5″), 55.8 (OCH_3), 49.4 (CH_2), 14.0 (CH_3). ^{15}N NMR (DMSO-d_6): δ 345 (N-2), 314 (N-1‴), 256 (N-1) 246 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.26 (d, J = 27 Hz, BF_4). HRMS (ESI^+): calcd for $C_{16}H_{17}N_4O^+$ [M^+], 281.1397; found, 281.1400.

Triazolium Salts 5a−e (Table 6).



*3,4-Diphenyl-1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-3-ium Triflate (**5a**, R^1 = R^2 = H).* Following the general procedure employing 2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (**1m**, 47 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). A brown greasy product was obtained (87 mg, 0.188 mmol, 94%). IR: 1593, 1491, 1439, 1253, 1223, 1150, 1028, 762, 692, 635 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.53 (s, 1H, H-5), 8.71−8.61 (m, 1H, H-6′), 7.97 (td, J = 7.7, 1.8 Hz, 1H, H-4′), 7.75−7.69 (m, 2H, H-3′, H-4″), 7.67−7.61 (m, 4H, H-2″, H-6″, H-3″, H-5″), 7.58−7.53 (m, 1H, H-4‴), 7.53−7.47 (m, 3H, H-5′, H-3‴, H-5‴), 7.44−7.38 (m, J = 5.3, 3.3 Hz, 2H, H-2‴, H-6‴), 6.19 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 151.7 (C-2′), 149.9 (C-6′), 142.8 (C-4), 137.8 (C-4′), 133.9 (C-1″), 132.1 (C-4″), 131.4 (C-4‴), 130.1 (C-3″,

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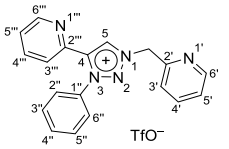
C-5″), 130.1 (C-3″, C-5″), 129.4 (C-3‴, C-5‴), 129.2 (C-2‴, C-6‴), 126.2 (C-2″, C-6″), 124.3 (C-5′), 123.6 (C-3′), 122.5 (C-1‴), 57.8 (CH_2). ^{15}N NMR (DMSO-d_6): δ 343 (N-2), 312 (N-1′), 250 (N-1, N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI$^+$): calcd for $C_{20}H_{17}N_4^+$ [M$^+$], 313.1448; found, 313.1445.

*3-Phenyl-1-(pyridin-2-ylmethyl)-4-(p-tolyl)-1H-1,2,3-triazol-3-ium Triflate (**5b**, R^1 = CH_3, R^2 = H).* Following the general procedure employing 2-((4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (**1n**, 50 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). A brown greasy product was obtained (81 mg, 0.196 mmol, 98%). IR: 1594, 1507, 1439, 1188, 1030, 817, 758, 731 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.48 (s, 1H, H-5), 8.65 (d, J = 4.2 Hz, 1H, H-6′), 7.97 (td, J = 7.7, 1.8 Hz, 1H, H-4′), 7.76−7.67 (m, 2H, H-3′, H-4″), 7.67−7.61 (m, 4H, H-2″, H-6″, H-3″, H-5″), 7.49 (dd, J = 6.8, 4.9 Hz, 1H, H-5′), 7.34−7.24 (m, 4H, H-2‴, H-6‴, H-3‴, H-5‴), 6.17 (s, 2H, CH_2), 2.32 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 151.7 (C-2′), 149.9 (C-6′), 142.9 (C-4), 141.6 (C-4‴), 137.8 (C-4′), 134.0 (C-1″), 132.1 (C-4″), 130.1 (C-3″, C-5″), 129.78 (C-5), 129.76 (C2‴, C-6‴/C-3‴, C-5‴), 129.21 (C2‴, C-6‴/C-3‴, C-5‴), 126.2 (C-2″, C-6″), 124.3 (C-5′), 123.6 (C-3′), 119.6 (C-2‴), 57.8 (CH_2), 21.0 (CH_3). ^{15}N NMR (DMSO-d_6): δ 343 (N-2), 312 (N-1′), 250 (N-1), 249 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_4^+$ [M$^+$], 327.1604; found, 327.1604.

*4-(4-Methoxyphenyl)-3-phenyl-1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-3-ium Triflate (**5c**, R^1 = OMe, R^2 = H).* Following the general procedure employing 2-((4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (**1o**, 53 mg, 0.2 mmol) and mesityl(phenyl)-iodonium triflate (**2a**, 170 mg, 0.36 mmol). A brown greasy product was obtained (86 mg, 0.175 mmol, 88%). IR: 1678, 1588, 1492, 1440, 1246, 1173, 1027, 833, 753, 691 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.45 (s, 1H), 8.71−8.61 (m, 1H), 8.01−7.93 (m, 1H), 7.77−7.61 (m, 6H), 7.49 (dd, J = 7.6, 4.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.16 (s, 2H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.4 (C-4‴), 151.8 (C-2′), 149.9 (C-6′), 142.8 (C-4), 137.8 (C-4′), 134.0 (C-1″), 132.1 (C-4″), 131.0 (C-2‴, C-6‴), 130.2 (C-3″, C-5″), 129.4 (C-5), 126.2 (C-2″, C-6″), 124.3 (C-5′), 123.6 (C-3′), 114.7 (C-3‴, C-5‴), 114.4 (C-1‴), 57.7 (CH_2), 55.5 (OCH_3). ^{15}N NMR (DMSO-d_6): δ 342 (N-2), 313 (N-1′), 250 (N-1, N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.75 (TfO). HRMS (ESI$^+$): calcd for $C_{21}H_{19}N_4O^+$ [M$^+$], 343.1553; found, 343.1554.

*3,4-Bis(4-methoxyphenyl)-1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-3-ium Tetrafluoroborate (**5d**, R^1 = R^2 = OMe).* Following the general procedure employing 2-((4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (**1o**, 53 mg, 0.2 mmol) and bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**, 154 mg, 0.36 mmol). The product was obtained as a brown solid (84 mg, 0.183 mmol, 91%). mp 92−96 °C. IR: 3115, 1609, 1506, 1254, 1179, 1014, 834, 716 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.40 (s, 1H, H-5), 8.69−8.60 (m, 1H, H-6′), 7.96 (td, J = 7.7, 1.8 Hz, 1H, H-4′), 7.71 (d, J = 7.8 Hz, 1H, H-3′), 7.60−7.55 (m, 2H, H-3″, H-6″), 7.48 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H, H-5′), 7.36−7.31 (m, 2H, H-2‴, H-6‴), 7.19−7.13 (m, 2H, H-3″, H-5″), 7.07−7.02 (m, 2H, H-3‴, H-5‴), 6.13 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3″), 3.78 (s, 3H, OCH_3‴). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 161.40 (C-4‴), 161.35 (C-4″), 151.8 (C-2′), 149.9 (C-6′), 142.8 (C-4), 137.9 (C-4′), 130.9 (C-2‴, C-6‴), 129.3 (C-6), 127.8 (C-2″, C-6″), 126.6 (C-1″), 124.3 (C-5′), 123.6 (C-3′), 115.2 (C-3″, C-5″), 114.7 (C-3‴, C-5‴), 114.5 (C-1‴), 57.7 (CH_2), 55.8 (OCH_3″), 55.5 (OCH_3‴). ^{15}N NMR (DMSO-d_6): δ 343 (N-2), 312 (N-1′), 251 (N-1), 247 (N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −148.23 (d, J = 26 Hz, BF_4). HRMS (ESI$^+$): calcd for $C_{22}H_{21}N_4O_2^+$ [M$^+$], 373.1659; found, 373.1660.

*3-Phenyl-4-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-3-ium Triflate (**5e**).*



Following the general procedure employing 2-((4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (**1p**, 47 mg, 0.2 mmol) and mesityl(phenyl)iodonium triflate (**2a**, 170 mg, 0.36 mmol). The product was obtained as brown oil (40 mg, 0.261 mmol, 43%). IR: 3094, 1592, 1574, 1495, 1439, 1253, 1223, 1149, 1049, 1028, 757, 691 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 9.71 (s, 1H, H-5), 8.64 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H, H-6′), 8.60 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H, H-6‴), 8.04−7.94 (m, 2H, H-4′, H-4‴), 7.74−7.61 (m, 7H, H-3′, Ph, H-3‴), 7.56 (ddd, J = 7.7, 4.8, 1.1 Hz, 1H, H-5‴), 7.49 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H, H-5′), 6.22 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 151.7 (C-2′), 150.3 (C-6‴), 149.8 (C-6′), 142.3 (C-2‴), 141.6 (C-4), 137.9 (C-4′/C-4‴), 137.8 (C-4′/C-4‴), 134.7 (C-1″), 132.0 (C-4″), 131.1 (C-5), 129.9 (C-3″, C-5″), 126.1 (C-5‴ and C-2″, C-6″), 124.8 (C-3‴), 124.3 (C-5′), 123.5 (C-3′), 57.8 (CH_2). ^{15}N NMR (DMSO-d_6): δ 345 (N-2), 312 (N-1′), 249 (N-1 and N-3). $^{19}F\{^1H\}$ NMR (471 MHz, DMSO-d_6): δ −77.76 (TfO). HRMS (ESI$^+$): calcd for $C_{19}H_{16}N_5^+$ [M$^+$], 314.1400; found, 314.1401.

*General Procedure for "One-Pot" Preparation of triazolium Salts **3a**, **4a**, and **5a** (Table 8).* A dry, nitrogen-flushed ACE tube, equipped with a magnetic stirring bar, was charged with organic azide **6** (1 mmol, 1 equiv), acetylene **7** (1 mmol, 1 equiv), phenyl-(mesityl)iodonium triflate **2a** (756 mg, 1.6 mmol, 1.6 equiv), and $Cu(PPh_3)_3Br$ (0.05 mmol, 47 mg, 5 mol %), and sealed. The reaction tube was placed in a preheated metal block at 130 °C and the reaction mixture was stirred for 3 h. Products were isolated as described in the above general procedures for the synthesis of the corresponding triazolium salt **3a**, **4a**, or **5a**. ^1H NMR spectra of isolated products were in agreement with the authentic samples prepared as described above.

*General Procedure for "One-Pot" Preparation of triazolium Salts **3a**, **4a**, and **4j** Starting from NaN_3 (Table 9).* A dry, nitrogen-flushed ACE tube, equipped with a magnetic stirring bar, was charged sodium azide (23 mg, 0.36 mmol, 1 equiv), acetylene **7** (0.36 mmol, 1 equiv), and iodonium salt **2** (0.936 mmol, 2.6 equiv). Then, $Cu(PPh_3)_3Br$ (0.02 mmol, 17 mg, 5 mol %) was added and the tube was sealed. The reaction tube was placed in a preheated metal block at 130 °C and the reaction mixture was stirred for 3 h. The products were isolated as described in the above general procedures for the synthesis of the corresponding triazolium salt **3a**, **4a**, or **4j**. ^1H NMR spectra of isolated products were in agreement with the authentic samples prepared as described above.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b02197.

Copies of NMR spectra (PDF)

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The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Marijan Kočevar on the occasion of his 70th birthday, recognizing his lifetime achievements in educational and scientific work.

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