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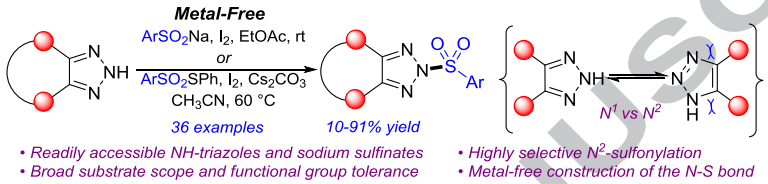

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Metal-free, highly regioselective sulfonylation of *NH*-1,2,3-triazoles with sodium sulfinates and thiosulfonates

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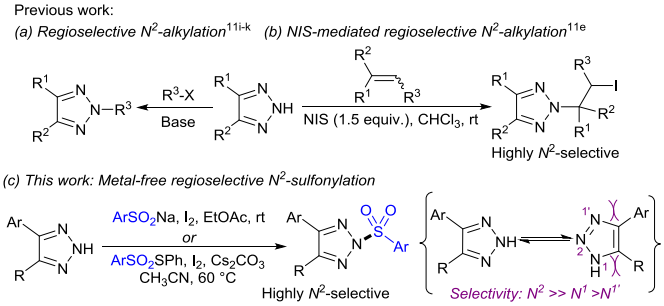
ABSTRACT

A convenient and metal-free protocol for the highly regioselective sulfonylation of *NH*-1,2,3-triazoles is described. A range of readily accessible *NH*-1,2,3-triazoles were sulfonylated with various aryl sulfinates in the presence of molecular iodine. The scope was extended to thiosulfonates as an efficient sulfonylating agent and nitrochromene derived triazoles were also explored for selective *N*-sulfonylation. A variety of synthetically viable N^2-sulfonyl triazoles were obtained in moderate to high yields with excellent regioselectivities *via* N-S bond construction under mild reaction conditions.

Amongst five-membered heteroaromatic compounds, 1,2,3-triazoles continue to occupy an important place in synthetic organic chemistry,[1] medicinal chemistry,[2] functional materials[3] and other fields.[4] Numerous reliable methodologies have been developed for the synthesis of N^1-substituted 1,2,3-triazoles, as exemplified by the 'click' reaction of organic azides with alkynes;[5] the condensation of organic azides with activated alkenes;[6] multicomponent strategies;[7] and azide-free syntheses.[8] Additionally, the organocatalyzed cycloaddition reactions of activated carbonyl compounds with organic azides to generate 1,4,5-trisubstituted 1,2,3-triazoles has grown remarkably in recent years.[9]

Generally, the above methods produce either N^1- or $N^{1'}$-substituted triazoles, thus the direct synthesis of N^2-substituted 1,2,3-triazoles remain little explored.[10] Most N^2-substituted 1,2,3-triazoles are obtained by the manipulation of *NH*-1,2,3-triazoles with suitable reactants.[11] The groups of Shi and Wang independently reported the alkylation of 4,5-disubstituted *NH*-1,2,3-triazoles to yield N^2-derivatives as the major isomer (Scheme 1a).[11i-k] Recently, Chen and co-workers employed the NIS-mediated regioselective N^2-alkylation of *NH*-1,2,3-triazoles with olefins (Scheme 1b).[11e] Despite these achievements, a general method is still lacking for the synthesis of N^2-sulfonyl 1,2,3-triazoles. Consequently, we envisaged the difficulty in achieving selective N^2-sulfonylation of *NH*-1,2,3-triazoles being due to low electron density at the N^2 position. In this regard, it is challenging to find a suitable sulfonylating agent to control the regioselectivity for N^2-sulfonylation.

On the other hand, the bench-stable, odourless and non-hygroscopic sodium sulfinates[12] have been employed for the formation of N-S bonds with primary and secondary amines.[13] In particular, the molecular iodine-mediated synthesis of sulfonamides[13b-e] attracted our attention because the reagents are inexpensive, non-toxic, and easy to handle. To the best of our knowledge, the sulfonylation of *NH*-1,2,3-triazoles is unexplored. Therefore, this fact motivated us to develop a new strategy for the synthesis of N^2-sulfonyl 1,2,3-triazoles *via* the iodine-mediated regioselective sulfonylation of *NH*-1,2,3-triazoles (Scheme 1c).



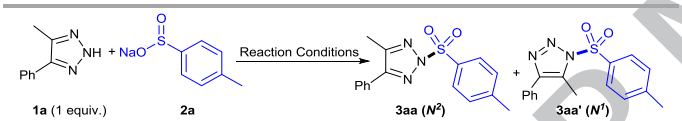
Scheme 1. Comparison of previous studies with our work.

In recent years, N^1-sulfonyl triazoles have been used to generate α–diazo imines as efficient carbene precursor in organic synthesis.[14] While N^1-sulfonyl triazoles were readily obtained by the reaction of sulfonyl azides with alkynes,[15] the synthesis of N^2-sulfonyl 1,2,3-triazoles has become highly desirable. Herein, we report the regioselective synthesis of N^2-sufonyl 1,2,3-triazoles *via* the

reaction of readily available *NH*-1,2,3-triazoles with sodium sulfinates and thiosulfonates in the presence of iodine.

Our investigation began with the identification of suitable reaction conditions to control the regioselectivity. Initial experiments were performed with 4-methyl-5-phenyl-*NH*-1,2,3-triazole (**1a**) and sodium *p*-toluenesulfinate (**2a**) as model substrates using iodine (Table 1). A mixture of regioisomers **3aa**/**3aa'** were formed in DCE, CH_2Cl_2 and 1,4-dioxane (Entries 1-3). Although the role of these solvents not entirely clear, the formation of a regioisomeric mixture (**3aa**/**3aa'**) was probably due to rapid interconversion of the isomeric triazole (N^1-H and N^2-H) of **1a**. Remarkably, a single regioisomer was observed for the tosylated triazole **3aa** in EtOH, EtOAc, CH_3CN and THF (Entries 4-7). Using 20 mol% and 50 mol% I_2 in EtOAc the reaction was sluggish at 60 °C (Entries 8 and 9). The use of EtOAc/H_2O (9:1) and **2a** (2 equiv.) did not show any significant improvement (Entries 10 and 11). To our delight, an excellent yield (94%) was achieved using excess iodine (1.1 equiv.) with **2a** (2 equiv.) in EtOAc at room temperature (Entry 12). The sulfonylation of **1a** was also observed with $PhI(OAc)_2$ and KI which provided **3aa** in moderate yields (Entries 13 and 14), whereas NBS afforded **3aa** in 74% yield with excellent regioselectivity (Entry 15).

Table 1. Optimization for the sulfonylation of triazole **1a** with **2a**.[a]

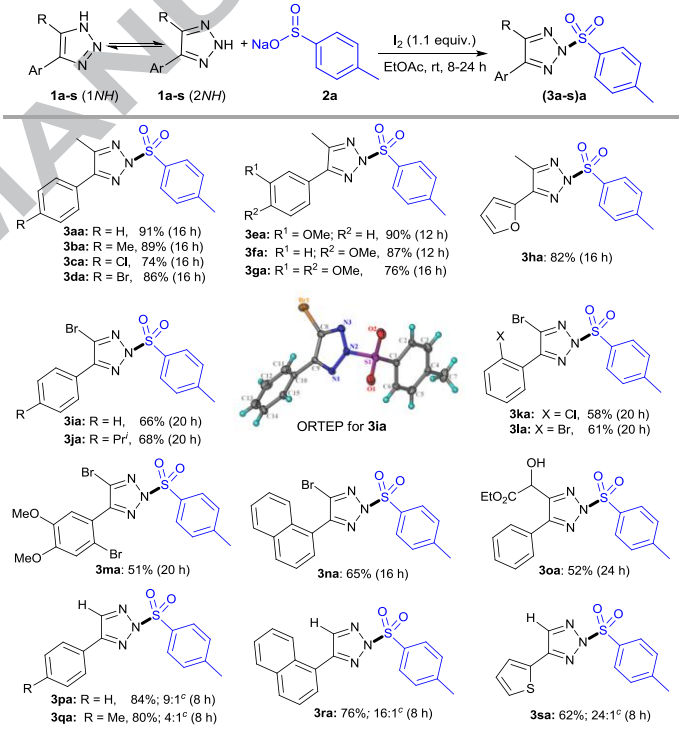


Entry	Reaction conditions	Time	Yield (N^2:N^1)[b]
1	**2a** (2.5 eq.), I_2 (1 eq.), DCE	10 h	78% (15:1)
2	**2a** (2.5 eq.), I_2 (1 eq.), CH_2Cl_2	10 h	76% (16:1)
3	**2a** (2.5 eq.), I_2 (1 eq.), Dioxane	10 h	85% (12:1)
4	**2a** (2.5 eq.), I_2 (1 eq.), EtOH	10 h	71% (1:0)
5	**2a** (2.5 eq.), I_2 (1 eq.), EtOAc	10 h	88% (1:0)
6	**2a** (2.5 eq.), I_2 (1 eq.), CH_3CN	10 h	80% (1:0)
7	**2a** (2.5 eq.), I_2 (1 eq.), THF	10 h	82% (1:0)
8	**2a** (2.5 eq.), I_2 (0.2 eq.), EtOAc, 60 °C	24 h	52% (1:0)
9	**2a** (2.5 eq.), I_2 (0.5 eq.), EtOAc, 60 °C	24 h	66% (1:0)
10	**2a** (2.5 eq.), I_2 (1 eq.), EtOAc/H_2O (9:1)	16 h	81% (1:0)
11	**2a** (2.0 eq.), I_2 (1.0 eq.), EtOAc	16 h	84% (1:0)
12	**2a (2.0 eq.), I_2 (1.1 eq.), EtOAc**	**16 h**	**94% (1:0)**
13	**2a** (2.5 eq.), $PhI(OAc)_2$ (1 eq.), EtOAc	24 h	42% (1:0)
14	**2a** (2.5 eq.), KI (1 eq.), EtOAc	24h	50% (1:0)
15	**2a** (2.5 eq.), NBS (1 eq.), EtOAc	24 h	74% (1:0)

[a] Reactions performed on a 0.2 mmol scale in solvent (1 mL) at room temperature. [b] Yields and regioselectivities based on the crude ^{1}H NMR spectra of **1a** using 1,2,4,5-tetramethylbenzene as an internal standard.

With the optimized conditions in hand, we then investigated the scope of the addition of various 4,5-disubstituted triazoles with sodium *p*-toluenesulfinate (**2a**). A broad range of mono- and disubstituted *NH*-1,2,3-triazoles were suitable substrates for the synthesis of N^2-tosylated triazoles in good to high yields (Table 2). In addition to **1a**, electron-rich and electron-poor groups on the aryl rings, such as methyl-, halo- and methoxy-substituents (**1b**-**g**), smoothly reacted with **2a** to give the desired 2-tosylated 1,2,3-trizoles (**3ba**–**ga**) in 74–90% yield. The heteroaryl substituted triazole (**1h**) was also a suitable substrate and provided the desired product **3ha** in 82% yield. Moreover, a variety of 4-bromo-5-aryl-*NH*-1,2,3-triazoles (**1i**-**n**) were also compatible substrates and provided the corresponding tosylated triazoles (**3ia**-**na**), albeit in lower yields. The structure and regioselectivity of **3ia** was further confirmed by single-crystal X-ray data analysis (see ESI).[16] The densely functionalised triazole (**1o**)[17] was also a good substrate and provided the desired product **3oa** in 52% yield. Generally, mono-substituted triazoles are challenging substrates to control the regioselectivity (see ESI for detailed optimization studies).[18] Regardless, the reaction of 4-phenyl-*NH*-1,2,3-triazole (**1p**) and 4-tolyl-*NH*-1,2,3-triazole (**1q**) with **2a** gave the corresponding sulfonylated products **3pa** and **3qa** as a 9:1 and 4:1 mixture of inseparable regioisomers, respectively. To our surprise, 1-naphthyl and thiophenyl derived triazoles gave the desired products **3ra** and **3sa** with high regioselectivities. Similar lower regioselectivities were also observed using 4-aryl-1,2,3-triazoles[11a,d,f] as substrates. Notably, these tosylated triazoles (**3pa-sa**) can be obtained by the debromination of 4-bromo triazoles (**3ia**-**na**) with high regioselectivities.[11b,j]

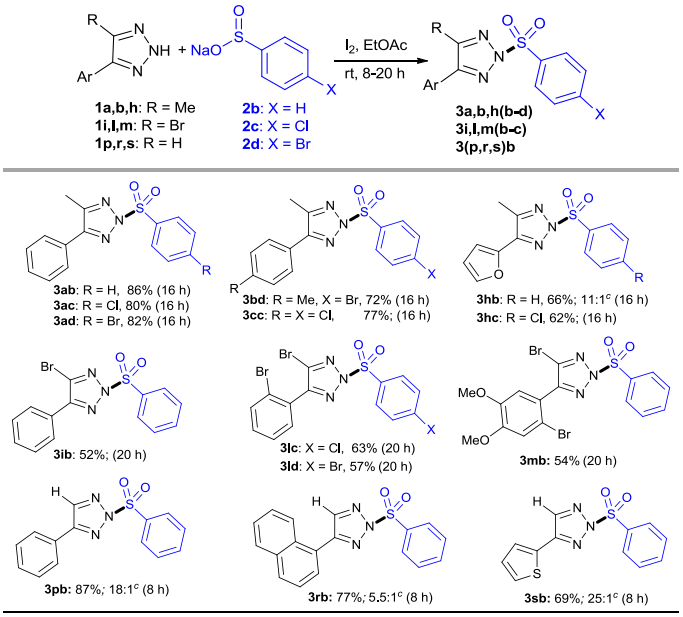
Table 2. I_2-mediated sulfonylation of various *NH*-triazoles (**1a-s**) with sodium *p*-toluenesulfinate (**2a**).[a,b]



[a] Reagents and conditions: **1a-s** (0.4 mmol, 1 eq.), sodium *p*-toluenesulfinate **2a** (2.0 eq.), I_2 (1.1 eq.), EtOAc (2 mL), room temperature. [b] Isolated yield after column chromatography. [c] Regioselectivities based on ^{1}H NMR spectroscopic analysis (see ESI).

To demonstrate the efficiency and practicality for the sulfonylation of triazoles, the substrate scope was extended to other sulfinate salts (Table 3). The reaction of 4-methyl-*NH*-triazoles with **2b**-**d** were investigated under the standard reaction conditions to obtain sulfonyl triazoles **3(a-c,h)b-d** in high yields and with excellent regioselectivities. Similarly, 4-bromo derived *N*-sulfonyl triazoles **3(i,m)b** and **3l(c,d)** were formed in good yields. As expected, the phenyl (**1p**), 1-naphthyl (**1r**) and thiophenyl (**1s**) derived triazoles were also sulfonylated. The high regioselectivity may be due to the methyl group and bromine atom blocking the N^1 reaction sites. Therefore, the C4 and C5 substituents on the triazole nucleus play an important role to provide predominantly the N^2-sulfonylated products (see ESI).

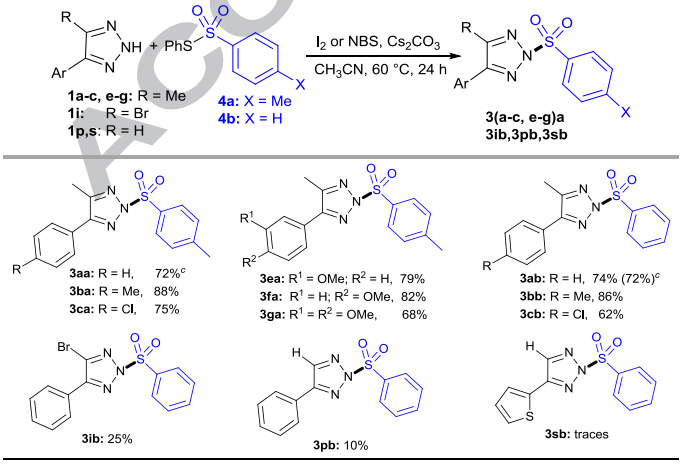
Table 3. Sulfonylation of *NH*-triazoles using various sulfinates (**2b-d**).[a,b]



[a] Reagents and conditions: triazole (0.4 mmol, 1 eq.), sodium sulfinate **2a** (2.0 eq.), I_2 (1.1 eq.), EtOAc (2 mL), room temperature. [b] Isolated yield after column chromatography. [c] Regioselectivities based on ^{1}H NMR spectroscopic analysis (see ESI).

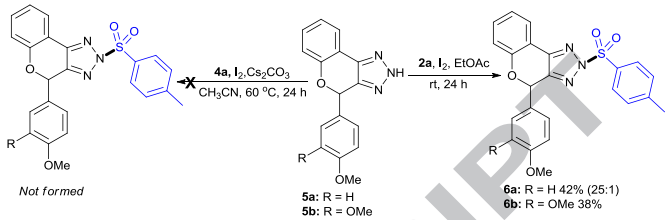
Recently, Jang and co-workers elegantly utilised thiosulfonates as a sulfonylating agent.[19] With a view to understand the generality of the presented methodology, thiosulfonates **4a** and **4b** were also examined. The reaction optimization was revisited using **1a** and **4a** as model compounds; the best results were achieved using a combination of I_2 (1.1 equiv.)/Cs_2CO_3 (1 equiv.) or NBS (2 equiv.)/Cs_2CO_3 (1 equiv.) in acetonitrile at 60 °C (Table 4). The sulfonylation of various triazoles with **4a** provided the desired N^2-tosylated triazoles **3(a-c,e-g)a** in high yields. Additionally, using **4b**, the corresponding N^2-sulfonylated triazoles **3(a-c)b** were obtained in good to high yields. The bromo derived triazole (**1i**) afforded **3ib** in only 25% yield, while the 4-phenyl (**1p**) and 4-thiophenyl (**1s**) triazoles were produced in trace amounts.

Table 4. Sulfonylation of *NH*-triazoles using thiosulfonates (**4a** and **4b**).[a,b]



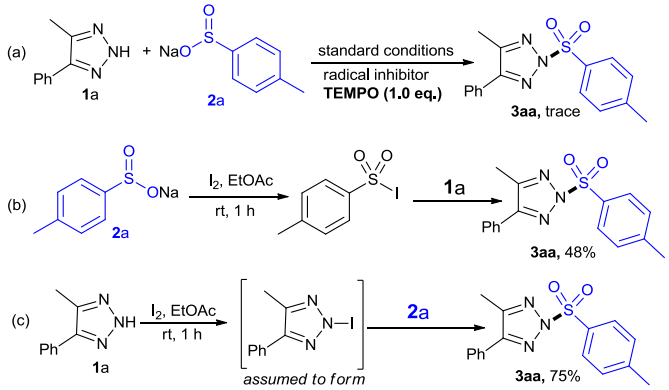
[a] Reagents and conditions: triazole (0.4 mmol, 1 eq.), thiosulfonate **4a/b** (2.0 eq.), I_2 (1.1 eq.)/Cs_2CO_3 (1 eq.) or NBS (2 eq.)/Cs_2CO_3 (1 eq.), CH_3CN (2 mL), 60 °C, 24 h. [b] Isolated yield after column chromatography. [c] Reaction conducted with NBS (see ESI).

To understand the generality of sulfonylation, the reaction scope was extended to nitrochromene derived triazoles. Accordingly, the sulfonylation of **5a** and **5b** with sodium *p*-toluenesulfinate **2a** under the standard reaction conditions gave N^2-tosylated triazoles **6a** and **6b** with lower yields in comparison with other triazoles (Scheme 2). Disappointingly, these triazoles failed to react with *S*-phenyl 4-methylbenzene-sulfonothioate **4a** under the standard reaction conditions.



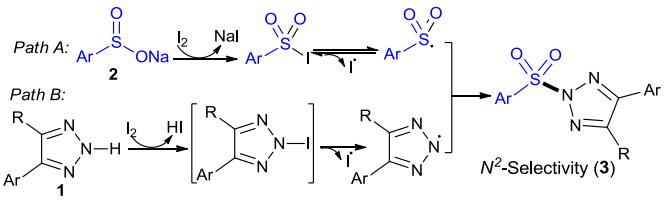
Scheme 2. Sulfonylation of nitrochromene derived triazoles. Reagents and conditions: **5a**,**b** (0.4 mmol, 1 eq.), **2a** (2.0 eq.), I_2 (1.1 eq.), EtOAc (2 mL), room temperature, 24 h; **5a**,**b** (0.4 mmol, 1 eq.), **4a** (2.0 eq.), I_2 (1.1 eq.)/Cs_2CO_3 (1 eq.), CH_3CN (2 mL), 60 °C, 24 h. [a] Isolated yield after column chromatography.

To gain insight to understand the reaction mechanism, control experiments were performed (Scheme 3). Using the radical scavenger TEMPO under the standard conditions, product **3aa** was observed in trace amounts, indicating that the reaction should proceed *via* a free-radical pathway (Scheme 3a). The known relatively unstable sulfonyl iodide, tosyl iodide (TsI),[20] was prepared by the reaction of 4-methylbenzene sodium sulfinate **2a** with molecular iodine. Subsequent treatment with **1a** provided the desired product in 48% yield (Scheme 3b). To further understand the role of iodine, triazole **1a** was treated with I_2 to presumably form the corresponding *N*-iodotriazole, followed by subsequent addition of sulfinate salt **2a** to afford **3aa** in 75% yield (Scheme 3c). Overall, these results suggest that the molecular iodine might be activating both reactants to form the N^2-sulfonylated products.



Scheme 3. Control experiments for mechanistic studies.

On the basis of experimental results and literature precedence,[13b-e] a plausible mechanism was proposed (Scheme 4). In path A, the reaction of sodium sulfinate **2** with molecular iodine could lead to the corresponding sulfonyl iodide intermediate.[20] The homolytic cleavage of sulfonyl iodide generates a sulfonyl radical which reacts with the internal nitrogen (N^2) of the triazole. Similarly, in path B, iodine might activate the internal nitrogen (N^2) of triazole **1** to give the N^2-iodotriazole, which reacts with sodium sulfinates **2** to give product **3**. Although the relatively low electron density at N^2 in comparison with the two terminal nitrogens (N^1 and $N^{1'}$),[11a,k] the high N^2-selectivity would be favoured due to the steric hindrance of the C4 and C5 substituents.



Scheme 4. Plausible mechanism for the N^2-sulfonylation of *NH*-triazoles.

In conclusion, we have successfully developed a highly regioselective, iodine-mediated sulfonylation reaction of *NH*-1,2,3-triazoles using sodium sulfinates and thiosulfonates to provide *N*-sulfonylated triazoles in moderate to high yields. This protocol is operationally simple and possesses a wide substrate scope, permitting the synthesis of a range of N^2-sulfonyl triazoles which can be difficult to prepare by other methods.

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References and Notes

1 For an excellent review on triazole applications, see: Huang, D., Zhao, P., Astruc, D., *Coord. Chem. Rev*. **2014**, *272*, 145.

2 Selected articles: (*a*) Mohammed, I., Kummetha, I. R., Singh, G., Sharova, N., Lichinchi, G., Dang, J., Stevenson, M., Rana, T. M., *J. Med. Chem*. **2016**, *59*, 7677; (*b*) Bai, H., Zhu, P., Wu, W., Li, J., Ma, Z., Zhang, W., Cheng, Y., Du, L., Li, M., *Med. Chem. Commun*. **2015**, *6*, 418; (*c*) Hsieh, H. Y., Lee, W. C., Senadi, G. C., Hu, W. P., Liang, J. J., Tsai, T. R., Chou, Y. W., Kuo, K. K., Chen, C. Y., Wang, J. J. *J. Med. Chem*., **2013**, *56*, 5422; (*d*) Thirumurugan, P., Matosiuk, D., Jozwiak, K. *Chem. Rev*., **2013**, *113*, 4905.

3 For selected articles on materials, see: (*a*) Reed, D. A., Xiao, D. J., Gonzalez, M. I., Darago, L. E., Herm, Z. R., Grandjean, F., Long, J. R., *J. Am. Chem. Soc*., **2016**, *138*, 5594; (*b*) Sood, R., Donnadio, A., Giancola, S., Kreisz, A., Jones, D. J., Cavaliere, S., *ACS Appl. Mater. Interfaces*, **2016**, *8*, 16897; (*c*) Shida, N., Ishiguro, Y., Atobe, M., Fuchigami, T., Inagi, S., *ACS Macro Lett*., **2012**, *1*, 656.

4 For recent review articles, see: (*a*) Schulze, B., Schubert, U. S., *Chem. Soc. Rev*., **2014**, *43*, 2522; (*b*) Byrne, J. P., Kitchen, J. A., Gunnlaugsson, T., *Chem. Soc. Rev*., **2014**, *43*, 5302.

5 For representative reviews, see: (*a*) Johansson, J. R., Beke-Somfai, T., Stålsmeden, A. S., Kann, N., *Chem. Rev*., **2016**, *116*, 14726 and references herein; (*b*) Liang, L., Astruc, D., *Coord. Chem. Rev*., **2011**, *255*, 2933; (*c*) Hein, J. E., Fokin, V. V., *Chem. Soc. Rev*., **2010**, *39*, 1302; (*d*) Meldal, M., Tornøe, C. W., *Chem. Rev*., **2008**, *108*, 2952.

6 (*a*) Chen, Y., Nie, G., Zhang, Q., Ma, S., Li, H., Hu, Q., *Org. Lett*., **2015**, *17*, 1118; (*b*) Li, W., Du, Z., Zhang, K., Wang, J., *Green Chem*., **2015**, *17*, 781; (*c*) Li, W., Wang, J., *Angew. Chem., Int. Ed*., **2014**, *53*, 14186; (*d*) Janreddy, D., Kavala, V., Kuo, C. W., Chen, C. W., Ramesh, C., Kotipalli, T., Kuo, T. S., Chen, M. L., He, C. H., Yao, C. F., *Adv. Synth. Catal*., **2013**, *355*, 2918.

7 For recent reviews on multicomponent strategies: (*a*) Chen, Z., Liu, Z., Cao, G., Li, H., Rena, H., *Adv. Synth. Catal*., **2017**, 359, 202; (*b*) Wei, F., Wang, W., Ma, Y., Tunga, C.-H., Xu, Z., *Chem. Commun*., **2016**, *52*, 14188; (*c*) Hassan, S., Müller, T. J. J.. *Adv. Synth. Catal*., **2015**, *357*, 617.

8 For selected reports for azide-free reactions, see: (*a*) Panda, S., Maity, P., Manna, D., *Org. Lett*., **2017**, *19*, 1534; (*b*) Bai, H.-W., Cai, Z.-J., Wang, S.-Y., Ji, S.-J., *Org. Lett*., **2015**, **17**, 2898; (*c*) Wan, J.-P., Cao, S., Liu, Y., *J. Org. Chem*., **2015**, *80*, 9028; (*d*) Chen, J.-H., Liu, S.-R., Chen, K., *Chem.-Asian J*., **2010**, *5*, 328.

9 Selected reports: (*a*) Thomas, J., Jana, S.. Liekens, S., Dehaen, W., *Chem. Commun*., **2016**, *52*, 9236; (*b*) Ramachary, D. B., Krishna, P. M., Gujral, J., Reddy, G. S., *Chem.-Eur. J*., **2015**, *21*, 16775; (*c*) Ramachary, D. B., Shashank, A. B., Karthik, S., *Angew. Chem., Int. Ed*., **2014**, *53*, 10420; (*d*) Li, W., Du, Z., Huang, J., Jia, Q., Zhang, K., Wang, J., *Green Chem*., **2014**, *16*, 3003; (*e*) Wang, L., Peng, S., Danence, L. J., Gao, Y., Wang, J., *Chem. - Eur. J*., **2012**, *18*, 6088.

10 (*a*) Kalisiak, J., Sharpless, K. B., Fokin, V. V., *Org. Lett*., **2008**, *10*, 3171; (*b*) Kamijo, S., Jin, T., Huo, Z., Yamamoto, Y., *J. Org. Chem.*, **2004**, *69*, 2386; (*c*) Kamijo, S., Jin, T., Huo, Z., Yamamoto, Y., *J. Am. Chem. Soc*., **2003**, *125*, 7786.

11 For the selective N^2-functionalization of triazoles, see: (*a*) Wei, H., Hu, Q., Ma, Y., Wei, L., Liu, J., Shi, M., Wang, F., *Asian J. Org. Chem*., **2017**, *6*, 662; (*b*) Deng, X., Lei, X., Nie, G., Jia, L., Li, Y., Chen, Y., *J. Org. Chem*., **2017**, *82*, 6163; (*c*) Motornov, V. A., Tabolin, A. A., Novikov, R. A., Nelyubina, Y. V., Ioffe, S. L., Smolyar, I. V., Nenajdenko, V. G., *Eur. J. Org. Chem*., **2017**, 6851; (*d*) Bhagat, U. K., Kamaluddin, Peddinti, R. K., *Tetrahedron Lett*., **2017**, *58*, 298; (*e*) Zhu, L.-L., Xu, X.-Q., Shi, J.-W., Chen, B.-L., Chen, Z., *J. Org. Chem*., **2016**, *81*, 3568; (*f*) Zhu, L.-L., Xu, X.-Q., Shi, J.-W., Chen, B.-L., Chen, Z., *J. Org. Chem*., **2016**, *81*, 3568; (*g*) Wen, J., Zhu, L.-L., Bi, Q.-W., Shen, Z.-Q., Li, X.-X., Li, X., Wang, Z., Chen, Z., *Chem. Eur. J*., **2014**, *20*, 974; (*h*) Ueda, S., Su, M., Buchwald, S. L., *Angew. Chem., Int. Ed*., **2011**, *50*, 8944; (*i*) Wang, X. J., Zhang, L., Krishnamurthy, D., Senanayake, C. H., Wipf, P., *Org. Lett*., **2010**, *12*, 4632; (*j*) Wang, X. J., Zhang, L., Lee, H., Haddad, N., Krishnamurthy, D., Senanayake, C. H., *Org. Lett*., **2009**, ***11***, 5026; (*k*) Chen, Y., Liu, Y., Petersen, J. L., Shi, X., *Chem. Commun*., **2008**, 3254.

12 For a review on sulfinate salts, see: Aziz, J., Messaoudi, S., Alami, M., Hamze, A., *Org. Biomol. Chem*., **2014**, *12*, 9743.

13 For the synthesis of sulfonamides using sodium sulfinates, see: (*a*) Jiang, Y.-y., Wang, Q.-Q., Liang, S., Hu, L.-M., Little, R. D., Zeng, C.-C., *J. Org. Chem*., **2016**, *81*, 4713; (*b*) Wei, W., Liu, C., Yang, D., Wen, J., You, J., Wang, H., *Adv. Synth. Catal*., **2015**, *357*, 987; (*c*) Buathongjan, C., Beukeaw, D., Yotphan, S., *Eur. J. Org. Chem*., **2015**, 1575; (*d*) Yang, K., Ke, M., Lin, Y., Song, Q., *Green Chem*., **2015**, *17*, 1395; (*e*) Pan, X., Gao, J., Liu, J., Lai, J., Jiang, H., Yuan, G., *Green Chem*., **2015**, *17*, 1400.

14 For representative recent reviews, see: (*a*) Jia, M., Ma, S., *Angew. Chem., Int. Ed*., **2016**, *55*, 9134; (*b*) Davies, H. M. L., Alford, J. S., *Chem. Soc. Rev*., **2014**, *43*, 5151; (*c*) Chattopadhyay, B., Gevorgyan, V., *Angew. Chem., Int. Ed*., **2012**, *51*, 862.

15 For the synthesis of N^1-sulfonyl-4-substituted triazoles, see: (*a*) Cano, I., Nicasio, M. C., Pérez, P. J., *Org. Biomol. Chem*., **2010**, *8*, 536; (*b*) Wang, F., Fu, H., Jiang, Y., Zhao, Y., *Adv. Synth. Catal*., **2008**, *350*, 1830. 46; For synthesis of N^1-sulfonyl-5-substituted triazoles: (*c*) Meza-Aviña, M. E., Patel, M. K., Lee, C. B., Dietz, T. J., Croatt, M. P., *Org. Lett*., **2011**, *13*, 2984.

16 The crystal structure of **3ia** was deposited in the Cambridge Crystallographic Data Centre (CCDC# 1816730).

17 Reddy, R. J., Waheed, Md., Karthik, T., Shankar, A., *New J. Chem*., **2018**, *42*, 980.

18 The N^2-regioselectivity of **3pa**, **3qa**, **3sa**, **3pb** and **3sb** was established on the basis of ^{1}H NMR data comparison with isomeric triazoles reported in the literature (see ESI, Table 2).

19 (*a*) Shyam, P. K., Jang, H.-Y., *J. Org. Chem*., **2017**, *82*, 1761; (*b*) Shyam, P. K., Son, S., Jang, H.-Y., *Eur. J. Org. Chem*., **2017**, 5025.

20 For the preparation of tosyl iodide, see: (*a*) Liu, L. K., Chi, Y., Jen, K.-Y., *J. Org. Chem*., **1980**, *45*, 406 (*b*) Nájera, C., Bald, B., Yus, M., *J. Chem. Soc. Perkin Trans. 1*, **1988**, 1029.

Highlights:

- A variety *NH*-triazoles have been accessed for regioselective sulfonylation.
- The metal-, ligand- and additive-free synthesis of N^2-sulfonyl triazoles.
- A wide range of N^2-sulfonyl triazoles have been prepared readily.
- This method is a simple, straightforward and broad substrate scope compatibility.