Organic LETTERS

Letter

pubs.acs.org/OrgLett

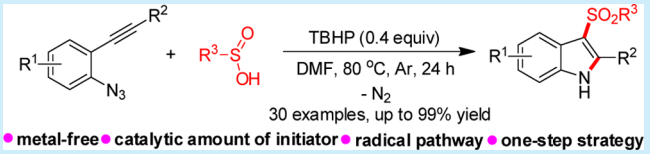
tert-Butyl Hydroperoxide (TBHP)-Initiated Vicinal Sulfonamination of Alkynes: A Radical Annulation toward 3-Sulfonylindoles

Fei Chen, Qiang Meng, Shang-Qing Han, and Bing Han*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, P. R. China

Supporting Information

ABSTRACT: A novel, efficient, and facile vicinal sulfonamination of alkynes by the reaction of accessible 2-alkynyl arylazides with sulfinic acids in the presence of *tert*-butyl hydroperoxide (TBHP) has been developed. This protocol utilizes sulfinic acids as the sulfonating reagent, azidos as the aminating reagent, and TBHP as the sulfonyl radical initiator. By using this protocol, a variety of potentially bioactive 3-sulfonylindoles were facilely synthesized via direct annulation.



The indole skeleton as a prevalent structure widely exists in many bioactive natural products and pharmaceuticals.[1] Among them, 3-sulfonylindole derivatives have served as novel HIV-1 non-nucleoside reverse-transcriptase inhibitors (e.g., **I**),[2] 5-HT_6 receptor ligands (e.g., **II**),[3] norepinephrine reuptake inhibitors and 5-HT_{2A} receptor antagonists (e.g., **III**),[4] and orexin receptor antagonists (e.g., **IV**)[5] due to their special chemical and biological properties (Figure 1). Thus, the

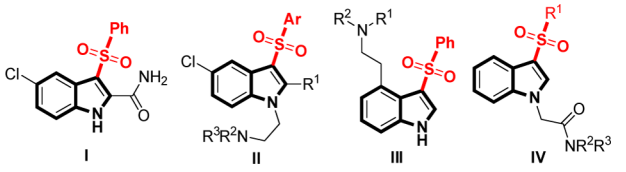
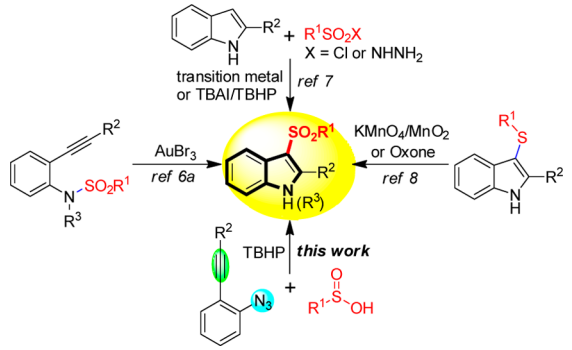


Figure 1. Biologically active 3-sulfonylindole derivatives.

efficient synthesis of 3-sulfonylindoles has drawn much attention from chemists and pharmacologists. To date, three general strategies have been achieved, including the indole annulation of suitable acyclic precursors,[6] direct C3-sulfonylation of indoles,[7] and the oxidation of the corresponding sulfides (Scheme 1).[8] However, the majority of these methods relate to either transition metal catalysts,[6a,b,7b−d] stepwise operation,[6c,d] or harsh conditions.[8] Therefore, the development of a convenient, metal-free, and one-pot approach to synthesize 3-sulfonylindoles from simple and readily available starting materials is still in demand.

With our continuing interest in the construction of structurally important heterocyclic scaffolds via radical cyclizations and annulations,[9] herein, we intend to establish a facile and efficient protocol for the synthesis of bioactive 3-sulfonylindoles by direct annulation of 2-alkynyl arylazides and sulfinic acids via a *tert*-butyl hydroperoxide (TBHP) initiated radical vicinal sulfonamination of alkynes under metal-free conditions (Scheme 1). Alkynes are one of the most common and useful functional groups, and their vicinal

Scheme 1. Strategies for the Synthesis of 3-Sulfonylindoles



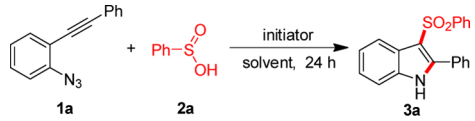
difunctionalization attract increasing attention from organic chemists.[10] In this context, this strategy not only presents the first example of radical vicinal sulfonamination of alkynes employing sufinic acids as the sulfonating reagent[11] and azidoes as the aminating reagent[12] but also realizes a direct annulation toward structurally important 3-sulfonylindoles. It is noteworthy that the efficient process can be initiated by a catalytic amount of environmentally friendly TBHP, which rendered this approach more attractive to practical synthesis and sustainable chemistry.

To achieve this idea, the reaction of 1-azido-2-(phenylethynyl)benzene (**1a**, 0.2 mmol) with benzenesulphinic acid (**2a**, 0.4 mmol) was chosen as a model reaction and stirred in CH_3CN at 80 °C for 24 h under oxidative conditions for the optimization investigation (Table 1). In the beginning, O_2 (1 atm) was used as the initiator, but the desired 2-phenyl-3-(phenylsulfonyl)-1*H*-indole **3a** was only obtained in less than 5% yield (Table 1, entry 1). To our delight, when a catalytic amount (0.2 equiv) of peroxides such as benzoyl peroxide (BPO), di-*tert*-butyl peroxide (DTBP), and TBHP (5−6 M in

Received: May 17, 2016

DOI: 10.1021/acs.orglett.6b01427
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	initiator	t (°C)	solvent	yield (%)[b]
1	O_2 (1 atm)	80	CH_3CN	<5
2	BPO (0.2 equiv)	80	CH_3CN	39
3	DTBP (0.2 equiv)	100	CH_3CN	63
4	TBHP (0.2 equiv)	80	CH_3CN	69
5	TBHP (0.3 equiv)	80	CH_3CN	75
6	TBHP (0.4 equiv)	80	CH_3CN	84
7	**TBHP (0.4 equiv)**	**80**	**DMF**	**87**
8	TBHP (0.4 equiv)	80	DMSO	45
9	TBHP (0.4 equiv)	80	1,4-dioxane	69
10	TBHP (0.4 equiv)	80	toluene	51
11	TBHP (0.5 equiv)	80	DMF	87
12	TBHP (0.6 equiv)	80	DMF	81
13	TBHP (0.4 equiv)	100	DMF	82
14[c]	TBHP (0.4 equiv)	80	DMF	75
15[d]	TBHP (0.4 equiv)	80	DMF	57
16[e]	TBHP (0.4 equiv)	80	DMF	75
17[f]	TBHP (0.4 equiv)	80	DMF	0
18[g]	TBHP (4.0 equiv)	80	DMF	24

[a]All reactions were carried out by using **1a** (0.2 mmol), **2a** (2.0 equiv), TBHP (5−6 M in decane), and solvent (1 mL) under argon (1 atm) and stirred for 24 h, except as noted. [b]Isolated yield. [c]TBHP (70% aqueous). [d]**2a** (1.2 equiv) was used. [e]**2a** (1.5 equiv) was used. [f]$PhSO_2Na$ (2.0 equiv) was used instead of **2a**. [g]$PhSO_2NHNH_2$ (2.0 equiv) was used instead of **2a**.

decane) were utilized as the initiator, the reaction took place smoothly and the results showed that TBHP was more efficient than others to deliver **3a** in 69% yield (Table 1, entries 2−4). The structure of **3a** was confirmed by a single-crystal X-ray diffraction study (Figure 2). With the increase of the usage

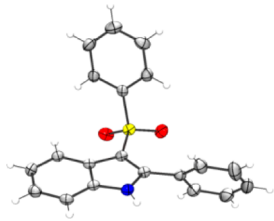
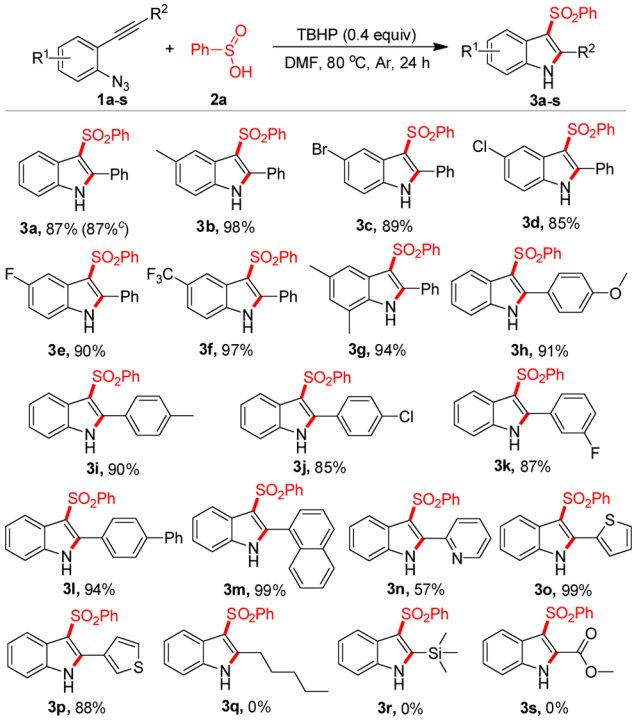


Figure 2. X-ray structure of **3a** (thermal ellipsoids are shown with 30% probability).

amount of TBHP to 0.3 equiv and 0.4 equiv, the yield of **3a** was increased to 75% and 84%, respectively (Table 1, entries 5 and 6). Screening other solvents, such as DMF, DMSO, 1,4-dioxane, and toluene, revealed that DMF was the best solvent and the yield of **3a** was further improved to 87% (Table 1, entries 7−10). However, increasing the usage amount of TBHP or raising the reaction temperature did not give a better result (Table 1, entries 11−13). The yield of **3a** was decreased to 75% when TBHP (70% aqueous) was used (Table 1, entry 14). In addition, the effects of the loading amount of sulfinic acid **2a** and other sulfonyl sources were also investigated, but the results obtained under these conditions were less satisfactory (Table 1, entries 15−18).

With the optimized conditions in hand (Table 1, entry 7), the scope of the reaction with various 2-alkynyl arylazides was investigated as shown in Scheme 2. First, the substitution

Scheme 2. Scope of 2-Alkynyl Arylazides[a,b]



[a]All reactions run in DMF (2.5 mL) using **1** (0.5 mmol), **2a** (1.0 mmol), and TBHP (0.2 mmol) at 80 °C under Ar for 24 h. [b]Isolated yields are shown. [c]**1a** (5 mmol) was used, and the corresponding product **3a** was obtained in 1.45 g.

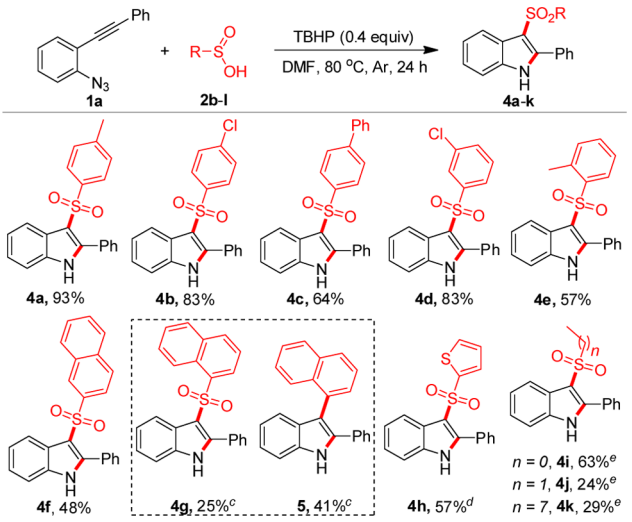
pattern on the aromatic ring of the arylazide moiety was explored. Using 4-phenyl with a wide range of electronic properties, substituted 2-phenylethynyl arylazides all proceeded well in the reaction, affording the desired 3-sulfonylindoles **3a−f** in excellent yields. When the phenyl bearing multisubstituent was incorporated in 2-phenylethynyl arylazide, for instance, a 4,6-dimethyl group, the reaction also proceeded smoothly and gave the corresponding products **3g** in 94% yield. Next, both aryl alkynyl and heterocyclic alkynyl substituted azidobenzenes were examined for the transformation. Phenylethynyl with a range of electronic properties substituents on the phenyl ring substituted azidobenzenes all proceeded well in the reaction, giving rise to the corresponding products **3h−k** in excellent yields. Other aryl alkynyls such as 4-biphenyl ethynyl, 1-naphthyl ethynyl, 2-pyridinyl ethynyl, and 2-/3-thienylethynyls incorporated into azidobenzenes were also tolerated well in the process, delivering the desired products **3l−p** in good to excellent yields. Unfortunately, aliphatic alkynyls such as 1-heptinyl and trimethylsilyl ethynyls involving substrates **1q** and **1r** were inert in the reaction, resulting in 0% yields for the corresponding products **3q** and **3r**, respectively; they were recovered in the reaction probably because of the lower stability of the in situ generated alkenyl radical derived from the addition of the sulphonyl radical to **1q** or **1r**. In addition, methyl propiolate substituted substrate **1s** only gave complicated compounds rather than the desired product **3s**. Notably, the reaction could be carried out in gram scale without

DOI: 10.1021/acs.orglett.6b01427
Org. Lett. XXXX, XXX, XXX−XXX

any difficulty, as it was demonstrated that the product **3a** was obtained in 87% yield (1.45 g) when 1-azido-2-(phenylethynyl)benzene (**1a**, 5 mmol) was used, displaying the pragmatic application of this method.

Having successfully achieved the cascade sequence with 2-alkynyl arylazides, we shifted our attention to explore the scope of sulfinic acids **2**. The reactions of a variety of sulfinic acids with **1a** were tested, and the results were illustrated in Scheme 3. Arylsulfinic acids bearing substituents such as *p*-Me, *p*-Cl, *p*-

Scheme 3. Scope of Sulfinic Acids[a,b]

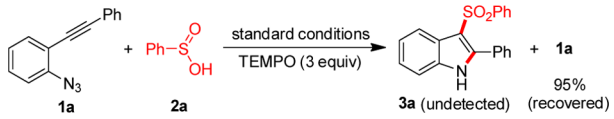


[a]All reactions run in DMF (2.5 mL) using **1a** (0.5 mmol), **2** (1.0 mmol), and TBHP (0.2 mmol) at 80 °C under Ar for 24 h. [b]Isolated yields. [c]**2h** (1.0 mmol) and TBHP (0.25 mmol) were divided into two equal parts and added per 12 h for 24 h. [d]**2i** (2.0 mmol) and TBHP (0.5 mmol) were divided into four equal parts and added per 12 h for 48 h. [e]**2j–l** (3.0 mmol) and TBHP (0.75 mmol) were divided into two equal parts and added per 12 h for 24 h.

Ph, and *m*-Cl on the phenyl ring gave the corresponding 3-sulfonylindoles **4a–d** in excellent yields. However, 2-methylbenzenesulfinic acid reacted with **1a** to afford **4e** in 57% yield, suggesting that the reaction was influenced by the steric effect. In addition, naphthalene-2-sulfinic acid was also suitable for this conversion, as demonstrated in the case of **4f**. When naphthalene-1-sulfinic acid **2h** was allowed to react with **1a**, the desired product **4g** was obtained in 25% yield accompanied by the unexpected product **5** in 41% yield, which indicates that the 1-naphthyl sulfonyl radical derived from sulfinic acid **2h** was more inclined to undergo desulfonylation under this circumstance. Furthermore, thiophene-2-sulfinic acid was a good sulfonating agent as well, providing **4h** in 57% yield. Remarkably, the reactions involving simple aliphatic sulfinic acids, such as methyl, ethyl, and octyl substituted sulfinic acids, were also successful and led to the desired products **4i–k** in 24–63% yields, demonstrating that aliphatic sulfinic acids were a good sulfonating reagent in the protocol as well.

To confirm that the reaction went through a radical process, a radical inhibition experiment was conducted as shown in Scheme 4. When the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyl-oxy (TEMPO) was added in the reaction system, the sulfonamination was absolutely inhibited and **1a** was almost completely recovered, attesting that a radical process is really involved.

Scheme 4. Control Experiment



Based on the experimental results and aforementioned control experiment, a proposed mechanism for this TBHP-initiated cascade sequence is illustrated in Figure 3. Initially,

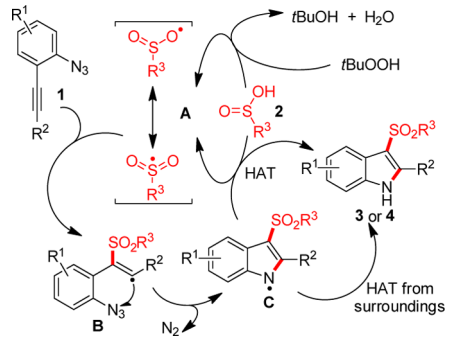


Figure 3. Proposed mechanism.

sulfinic acid **2** reacts with TBHP under heating to form the corresponding radical **A**, which can be drawn as the resonance structures sulfinic acid and sulfonyl radicals. Subsequently, the sulfonyl radical adds to the alkynyl moiety of **1** to generate the intermediate **B**, which immediately undergoes intramolecular cyclization of the alkenyl radical with an azido moiety to yield the N-radical intermediate **C** along with the release of N_2. Finally, the intermediate **C** abstracts a hydrogen atom from sulfinic acid **2** or the surroundings to produce 3-sulfonylindole **3** or **4**.

In conclusion, we have demonstrated a facile, metal-free, and direct annulation approach for access to a variety of structurally important 3-sulfonylindoles via a TBHP-initiated cascade sulfonation/cyclization process by the reaction of sulfinic acids with available 2-alkynyl arylazides. This protocol not only provides a novel method for the vicinal sulfonamination of alkynyls but also provides a general approach for the synthesis of 3-sulfonylindole frameworks that are important in medicinal and biological chemistry. Further studies of the radical tandem reactions constructing heterocyclic scaffolds are in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01427.

Detailed experimental procedures and spectral data for all products (PDF)

Crystallographic data for compound **3a** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hanb@lzu.edu.cn.

Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.orglett.6b01427
Org. Lett. XXXX, XXX, XXX–XXX

■ ACKNOWLEDGMENTS

We thank the NNSFC (21422205 and 21272106), the Program for New Century Excellent Talents in University (NCET-13-0258), the Changjiang Scholars and Innovative Research Team in University (IRT-15R28), the "111" project, and the Fundamental Research Funds for the Central Universities (lzujbky-2016-ct02 and lzujbky-2016-ct08) for financial support.

■ REFERENCES

(1) For reviews on indole-containing natural products, see: (a) Ishikura, M.; Abe, T.; Choshi, T.; Hibino, S. *Nat. Prod. Rep.* **2013**, *30*, 694−752. (b) Higuchi, K.; Kawasaki, T. *Nat. Prod. Rep.* **2007**, *24*, 843−868. For examples of biological activities of indoles, see: (c) Biswal, S.; Sahoo, U.; Sethy, S.; Kumar, H. K. S.; Banerjee, M. *Asian J. Pharm. Clin. Res.* **2012**, *5*, 1−6. (d) Kochanowska-Karamyan, A. J.; Hamann, M. T. *Chem. Rev.* **2010**, *110*, 4489−4497.

(2) (a) Gao, D.; Back, T. G. *Synlett* **2013**, *24*, 389−393. (b) Silvestri, R.; Martino, G. D.; Regina, G. L.; Artico, M.; Massa, S.; Vargiu, L.; Mura, M.; Loi, A. G.; Marceddu, T.; Colla, P. L. *J. Med. Chem.* **2003**, *46*, 2482−2493. (c) Williams, T. M.; Ciccarone, T. M.; MacTough, S. C.; Rooney, C. S.; Balani, S. K.; Condra, J. H.; Emini, E. A.; Goldman, M. E.; Greenlee, W. J.; Kauffman, L. R.; O'Brien, J. A.; Sardana, V. V.; Schleif, W. A.; Theoharides, A. D.; Anderson, P. S. *J. Med. Chem.* **1993**, *36*, 1291−1294.

(3) (a) Bernotas, R. C.; Antane, S.; Shenoy, R.; Le, V. D.; Chen, P.; Harrison, B. L.; Robichaud, A. J.; Zhang, G. M.; Smith, D.; Schechter, L. E. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1657−1660. (b) Bernotas, R.; Lenicek, S.; Antane, S.; Zhang, G. M.; Smith, D.; Coupet, J.; Harrison, B.; Schechter, L. E. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 5499−5502.

(4) Heffernan, G. D.; Coghlan, R. D.; Manas, E. S.; McDevitt, R. E.; Li, Y.; Mahaney, P. E.; Robichaud, A. J.; Huselton, C.; Alfinito, P.; Bray, J. A.; Cosmi, S. A.; Johnston, G. H.; Kenney, T.; Koury, E.; Winneker, R. C.; Deecher, D. C.; Trybulski, E. J. *Bioorg. Med. Chem.* **2009**, *17*, 7802−7815.

(5) Bentley, J. M.; Davenport, T.; Slack, M. *PCT Int. Appl.* WO 2011138265 A2 20111110.

(6) (a) Nakamura, I.; Yamagishi, U.; Song, D.; Konta, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 2284−2287. (b) Stokes, B. J.; Liu, S.; Driver, T. G. *J. Am. Chem. Soc.* **2011**, *133*, 4702−4705. (c) Kobayashi, K.; Kobayashi, A.; Ezaki, K. *Tetrahedron* **2013**, *69*, 7936−7942. (d) Gao, D.; Back, T. G. *Chem. - Eur. J.* **2012**, *18*, 14828−14840.

(7) (a) Qiu, J. K.; Hao, W. J.; Wang, D. C.; Wei, P.; Sun, J.; Jiang, B.; Tu, S. J. *Chem. Commun.* **2014**, *50*, 14782−14785. (b) Rahman, M.; Ghosh, M.; Hajra, A.; Majee, A. *J. Sulfur Chem.* **2013**, *34*, 342−346. (c) Tocco, G.; Begala, M.; Esposito, F.; Caboni, P.; Cannas, V.; Tramontano, E. *Tetrahedron Lett.* **2013**, *54*, 6237−6241. (d) Yadav, J. S.; Reddy, B. V. S.; Krishna, A. D.; Swamy, T. *Tetrahedron Lett.* **2003**, *44*, 6055−6058.

(8) (a) Chen, Y.; Cho, C. H.; Shi, F.; Larock, R. C. *J. Org. Chem.* **2009**, *74*, 6802−6811. (b) Vedejs, E.; Little, J. D. *J. Org. Chem.* **2004**, *69*, 1794−1799.

(9) (a) Yang, X.-L.; Peng, X.-X.; Chen, F.; Han, B. *Org. Lett.* **2016**, *18*, 2070−2073. (b) Chen, F.; Yang, X.-L.; Wu, Z.-W.; Han, B. *J. Org. Chem.* **2016**, *81*, 3042−3050. (c) Yang, X.-L.; Long, Y.; Chen, F.; Han, B. *Org. Chem. Front.* **2016**, *3*, 184−189. (d) Duan, X.-Y.; Jia, P.-P.; Zhang, M.; Han, B. *Org. Lett.* **2015**, *17*, 6022−6025. (e) Duan, X.-Y.; Zhou, N.-N.; Fang, R.; Yang, X.-L.; Yu, W.; Han, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 3158−3162. (f) Peng, X.-X.; Deng, Y.-J.; Yang, X.-L.; Zhang, L.; Yu, W.; Han, B. *Org. Lett.* **2014**, *16*, 4650−4653. (g) Yang, X.-L.; Chen, F.; Zhou, N.-N.; Yu, W.; Han, B. *Org. Lett.* **2014**, *16*, 6476−6479. (h) Duan, X.-Y.; Yang, X.-L.; Fang, R.; Peng, X.-X.; Yu, W.; Han, B. *J. Org. Chem.* **2013**, *78*, 10692−10704. (i) Han, B.; Yang, X.-L.; Fang, R.; Yu, W.; Wang, C.; Duan, X.-Y.; Liu, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 8816−8820. (j) Han, B.; Yang, X.-L.; Wang, C.; Bai, Y.-W.; Pan, T.-C.; Yu, W. *J. Org. Chem.* **2012**, *77*, 1136−1142. (k) Han, B.; Wang, C.; Han, R.-F.; Yu, W.; Duan, X.-Y.; Fang, R.; Yang, X.-L. *Chem. Commun.* **2011**, *47*, 7818−7820. (l) Chen, Y.-X.; Qian, L.-F.; Zhang, W.; Han, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9330−9333.

(10) For recent selected examples on difunctionalization of alkynes, see: (a) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *J. Am. Chem. Soc.* **2013**, *135*, 11481−11484. (b) Handa, S.; Fennewald, J. C.; Lipshutz, B. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 3432−3435. (c) Zhang, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 28−29. (d) Wang, X.; Studer, A. *J. Am. Chem. Soc.* **2016**, *138*, 2977−2980. (e) Hartmann, M.; Daniliuc, C. G.; Studer, A. *Chem. Commun.* **2015**, *51*, 3121−3123. (f) He, C.; Hao, J.; Xu, H.; Mo, Y.; Liu, H.; Han, J.; Lei, A. *Chem. Commun.* **2012**, *48*, 11073−11075. (g) He, C.; Guo, S.; Ke, J.; Hao, J.; Xu, H.; Chen, H.; Lei, A. *J. Am. Chem. Soc.* **2012**, *134*, 5766−5769. (h) Peng, H.; Akhmedov, N. G.; Liang, Y. F.; Jiao, N.; Shi, X. *J. Am. Chem. Soc.* **2015**, *137*, 8912−8915. (i) Li, X.; Li, X.; Jiao, N. *J. Am. Chem. Soc.* **2015**, *137*, 9246−9249. (j) Too, P. C.; Chiba, S. *Chem. Commun.* **2012**, *48*, 7634−7636.

(11) For recent selected examples on sulfinic acids as precursors of sulfonyl radicals, see: (a) Lu, Q.; Zhang, J.; Wei, F.; Qi, Y.; Wang, H.; Liu, Z.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7156−7159. (b) Yuan, Z.; Wang, H. Y.; Mu, X.; Chen, P.; Guo, Y. L.; Liu, G. *J. Am. Chem. Soc.* **2015**, *137*, 2468−2471. (c) Shen, T.; Yuan, Y.; Song, S.; Jiao, N. *Chem. Commun.* **2014**, *50*, 4115−4118. (d) Yang, W.; Yang, S.; Li, P.; Wang, L. *Chem. Commun.* **2015**, *51*, 7520−7523. (e) Wei, W.; Wen, J.; Yang, D.; Du, J.; You, J.; Wang, H. *Green Chem.* **2014**, *16*, 2988−2991. For recent selected examples on other precursors of sulfonyl radicals, see: (f) Chen, Z. Z.; Liu, S.; Hao, W. J.; Xu, G.; Wu, S.; Miao, J. N.; Jiang, B.; Wang, S. L.; Tu, S. J.; Li, G. *Chem. Sci.* **2015**, *6*, 6654−6658. (g) Zhang, L.; Chen, S.; Gao, Y.; Zhang, P.; Wu, Y.; Tang, G.; Zhao, Y. *Org. Lett.* **2016**, *18*, 1286−1289. (h) Jiang, Y.; Loh, T.-P. *Chem. Sci.* **2014**, *5*, 4939−4943.

(12) For recent selected examples on organic azides as the nitrogen source in the synthesis of nitrogen-bearing heterocycles, see: (a) Alt, I. T.; Plietker, B. *Angew. Chem., Int. Ed.* **2016**, *55*, 1519−1522. (b) Motiwala, H. F.; Fehl, C.; Li, S. W.; Hirt, E.; Porubsky, P.; Aubé, J. *J. Am. Chem. Soc.* **2013**, *135*, 9000−9009. (c) Stenehjem, E. D.; Ziatdinov, V. R.; Stack, T. D. P.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2013**, *135*, 1110−1116. (d) Yu, D. G.; Suri, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 8802−8805. (e) Wang, Y. F.; Toh, K. K.; Lee, J. Y.; Chiba, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5927−5931. (f) Chiba, S.; Xu, Y. J.; Wang, Y. F. *J. Am. Chem. Soc.* **2009**, *131*, 12886−12887. (g) Chiba, S.; Zhang, L.; Lee, J. Y. *J. Am. Chem. Soc.* **2010**, *132*, 7266−7267. (h) Yang, T.; Zhu, H.; Yu, W. *Org. Biomol. Chem.* **2016**, *14*, 3376−3384. (i) Peng, J.; Xie, Z.; Chen, M.; Wang, J.; Zhu, Q. *Org. Lett.* **2014**, *16*, 4702−4705. (j) Tang, C.; Yuan, Y.; Jiao, N. *Org. Lett.* **2015**, *17*, 2206−2209. (k) Shen, T.; Huang, X.; Liang, Y. F.; Jiao, N. *Org. Lett.* **2015**, *17*, 6186−6189. (l) Wang, X.; Jiao, N. *Org. Lett.* **2016**, *18*, 2150−2153. (m) Zhu, X.; Chiba, S. *Chem. Commun.* **2016**, *52*, 2473−2476. (n) Wang, Y. F.; Toh, K. K.; Ng, E. P. J.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 6411−6421. (o) Wang, Y. F.; Chiba, S. *J. Am. Chem. Soc.* **2009**, *131*, 12570−12572. (p) Qiao, J.-B.; Zhao, Y.-M.; Gu, P. *Org. Lett.* **2016**, *18*, 1984−1987.

DOI: 10.1021/acs.orglett.6b01427
Org. Lett. XXXX, XXX, XXX−XXX