Advanced Synthesis & Catalysis

## Accepted Article

**Title:** TBAI/K2S2O8 Initiated Radical Cyclization to Synthesize β-Arylsulfonyl Naphthalenes from Homopropargylic Alcohols and Sulfonyl Hydrazides

**Authors:** xiaodong yang, lianbiao zhao, bingxiang yuan, zhenjie qi, and Ru-Long Yan



**To be cited as:** *Adv. Synth. Catal.* 10.1002/adsc.201700634

**Link to VoR:** http://dx.doi.org/10.1002/adsc.201700634

10.1002/adsc.201700634



**DOI: 10.1002/adsc.201**((will be filled in by the editorial staff))

# TBAI/$K_2S_2O_8$ Initiated Radical Cyclization to Synthesize β- Arylsulfonyl Naphthalenes from Homopropargylic Alcohols and Sulfonyl Hydrazides

Xiaodong Yang,[†] Lianbiao Zhao,[‡] Bingxiang Yuan,[†] Zhenjie Qi,[†] Rulong Yan*[†]

[†] State Key Laboratory of Applied Organic Chemistry, Key laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Department of Chemistry, Lanzhou University, Lanzhou, Gansu, China
[‡] College of Chemical Engineering, Northwest University for Nationalities, Lanzhou, Gansu, China

Fax: 0931-8912596 E-mail: yanrl@lzu.edu.cn

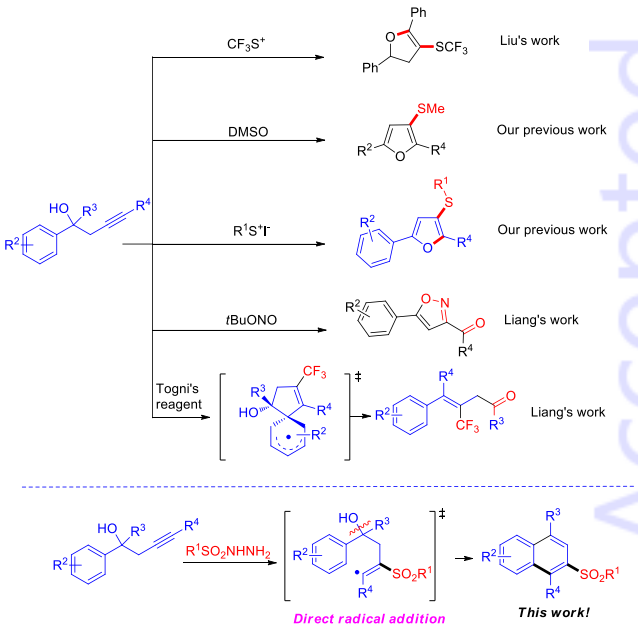
Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

**Abstract.** A metal-free radical addition method for the synthesis of *β*-arylsulfonyl naphthalenes with homopropargylic alcohols and sulfonyl hydrazides has been developed. In this reaction, sulfonyl hydrazide is employed as the source of sulfonyl radical to produce the desired sulfone directly. There is the first example for homopropargylic alcohol through direct intramolecular addition of vinyl radical to arenes with sulfonyl radical, which is initiated by the TBAI/$K_2S_2O_8$ reaction system and generates the desired products in moderate yields.

**Keywords:** *β*- arylsulfonyl naphthalenes; homopropargylic alcohols; sulfonyl hydrazides

Organosulfones motifs represent as privileged structure in the fields of organic synthesis, pharmaceutical industry, agrochemicals as well as materials science.[1] Particularly, the sulfones have been used as drug candidates for anticancer, HIV and Parkinson's diseases for its significant biological activities.[2] On the other hand, desulfonylation reactions have also been flourished in the total synthesis through functional group transformations (FGTs) because the sulfonyl is a good leaving group.[3] Common strategies for sulfones preparation mainly include the introduction sulfonyl group with sulfonylating reagents and oxidation of the sulfide.[4] Compared to the traditional sulfonylating reagents, such as sodium sulfinate, arylsulfinic acids, sulfonyl halides,[5] sulfonyl hydrazides have emerged as ideal sulfonylating agents because of its commercial availability, stability and high reactivity.[6] Recently, radical-triggered addition of sulfonyl radical to alkynes has drawn more attentions for its offering straightforward approaches to synthesize sulfones. Several elegant and significant works about sulfonyl radical addition to alkynes have been reported by the group of Tian, Tu, Li, Breit, Wang and so on.[7] Due to the wide applications of sulfone, it is of great interest to develop efficient and direct method for the construction of sulfone.

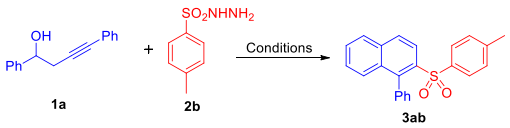



**Scheme 1.** The reactions of homopropargylic alcohols

The homopropargylic alcohols, interesting and useful substrates, have been heavily studied recent years.[8] The radical rearrangement and nucleophilic addition methods empolying homopropargylic alcohol as substrate had been well developed in the past several years. In the field of nucleophilic

10.1002/adsc.201700634

**Table 1**. Optimization of reaction conditions [a]

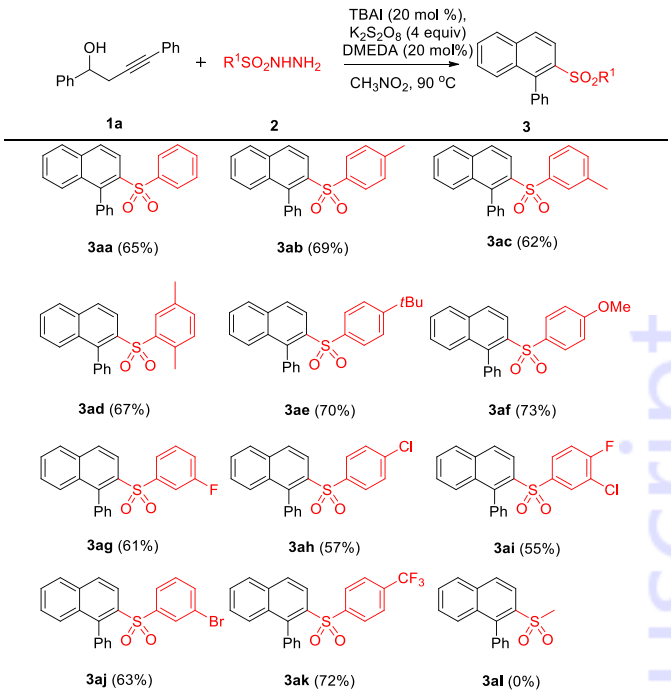



| entry | catalyst(20 mol %) | oxidant (equiv) | additives (20 mol %) | solvent | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | TBAI | $K_2S_2O_8$ (3) | - | DCE | 45 |
| 2 | TBAI | $K_2S_2O_8$ (3) | - | $CH_3NO_2$ | 53 |
| 3 | TBAI | $K_2S_2O_8$ (3) | - | DMF | trace |
| 4 | TBAI | $K_2S_2O_8$ (3) | - | DMSO | trace |
| 5 | TBAI | $K_2S_2O_8$ (3) | - | $CH_3CN$ | 36 |
| 6 | TBAI | $K_2S_2O_8$ (3) | - | EtOH | - |
| 7 | TBAI | $K_2S_2O_8$ (4) | - | $CH_3NO_2$ | 61 |
| 8 | TBAI | TBHP (4) | - | $CH_3NO_2$ | 41 |
| 9 | TBAI | TBP (4) | - | $CH_3NO_2$ | - |
| 10 | TBAI | Oxone® (4) | - | $CH_3NO_2$ | - |
| 11 | TBAI | $K_2S_2O_8$ (4) | PivOH | $CH_3NO_2$ | 43 |
| 12 | TBAI | $K_2S_2O_8$ (4) | $CF_3COOH$ | $CH_3NO_2$ | 37 |
| 13 | TBAI | $K_2S_2O_8$ (4) | TMEDA | $CH_3NO_2$ | 55 |
| 14 | TBAI | $K_2S_2O_8$ (4) | $Et_3N$ | $CH_3NO_2$ | 62 |
| 15 | TBAI | $K_2S_2O_8$ (4) | HMPA | $CH_3NO_2$ | 59 |
| **16** | **TBAI** | **$K_2S_2O_8$ (4)** | **DMEDA** | **$CH_3NO_2$** | **69** |
| 17 | KI | $K_2S_2O_8$ (4) | DMEDA | $CH_3NO_2$ | 49 |
| 18 | $NH_4I$ | $K_2S_2O_8$ (4) | DMEDA | $CH_3NO_2$ | 35 |
| 19 | $I_2$ | $K_2S_2O_8$ (4) | DMEDA | $CH_3NO_2$ | 13 |

[a] Reaction conditions: **1a** (0.3 mmol), **2b** (0.45 mmol), solvent (2 mL). [b] Yields of isolated products. Entry in bold highlights optimized reaction conditions, and the reaction time was monitored by TLC. TBAI = Tetrabutylammonium iodide, TBP = Ditertbutyl peroxide, DMEDA = *N*,*N*-Dimethylethanediamine, TMEDA = Tetramethylethylenediamine, HMPA = Hexamethylphosphoric triamide, DCE = Dichloroethane.

addition, Liu's group had reported the approach for the synthesis *SCF*$_3$-substituted dihydrofurans with homopropargylic alcohols and trifluoromethanesulfenamide (Scheme 1).[9] Our group also had developed two methods for the construction sulfanylfurans and 3-methylthiofurans with homopropargylic alcohols and sulfonyl hydrazides/DMSO (Scheme 1).[10] In the field of radical rearrangement, great progress had been achieved by the group of liang (Scheme 1). In 2014, Liang' group developed an unprecedented one pot reaction of homopropargylic alcohols that involved copper-catalyzed trifluoromethylation, 1,4-aryl migration, and formation of a carbonyl group. [11] To our best knowledge, the formation of *β*-arylsulfonyl naphthalenes from homopropargylic alcohols and sulfonyl hydrazides through direct radical addition has not been explored. Intrigued by the utilization of arylsulfonohydrazides for the formation of the *S*-containing molecules,[12] herein, we developed a metal-free approach to synthesize *β*-arylsulfonyl naphthalenes from homopropargylic alcohols and sulfonyl hydrazides *via* direct radical addition.

**Scheme 2.** The scope of substituted sulfonyl hydrazides




Reaction conditions: **1a** (0.3 mmol), **2** (0.45 mmol), TBAI (20 mol %), $K_2S_2O_8$ (1.2 mmol), DMEDA (20 mol %), $CH_3NO_2$ (2 mL), 100 °C.

Initially, 1,4-diphenylbut-3-yn-1-ol (**1a**) and *p*-toluenesulfonyl hydrazide (**2b**) were chose as the model substrates to optimize reaction conditions. While TBAI (20 mol %) and $K_2S_2O_8$ (3 equiv) were used in this reaction, radical cyclization occurred to give the desired product 1-phenyl-2-tosylnaphthalene (**3ab**) in 45% yield with DCE as solvent (Table 1, entry 1). After confirming the structure of compound **3ab** by the single crystal X-ray analysis (Figure 1),[13] different solvents were evaluated and $CH_3NO_2$ was found to be the most efficient solvent for this transformation (Table 1, entry 1-6). The yield of **3ab** was slightly improved when $K_2S_2O_8$ was increased to 4 equiv for this reaction (Table 1, entry 7). Then various oxidants, such as TBHP, TBP, Oxone® were also tested, no better results were obtained (Table 1, entries 8-11). Further investigation was focused on introducing the acids or bases to this reaction system. The yields of **3ab** were decreased when acids were added (Table 1, entries 11, 12). To our delight, the base DMEDA promoted the reaction and the yield

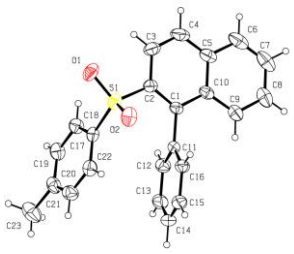
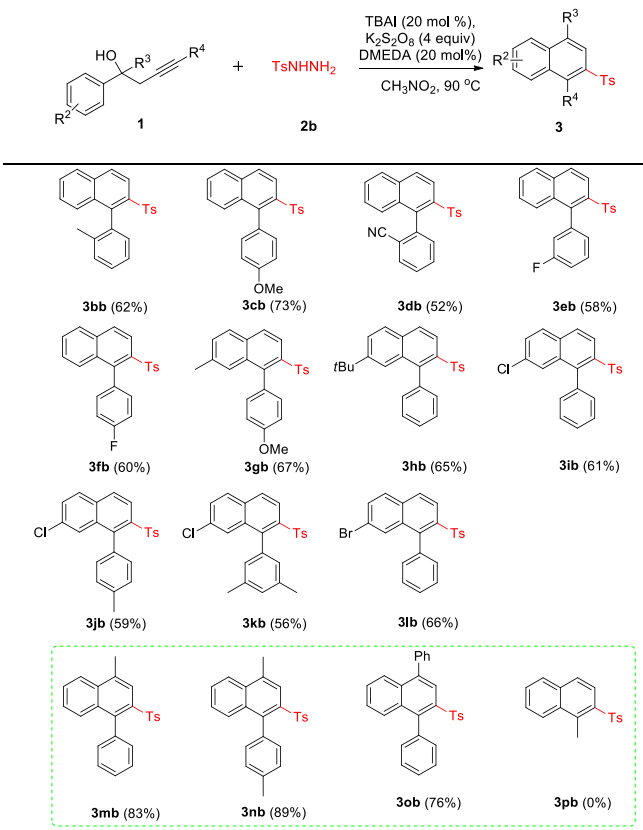


Figure 1. The X-ray Structure of **3ab**.

10.1002/adsc.201700634

**Scheme 3**. The scope of substituted homopropargylic alcohols and sulfonyl hydrazides



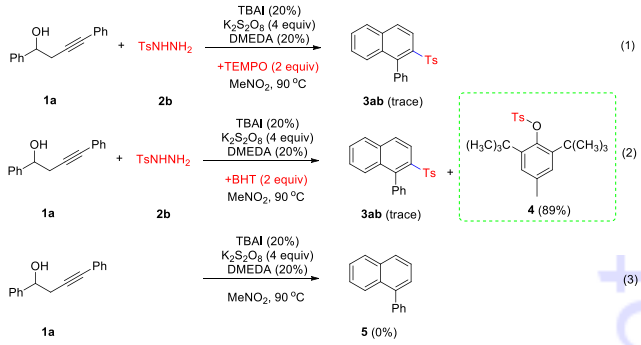

Reaction conditions: **1** (0.3 mmol), **2b** (0.45 mmol), TBAI (20 mol %), $K_2S_2O_8$ (1.2 mmol), DMEDA (20 mol %), $CH_3NO_2$ (2 mL), 100 °C.

was improved to 69% (Table 1, entries 13-19). Finally, different iodine sources were also investigated and TBAI was proved to be the best catalyst for this reaction (Table 1, entries 17-19). After screening other reaction parameters, the optimized reaction system was established as Table 1, entry 16.

With the optimized conditions in hand, the scope of substituted sulfonyl hydrazides was examined and the results are illustrated in Scheme 2. Arylsulfonohydrazides with various the *m*-, *o*-, *p*-substituents reacted with substrate **1a** smoothly, generating the desired substituted *β*-arylsulfonyl naphthalenes in moderate yields. Substituted sulfonyl hydrazides with both electron-withdrawing and electron-donating groups, such as alkyl, methoxyl, fluoro, chloro, bromo and trifluoromethyl all survived in this process and the reactions were less affected by the nature of groups on the benzene ring of sulfonyl hydrazides. When methanesulfonyl hydrazide **2l** was subjected to the standard condition, no desired product was detected, probably due to the instability of methanesulfonyl radicals. It is known that generation of methanesulfonyl radicals is often followed by beta-scission to yield a methyl radical.

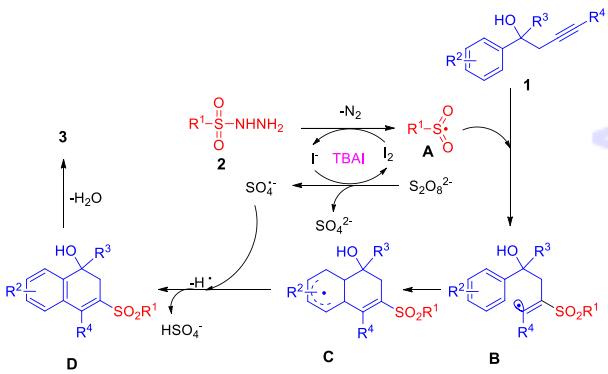
After successfully evaluating the various sulfonyl hydrazides, we next extended our investigation to the scope of substituted homopropargylic alcohols. As conceived, various homopropargylic alcohols with Me, MeO, *t*Bu, F, Cl, Br and CN groups on the benzene ring were transformed well under the optimized conditions and gave the corresponding *β*-arylsulfonyl naphthalenes in 52-73% yields (Scheme 3). Moreover, more challenging substrates **1m**, **1n**, and **1o** were also tolerated well and generated the desired products **3mb**, **3lb**, and **3ob** in 83%, 89%, 76% yields respectively. Unfortunately, the homopropargylic alcohols with alkyl group performed unsuccessfully in this process and no desired product was obtained.

**Scheme 4**. Control experiments




To gain some mechanistic insights, several control experiments were carried out and the results are shown in Scheme 4. The reaction was significantly inhibited when 2.0 equiv of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was employed. When the radical scavenger of 2,6-di-tert-butyl-4-methyl-phenol (BHT) was used for this reaction, the product **3ab** was almost not detected and a product 2,6-di-tert-butyl-4-methylphenyl-4-methylbenzene sulfonate **4** was isolated in 89% yield, which was confirmed by NMR and HMRS spectroscopy (Scheme 4, entry 2). This result suggested that sulfonyl radical should be the important radical intermediate for this transformation. Furthermore, no desired product **5** was detected without substrate **2b** under the standard conditions.

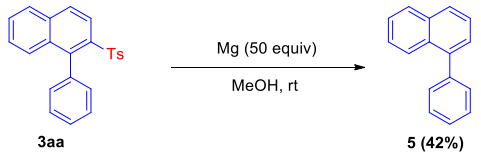
**Scheme 5**. Proposed mechanism




Based on these experimental results and previous mechanistic studies, a plausible mechanism is proposed in Scheme 5. Firstly, a sulfonyl radical **A** is generated from sulfonyl hydrazides **2** by

TBAI/$K_2S_2O_8$ with releasing $N_2$. Next, the vinyl radical intermediate **B** is obtained from the the sulfonyl radical **A** addition to homopropargylic alcohol **1**.[6a-f] Furthermore, the vinyl radical **B** undergoes intramolecular cyclization to synthesis new radical intermediate **C**.[3a, 6e, 6l, 6t, 6z] Then the intermediate **D** is produced via losing hydrogen radical directly. Finally, the desired naphthalene **3** is afforded through water elimination.

**Scheme 6**. The transformation of removing the sulfonyl group




The versatility of the product **3aa** is shown by further transformations to valuable product (Scheme 6). Removing the sulfonyl group of the product **3aa** had been operated with magnesium turnings under mild conditions,[14] thus yielding the 1-phenylnaphthalene **5** in moderate yield.

In summary, we have developed a straightforward method for the synthesis of substituted *β*-arylsulfonyl naphthalenes with homopropargylic alcohols and sulfonyl hydrazides, affording densely functionalized, substituted sulfones in moderate yields with high regioselectivity. This method constitutes a concise approach to substituted sulfones through tandem intermolecular radical addition and cyclization with no requirement of metal catalysis.

## Experimental Section

**General procedure for synthesis of *β*-Arylsulfonyl naphthalenes with homopropargylic alcohols and sulfonylhydrazines:**

The homopropargylic alcohols (**1a**, 0.3 mmol), sulfonylhydrazines (**2b**, 0.45 mmol), TBAI (20 mol %), $K_2S_2O_8$ (4 equiv), DMEDA (20 mol %) were mixed in $CH_3NO_2$ (2 mL) and this mixture was carried out under $N_2$ at 100 °C for 12 h. Then the reaction mixture was cooled to room temperature, and then extracted with ethyl acetate (15 ml×3). The combined organic phase was dried over anhydrous $Na_2SO_4$. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (10:1) to afford the desired *β*-arylsulfonyl naphthalenes **3ab** (74.1 mg, 69% yield).

## Acknowledgements

*This work was supported by National Natural Science Foundation of China (21672086, 21462035), Gansu Province Science Foundation for Youths (1606RJYA260) and the Fundamental Research Funds for the Central Universities (lzujbky-2016-39).*

## References

[1] For selected examples, see: a) C. Napier, M. Stewart, H. Melrose, B. Hopkins, A. McHarg, R. Wallis, *Eur. J. Pharmacol*. **1999**, *375*, 61; b) K. G. Petrov, Y. Zhang, M. Carter, G. S. Cockerill, S. Dickerson, C. A. Gauthier, Y. Guo, R. A. Mook, Rusnak, D. W.; Walker, A. L.; Wood, E. R.; Lackey, K. E. *Bioorg. Med. Chem. Lett*. **2006**, *16*, 4686; c) M. Artico, R. Silvestri, S. Massa, A. G. Loi, S. Corrias, G. Piras, P. L. Colla, *J. Med. Chem*. **1996**, *39*, 522; d) I. D. Kerr, J. H. Lee, C. J. Farady, R. Marion, M. Rickert, M. Sajid, K. C. Pandey, C. R. Caffery, J. Legac, E. Hansell, J. H. Mckerrow, C. S. Craik, P. J. Rosenthal, L. S. Brinen, *J. Biol. Chem*. **2009**, *284*, 25697.

[2] a) S. Sciabola, E. Carosati, M. Baroni, R. Mannhol, *J. Med. Chem.* **2005**, *48*, 3756; b) L. Llauger, H. He, J. Kim, J. Aguirre, N. Rosen, U. Peters, P. Davies, G. J. Chiosis, *J. Med. Chem.* **2005**, *48*, 2892; c) N. Neamati, A. Mazumder, H. Zhao, S. Sunder, T. R. Burke, R. J. Schultz, Y. Pommier, *Antimicrob. Agents Chemother*. **1997**, *41*, 385.

[3] a) Y.-L. Zhu, B. Jiang, W.-J. Hao, J.-K. Qiu, J. Sun, D.-C. Wang, P. Wei, A.-F. Wang, G.-G. Li, S.-J. Tu, *Org. Lett*. **2015**, *17*, 6078; b) H. Guo, Q. Xu, O. Kwon, *J. Am. Chem. Soc.* **2009**, *131*, 6318; c) K. Inanaga, T. Fukuyama, M. Kubota, Y. Komatsu, H. Chiba, A. Kayano, K. Tagami, *Org. Lett*. **2015**, *17*, 3158.

[4] M. P. Bertrand, C. Ferreri, *in Radicals in Organic Synthesis, ed. P. Renaud and M. Sibi*, Wiley-VCH, Weinheim. **2001**, *2*, 485–504.

[5] a) M. Rahimizadeh, G. Rajabzadeh, S. M. Khatami, H. Eshghi, A. Shiri, *J. Mol. Catal. A* **2010**, *323*, 59; b) A. Rostami, J. Akradi, *Tetrahedron Lett.* **2010**, *51*, 3501; c) W. F. Lo, H. M. Kaiser, M. Beller, M. K. Tse, *Org. Lett.* **2007**, *9*, 3405; d) A. Kar, I. A. Sayyed, W. F. Lo, H. M. Kaiser, M. Beller, M. K. Tse, *Org. Lett.* **2007**, *9*, 3405, e) V. G. Pandya, S. B. Mhaske, *Org. Lett.* **2014**, *16*, 3836; f) S. Liang, R.-Y. Zhang, L.-Y. Xi, S.-Y. Chen, X.-Q. Yu, *J. Org. Chem.* **2013**, *78*, 11874; j) C.-R. Liu, M.-B. Li, D.-J. Cheng, C.-F. Yang, S.-K. Tian, *Org. Lett.* **2009**, *11*, 2543; h) C. Waldmann, O. Schober, G. Haufe, K. Kopka, *Org. Lett.* **2013**, *15*, 2954; i) A. Shavnya, K. D. Hesp, V. Mascitti, A. C. Smith, *Angew. Chem., Int. Ed.* **2015**, *54*, 13571; j) X. D. Tang, L. B. Huang, C. R. Qi, X. Wu, W. Q. Wu, H. F. Jiang, *Chem. Commun.* **2013**, *49*, 6102; k) J. D. Liu. S. B. Zhuang, Q. W. Gui, X. Chen, Z. Y. Yang, Z. Tan, *Eur. J. Org. Chem*. **2014**, *2014*, 3196; l) B. N. Du, P. Qian, Y. Wang, H. B. Mei, J. L. Han, Y. Pan, *Org. Lett*. **2016**, *18*, 4144; m) W. Wei, J. W. Wen, D. S. Yang, J. Du, You, J. M.; Wang, H. *Green Chem.* **2014**, *16*, 2988; n) Q. Q. Lu, J. Zhang, G. L. Zhao, Y. Qi, H. M. Wang, A. W. Lei, *J. Am. Chem. Soc*. **2013**, *135*, 11481; o) M. Chen, Z.-T. Huang, Q.-Y. Zheng, *Org. Biomol. Chem*. **2014**, *12*, 9337; p) R. P. Nair, T. H. Kim, B. J. Frost, *Organometallics*. **2009**, *28*, 4681; q)

S.-K. Kang, H.-W. Seo, Y.-H. Ha, *Synthesis*, **2001**, *2001*, 1321.

[6] a) Y.-L. Zhu, B. Jiang, W.-J. Hao, A.-F. Wang, J.-K. Qiu, P. Wei, D.-C. Wang, G.-G. Li, S.-J. Tu, *Chem. Commun*. **2016**, *52*, 1907;b) X. Q. Li, X. S. Xu, P. Z. Hu, X. Q. Xiao, C. *J*. Zhou, *Org. Chem*. **2013**, *78*, 7343; c) J. Zhang, Y. Shao, H. X. Wang, Q. Luo, J. J. Chen, D. M. Xu, X. B. Wan, *Org. Lett*. **2014**, *16*, 3312; d) G. W. Rong, J. C. Mao, H. Yan, Y. Zheng, G. Q. Zhang, *J. Org. Chem*. **2015**, *80*, 4697; e) Z. Yang, W.-J. Hao, S.-L. Wang, J.-P. Zhang, Bo. Jiang, G.-G. Li, S.-J. Tu, *J. Org. Chem*. **2015**, *80*, 9224; f) Lan. Zheng, Z. Z. Zhou, Y.-T. He, L.-H. Li, J.-W. Ma, Y.-F. Qiu, P.-X. Zhou, X.-Y. Liu, P.-F. Xu, Y.-M. Liang, *J. Org. Chem*. **2016**, *81*, 66; g) F.-L. Yang, S.-K. Tian, *Angew. Chem., Int. Ed*. **2013**, *52*, 4929; h) F.-L. Yang, F.-X. Wang, T.-T. Wang, Y.-J. Wang, S.-K. Tian, *Chem. Commun*. **2014**, *50*, 2111; i) F.-L. Yang, X.-T. Ma, S.-K. Tian, *Chem. Eur. J*. **2012**, *18*, 1582; j) T.-T. Wang, F.-X. Wang, F.-L. Yang, S.-K. Tian, *Chem. Commun.* **2014**, *50*, 3802; k) W.-J. Hao, Y. Du, D. Wang, B. Jiang, Q. Gao, S.-J. Tu, G. G. Li, *Org. Lett.* **2016**, *18*, 1884; l) Z.-Z. Chen, S. Liu, W.-J. Hao, G. Xu, S. Wu, J.-N. Miao, B. Jiang, S.-L. Wang, S.-J. Tu, G. G. Li, *Chem. Sci*. **2015**, *6*, 6654; m) S. R. Guo, W.-M. He, J.-N. Xiang, Y.-Q. Yuan, *Chem. Commun.* **2014**, *50*, 8578; n) X. Li, Y. Xu, W. Wu, C. Jiang, C. Qi, H. Jiang, *Chem. Eur. J*. **2014**, *20*, 7911; o) R, Singh, B. K. Allam, N. Singh, K. Kumari, S. K. Singh, K. N. Singh, *Adv. Synth. Catal*. **2015**, *357*, 1181; p) U. Wille, *Chem. Rev*. **2013**, *113*, 813; q) T. Besset, T. Poisson, X. Pannecoucke, *Eur. J. Org. Chem*. **2015**, *2015*, 2765; r) T. Wang, N. Jiao, *Acc. Chem. Res*. **2014**, *47*, 1137; s) D. Leca, L. Fensterbank, E. Lacote, M. Malacria, *Chem. Soc. Rev*. **2005**, *34*, 858; t) J. Wen, W. Wei, S. Xue, D. Yang, Y. Lou, C. Gao, H. Wang, *J. Org. Chem*. **2015**, *80*, 4966; u) S. Li, X. Li, F. Yang, Y. Wu, *Org. Chem. Front*. **2015**, *2*, 1076; v) X. Li, X. Shi, M. Fang, X. Xu, *J. Org. Chem*. **2013**, *78*, 9499; w) J.-K. Qiu, B. Jiang, Y.-L. Zhu, W.-J. Hao, D.-C. Wang, J. Sun, P. Wei, S.-J. Tu, G. Li, *J. Am. Chem. Soc*. **2015**, *137*, 8928; x) B. Jiang, Y. Ning, W. Fan, S.-J. Tu, G. G. Li, *J. Org. Chem*. **2014**, *79*, 4018.

[7] a) G. C. Senadi, B.-C. Guo, W.-P. Hu, J.-J. Wang, *Chem. Commun.* **2016**, *52*, 11410; b) W. Wei, J. W. Wen, D. S. Yang, M. Y. Guo, Y. Y. Wang, J. M. You, H. Wang, *Chem. Commun*. **2015**, *51*, 768; c) J.-K. Qiu, W.-J. Hao, D.-C. Wang, P. Wei, J. Sun, B. Jiang, S.-J. Tu, *Chem. Commun.* **2014**, *50*, 14782; d) S. Tang, Y. Wu, W. Q. Liao, R. P. Bai, C. Liu, A. W. Lei, *Chem. Commun.* **2014**, *50*, 4496; f) W. Wei, C. L. Liu, D. S. Yang, J. W. Wen, J. M. You, Y. R. Suo, H. Wang, *Chem. Commun.* **2013**, *49*, 10239; h) K. Xu, V. Khakyzadeh, T. Bury, B. Breit, *J. Am. Chem. Soc.* **2014**, *136*, 16124; i) J. Sun, J.-K. Qiu, Y.-L. Zhu, C. Guo, W.-J. Hao, B. Jiang, S.-J. Tu, *J. Org. Chem*. **2015**, *80*, 8217; l) Y. Su, X. J. Zhou, C. L. He, W. Zhang, X. Ling, X. Xiao, *J. Org. Chem.* **2016**, *81*, 4981; m) Y. X. Wang, L. Ma, M. H. Ma, H. Zheng, Y. Shao, X. B. Wan, *Org. Lett.* **2016**, *18*, 5082; n) R. Fu, W.-J. Hao, Y.-N. Wu, N.-N. Wang, S.-J. Tu, G.-G. Li, B. Jiang, *Org. Chem. Front.* **2016**, *3*, 1452; o) R. Singh, B. K. Allam, N. Singh, K. Kumari, S. K. Singh, K. N. Singh, *Org. Lett*. **2015**, *17*, 2656. p) F.-L. Yang, S.-K. Tian, Tetrahedron Lett. **2017**, *58*, 487.

[8] a) D. Zhang, J. M. Ready, *J. Am. Chem. Soc*. **2006**, *128*, 15050; b) V. Belting, N. Krause, *Org. Lett.*, **2006**, *8*, 4489; c) S. Antoniotti, E. Genin, V. Michelet, J.-P. Genet, *J. Am. Chem. Soc.*, **2005**, *127*, 9976; d) C.-W. Chen, T.-Y. Luh, *J. Org. Chem.*, **2008**, *73*, 8357; e) A. K. Saikia, P. Ghosh, A. K. Kautarya, *RSC Adv.*, **2016**, *6*, 44774; f) T. Shi, X. Guo, S. Teng, W. Hu, *Chem. Commun.* **2015**, *51*, 15204.

[9] D.-Q. Chen, P. Gao, P.-X. Zhou, X.-R. Song, Y.-F. Qiu, X.-Y. Liu, Y.-M. Liang, *Chem. Commun.* **2015**, *51*, 6637.

[10] a) X. Yang, R. Yan, *Org. Biomol. Chem.* **2017**, *15*. 3571; b) Z. An, Y. She, X. Yang, X. Pang, R. Yan, *Org. Chem. Front.* **2016**, *3*, 1746.

[11] a) P. Gao, H.-X. Li, X.-H. Hao, D.-P. Jin, D.-Q. Chen, X.-B. Yan, X.-X. Wu, X.-R. Song, X.-Y. Liu, Y.-M. Liang, *Org. Lett.* **2014**, *16*, 6298; b) P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu, Y.-M. Liang, *Angew. Chem., Int. Ed.* **2014**, *53*, 7629.

[12] a) X. Kang, R. Yan, G. Yu, X. Pang, X. Liu, X. Li, L. Xiang, G. Huang, *J. Org. Chem.* **2014**, *79*, 10605; b) X. Pang, L. Xiang, X. Yang, R. Yan, *Adv. Synth. Catal*. **2016**, *358*, 321.

[13] CCDC-1561459 contains the supplementary crystallographic data (3ab) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] A. Neo, C. Lopez, V. Romero, B. Antelo, J. Delamano, A. Perez, D. Fernandez, J. Almeida, L. Castedo, G. Tojo, *J. Org. Chem.* **2010**, *75*, 6764.

10.1002/adsc.201700634

**UPDATE**

# TBAI/$K_2S_2O_8$ Initiated Radical Cyclization to Synthesize $\beta$- Arylsulfonyl Naphthalenes from Homopropargylic Alcohols and Sulfonyl Hydrazides

*Adv. Synth. Catal.* **Year**, *Volume*, Page – Page

Xiaodong Yang,[†] Lianbiao Zhao,[‡] Bingxiang Yuan,[†] Zhenjie Qi,[†] Rulong Yan*[†]