ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Org. Chem. Front.*, 2018, **5**, 2604

Metal-free deoxygenative sulfonylation of quinoline *N*-oxides with sodium sulfinates *via* a dual radical coupling process†

Long-Yong Xie,[a] Sha Peng,[a] Fang Liu,[a] Guan-Rong Chen,[a] Wen Xia,[b] Xianyong Yu,[b] Wen-Feng Li,[c] Zhong Cao[c] and Wei-Min He *[a]

Received 3rd July 2018,
Accepted 27th July 2018

DOI: 10.1039/c8qo00661j

rsc.li/frontiers-organic

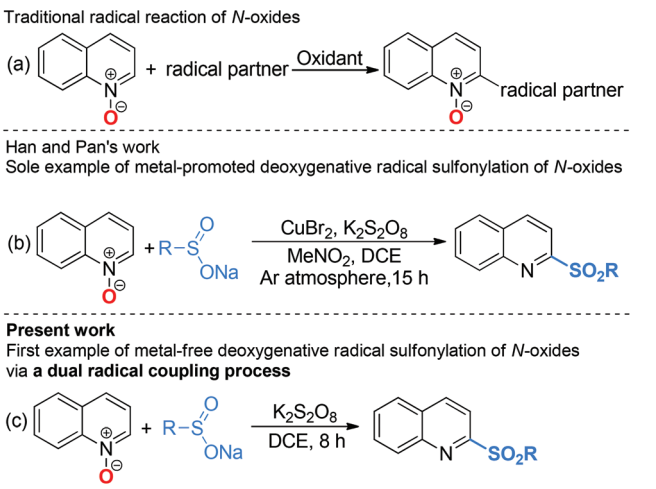
The first example of a metal- and reductant-free deoxygenative sulfonylation of quinoline *N*-oxides with sodium sulfinates *via* a dual radical coupling process is reported. In this reaction, sodium sulfinates play dual roles of a sulfonylation reagent and activating agent. This procedure is expected to complement the current methods for the radical reaction of quinoline *N*-oxides.

Published on 07 Ogos 2018. Downloaded on 17/10/2025 6:48:42 PG.

Introduction

Radical chemistry has played an increasingly important role in modern synthesis. The utilization of a controlled radical reaction to synthesize structurally diverse organic molecules has been of increasing interest in both academia and industry.[1] In recent decades, a large number of radical reactions have been catalyzed by various transition metal complexes, which result in inevitable metal residuals in the terminal products and disposal of these metal salts often causes environmental pollution.[2] Therefore, the development of metal-free radical reactions is of great importance and has been extensively studied over the past years.

The C–H bond functionalization of quinoline *N*-oxides has received extensive attention in organic synthesis, as it has been demonstrated to be a powerful and versatile tool for direct incorporation of new functionalities at the C-2[3] and C-8 positions[4] of quinoline skeletons with excellent atom economy. However, although the nucleophilic addition to quinoline *N*-oxides generating 2-substituted quinolines has been well established, direct construction of such motifs[5] *via* radical pathways remains a long-standing challenge. In fact, most radical reactions of quinoline *N*-oxides through C–H bond activation result in substituted quinoline *N*-oxides (Scheme 1a).[6] These protocols require additional deoxygenative functionalization with superstoichiometric amounts of harmful reagents as reductants for obtainment of the expected 2-substituted quinolines. The one-pot synthesis of 2-sulfonylquinolines from quinoline *N*-oxides through C–H bond activation[7] has attracted considerable attention due to their potential biological activities and valuable synthetic utilities as well as the availability of readily accessible quinoline *N*-oxides.[8] However, to the best of our knowledge, the only example of direct synthesis of 2-sulfonylquinolines *via* deoxygenative radical sulfonylation[9] of quinoline *N*-oxides in the presence of copper salts as the catalyst under an argon atmosphere was reported by Pan and Han (Scheme 1b).[10] Considering the inconveniences and manufacturing costs in eliminating the trace metal contami-



Scheme 1 Radical coupling reactions of *N*-oxides.

[a]*Hunan Provincial Engineering Research Center for Ginkgo biloba, Hunan University of Science and Engineering, Yongzhou 425100, China. E-mail: weiminhe2016@yeah.net*
[b]*Key Laboratory of Theoretical Organic Chemistry and Functional Molecule of Ministry of Education, Hunan University of Science and Technology, Xiangtan 411201, China*
[c]*Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, Changsha, 410114, China*

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8qo00661j

This journal is © the Partner Organisations 2018

Published on 07 Ogos 2018. Downloaded on 17/10/2025 6:48:42 PG.

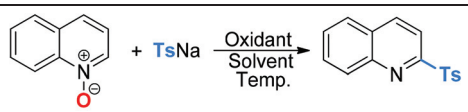
nation, especially for the late-stage functionalization of pharmacologically active compounds, a metal-free radical reaction for the synthesis of 2-sulfonylquinolines would be greatly desired. As part of our program devoted to the study of eco-friendly organic synthesis,[11] herein, we report for the first time a facile metal- and reductant-free protocol for the direct construction of 2-sulfonylquinolines *via* a dual radical coupling process (Scheme 1c).

Results and discussion

Our investigation started with the cross coupling reaction of quinoline *N*-oxide (**1a**) and sodium *p*-toluensulfinate (**2a**, 2 equiv.) in the presence of $K_2S_2O_8$ (1.2 equiv.) in 1,2-dichloroethane (DCE) at 100 °C for 8 h, and it led to the production of the desired 2-tosylquinoline **3aa** in 55% yield based on 65% conversion of the starting material **1a** (Table 1, entry 1). No 4-sulfonylquinoline was observed. Increasing the amount of oxidant to 2 equiv. resulted in the complete consumption of **1a** and an 85% yield of **3aa** (entry 2). However, further increasing the loading of $K_2S_2O_8$ was not beneficial for the reaction (entry 3). Unexpectedly, inferior outcomes of the reaction were detected when employing related persulfate salt oxidants (entries 4–6), whereas a markedly lower yield of **3aa** or no reaction was observed when organic oxidants were used (entries 7–12). The solvent also played a key role in the reaction outcome. Among the solvents examined, DCE proved to be the best for this reaction (entries 2, 13–17). Performing the transformation at a concentration of 0.1 M did not affect the reaction outcome; however, a higher concentration of 0.25 M was chosen that reduces solvent waste (entries 18 *vs.* 1). Further increasing the concentration of **1a** resulted in a slightly decreased yield (entry 19). Increasing the reaction temperature from 100 °C to 110 °C did not improve the reaction outcome, whereas a distinct decrease in the yield of **3aa** and the **1a** conversion was detected when the temperature was decreased to 90 °C (entries 20 and 21). Furthermore, reducing the amount of **2a** led to a decrease in the yield of **3aa** (entry 22). No reaction occurred in the absence of $K_2S_2O_8$, and the raw material **1a** was quantitatively recovered (entry 23).

The optimal reaction conditions (Table 1, entry 18) were applicable for the oxidative coupling reaction of quinoline *N*-oxides and sodium sulfinates. As shown in Table 2, quinoline *N*-oxides bearing sterically hindered, electron-rich or electron-poor substituents in the quinoline ring all reacted well to yield the desired sulfonated products in moderate to good yields (**3aa–3pa**). Notably, a variety of functional groups are tolerated, including methyl (**3aa–3ga**), isopropyl (**3ha**), methoxy (**3ia**), phenyl (**3ja**), fluoride (**3ka**), chloride (**3la** and **3ma**) and bromide (**3na–3pa**). When isoquinoline *N*-oxide **1q** was employed as the substrate, a total 78% yield of the isomer

Table 1 Optimization of reaction conditions[a]

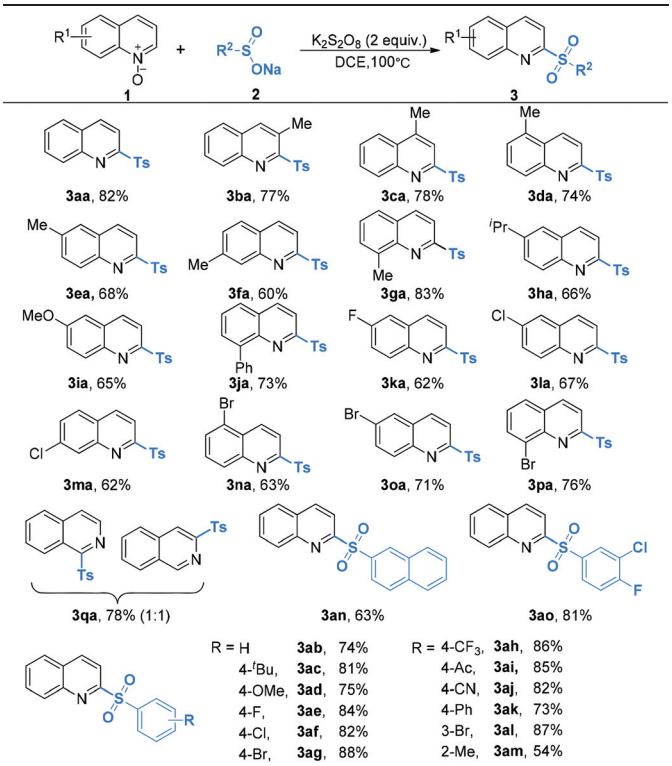


1a 2a 3aa

Entry	Oxidant (equiv.)	Solvent (mL)	Temp.	Yield[b] (%)
1	$K_2S_2O_8$ (1.2)	DCE (1)	100 °C	55
2	$K_2S_2O_8$ (2)	DCE (1)	100 °C	85
3	$K_2S_2O_8$ (2.5)	DCE (1)	100 °C	85
4	$Na_2S_2O_8$ (2)	DCE (1)	100 °C	68
5	$(NH_4)_2S_2O_8$ (2)	DCE (1)	100 °C	61
6	Oxone (2)	DCE (1)	100 °C	36
7	$PhI(OAc)_2$ (2)	DCE (1)	100 °C	21
8	PCC (2)	DCE (1)	100 °C	N.R.
9	*m*-CPBA (2)	DCE (1)	100 °C	N.R.
10	TBHP (2)	DCE (1)	100 °C	N.R.
11	H_2O_2 (2)	DCE (1)	100 °C	N.R.
12	O_2 balloon	DCE (1)	100 °C	N.R.
13	$K_2S_2O_8$ (2)	MeCN (1)	100 °C	52
14	$K_2S_2O_8$ (2)	$MeNO_2$ (1)	100 °C	56
15	$K_2S_2O_8$ (2)	DMSO (1)	100 °C	32
16	$K_2S_2O_8$ (2)	DMF (1)	100 °C	41
17	$K_2S_2O_8$ (2)	THF (1)	100 °C	N.R.
18	**$K_2S_2O_8$ (2)**	**DCE (0.4)**	**100 °C**	**85**
19	$K_2S_2O_8$ (2)	DCE (0.3)	100 °C	70
20	$K_2S_2O_8$ (2)	DCE (0.4)	110 °C	83
21	$K_2S_2O_8$ (2)	DCE (0.4)	90 °C	45
22[c]	$K_2S_2O_8$ (2)	DCE (0.4)	100 °C	73
23	—	DCE (1)	100 °C	N.R.

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), oxidant, solvent, 100 °C, 8 h. [b] Estimated by ^{1}H NMR using diethyl phthalate as the internal reference. [c] 1.5 equiv. of **2a** were used. N.R: no reaction.

Table 2 Reaction scope[a]



[a] All reactions were carried out in a sealed tube in the presence of **1** (0.3 mmol), **2** (0.6 mmol), $K_2S_2O_8$ (0.6 mmol) and DCE (1.2 ml); isolated yields are reported.

Published on 07 Ogos 2018. Downloaded on 17/10/2025 6:48:42 PG.

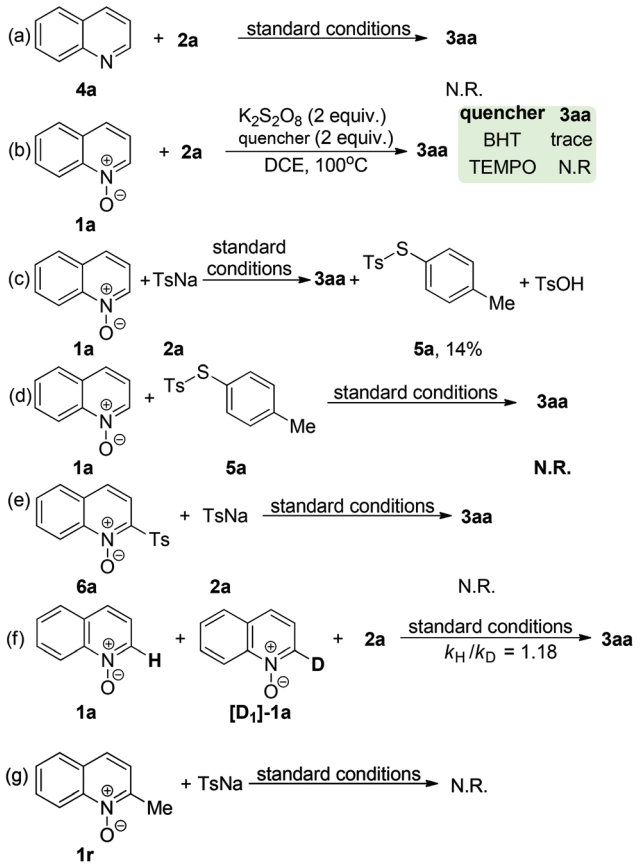
products **3qa-1** and **3qa-2** was obtained in a 1 : 1 ratio. However, when pyridine *N*-oxide or quinoxaline *N*-oxide was used as the substrate, only a trace amount of the tosylation product could be detected.

Sodium arenesulfinates with various synthetically useful functional groups present on the phenyl ring such as alkyl (Me and *t*-Bu), methoxyl, halo (F, Cl and Br), trifluoromethyl, acetyl, nitrile and phenyl were well compatible (**3ab–3am**). Regardless of their electronic characteristics, quinoline *N*-oxides coupled smoothly with sodium arenesulfinates bearing both electron-donating and electron-deficient substituents, to produce the expected products in moderate to excellent yields. Furthermore, the yield was slightly lower in the case of *ortho*-substituted sodium arenesulfinate (**3am**) than those obtained with the *para*-substituted ones, which might be due to steric factors. Moreover, di-substituted aryl sulfinates and 2-naphthalenesulfinates also afforded the corresponding compounds in good yields (**3an** and **3ao**). When sodium thiophene-2-sulfinate or sodium pyridine-3-sulfinate was used as the substrate, no sulfonylation product was formed and the quinoline *N*-oxide starting material was quantitatively recovered. No sulfonylation reaction occurred when an aliphatic sodium sulfinate was employed as the substrate, which might be ascribed to the unstable aliphatic sulfonyl intermediate.

Finally, we investigated the scalability of this new sulfonylation reaction. More than 1 g of quinoline *N*-oxide **1a** and sodium *p*-toluensulfinate **2a** was subjected to the standard reaction conditions (Scheme 2). As anticipated, the reaction proceeded well by delivering **3aa** in 78% yield.

To understand the reaction mechanism of the present oxidative coupling reaction, a series of control experiments were conducted. Firstly, no sulfonylation reaction occurred between quinoline **4a** and **2a** under optimal reaction conditions, which indicated that the N–O group played a key role in the transformation (Scheme 3a). Secondly, when **1a** was treated under standard reaction conditions in the presence of 2 equiv. of radical scavenger (TEMPO or BTH) (Scheme 3b), the reaction was completely inhibited. To further verify whether the radical species is involved in the overall chemical process, electron paramagnetic resonance (EPR) experiments were carried out to gain insight into the radical coupling reaction. When $K_2S_2O_8$ with **2a** in DCE at room temperature was tested, no radical signal (g = 2.003, AN = 1.43 mT, AHβ = 1.36 mT, AHγ = 0.21 mT) was observed (Fig. 1a). An oxygen-centered sulfate radical could also be detected through treatment of $K_2S_2O_8$ in DCE at 80 °C for 5 min (Fig. 1b). After the reaction of **2a** and $K_2S_2O_8$ in DCE at 80 °C, the signal of the sulfur-centered 4-methylbenzenesulfonyl radical (g = 2.002, AN = 1.54 mT, AH = 2.206 mT) was clearly observed (Fig. 1c).[12] These observations suggested that both an oxygen-centered sulfate radical and a sulfur-centered 4-methylbenzenesulfonyl radical were generated in this reaction. ^{1}H NMR analysis can provide valuable information about the reaction process. Pleasingly, a characteristic spectrum was obtained when the reaction mixture was investigated by ^{1}H NMR. Both the *S*-*p*-tolyl

Scheme 2 Gram-scale synthesis.



Scheme 3 Control experiments.

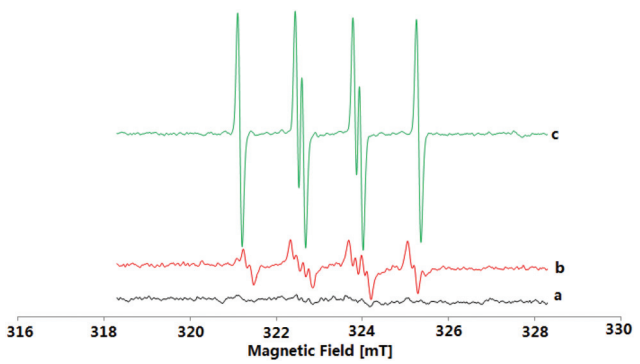
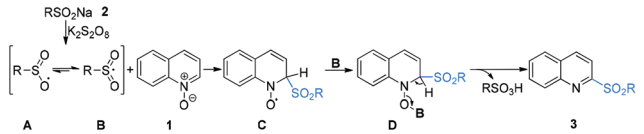


Fig. 1 Electron paramagnetic resonance experiments (a) $K_2S_2O_8$ + TsNa-DCE-RT-5 min; (b) $K_2S_2O_8$-DCE-80 °C-5 min, g = 2.003, AN = 1.43 mT, AHβ = 1.36 mT, AHγ = 0.21 mT, an oxygen-centered sulfate radical; (c) $K_2S_2O_8$ + TsNa-DCE-80 °C-5 min, g = 20 056, AN = 1.39 mT, AH = 1.48 mT, a sulfur-centered 4-methylbenzenesulfonyl radical.

This journal is © the Partner Organisations 2018



Scheme 4 Proposed mechanism.

4-methylbenzenesulfonothioate (**5a**) and TsOH were detected by ^{1}H NMR and MS (Scheme 3c). Further treatment of **1a** with **5a** and **6a** with **2a** under standard reaction conditions could not produce the desired **3aa** (Schemes 3d and 3e), which indicated that **5a** and **6a** might not be the possible reaction intermediates. A clear kinetic isotope effect value (1.18) of the competitive intermolecular experiment involving a 1 : 1 mixture of **1a**/[D1]-**1a** was observed (Scheme 3f), which revealed that the scission of the quinoline *N*-oxide C(sp_2)–H bond may not be involved in the rate-limiting step. Treatment of 2-methylquinoline *N*-oxide **1r** under standard reaction conditions could not deliver the sulfonylation product and the starting material 2-methylquinoline *N*-oxide was quantitatively recovered.

According to the mechanism research in previous literature[10] and the above experimental observation, a plausible reaction mechanism is proposed as shown in Scheme 4. First, in the presence of $K_2S_2O_8$, sodium arenesulfinate **2** was easily transformed into an oxygen-centered radical **A** resonating with the sulfonyl radical **B** *via* single electron transfer (SET).[9a,13] Subsequently, the radical **B** reacted with quinoline *N*-oxide **1** through a Minisci-like radical reaction to produce an intermediate **C**. Then, the intermediate **C** coupled with the oxygen-centered sulfate radical **B** to form intermediate **D**, which underwent an aromatization reaction to account for the formation of 2-sulfonylquinoline **3** with concomitant release of sulfonic acid.

Conclusions

In conclusion, we have reported the first example of a metal- and reductant-free deoxygenative sulfonylation of quinoline *N*-oxides with sodium sulfinates *via* a dual radical coupling process. Various functional groups in both quinoline *N*-oxides and arenesulfinates are accepted to afford a broad range of 2-sulfonylquinoline derivatives. In this reaction, sodium sulfinates play dual roles of an oxidant and activating agent. A possible mechanism is proposed on the basis of detailed mechanistic studies and suggests that *in situ* generation of sulfonyl radicals might be a key factor for obtaining deoxygenative sulfonated products. This procedure is expected to complement the current methods for Minisci-type radical-coupling reaction.

Experimental

General procedure for the synthesis of compound 3

In a pressure tube were consecutively placed quinoline *N*-oxides **1** (0.3 mmol), DCE (1.2 mL), sodium sulfinates **2** (0.6 mmol) and $K_2S_2O_8$ (0.6 mmol), and then the mixtures were heated to 100 °C. The progress of the reaction was monitored by TLC. The reaction typically took 8 h–12 h. Upon completion, the reaction was cooled to room temperature, and then water (5 mL) was added to the reaction mixture; it was extracted with CH_2Cl_2 (5 mL × 3) and the organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10 : 1–4 : 1) to obtain 2-sulfonylquinolines **3**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the financial support from the post-funded projects of Hunan University of Science and Engineering, the National Natural Science Foundation of China (No. 21273068 and 21545010), the Scientific Research Hunan Provincial Education Department (No. 17A081) and the 9th Science and Technology Innovation Program (2017) of China Hunan Provincial Science & Technology Department.

Notes and references

1 (*a*) A. Studer and P. Curran Dennis, *Angew. Chem., Int. Ed.*, 2015, **55**, 58; (*b*) M. Yan, J. C. Lo, J. T. Edwards and P. S. Baran, *J. Am. Chem. Soc.*, 2016, **138**, 12692; (*c*) M. Zhang, Q.-Y. Fu, G. Gao, H.-Y. He, Y. Zhang, Y.-S. Wu and Z.-H. Zhang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 6175; (*d*) T. Xiong and Q. Zhang, *Chem. Soc. Rev.*, 2016, **45**, 3069; (*e*) Y. Yang, J. Lan and J. You, *Chem. Rev.*, 2017, **117**, 8787; (*f*) H. Yi, G. Zhang, H. Wang, Z. Huang, J. Wang, A. K. Singh and A. Lei, *Chem. Rev.*, 2017, **117**, 9016.

2 (*a*) L. J. Sebren, J. J. Devery and C. R. J. Stephenson, *ACS Catal.*, 2014, **4**, 703; (*b*) W. Wei, C. Liu, D. Yang, J. Wen, J. You, Y. Suo and H. Wang, *Chem. Commun.*, 2013, **49**, 10239; (*c*) D. Liu, C. Liu, H. Lia and A. Lei, *Chem. Commun.*, 2014, **50**, 3623; (*d*) W. Wei, J. Wen, D. Yang, M. Wu, J. You and H. Wang, *Org. Biomol. Chem.*, 2014, **12**, 7678.

3 (*a*) J. Wu, X. Cui, L. Chen, G. Jiang and Y. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 13888; (*b*) H. Wang, X. Cui, Y. Pei, Q. Zhang, J. Bai, D. Wei and Y. Wu, *Chem. Commun.*, 2014, **50**, 14409; (*c*) O. V. Larionov, D. Stephens, A. Mfuh and G. Chavez, *Org. Lett.*, 2014, **16**, 864; (*d*) A. T. Londregan, K. Burford, E. L. Conn and K. D. Hesp, *Org. Lett.*, 2014, **16**, 3336; (*e*) D. Wang, H. Jia, W. Wang and Z. Wang, *Tetrahedron Lett.*, 2014, **55**, 7130; (*f*) X. Chen, X. Cui, F. Yang and Y. Wu, *Org. Lett.*, 2015, **17**, 1445; (*g*) L. Bering and A. P. Antonchick, *Org. Lett.*, 2015, **17**, 3134; (*h*) V. V. Pagar and R.-S. Liu, *Org. Biomol. Chem.*, 2015, **13**, 6166; (*i*) D. Wang, Y. Wang, J. Zhao, L. Li, L. Miao,

Published on 07 Ogos 2018. Downloaded on 17/10/2025 6:48:42 PG.

Published on 07 Ogos 2018. Downloaded on 17/10/2025 6:48:42 PG.

D. Wang, H. Sun and P. Yu, *Tetrahedron*, 2016, **72**, 5762; (*j*) A. Biswas, U. Karmakar, A. Pal and R. Samanta, *Chem. – Eur. J.*, 2016, **22**, 13826; (*k*) D. Wang, J. Zhao, Y. Wang, J. Hu, L. Li, L. Miao, H. Feng, L. Désaubry and P. Yu, *Asian J. Org. Chem.*, 2016, **5**, 1442; (*l*) R. Kumar, I. Kumar, R. Sharma and U. Sharma, *Org. Biomol. Chem.*, 2016, **14**, 2613; (*m*) G. E. M. Crisenza, E. M. Dauncey and J. F. Bower, *Org. Biomol. Chem.*, 2016, **14**, 5820; (*n*) Y. Lian, S. B. Coffey, Q. Li and A. T. Londregan, *Org. Lett.*, 2016, **18**, 1362; (*o*) H. Xia, Y. Liu, P. Zhao, S. Gou and J. Wang, *Org. Lett.*, 2016, **18**, 1796; (*p*) S. K. Aithagani, M. Kumar, M. Yadav, R. A. Vishwakarma and P. P. Singh, *J. Org. Chem.*, 2016, **81**, 5886; (*q*) L.-Y. Xie, Y. Duan, L.-H. Lu, Y.-J. Li, S. Peng, C. Wu, K.-J. Liu, Z. Wang and W.-M. He, *ACS Sustainable Chem. Eng.*, 2017, **5**, 10407; (*r*) Z. Zhang, C. Pi, H. Tong, X. Cui and Y. Wu, *Org. Lett.*, 2017, **19**, 440; (*s*) D. Wang, Y. Wang, J. Zhao, M. Shen, J. Hu, Z. Liu, L. Li, F. Xue and P. Yu, *Org. Lett.*, 2017, **19**, 984; (*t*) X. Yu, S. Yang, Y. Zhang, M. Guo, Y. Yamamoto and M. Bao, *Org. Lett.*, 2017, **19**, 6088; (*u*) W.-Z. Bi, K. Sun, C. Qu, X.-L. Chen, L.-B. Qu, S.-H. Zhu, X. Li, H.-T. Wu, L.-K. Duan and Y.-F. Zhao, *Org. Chem. Front.*, 2017, **4**, 1595; (*v*) Y.-P. Han, X.-S. Li, X.-Y. Zhu, M. Li, L. Zhou, X.-R. Song and Y.-M. Liang, *J. Org. Chem.*, 2017, **82**, 1697; (*w*) D. Zhang, K. Qiao, J. Hua, Z. Liu, H. Qi, Z. Yang, N. Zhu, Z. Fang and K. Guo, *Org. Chem. Front.*, 2018, **5**, 2340.

4 (*a*) J. Jeong, P. Patel, H. Hwang and S. Chang, *Org. Lett.*, 2014, **16**, 4598; (*b*) U. Sharma, Y. Park and S. Chang, *J. Org. Chem.*, 2014, **79**, 9899; (*c*) H. Hwang, J. Kim, J. Jeong and S. Chang, *J. Am. Chem. Soc.*, 2014, **136**, 10770; (*d*) D. E. Stephens, J. Lakey-Beitia, G. Chavez, C. Ilie, H. D. Arman and O. V. Larionov, *Chem. Commun.*, 2015, **51**, 9507; (*e*) D. E. Stephens, J. Lakey-Beitia, A. C. Atesin, T. A. Ateşin, G. Chavez, H. D. Arman and O. V. Larionov, *ACS Catal.*, 2015, **5**, 167; (*f*) D. Gwon, H. Hwang, H. K. Kim, S. R. Marder and S. Chang, *Chem. – Eur. J.*, 2015, **21**, 17200; (*g*) X. Chen, X. Cui and Y. Wu, *Org. Lett.*, 2016, **18**, 2411; (*h*) X. Chen, X. Cui and Y. Wu, *Org. Lett.*, 2016, **18**, 3722; (*i*) D. Kalsi, R. A. Laskar, N. Barsu, J. R. Premkumar and B. Sundararaju, *Org. Lett.*, 2016, **18**, 4198.

5 (*a*) G. Li, C. Jia and K. Sun, *Org. Lett.*, 2013, **15**, 5198; (*b*) C. Zhu, M. Yi, D. Wei, X. Chen, Y. Wu and X. Cui, *Org. Lett.*, 2014, **16**, 1840; (*c*) W. Sun, M. Wang, Y. Zhang and L. Wang, *Org. Lett.*, 2015, **17**, 426; (*d*) G. Li, C. Jia, K. Sun, Y. Lv, F. Zhao, K. Zhou and H. Wu, *Org. Biomol. Chem.*, 2015, **13**, 3207; (*e*) M. Li, X. Li, H. Chang, W. Gao and W. Wei, *Org. Biomol. Chem.*, 2016, **14**, 2421; (*f*) A. K. Jha and N. Jain, *Chem. Commun.*, 2016, **52**, 1831; (*g*) H. Yu, C. A. Dannenberg, Z. Li and C. Bolm, *Chem.– Asian J.*, 2016, **11**, 54; (*h*) R. Kumar, R. Kumar, A. K. Dhiman and U. Sharma, *Asian J. Org. Chem.*, 2017, **6**, 1043.

6 (*a*) Z. Wu, C. Pi, X. Cui, J. Bai and Y. Wu, *Adv. Synth. Catal.*, 2013, **355**, 1971; (*b*) X. Chen, C. Zhu, X. Cui and Y. Wu, *Chem. Commun.*, 2013, **49**, 6900; (*c*) W. Sun, Z. Xie, J. Liu and L. Wang, *Org. Biomol. Chem.*, 2015, **13**, 4596; (*d*) P. Li, J. Zhao, C. Xia and F. Li, *Org. Chem. Front.*, 2015, **2**, 1313; (*e*) G. Li, S. Yang, B. Lv, Q. Han, X. Ma, K. Sun, Z. Wang, F. Zhao, Y. Lv and H. Wu, *Org. Biomol. Chem.*, 2015, **13**, 11184; (*f*) J. Zhao, P. Li, C. Xia and F. Li, *RSC Adv.*, 2015, **5**, 32835; (*g*) L. Fan, T. Wang, Y. Tian, F. Xiong, S. Wu, Q. Liang and J. Zhao, *Chem. Commun.*, 2016, **52**, 5375; (*h*) J.-W. Yuan, S.-N. Liu and L.-B. Qu, *Tetrahedron*, 2017, **73**, 2267; (*i*) W.-M. Zhang, J.-J. Dai, J. Xu and H.-J. Xu, *J. Org. Chem.*, 2017, **82**, 2059; (*j*) J.-W. Yuan, W.-J. Li and Y.-M. Xiao, *Tetrahedron*, 2017, **73**, 179.

7 (*a*) Z. Wu, H. Song, X. Cui, C. Pi, W. Du and Y. Wu, *Org. Lett.*, 2013, **15**, 1270; (*b*) K. Sun, X.-L. Chen, X. Li, L.-B. Qu, W.-Z. Bi, X. Chen, H.-L. Ma, S.-T. Zhang, B.-W. Han, Y.-F. Zhao and C.-J. Li, *Chem. Commun.*, 2015, **51**, 12111; (*c*) Y. Su, X. Zhou, C. He, W. Zhang, X. Ling and X. Xiao, *J. Org. Chem.*, 2016, **81**, 4981; (*d*) R. Wang, Z. Zeng, C. Chen, N. Yi, J. Jiang, Z. Cao, W. Deng and J. Xiang, *Org. Biomol. Chem.*, 2016, **14**, 5317; (*e*) W.-K. Fu, K. Sun, C. Qu, X.-L. Chen, L.-B. Qu, W.-Z. Bi and Y.-F. Zhao, *Asian J. Org. Chem.*, 2017, **6**, 492; (*f*) L. Sumunnee, C. Buathongjan, C. Pimpasri and S. Yotphan, *Eur. J. Org. Chem.*, 2017, **2017**, 1025; (*g*) L.-Y. Xie, Y.-J. Li, J. Qu, Y. Duan, J. Hu, K.-J. Liu, Z. Cao and W.-M. He, *Green Chem.*, 2017, **19**, 5642.

8 (*a*) J. A. Bull, J. J. Mousseau, G. Pelletier and A. B. Charette, *Chem. Rev.*, 2012, **112**, 2642; (*b*) G. Yan, A. J. Borah and M. Yang, *Adv. Synth. Catal.*, 2014, **356**, 2375; (*c*) Y. Wang and L. Zhang, *Synthesis*, 2015, 289.

9 Selected examples of radical sulfonylation reaction: (*a*) D. Xia, Y. Li, T. Miao, P. Li and L. Wang, *Chem. Commun.*, 2016, **52**, 11559; (*b*) R. Fu, W.-J. Hao, Y.-N. Wu, N.-N. Wang, S.-J. Tu, G. Li and B. Jiang, *Org. Chem. Front.*, 2016, **3**, 1452; (*c*) Y.-L. Zhu, B. Jiang, W.-J. Hao, A.-F. Wang, J.-K. Qiu, P. Wei, D.-C. Wang, G. Li and S.-J. Tu, *Chem. Commun.*, 2016, **52**, 1907; (*d*) Y.-y. Jiang, Q.-Q. Wang, S. Liang, L.-M. Hu, R. D. Little and C.-C. Zeng, *J. Org. Chem.*, 2016, **81**, 4713; (*e*) W. Wei, H. Cui, D. Yang, X. Liu, C. He, S. Dai and H. Wang, *Org. Chem. Front.*, 2017, **4**, 26; (*f*) B. Wang, L. Tang, L. Liu, Y. Li, Y. Yang and Z. Wang, *Green Chem.*, 2017, **19**, 5794; (*g*) W. Wei, H. Cui, D. Yang, H. Yue, C. He, Y. Zhang and H. Wang, *Green Chem.*, 2017, **19**, 5608; (*h*) J.-P. Wan, S. Zhong, Y. Guo and L. Wei, *Eur. J. Org. Chem.*, 2017, 4401; (*i*) L. Wang, H. Yue, D. Yang, H. Cui, M. Zhu, J. Wang, W. Wei and H. Wang, *J. Org. Chem.*, 2017, **82**, 6857; (*j*) X. Wan, K. Sun and G. Zhang, *Sci. China: Chem.*, 2017, **60**, 353; (*k*) J. Xu, X. Yu, J. Yan and Q. Song, *Org. Lett.*, 2017, **19**, 6292; (*l*) J. Yan, J. Xu, Y. Zhou, J. Chen and Q. Song, *Org. Chem. Front.*, 2018, **5**, 1483; (*m*) Z. Peng, X. Zheng, Y. Zhang, D. An and W. Dong, *Green Chem.*, 2018, **20**, 1760.

10 B. Du, P. Qian, Y. Wang, H. Mei, J. Han and Y. Pan, *Org. Lett.*, 2016, **18**, 4144.

11 (*a*) Y. Pan, G.-W. Chen, C.-H. Shen, W. He and L.-W. Ye, *Org. Chem. Front.*, 2016, **3**, 491; (*b*) C. Wu, Z. Wang, Z. Hu, F. Zeng, X.-Y. Zhang, Z. Cao, Z. Tang, W.-M. He and X.-H. Xu, *Org. Biomol. Chem.*, 2018, **16**, 3177; (*c*) C. Wu, J. Wang, X.-Y. Zhang, G.-K. Jia, Z. Cao, Z. Tang, X. Yu, X. Xu and W.-M. He, *Org. Biomol. Chem.*, 2018, **16**, 5050;

 This journal is © the Partner Organisations 2018

(*d*) J.-X. Tan, Y. Guo, F. Zeng, G.-R. Chen, L.-Y. Xie and W.-M. He, *Chin. J. Org. Chem.*, 2018, **38**, 1740; (*e*) Z. Wang, L. Yang, H.-L. Liu, W.-H. Bao, Y.-Z. Tan, M. Wang, Z. Tang and W.-M. He, *Chin. J. Org. Chem.*, 2018, DOI: 10.6023/cjoc201805033; (*f*) K.-J. Liu, Y.-L. Fu, L.-Y. Xie, C. Wu, W.-B. He, S. Peng, Z. Wang, W.-H. Bao, Z. Cao, X. Xu and W.-M. He, *ACS Sustainable Chem. Eng.*, 2018, **6**, 4916; (*g*) W. Li, G. Yin, L. Huang, Y. Xiao, Z. Fu, X. Xin, F. Liu, Z. Li and W. He, *Green Chem.*, 2016, **18**, 4879; (*h*) C. Wu, X. Xin, Z.-M. Fu, L.-Y. Xie, K.-J. Liu, Z. Wang, W. Li, Z.-H. Yuan and W.-M. He, *Green Chem.*, 2017, **19**, 1983; (*i*) L.-Y. Xie, J. Qu, S. Peng, K.-J. Liu, Z. Wang, M.-H. Ding, Y. Wang, Z. Cao and W.-M. He, *Green Chem.*, 2018, **20**, 760; (*j*) K.-J. Liu, S. Jiang, L.-H. Lu, L.-L. Tang, S.-S. Tang, H.-S. Tang, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, **20**, 3038; (*k*) C. Wu, L.-H. Lu, A.-Z. Peng, G.-K. Jia, C. Peng, Z. Cao, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, DOI: 10.1039/C8GC00491A.

12 G. R. Buettner, *Free Radical Biol. Med.*, 1987, **3**, 259.

13 (*a*) D. Xia, T. Miao, P. Li and L. Wang, *Chem. – Asian J.*, 2015, **10**, 1919; (*b*) W. Wei, J. Wen, D. Yang, J. Du, J. You and H. Wang, *Green Chem.*, 2014, **16**, 2988.

Published on 07 Ogos 2018. Downloaded on 17/10/2025 6:48:42 PG.