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原位生成的磺酸催化 *N*-磺酰基-1,2,3-三氮唑与醇偶联高区域选择性合成 N^2-取代 1,2,3-三氮唑

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摘要 1,2,3-三氮唑 N^1、N^3 原子电子云比 N^2 原子电子云更加富集, 更容易发生各类化学转化, 因此其研究更为充分. 相较而言, 高区域选择性合成 N^2-1,2,3-三氮唑的研究相对有限. 采用天然来源且价廉易得的醇替代卤代试剂, 与 *N*-磺酰基-1,2,3-三氮唑偶联, 在无需添加任何催化剂或添加剂条件下, 通过原位生成的磺酸催化, 高区域选择性、高收率(68%～83%)地合成了 N^2-取代 1,2,3-三氮唑. 该反应具有广阔的底物适应性, 芳基苄醇和烷基醇等都具有良好的官能团兼容性. 初步机理研究显示, *N*-磺酰基-1,2,3-三氮唑水解产生的甲基磺酸有效催化了反应中的亲核取代过程, 并通过热稳定中间体 N^2H-1,2,3-三氮唑实现了高区域选择性.

关键词 高区域选择性; 无金属催化; N^2-取代 1,2,3-三氮唑; 绿色合成

High Regioselective Synthesis of N^2-Substituted-1,2,3-triazole via *N*-Sulfonyl-1,2,3-triazole Coupling with Alcohol Catalyzed by *in-situ* Generated Sulfonic Acid

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Abstract The green and highly efficient synthesis of N^2-substituted 1,2,3-triazoles remains challenging due to the lower electron density at the N^2-atom than that at two terminal nitrogen atoms (N^1 and N^3) of the triazole heterocycle. Cheap and easily available alcohols were developed as starting points to couple with *N*-sulfonyl-1,2,3-triazole instead of halogenated reagents catalyzed by *in-situ* generated sulfonic acid. The resulting products, N^2-substituted 1,2,3-triazoles, were obtained with high regioselectivity and in good yields (68%～83%) without any additional catalysts or additives. The reaction has a broad substrate adaptability and functional group compatibility, including aryl benzyl and alkyl alcohols. Preliminary mechanistic studies indicate that methanesulfonic acid (MsOH) which *in situ* produced by the hydrolysis of *N*-sulfonyl-1,2,3-triazoles promoted the reaction, and high regioselectivity was promoted through the thermally stable intermediate N^2H-1,2,3-triazole.

Keywords high regioselectivity; free-catalysis; N^2-substituted 1,2,3-triazole; green synthesis

1 Introduction

N^2-Substituted 1,2,3-triazoles are present in numerous natural products, pharmaceuticals and functional materials.[1] Hence, it is extremely valuable to develop an efficient and highly regioselective method for the preparation of N^2-substituted 1,2,3-triazoles. However, the synthesis of N^2-substituted 1,2,3-triazoles remains challenging due to the lower electron density at the N^2-atom than that at two terminal nitrogen atoms (N^1 and N^3) of the triazole heterocycle, which has limited their further application.[2]

Several elegant strategies have been established to access N^2-substituted 1,2,3-triazoles (Scheme 1). For example, Wang[3] and Shi[2] developed a method for the synthesis of N^2-substituted triazoles by introducing bulky groups (such as bromine atom) at positions 4 and 5 of 1,2,3-triazoles to lower the electron density or increase the steric hindrance at N^1 and N^3 (Scheme 1, a). The resulting enhanced reactivity at the N^2 atom enabled an efficient synthesis of N^2-substituted 1,2,3-triazoles. However, the protocol suffered from a substrate scope limitation. Shi and Chen's group[4] also reported a high regioselective synthe-

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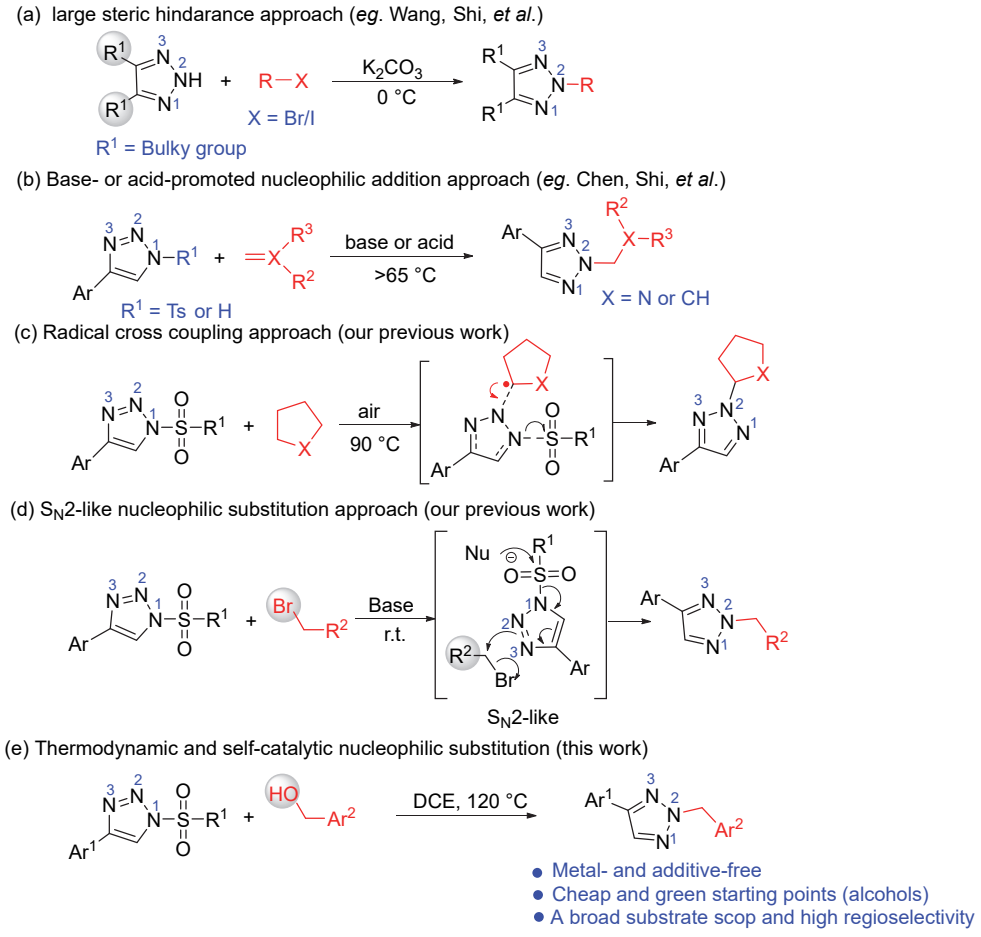
sis of N^2-substituted triazoles by a base or acid-induced N^2 nucleophilic addition of *N*-sulfonyl-1,2,3-triazoles to iminium ion or olefins, respectively (Scheme 1, b). High regioselectivity of this approach was dictated by the key intermediate 4-phenyl-2*H*-1,2,3-triazoles (**4a**), which was generated from the hydrolysis of *N*-sulfonyl-1,2,3-triazole as a more stable tautomer than the other one (4-phenyl-1*H*-1,2,3-triazoles, **4a'**) at high temperature. Very recently, our group developed an efficient strategy for the synthesis of N^2-substituted triazoles by oxidative C(sp^3)—H amination of tetrahydrofuran via a radical-initiated S_N2-like coupling. This approach also somewhat suffered from a substrate scope limitation (Scheme 1, c).[5] We then developed an approach to orient highly regioselective N^2-substituted 1,2,3-triazoles by a base-promoted S_N2-like nucleophilic substitution of haloalkanes (Scheme 1, d).[6] The developed method is highly efficient under mild conditions (room temperature) with a broad substrate scope. However, the use of halogenated substrates has certain limitations, such as the generation of toxic and harmful by-products, which is not environmentally friendly. Thus, it is highly desirable to develop alternative methods that are environmentally friendly and process efficient, using readily available and less toxic substrates, such as using alcohol as alkylating reagents to replace organic halides.

N-Sulfonyl-1,2,3-triazoles, which can be easily prepared from copper(I)-catalyzed azide-alkyne cycloadditions,[7] have been utilized as one of the most important precursors of carbene to access other heterocycles by a variety of chemical transformations.[8] Over the past decades, many legend transformations of *N*-sulfonyl-1,2,3-triazoles were developed by Fokin,[9] Gevorgyan,[10] Li,[11] and other groups.[12] Despite the inherently strong C—O bonds in alcohols, numerous methods via dehydroxylation of alcohols cross-coupling with nucleophiles to construct various complex molecules have been established.[13] Thus, we were curious whether alcohols would react with *N*-sulfonyl-1,2,3-triazole via nucleophilic substitution reaction to afford N^2-substituted 1,2,3-triazoles. It remains challenging to promote the envisioned reaction and several main competitive transformations will occur. For example, *N*-sulfonyl-1,2,3-triazoles readily undergo a ring-opening process followed by a carbene or *N*-sulfonyl ketenimine formation under heating.[14] N^1 and N^3-selective competitive reactions are also big challenges.

2 Results and discussion

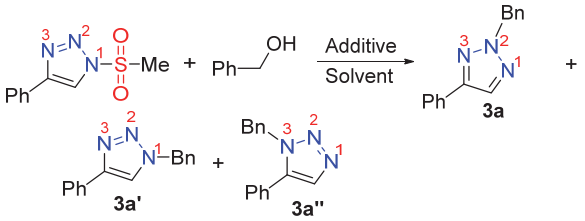
Benzyl carbocations are readily generated from benzyl alcohols under an acidic environment and relatively stable



Scheme 1 Highly regioselective synthesis of N^2-substituted 1,2,3-triazoles

for fruitful transformations.[15] Then *N*-sulfonyl-1,2,3-triazole (**1a**) and benzyl alcohol (**2a**) were used to test the reaction. The coupling reaction of **1a** (0.2 mmol) and **2a** (2.0 mmol) was initially examined using dichloroethane (DCE) as the reaction solvent and TsOH (0.4 mmol) as additive at room temperature. No desired coupling products **3a**/**3a'** were observed (Table 1, Entry 1). Raising the reaction temperature to 50 ℃ or 80 ℃ still failed to give the desired product (Table 1, Entries 2, 3). Further raising the temperature to 100 ℃ gratifyingly offered the desired N^2-product **3a** in 50% isolated yield (Table 1, Entry 4). The N^1-product **3a'** was also obtained in 5% isolated yield. The reaction yield was further improved to 80% yield for **3a** when the reaction temperature was continuously raised to 120 ℃ (Table 1, Entry 5). At a higher temperature than 120 ℃, the yield decreased slightly (Table 1, Entry 6). Increasing the amount of additive has no obvious effect on the yield (Table 1, Entry 7). Interestingly, the reaction even proceeded successfully to afford the N^2-product **3a** in 82% yield in the absence of TsOH (Table 1, Entry 8). With the optimal temperature 120 ℃, screening of solvent did not improve the reaction yield (Table 1, Entries 9～12). Decreasing the amount of benzyl alcohol to 5 equiv. did not affect the reaction, but further decreasing the amount to 3 equiv. led to a diminished yield of N^2-product (Table 1, Entries 13, 14).

Table 1 Optimization of the reaction conditions[a]



Entry	Additive	Solvent	Temp./℃	Yield[b]/%	
				3a	**3a'**
1	TsOH	DCE	rt	n.d.	n.d.
2	TsOH	DCE	50	n.d.	n.d.
3	TsOH	DCE	80	n.d.	n.d.
4	TsOH	DCE	100	50	5
5	TsOH	DCE	120	80	8
6	TsOH	DCE	130	76	10
7[c]	TsOH	DCE	120	80	10
8	None	DCE	120	82	12
9	None	PhMe	120	72	8
10	None	CH_3CN	120	63	10
11	None	DMF	120	45	5
12	None	DMSO	120	55	7
13[d]	None	DCE	120	82	12
14[e]	None	DCE	120	52	6
15	None	DCE	120	45	5

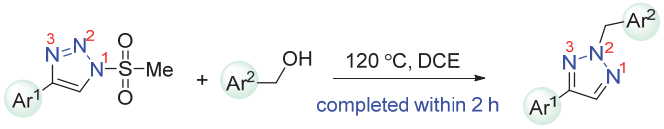
[a] Unless otherwise noted, all reactions were carried out on a 0.2 mmol scale with n(**1a**)∶n(**2a**)=1∶10, and additive (0.4 mmol) in solvent (2.0 mL) at the specified reaction temperature in air for 2 h. DMF=*N*,*N*-dimethylformamide, DMSO=dimethyl sulfoxide. [b] Isolated yield. [c] Using 4.0 equiv. of TsOH. [d] Using 5.0 equiv. of benzyl alcohol. [e] Using 3.0 equiv. of benzyl alcohol.

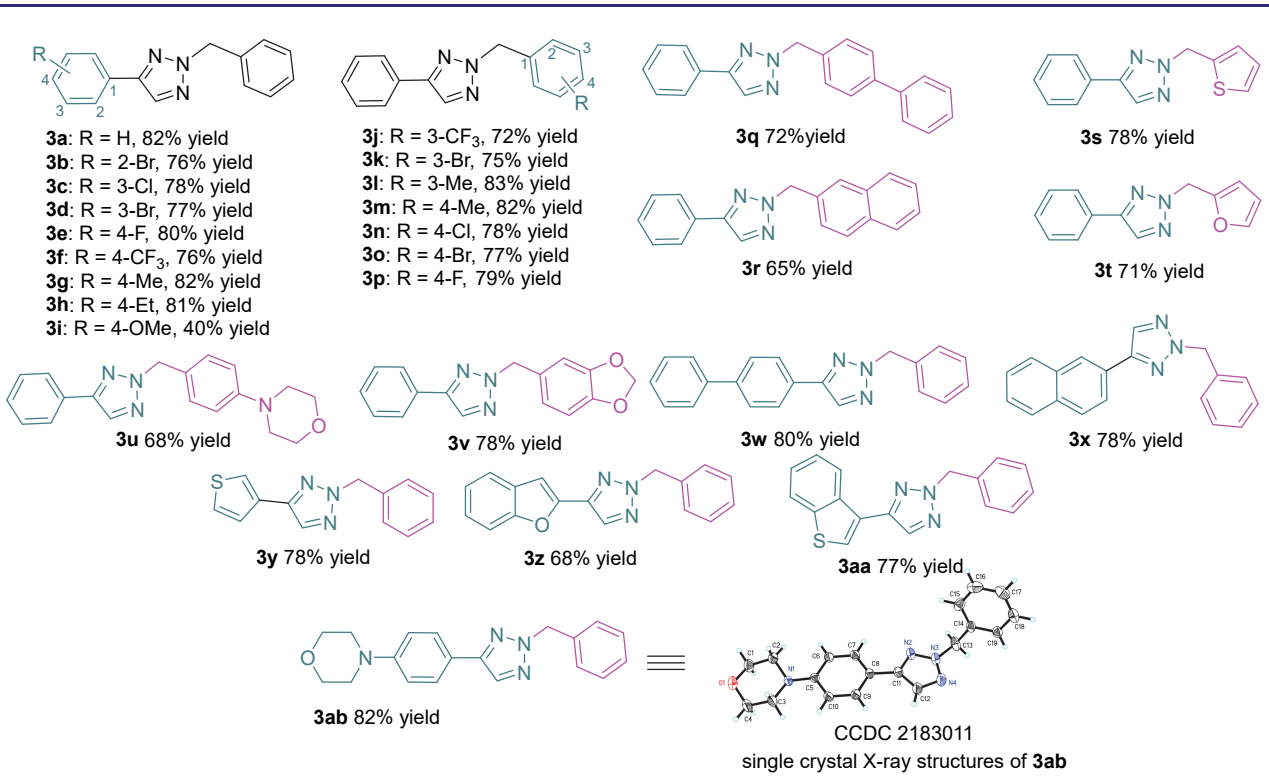
N-Tosyl-1,2,3-triazole was not well applicable in the reaction due to the production of *α*-cyano sulfone via ketenimines pathway (Table 1, Entry 15).[16] Overall, it was found that the optimal reaction conditions involved using DCE as the solvent at 120 ℃ in air without any additives. The model reaction was completed within 2 h. N^1-Substituted triazole was always observed as the main by-product and trace amounts of N^3-substituted triazole could be monitored by liquid chromatograph mass spectrometer (LCMS) (≈2%).

With the optimized conditions in hand, the substrate scope was subsequently investigated (Table 2). Neither electron-withdrawing nor electron-donating substituents on the phenyl group in *N*-sulfonyl-1,2,3-triazole affected the yields (**3b**～**3h**, 76%～82%). Strong electron donor group 4-OMe substituent on the phenyl group in *N*-sulfonyl-1,2,3-triazole was unfavorable for the reaction affording the product in a low yield of 40% (**3i**). Either benzyl alcohols containing electron-withdrawing or electron-donating substituents at the *para* or *meta* position of the phenyl group transformed smoothly into the desired products in high yields (**3j**～**3p**, 76%～82%). Naphthalene-2-ylmethanol (**2i**) and [1,1'-biphenyl]-4-ylmethanol (**2j**) also afforded the corresponding product in 72% (**3q**) and 65% (**3r**) yields, respectively. In addition, aromatic heterocyclic alcohol, including thiophene-2-ylmethanol (**2k**), furan-2-ylmethanol (**2l**), (4-morpholinophenyl)methanol (**2m**) and benzo[*d*]-[1,3]dioxol-5-ylmethanol (**2n**), reacted well and afforded moderate to good yields (**3s**～**3v**, 68%～78%). The *N*-sulfonyl-1,2,3-triazole with biphenyl (**1j**) or naphthalene (**1k**) substitution also delivered the desired product in good yields (**3w**, 80% yield; **3x**, 78% yield). The triazoles possessing heterocyclic groups at the 4-position of the phenyl ring (**1l**～**1o**) were then examined and it was found that they all reacted well with benzyl alcohol to afford the corresponding products (**3y**～**3ab**) in good yields (68%～82%). In all cases, the main by-product was N^1-alkylated **3'**. Trace amounts of NH-1,2,3-triazole **4** from desulfonylation and N^3-alkylated byproduct were also observed in some cases. The products were determined to be N^2-selective using single-crystal X-ray analysis of **3ab**, and the other products were tentatively assigned by analogy.

Alkyl-substituted alcohols have also been used to explore the reactions (Table 3). When methanol was tested to react with *N*-sulfonyl-1,2,3-triazole, N^1-substituted 1,2,3-triazole (**3ac**) was accidentally formed in 70% isolated yield with by-product of 4-phenyl-1*H*-1,2,3-triazole (**4a**, 20% yield). For the substrates with electron-withdrawing or electron-donating groups on the aromatic ring of *N*-sulfonyl-1,2,3-triazoles, the N^1-products were afforded in moderate yields (**3ad**, 65% yield; **3ae**, 68% yield). Only a trace of N^1-products (≈5%) can be observed when ethanol reacted with **1a**, which may be attributed to that ethanol can produce the corresponding carbocation effectively in this reaction. The product **3ae** was determined to be an N^1-substituted triazole by single-crystal X-ray analysis. The mechanism of the N^1-selectivity for methanol is not clear, and it may be due to

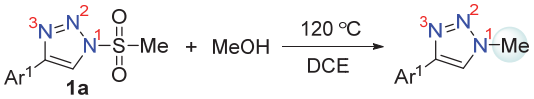
Table 2 Scope of substrates

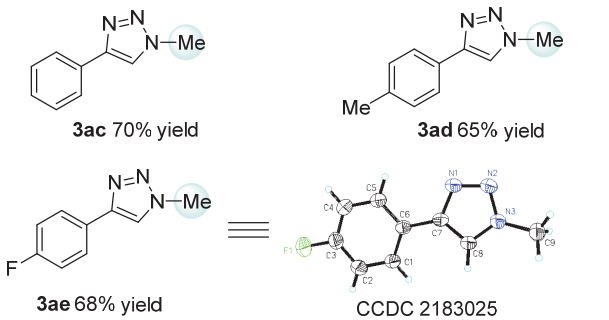




the much lower $D(R^{+}\text{-}H^{-})$ (heterolytic bond dissociation energy) value of methyl carbocation.[17] The control experiment was performed by using N^2-methyl-1,2,3-triazole to reflux under the identified conditions and no N^1-methyl-1,2,3-triazole was detected. The results exclude that the N^1 product was yielded via the migration of methyl group from N^2 to N^1 atom.

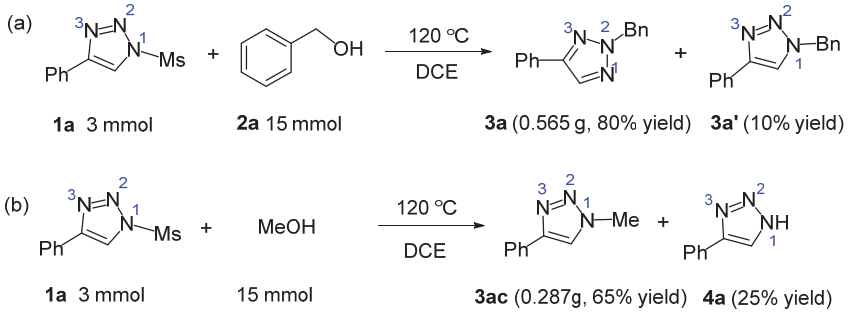
Table 3 Reaction of *N*-sulfonyl-1,2,3-triazole with methanol



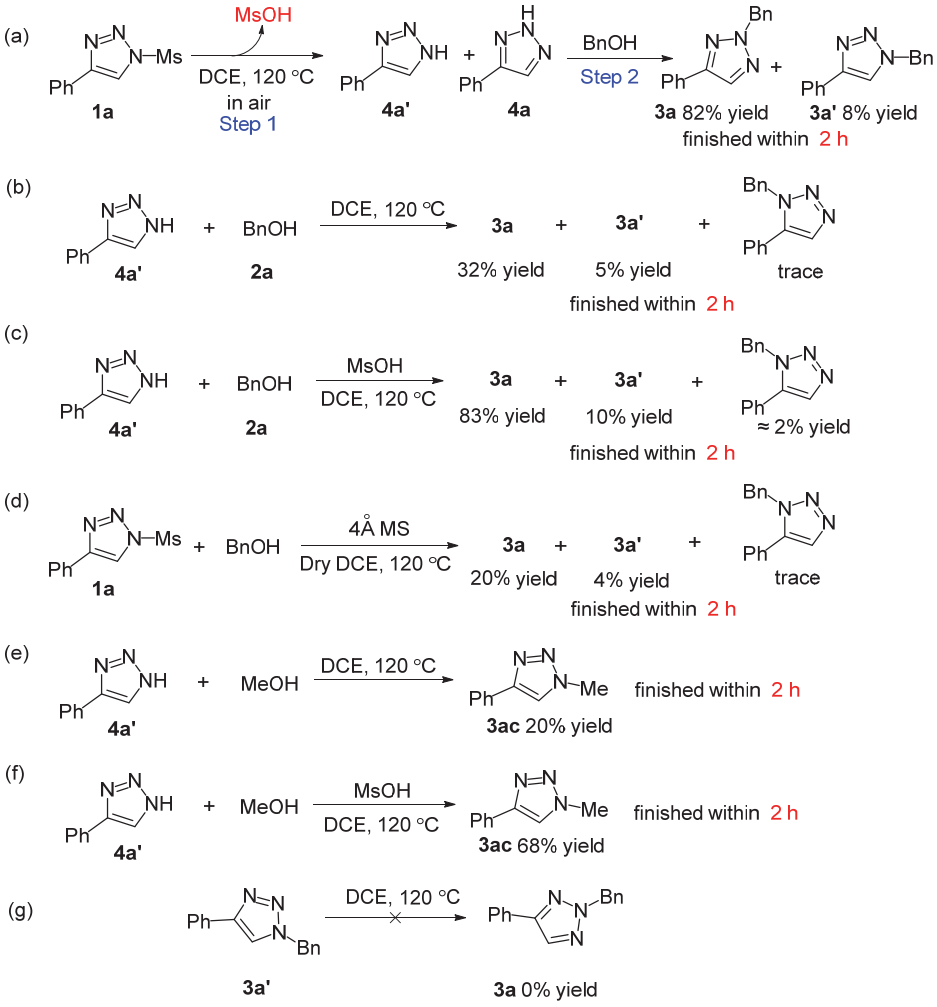


To demonstrate the practicality of the reaction for organic synthesis, a gram-scale synthesis was performed (Scheme 2). The coupling of **1a** (3.0 mmol, 0.669 g) with **2a** (15.0 mmol, 1.622 g) delivered the desired product **3a** with a comparable yield (0.565 g, 80% yield), and the coupling of **1a** (3.0 mmol, 0.669 g) with methanol (15.0 mmol, 0.48 g) also gave the N^1-product **3ac** with a moderate yield (0.287g, 65% yield).

To gain insight into the reaction mechanism, a series of control experiments were conducted. First, *N*-sulfonyl-1,2,3-triazole (**1a**) was desulfonylated in DCE for 2 h to generate 4-phenyl-1*H*-1,2,3-triazole (**4a'**) and 4-phenyl-2*H*-1,2,3-triazole (**4a**), releasing 1 equiv. of methanesulfonic acid (MsOH). When benzyl alcohol (**2a**) was subsequently added, the coupling N^2-product **3a** and N^1-product **3a'** were formed in 82% and 8% isolated yields, respectively (Scheme 3, a). When **4a'** was isolated to react with benzyl alcohol without MsOH, the yield of **3a** was reduced to 32% (Scheme 3, b). In the presence of 1.0 equiv. of MsOH, **4a'** reacted with benzyl alcohol smoothly and a similar yield of **3a** was obtained (83%, Scheme 3, c). Furthermore, the reaction proceeded not well and only afforded the desired product in 20% yield with ultra dry solvent and 4 Å molecular sieves within 2 h (Scheme 3, d). When methanol reacted with **4a'** with and without methanesulfonic acid (Scheme 3, e and f), the yields were 68% and 20%, respec-



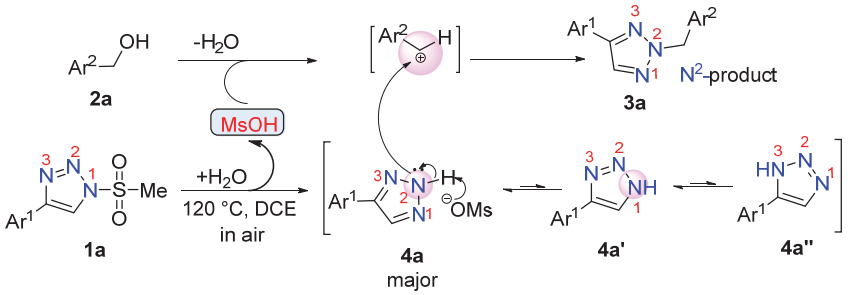
Scheme 2 Gram-scale synthesis of compounds **3a** and **3ac**



Scheme 3 Control experiments

tively. These results demonstrated that **4a**/**4a'** was the main intermediate to couple with benzyl alcohol and methanesulfonic acid (MsOH) which was *in situ* produced by hydrolysis of *N*-sulfonyl-1,2,3-triazole to activate alcohol hydroxyl groups and catalyze the transformation. In addition, N^1-Bn-1,2,3-triazole (**3a'**) was refluxed under the identified conditions and no N^2-product was observed (Scheme 3, g).

Based on the above control experiments, the following mechanism was proposed (Scheme 4). The sulfonyl group of *N*-sulfonyl-1,2,3-triazoles can undergo elimination to afford 4-phenyl-1*H*-1,2,3-triazoles, 4-phenyl-2*H*-1,2,3-triazoles and 4-phenyl-3*H*-1,2,3-triazoles as nucleophilic intermediates at high temperature. The intermediates were converted into a more stable form (4-phenyl-2*H*-1,2,3-triazole) at a higher temperature.[4] Methanesulfonic acid (MsOH) was *in situ* produced from the hydrolysis of *N*-sulfonyl-1,2,3-triazole which promoted the protonation and dehydroxylation of the alcohols to generate the carbocation. Then, 4-phenyl-2*H*-1,2,3-triazole reacted with benzyl carbocations by S_N1 nucleophilic substitution reaction to afford the N^2-substituted triazoles.



Scheme 4 Possible mechanism

3 Conclusions

An efficient, metal-free synthesis of N^2-substituted 1,2,3-triazoles with high regioselective from *N*-sulfonyl-1,2,3-triazoles and aryl benzyl alcohol was developed. Methanesulfonic acid (MsOH) which is *in situ* produced by hydrolysis of *N*-sulfonyl-1,2,3-triazoles promotes the reaction. In this reaction, a wide range of easily accessible and environmentally friendly alcohols as starting materials can tolerate this reaction well, and evaluations of the bioactivity of the resulting products for anticancer activity are ongoing in our laboratory.

4 Experimental section

4.1 General information

All reactions and manipulations were carried out under an air atmosphere in a 4 mL sealed vial equipped with a stir bar. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using a Brucker 400 MHz spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard ($\delta=0$) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta=77.0$) for ^{13}C NMR. High-resolution mass spectrometry (HRMS) was performed on an IonSpec FT-ICR or a Waters Micromass Q-TOF micro Synapt High-Definition mass spectrometers. Mass spectra were recorded on the a HP-5989 instrument by ESI methods. The X-ray diffraction analysis was performed using a Bruker Smart-1000 X-ray diffractometer.

4.2 General procedures for products 3

In a 4 mL sealed vial equipped with a stir bar, *N*-sulfonyl-1,2,3-triazoles **1** (0.2 mmol) and dichloroethane (2 mL) were added. Then the benzyl alcohol **2** (1.0 mmol) were added to the mixture. The vial was tightly capped and stirred for 2 h at 120 ℃. After completion of the reaction, the mixture was cooled to room temperature and purified by column chromatography using petroleum ether/ethyl acetate mixture ($V:V=30:1$) as eluent to afford products **3** in high yield and purity.

2-Benzyl-4-phenyl-2*H*-1,2,3-triazole (**3a**):[18] 82% yield (38 mg) as a white solid. m.p. 78～79 ℃ (lit.[18] 78～80 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.87 (s, 1H), 7.79 (d, $J=7.4$ Hz, 2H), 7.42 (t, $J=7.5$ Hz, 2H), 7.38～7.30 (m, 6H), 5.63 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.1, 135.3, 131.4, 130.3, 128.8, 128.7, 128.4, 128.3, 127.9, 125.9, 58.7.

2-Benzyl-4-(2-bromophenyl)-2*H*-1,2,3-triazole (**3b**): 76% yield (40 mg) as a white solid. m.p. 76～78 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 8.14 (s, 1H), 7.75 (d, $J=7.7$ Hz, 1H), 7.66 (d, $J=8.0$ Hz, 1H), 7.39～7.32 (m, 6H), 7.21 (t, $J=7.7$ Hz, 1H), 5.65 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 146.5, 135.1, 134.4, 133.6, 131.34, 131.0, 129.6, 128.8, 128.3, 128.0, 127.5, 121.8, 58.7; HRMS (ESI) calcd for $C_{15}H_{13}BrN_3Na$ $[M+Na]^+$ 314.0212, found 314.0217.

2-Benzyl-4-(3-chlorophenyl)-2*H*-1,2,3-triazole (**3c**): 78% yield (42 mg) as a white solid. m.p. 86～88 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.85 (s, 1H), 7.79 (s, 1H), 7.65 (d, $J=7.2$ Hz, 1H), 7.39～7.28 (m, 7H), 5.62 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 146.8, 135.1, 134.8, 132.1, 131.5, 130.1, 128.8, 128.4, 128.1, 126.1, 124.0, 58.8; HRMS (ESI) calcd for $C_{15}H_{12}ClN_3Na$ $[M+Na]^+$ 292.0612, found 292.0620.

2-Benzyl-4-(3-bromophenyl)-2*H*-1,2,3-triazole (**3d**): 77% yield (48 mg) as a white solid. m.p. 64～66 ℃; ^{1}H NMR (400 MHz, Chloroform-d) δ: 7.96 (s, 1H), 7.85 (s, 1H), 7.70 (d, $J=7.7$ Hz, 1H), 7.47 (d, $J=7.9$ Hz, 1H), 7.38～7.32 (m, 5H), 7.31～7.25 (m, 1H), 5.62 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 146.6, 135.1, 132.4, 131.5, 131.3, 130.4, 128.9, 128.8, 128.4, 128.1, 124.4, 123.1, 58.9; HRMS (ESI) calcd for $C_{15}H_{13}BrN_3$ $[M+H]^+$ 314.0287, found 314.0279.

2-Benzyl-4-(4-fluorophenyl)-2*H*-1,2,3-triazole (**3e**): 80% yield (40 mg) as a white solid. m.p. 52～54 ℃ (lit.[18] 53～55 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.81 (s, 1H), 7.78～7.72 (m, 2H), 7.37～7.32 (m, 5H), 7.11 (t, $J=8.7$ Hz, 2H), 5.61 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ: −113.13; ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 162.8 (d, $J=247.6$ Hz), 147.2, 135.2, 131.1, 128.8, 128.3, 128.1, 12s7.7 (d, $J=8.2$ Hz), 126.6 (d, $J=3.3$ Hz), 115.8 (d, $J=21.7$ Hz), 58.7.

2-Benzyl-4-(4-trifluoromethylphenyl)-2*H*-1,2,3-triazole (**3f**): 76% yield (46 mg) as a white solid. m.p. 55～56 ℃ (lit.[18] 55～57 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.91 (d, $J=3.3$ Hz, 2H), 7.88 (s, 1H), 7.67 (d, $J=8.2$ Hz, 2H), 7.38～7.31 (m, 5H), 5.63 (s, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ: −62.62; ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 146.7, 135.1, 133.8, 131.8, 130.2 (d, $J=32.6$

Hz), 128.8, 128.4, 128.1, 126.1, 125.8 (q, J=3.8 Hz), 124.1 (d, J=271.9 Hz), 58.9.

2-Benzyl-4-(*p*-tolyl)-2*H*-1,2,3-triazole (**3g**): 82% yield (41 mg) as a white solid. m.p. 64～66 ℃ (lit.[6] 64～66 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.82 (s, 1H), 7.67 (d, J=8.1 Hz, 2H), 7.35～7.31 (m, 5H), 7.22 (d, J=7.9 Hz, 2H), 5.61 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.1, 138.3, 135.4, 131.2, 129.5, 128.7, 128.2, 127.9, 127.5, 125.8, 58.6, 21.3.

2-Benzyl-4-(4-ethylphenyl)-2*H*-1,2,3-triazole (**3h**): 82% yield (41 mg) as a white solid. m.p. 73～75 ℃ (lit.[6] 73～75 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.83 (s, 1H), 7.68 (d, J=7.6 Hz, 2H), 7.35～7.31 (m, 5H), 7.23 (d, J=7.7 Hz, 2H), 5.62 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.1, 144.7, 135.4, 131.2, 128.7, 128.3, 128.2, 127.9, 127.7, 125.9, 58.6, 28.7, 15.5.

2-Benzyl-4-(4-methoxyphenyl)-2*H*-1,2,3-triazole (**3i**): 40% yield (21 mg) as a white solid. m.p. 78～79 ℃ (lit.[18] 79～81 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.78 (s, 1H), 7.71 (d, J=8.6 Hz, 2H), 7.36～7.28 (m, 5H), 6.94 (d, J=8.6 Hz, 2H), 5.60 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 159.8, 147.9, 135.4, 130.9, 128.7, 128.2, 127.9, 127.2, 123.0, 114.2, 58.6, 55.3.

4-Phenyl-2-(3-trifluoromethylbenzyl)-2*H*-1,2,3-triazole (**3j**): 72% yield (43 mg) as a white solid. m.p. 73～75 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.89 (s, 1H), 7.81～7.77 (m, 2H), 7.63 (s, 1H), 7.59 (d, J=7.6 Hz, 1H), 7.54～7.46 (m, 2H), 7.43 (t, J=7.4 Hz, 2H), 7.39～7.33 (m, 1H), 5.68 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.44, 136.23, 131.75, 131.32 (d, J=1.0 Hz), 131.04, 130.12, 129.37, 128.92, 128.62, 125.98, 125.23 (q, J=3.7 Hz), 124.81 (q, J=3.7 Hz), 58.10; HRMS (ESI) calcd for $C_{16}H_{13}F_3N_3$ [M+H]$^+$ 304.1022, found 304.1026.

2-(3-Bromobenzyl)-4-phenyl-2*H*-1,2,3-triazole (**3k**): 75% yield (47 mg) as a white solid. m.p. 55～57 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.88 (s, 1H), 7.79 (d, J=7.5 Hz, 2H), 7.50 (s, 1H), 7.47～7.40 (m, 3H), 7.35 (t, J=7.3 Hz, 1H), 7.29～7.19 (m, 2H), 5.59 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.3, 137.4, 131.6, 131.4, 131.1, 130.3, 130.1, 128.9, 128.5, 126.5, 125.9, 122.8, 57.9; HRMS (ESI) calcd for $C_{15}H_{13}BrN_3$ [M+H]$^+$ 314.0220, found 314.0225.

2-(3-Methylbenzyl)-4-phenyl-2*H*-1,2,3-triazole (**3l**): 83% yield (41 mg) as a white solid. m.p. 52～54 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.86 (s, 1H), 7.79 (d, J=7.8 Hz, 2H), 7.42 (t, J=7.6 Hz, 2H), 7.35 (d, J=7.5 Hz, 1H), 7.26～7.21 (m, 1H), 7.18～7.10 (m, 3H), 5.58 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 147.9, 138.5, 135.2, 131.4, 130.4, 129.1, 128.8, 128.7, 128.4, 125.9, 125.1, 58.7, 21.4; HRMS (ESI) calcd for $C_{16}H_{15}N_3Na$ [M+Na]$^+$ 272.1158, found 272.1149.

2-(4-Methylbenzyl)-4-phenyl-2*H*-1,2,3-triazole (**3m**): 82% yield (40 mg) as a white solid. m.p. 58～60 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.84 (s, 1H), 7.79～7.78 (m, 1H), 7.77 (s, 1H), 7.45～7.39 (m, 2H), 7.36～7.30 (m, 1H), 7.25 (s, 2H), 7.15 (d, J=7.9 Hz, 2H), 5.58 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 147.9, 138.1, 132.3, 131.3, 130.4, 129.4, 128.8, 128.3, 128.1, 125.9, 58.5, 21.1; HRMS (ESI) calcd for $C_{16}H_{15}N_3Na$ [M+Na]$^+$ 272.1158, found 272.1153.

2-(4-Chlorobenzyl)-4-phenyl-2H-1,2,3-triazole (**3n**): 78% yield (42 mg) as a white solid. m.p. 50～52 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.86 (s, 1H), 7.80～7.76 (m, 2H), 7.42 (t, J=7.5 Hz, 2H), 7.38～7.26 (m, 4H), 5.58 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.2, 134.3, 133.7, 131.5, 130.2, 129.4, 129.1, 128.9, 128.5, 125.9, 57.9; HRMS (ESI) calcd for $C_{15}H_{13}ClN_3$ [M+H]$^+$ 270.0707, found 270.0702.

2-(4-Bromobenzyl)-4-phenyl-2*H*-1,2,3-triazole (**3o**): 77% yield (48 mg) as a white solid. m.p. 60～62 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.86 (s, 1H), 7.77 (d, J=7.2 Hz, 2H), 7.48 (d, J=8.4 Hz, 2H), 7.42 (t, J=7.4 Hz, 2H), 7.35 (t, J=7.3 Hz, 1H), 7.28～7.20 (m, 2H), 5.57 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.2, 134.2, 131.9, 131.6, 130.2, 129.7, 128.9, 128.5, 125.9, 122.4, 58.1; HRMS (ESI) calcd for $C_{15}H_{13}BrN_3$ [M+H]$^+$ 314.0228, found 314.0221.

2-(4-Fluorobenzyl)-4-phenyl-2*H*-1,2,3-triazole (**3p**): 79% yield (40 mg) as a white solid. m.p. 46～48 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.86 (s, 1H), 7.78 (d, J=7.4 Hz, 2H), 7.42 (t, J=7.5 Hz, 2H), 7.35 (dd, J=8.1, 5.5 Hz, 3H), 7.03 (t, J=8.6 Hz, 2H), 5.58 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 162.7 (d, J=247.0 Hz), 148.1, 131.5, 131.1 (d, J=3.2 Hz), 130.2, 129.9 (d, J=8.3 Hz), 128.9, 128.5, 125.9, 115.7 (d, J=21.7 Hz), 57.9; HRMS (ESI) calcd for $C_{15}H_{13}FN_3$ [M+H]$^+$ 254.1025, found 254.1029.

2-([1,1'-Biphenyl]-4-ylmethyl)-4-phenyl-2*H*-1,2,3-triazole (**3q**): 72% yield (45 mg) as a white solid. m.p. 56～58 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.90 (s, 1H), 7.86 (d, J=8.3 Hz, 2H), 7.67 (s, 1H), 7.64 (d, J=4.7 Hz, 2H), 7.62 (s, 1H), 7.45 (t, J=7.6 Hz, 2H), 7.35 (td, J=6.8, 5.2, 3.3 Hz, 6H), 5.64 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 147.7, 141.2, 140.5, 135.3, 131.5, 129.3, 128.9, 128.8, 128.3, 128.1, 127.6, 127.5, 127.1, 126.3, 58.7; HRMS (ESI) calcd for $C_{21}H_{18}N_3$ [M+H]$^+$ 312.1503, found 312.1495.

2-(Naphthalen-2-ylmethyl)-4-phenyl-2*H*-1,2,3-triazole (**3r**): 65% yield (37 mg) as a white solid. m.p. 62～64 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 8.24 (d, J=8.3 Hz, 1H), 7.91～7.85 (m, 3H), 7.80 (d, J=7.2 Hz, 2H), 7.56 (d, J=7.2 Hz, 1H), 7.53～7.48 (m, 2H), 7.47～7.42 (m, 3H), 7.36 (d, J=7.3 Hz, 1H), 6.10 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 147.9, 133.8, 131.3, 131.1, 130.4, 129.3, 128.9, 128.8, 128.4, 127.6, 126.8, 126.1, 125.9, 125.4, 123.3, 56.8; HRMS (ESI) calcd for $C_{19}H_{15}N_3Na$ [M+Na]$^+$ 308.1158, found 308.1151.

4-Phenyl-2-(thiophen-2-ylmethyl)-2*H*-1,2,3-triazole (**3s**): 78% yield (38 mg) as a white solid. m.p. 65～67 ℃ (lit.[6] 64～66 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.86 (s, 1H), 7.79 (d, J=1.4 Hz, 1H), 7.78～7.77 (m, 1H), 7.44～7.39 (m, 2H), 7.37～7.32 (m, 1H), 7.28 (dd, J=5.1, 1.2 Hz, 1H), 7.17～7.14 (m, 1H), 6.98 (dd, J=5.1, 3.5 Hz, 1H), 5.79 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 148.2,

136.8, 131.5, 130.2, 128.8, 128.5, 127.6, 127.1, 126.5, 125.9, 53.2.

2-(Furan-2-ylmethyl)-4-phenyl-2*H*-1,2,3-triazole (**3t**): 78% yield (32 mg) as a white solid. m.p. 66～68 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.86 (s, 1H), 7.79 (d, *J*=1.4 Hz, 1H), 7.78～7.76 (m, 1H), 7.45～7.39 (m, 3H), 7.37～7.33 (m, 1H), 6.46 (d, *J*=3.3 Hz, 1H), 6.37 (dd, *J*=3.2, 1.9 Hz, 1H), 5.62 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 148.2, 148.1, 143.2, 131.6, 130.2, 128.8, 128.5, 126.1, 110.6, 109.8, 51.3; HRMS (ESI) calcd for $C_{13}H_{12}N_3ONa$ $[M+Na]^+$ 248.0794, found 248.0788.

4-(4-((4-Phenyl-2*H*-1,2,3-triazol-2-yl)methyl)phenyl)morpholine (**3u**): 68% yield (44 mg) as a white solid. m.p. 62～63 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.86 (s, 1H), 7.82～7.78 (m, 2H), 7.44 (t, *J*=7.4 Hz, 2H), 7.36～7.32 (m, 3H), 6.90 (d, *J*=8.7 Hz, 2H), 5.56 (s, 2H), 3.88～3.85 (m, 4H), 3.18～3.15 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 151.2, 147.8, 131.3, 130.4, 129.3, 128.8, 128.3, 126.4, 125.9, 115.6, 66.8, 58.3, 49.1; HRMS (ESI) calcd for $C_{19}H_{21}N_4O$ $[M+H]^+$ 321.1710, found 321.1718.

2-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-4-phenyl-2*H*-1,2,3-triazole (**3v**): 78% yield (43 mg) as a white solid. m.p. 56～58 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.85 (s, 1H), 7.78 (d, *J*=7.3 Hz, 2H), 7.42 (t, *J*=7.5 Hz, 2H), 7.34 (t, *J*=7.3 Hz, 1H), 6.87 (d, *J*=8.2 Hz, 2H), 6.78 (d, *J*=7.7 Hz, 1H), 5.94 (s, 2H), 5.52 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 148.1, 147.9, 147.7, 131.4, 130.3, 128.9, 128.8, 128.4, 125.9, 121.8, 108.6, 108.4, 101.2, 58.5; HRMS (ESI) calcd for $C_{16}H_{13}N_3O_2Na$ $[M+Na]^+$ 302.0900, found 302.0897.

4-([1,1'-Biphenyl]-4-yl)-2-benzyl-2*H*-1,2,3-triazole (**3w**): 80% yield (50 mg) as a white solid. m.p. 95～97 ℃; ^{1}H NMR (400MHz, Chloroform-*d*) *δ*: 7.90 (s, 1H), 7.86 (d, *J*=8.3 Hz, 2H), 7.67 (s, 1H), 7.64 (d, *J*=4.7 Hz, 2H), 7.62 (s, 1H), 7.45 (t, *J*=7.6 Hz, 2H), 7.38～7.32 (m, 6H), 5.64 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 147.7, 141.2, 140.5, 135.3, 131.5, 129.3, 128.9, 128.8, 128.3, 128.0, 127.6, 127.5, 127.1, 126.3, 58.79; HRMS (ESI) calcd for $C_{21}H_{18}N_3$ $[M+H]^+$ 312.1452, found 312.1458.

2-Benzyl-4-(naphthalen-2-yl)-2*H*-1,2,3-triazole (**3x**): 78% yield (40 mg) as a white solid. m.p. 90～92 ℃ (lit.[18] 91～93 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 8.26 (s, 1H), 8.00 (s, 1H), 7.96～7.83 (m, 4H), 7.54～7.47 (m, 2H), 7.43～7.32 (m, 5H), 5.68 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 148.1, 135.3, 133.5, 133.3, 131.7, 128.8, 128.6, 128.3, 128.2, 128.1, 127.8, 127.7, 126.5, 126.3, 124.7, 123.9, 58.8.

2-Benzyl-4-(thiophen-3-yl)-2*H*-1,2,3-triazole (**3y**): 78% yield (37 mg) as a white solid. m.p. 55～57 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.76 (s, 1H), 7.63～7.61 (m, 1H), 7.45 (d, *J*=4.9 Hz, 1H), 7.40～7.37 (m, 1H), 7.36～7.32 (m, 5H), 5.61 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 144.2, 135.3, 131.6, 131.6, 128.8, 128.3, 127.9, 126.4, 125.9, 121.6, 58.6; HRMS (ESI) calcd for $C_{13}H_{12}N_3S$ $[M+H]^+$ 242.0707, found 242.0715.

4-(Benzofuran-2-yl)-2-benzyl-2*H*-1,2,3-triazole (**3z**): 88% yield (37 mg) as a white solid. m.p. 53～55 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.96 (s, 1H), 7.59 (d, *J*=7.4 Hz, 1H), 7.54 (d, *J*=8.1 Hz, 1H), 7.39～7.27 (m, 6H), 7.26～7.21 (m, 1H), 7.08 (s, 1H), 5.65 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 154.8, 147.6, 140.2, 134.9, 132.3, 128.8, 128.5, 128.4, 128.1, 124.8, 123.2, 121.2, 111.4, 103.5, 58.9; HRMS (ESI) calcd for $C_{17}H_{14}N_3O$ $[M+H]^+$ 276.1122, found 276.1128.

4-(Benzo[*b*]thiophen-3-yl)-2-benzyl-2*H*-1,2,3-triazole (**3aa**): 77% yield (44 mg) as a white solid. m.p. 62～63 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 8.47 (d, *J*=8.0 Hz, 1H), 7.96 (s, 1H), 7.92 (d, *J*=8.0 Hz, 1H), 7.73 (s, 1H), 7.51～7.46 (m, 1H), 7.45～7.32 (m, 6H), 5.71 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 143.7, 140.5, 136.9, 135.3, 132.6, 128.8, 128.4, 128.1, 126.5, 124.8, 124.8, 124.5, 123.9, 122.7, 58.8; HRMS (ESI) calcd for $C_{17}H_{14}N_3S$ $[M+H]^+$ 291.0809, found 291.0812.

4-(4-(2-Benzyl-2*H*-1,2,3-triazol-4-yl)phenyl)morpholine (**3ab**): 82% yield (52 mg) as a white solid. m.p. 68～70 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.78 (s, 1H), 7.69 (d, *J*=8.7 Hz, 2H), 7.36～7.29 (m, 5H), 6.94 (d, *J*=8.7 Hz, 2H), 5.60 (s, 2H), 3.89～3.85 (m, 4H), 3.23～3.15 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 151.3, 148.1, 135.5, 130.8, 128.7, 128.2, 127.9, 126.9, 121.9, 115.5, 66.8, 58.6, 48.9; HRMS (ESI) calcd for $C_{19}H_{21}N_4O$ $[M+H]^+$ 320.1678, found 320.1689.

1-Methyl-4-phenyl-1*H*-1,2,3-triazole (**3ac**): 70% yield (22 mg) as a white solid. m.p. 111～113 ℃ (lit.[19a] 112～115 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.82 (d, *J*=7.3 Hz, 2H), 7.74 (s, 1H), 7.42 (t, *J*=7.6 Hz, 2H), 7.33 (t, *J*=7.4 Hz, 1H), 4.14 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 148.1, 130.6, 128.8, 128.1, 125.7, 120.6, 36.7.

1-Methyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (**3ad**): 65% yield (22 mg) as a white solid. m.p. 131～133 ℃ (lit.[19a] 132～134 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.70 (s, 1H), 7.68 (s, 2H), 7.21 (d, *J*=7.9 Hz, 2H), 4.07 (d, *J*=2.3 Hz, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 148.1, 137.9, 129.5, 127.8, 125.6, 120.3, 36.7, 21.2.

4-(4-Fluorophenyl)-1-methyl-1*H*-1,2,3-triazole (**3ae**): 68% yield (24 mg) as a white solid. m.p. 111～112 ℃ (lit.[19b] 112～113 ℃); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.76 (dd, *J*=8.6, 5.4 Hz, 2H), 7.69 (s, 1H), 7.08 (t, *J*=8.7 Hz, 2H), 4.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) *δ*: 162.6 (d, *J*=247.2 Hz), 147.1, 127.4 (d, *J*=8.1 Hz), 126.8 (d, *J*=3.2 Hz), 120.4, 115.8 (d, *J*=21.8 Hz), 36.7.

Supporting Information The detailed procedure for the synthesis of **3**, copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR of compounds **3a**～**3ae**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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