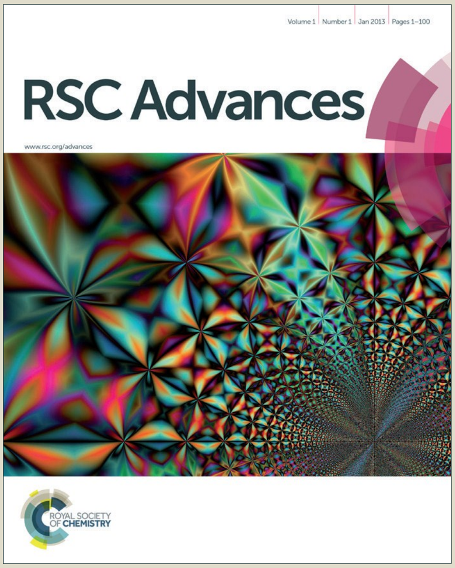
RSC Advances

This article can be cited before page numbers have been issued, to do this please use: G. Nie, X. Deng, X. Lei, Q. Hu and Y. Chen, *RSC Adv.*, 2016, DOI: 10.1039/C6RA17842A.



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

View Article Online
DOI: 10.1039/C6RA17842A

Journal Name

COMMUNICATION

Mn(III)-Mediated Regioselective Synthesis of (E)-Vinyl Sulfones from Sodium Sulfinates and Nitro-olefins

Received 00th January 20xx,
Accepted 00th January 20xx

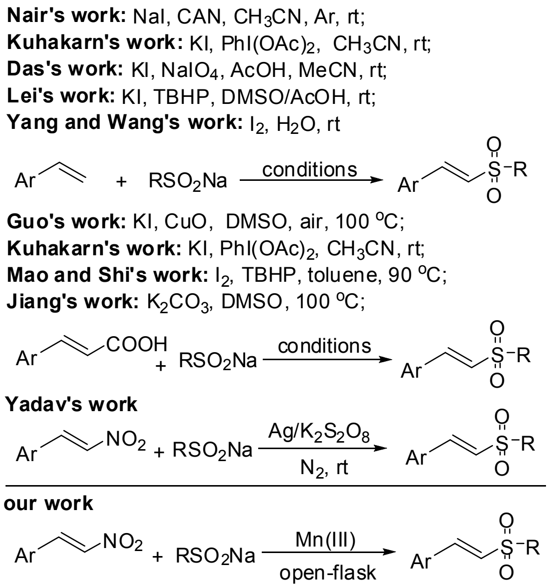
DOI: 10.1039/x0xx00000x

www.rsc.org/

Gang Nie, Xiaocong Deng, Xue Lei, Qinquan Hu, and Yunfeng Chen*

An efficient Mn(III)-mediated coupling reaction of sodium sulfinates with nitro-olefins has been developed, this reaction proceeds in a mild and open-flask condition to afford (E)-vinyl sulfones with high regioselectivities and in good to excellent yields. The control experiments revealed that this transformation could involve a radical process.

Vinyl sulfones are important structural synthons in the synthetic organic chemistry, which are good Michael acceptors and also easy to participate in cycloaddition reactions.[1] Nowadays, its derivatives have also shown a widely biological and pharmacological activities.[2] So far, many conventional approaches for the synthesis of vinyl sulfones have been established, including the oxidation of the corresponding sulfides,[3] β-elimination of selenosulfones and halosulfones,[4] and addition of sulfonyl chloride to alkynes/alkenes.[5] In recent years, sodium sulfinate and sulfonyl hydrazine have been utilized to react with different partners for synthesis of vinyl sulfones, probably due to their good stability and ease of handling.[6] The direct addition of sodium sulfinates to terminal aromatic alkynes[7] and propiolic acid[8] in the presence of Cu or Pd catalysts could give vinyl sulfones with high yields and regioselectivities. At the same time, alkenes are also good reaction partners to produce vinyl sulfones via oxidative coupling reactions with sodium sulfinates (**Scheme 1**).[9] For instance, Nair's group reported one-pot synthesis of vinyl sulfones via CAN-mediated reaction of aryl sulfinates and alkenes.[9a] Lately, KI/PhI(OAc)$_2$[9b], KI/NaIO$_4$[9c], KI/TBHP[9d] together with stoichiometric I$_2$[9e] and other methods[9k-m] have also been developed by different groups. The cinnamic acids can undergo decarboxylation in many reaction systems.[10] Guo's group designed a copper-catalyzed aerobic oxidative decarboxylative sulfonylation reaction to synthesize vinyl sulfones by using cinnamic acids and sodium sulfinates as the starting materials.[10c] Interestingly, Jiang and co-workers revealed a transition metal-free base-promoted variant, which made this transformation greener.[10d] Nitro-olefins are relatively stable, simple to be obtained by Henry reaction from aldehyde and nitromethane, which have been widely used to synthesize useful organic molecules. In some cases, the nitro-olefins are equivalent to alkyne synthon by the elimination of HNO$_2$ or an oxidative dehydrogenation process. For example, nitro-olefins are good partners for the synthesis of *NH*-1,2,3-triazoles and NO$_2$-substituted 1,2,3-triazoles.[11]



Scheme 1. Synthesis of vinyl sulfones from sodium sulfinates and alkenes.

In fact, Yadav's group reported a silver-catalyzed coupling reaction of nitro-olefins and sodium sulfinates in the presence of oxidant and under nitrogen atmosphere.[12] Encouraged by this work, we wanted to develop other methods, especially cheaper metal salts and simpler operation to make this transformation more applicable. Herein, we reported an efficient synthesis of (E)-vinyl sulfones by Mn(III)-mediated coupling reaction of nitro-olefins with sodium sulfinates under air.

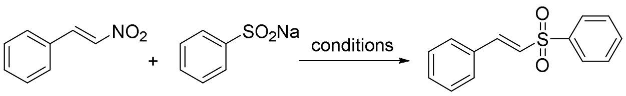
---

*School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430073, People's Republic of China E-mail: yfchen@wit.edu.cn

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6RA17842A

Table 1. Optimization of the Reaction Conditions [a]



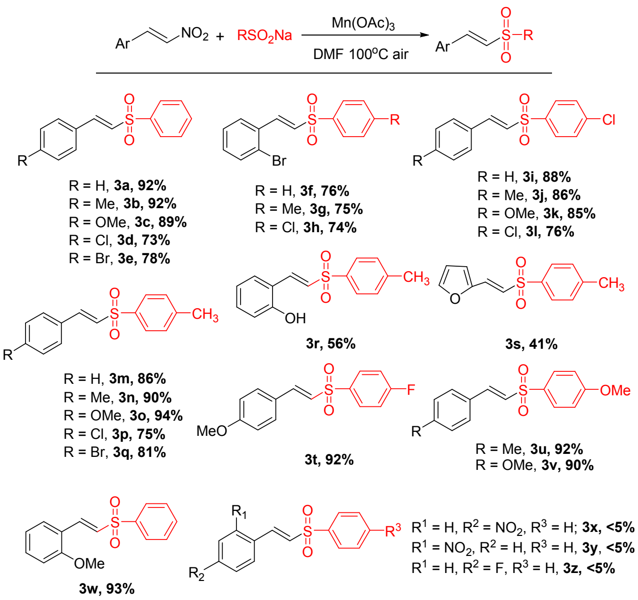
1a 2a 3a

Entry	Oxidant	Oxidant(equiv)	Solvent	Temp(°C)	Yield[c](%)
1	I_2	2.5	DMF	rt	trace
2	KI/TBHP	0.2/2.5	DMF	rt	trace
3	TBHP	2.5	DMF	rt	16
4	DTBP	2.5	DMF	rt	19
5	$K_2S_2O_8$	2.5	DMF	rt	14
6	$Fe(NO_3)_3$	2.5	DMF	rt	17
7	$FeCl_3$	2.5	DMF	rt	13
8	$CuSO_4$	2.5	DMF	rt	trace
9	$Mn(OAc)_3$	2.5	DMF	rt	38
10	$AgNO_3$	2.5	DMF	rt	nd[b]
11	$AgNO_3$/ $K_2S_2O_8$	0.2/2.5	DMF	rt	nd
12	$Mn(OAc)_3$	3	DMF	rt	46
13	$Mn(OAc)_3$	3	DMF	40	59
14	$Mn(OAc)_3$	3	DMF	60	65
15	$Mn(OAc)_3$	3	DMF	80	77
16	$Mn(OAc)_3$	3	DMF	100	92
17	$Mn(OAc)_3$	0.2	DMF	100	33
18	$Mn(OAc)_3$	2	DMF	100	84
19	$Mn(OAc)_3/K_2S_2O_8$	0.2/3	DMF	100	56
20	$Mn(OAc)_3$	3	toluene	100	nd
21	$Mn(OAc)_3$	3	AcOH	100	47
22	$Mn(OAc)_3$	3	EtOH	100	14
23	$Mn(OAc)_3$	3	DMSO	100	45
24	$Mn(OAc)_3$	3	H_2O	100	37
25[d]	$Mn(OAc)_3$	3	DMF	100	90

[a] Reaction conditions: nitro-benzeneolefin (**1a**) (0.3 mmol), sodium benzenesulfinate (**2a**) (2 equiv, 0.6 mmol), solvent (5 mL), 8 h, air. [b] nd, not detected, [c] Isolated yield, [d] Argon atmosphere.

Our studies began by examining the reaction between nitro-olefin (**1a**) and sodium benzenesulfinate (**2a**) in the presence of a stoichiomertic I_2 in DMF at room temperature under air (**Table 1, entry 1**), the corresponding product **3a** was not observed at all, and KI/TBHP system gave the same result too (**entry 2**). However, TBHP, DTBP and $K_2S_2O_8$ could promote this reaction despite low yields (**entries 3-5**). Then, other metal salts oxidants such as $Fe(NO_3)_3$, $FeCl_3$, $Mn(OAc)_3$, and $CuSO_4$ were tested, $Mn(OAc)_3$ showed superior reactivity towards this coupling reaction and the yield of **3a** increased to 38% (**entries 6-9**). By contrast with Yadav's protocol, $AgNO_3$ was also introduced into this reaction, but the product **3a** was not observed at all, $AgNO_3/K_2S_2O_8$ system also gave the same result (**entries 10 and 11**), which revealed that the silver salt system could not work in this case. To further improve the yield of **3a**, different reaction temperatures were set, the yield of the expected product **3a** increased to 92% when the reaction temperature reached up to 100 °C (**entries 12-16**). Attempts to reduce the amount of $Mn(OAc)_3$ failed, and $Mn(OAc)_3/K_2S_2O_8$ system gave inferior result (**entries 17-19**). Meanwhile, various solvents were examined, which indicated that the reaction performed in DMF was significantly better than those in toluene, AcOH, EtOH, DMSO or H_2O (**entries 20-24**). Under argon atmosphere, the yield of **3a** was similar to the open flask condition **(entry 25)**.

Table 2. Substrate Scope for the Synthesis of Various Vinyl Sulfones[a]



[a] Reaction conditions: nitroolefins (0.3 mmol), sodium sulfinates (0.6 mmol, 2 equiv), $Mn(OAc)_3$ (0. 9 mmol, 3 equiv), DMF (5mL), 100°C, air. [b] Isolated yield.

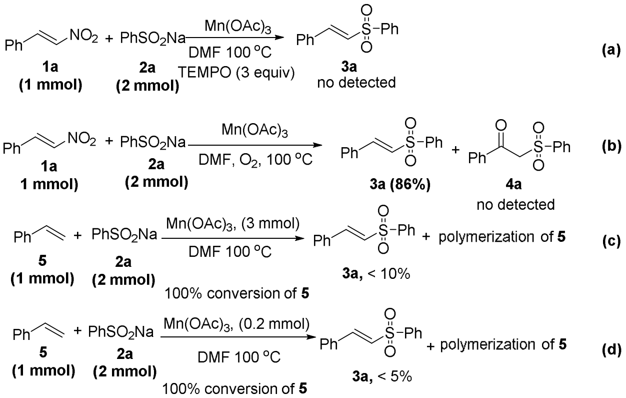
With the optimized protocol in hand, we further examined the scope and limitation of this coupling reaction between different nitro-olefins and sodium sulfinates, and the results are summarized in **Table 2**. Nitro-olefins with electron-donating functional group such as OMe, Me have higher yield than those with electron-drawing group such as Cl, Br. For instance, Nitro-olefins with electron-donating functional group gave the corresponding product in 86-93% yields (**3a-c, 3i-k, 3m-o, 3u-3v, 3w**). Instead, Nitro-olefins with electron-drawing group gave 73-81% yields of the products **(3d-e, 3h, 3l, 3p-q)**. It is noteworthy that sodium sulfinates with electron-donating groups and withdrawing groups have no significant influence on the transformation (**3v, 3t**). Furthermore, acid-sensitive furanyl-substituted nitro-olefin was also suitable substrate to react with sodium sulfinate, the furanyl-substituted vinyl sulfone (**3s**) was obtained in 41% isolated yield. Unfortunately, nitro-olefins with NO_2 group couldn't give the corresponding products **(3x-z)**.[13]

To gain insights into mechanism of the reaction, nitro-olefin (**1a**) and sodium benzenesulfinate (**2a**) reacted in the presence

View Article Online
DOI: 10.1039/C6RA17842A

of 2,2,6,6-tetramethylpiperidinooxy (**TEMPO, 3eq**) which is a radical scavenger under standard condition (**Scheme 2**). However, **3a** was no detected, which implied that this reaction could involve a radical process. Under oxygen atmosphere, the reaction only gave the desired product **3a**, while assumed oxidative product **4a** was not detected, which showed that Mn(III) could not promote a metal-catalyzed oxidization process.[14]

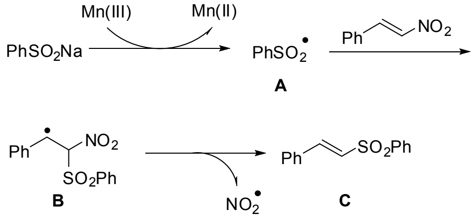
Scheme 2. Control Experiments



Furthermore, in order to reveal the role of the nitro group in this reaction, we reconsidered the reaction between styrene and sodium sulfinates, most of which need I_2 or I^-/oxidants, and Lei disclosed that I_2 system involve a HI elimination similar to the β-hydride elimination of transition metals process to achieve alkenylation for the formation of vinyl sulfones.[9h] Then the reactions between styrene and sodium sulfinates in the presence of $Mn(OAc)_3$ were investigated. Under our standard condition, the reaction between styrene (**5**) and sodium sulfinates in the presence of three equivalent or catalytic amount of $Mn(OAc)_3$ induce the 100% conversion of styrene, however, the desired vinyl sulfone **3a** was detected in less than 10% yield, most of styrene was polymerized. This result showed that Mn(III) could not react with the carbon radical, the successively β-hydride elimination process didn't exist. By contrast, a potential elimination of nitro radical should be involved during the coupling of nitro-olefins with sodium sulfinates.

On the basis of the results described above and previous literature reports,[12, 15] a plausible mechanism was proposed in **Scheme 3**. Firstly, a radical **A** was initially formed through the oxidation of sodium sulfinate by Mn(III) under heating. Next, intermediate **B** was generated through the trans-addition of **A** to the nitro-olefin. Then, intermediate **B** eliminated a nitro radical to give product **C**. The nitro radical may be quenched by other radical species or $Mn(OAc)_3$, that's the reason why too much excess amount of $Mn(OAc)_3$ was needed.

Scheme 3. A plausible mechanism



In summary, we have developed an efficient Mn(III)-mediated synthesis of (E)-vinyl sulfones through coupling reactions of sodium sulfinates with nitro-olefins. The synthetic method presented many advantages such as cheap metal, simple operation, easily available substrate, and good yields, which is promising for practical applications in relevant industry and manufacture in the future.

We are grateful to the National Natural Science Foundation of China (21002076), the Scientific Research Foundation for the Returned Overseas Chinese Scholars for financial support. We also thank NO.CX2015151, supported by Graduate Innovative Fund of Wuhan Institute of Technology.

Notes and references

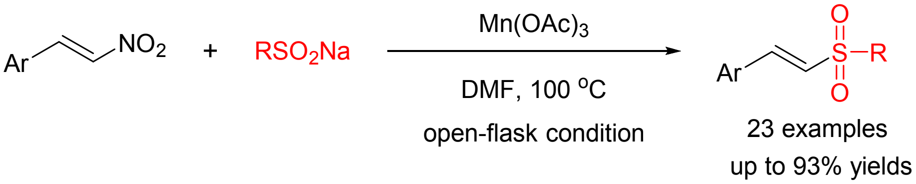
1. (a) A. K. Musser, P. L. Fuchs, *J. Org. Chem*. 1982, **47**, 3121; (b) R. V. C. Carr, R. V. Williams, L. A. Paquette, *J. Org. Chem*. 1983, **48**, 4976; (c) W. A. Kinney, G. D. Crouse, L. A. Paquette, *J. Org. Chem*. 1983, **48**, 4986; (d) T. Llamas, R. G. Arrayas, J. C. Carretero, *Org. Lett.* 2006, **8**, 1795; (e) G. Liang, M. C Tong, C. J. Wang, *Adv Synth Catal.* 2009, **351**, 3101; (f) S. Dey, D. Datta, T. Pathak, *Synlett*. 2011, 2521; (g) D. Sahu, S. Dey, T. Pathak, B. Ganguly, *Org. Lett.* 2014, **16**, 2100; (h) J. R. Bull, K. Bischofberger, *J. Chem. Soc., Perkin Trans. 1* 1991, 2859; (i) T. Llamas, R. G. Arrayas, J. C. Carretero, *Synthesis-Stuttgart.* 2007, 950; (j) J. K. Laha, *Chem Nat Compd*. 2010, **46**, 254; (k) J. Yang, W. Yin, R. Liu, C. Chu, *Chin. J. Chem.* 2012, **30**, 2786; (l) M. I. Pleshchev, V. V. Kachala, A. S. Goloveshkin, I. S. Bushmarinov, V. V. Kuznetsov, D. V. Khakimov, N. N. Makhova, *Mendeleev Commun*. 2013, **23**, 271; (m) V. A. Vasin, V. V. Razin, E. V. Bezrukova, D. Y. Korovin, P. S. Petrov, N. V. Somov, *Russ. J. Org. Chem.* 2015, **51**, 1144.
2. (a) S. Liu, R. P. Hanzlik, *J. Med. Chem*. 1992, **35**, 1067; (b) J. T. Palmer, D. Rasnick, J. L. Klaus, D. Brömme, *J. Med. Chem.* 1995, **38**, 3193; (c) W. R. Roush, S. L. Gwaltney II, J. Cheng, K. A. Scheidt, J. H. McKerrow, E. Hansell, *J. Am. Chem. Soc.* 1998, **120**, 10994; (d) J. J. Reddick, J. Cheng, W. R. Roush, *Org. Lett.* 2003, **5**, 1967; (e) G. Wang, U. Mahesh, G. Y. J. Chen, S. Yao, *Org. Lett*. 2003, **5**, 737; (f) B. R. Shenai, B. J. Lee, A. Alvarez-Hernandez, P. Y. Chong, C. D. Emal, R. J. Neitz, W. R. Roush, P. J. Rosenthal, *Antimicrob. Agents Chemother*. 2003, **47**, 154; (g) B. A. Frankel, M. Bentley, R. G. Kruger, D. G. McCafferty, *J. Am. Chem. Soc.* 2004, **126**, 3404; (h) D. C. Meadows, T. Sanchez, N. Neamati, T. W. North, J. Gervay-Hague, *Bioorg. Med. Chem*. 2007, **15**, 1127; (i) M. Uttamchandani, K. Liu, R. C. Panicker, S. Yao, *Chem. Commun.* 2007, 1518; (j) K. Steert, I. El-Sayed, P. Vander Veken, A. Krishtal, C. Van Alsenoy, G. D. Westrop, J.

View Article Online
DOI: 10.1039/C6RA17842A

C. Mottram, G. H. Coombs, K. Augustyns, A. Haemers, *Bioorg. Med. Chem. Lett.* 2007, **17**, 6563; (k) R. Ettari, E. Nizi, M. E. D. Francesco, M.-A. Dude, G. Pradel, R. Vičík, T. Schirmeister, N. Micale, S. Grasso, M. Zappalà, *J. Med. Chem.* 2008, **51**, 988; (l) S. Y. Woo, J. H. Kim, M. K. Moon, S.-H. Han, S. K. Yeon, J. W. Choi, B. K. Jang, H. J. Song, Y. G. Kang, J. W. Kim, J. Lee, D. J. Kim, O. Hwang, K. D. Park, *J. Med. Chem.* 2014, **57**, 1473.

3. (a) A. A. Lindén, L. Krüger, J. Bäckvall, *J. Org. Chem*. 2003, **68**, 5890; (b) F. G. Gelalcha, B. Schulze, *J. Org. Chem*. 2002, **67**, 8400; (c) M. Matteucci, G. Bhalay M. Bradley, *Org. Lett.* 2003, **5**, 235.
4. (a) J. Sinnreich, M. Asscher*, J. Chem. Soc. Perkin Trans. 1* 1972, 1543; (b) P. B. Hopkins, P. L. Fuchs, *J. Org. Chem*. 1978, **43**, 1208; (c) R. V. C. Carr, R. V. Williams, L. A. Paquette, *J. Org. Chem*. 1983, **48**, 4976. (d) F. E. K. Kroll, R. Morphy, D. Rees, D. Gani, *Tetrahedron Lett*. 1997, **38**, 8573.
5. (a) L. M. Harwood, M. Julia, G. Le Thuillier, *Tetrahedron.* 1980, **36**, 2483; (b) S. Zhu, C. Qin, G. Xu, Q. Chu, *Tetrahedron Lett*. 1998, **39**, 5265; (c) T. G. Back, S. Collins, *J. Org. Chem*. 1981, **46**, 3249; (d) V. Nair, A. Augustine, S. B. Panicker, T. D. Suja, S. Mathai, *Res. Chem. Intermed*. 2003, **29**, 213; (e) H. Qian, X. Huang, *Synlett.* 2001, 1913.
6. (a) X. Li, X. Xu, C. Zhou, *Chem. Commun*. 2012, **48**, 12240; (b) X. Q. Li, X. Shi, M. Fang, X. Xu, *J. Org. Chem*. 2013, **78**, 9499; (c) X. Li, Y. Xu, W. Wu, C. Jiang, C. Qi, H. Jiang, *Chem. Eur. J.* 2014, **20**, 7911; (d) G. Rong, J. Mao, H. Yan, Y. Zheng, G. Zhang, *J. Org. Chem*. 2015, **80**, 4697; (e) S. Li, X. Li, F. Yang, Y. Wu, *Org. Chem. Fron*. 2015, **2**, 1076.
7. (a) G. M. Shelke, V. K. Rao, K. Pericherla, A. Kumar, *Synlett*. 2014, **25**, 2345; (b) Y. Xu, J. Zhao, X. Tang, W. Wu, H. Jiang, *Adv Synth Catal*. 2014, **356**, 2029; (c) N. Taniguchi, *Synlett.* 2012, **23**, 1245; (d) N. Taniguchi, *Tetrahedron*. 2014, **70**, 1984; (e) W. Wei, J. Li, D. Yang, J. Wen, Y. Jiao, J. You, H. Wang, *Org. Biomol. Chem.* 2014, **12**, 1861; (f) Q. Xue, Z. Mao, Y. Shi, H. Mao, Y. Cheng, C. Zhu, *Tetrahedron Lett*. 2012, **53**, 1851; (g) J. L. G. Ruano, J. Alemán, C. G. Paredes, *Org. Lett*. 2006, **8**, 2683
8. (a) G. Rong, J. Mao, H. Yan, Y. Zheng, G. Zhang, *J. Org. Chem*. 2015, **80**, 7652; (b) J. Meesin, P. Katrun, V. Reutrakul, M. Pohmakotr, D. Soorukram, C. Kuhakarn, *Tetrahedron*. 2016, **72**, 1440.
9. (a) V. Nair, A. Augustine, T. G. George, L. G. Nair, *Tetrahedron. Lett.* 2001, **42**, 6763; (b) P. Katrun, S. Chiampanichayakul, K. Korworapan, M. Pohmakotr, V. Reutrakul, T. Jaipetch, C. Kuhakarn, *Eur. J. Org. Chem.* 2010, 5633; (c) N. Kamigata, H. Sawada, M. Kobayashi, *J. Org. Chem.* 1983, **48**, 3793; d) N. Taniguchi, *Synlett.* 2011, 1308; (e) V. Nair, A. Augustine, T. D. Suja, *Synthesis.* 2002, 2259; (f) B. Das, M. Lingaiah, K. Damodar, N. Bhunia, *Synthesis.* 2011, 2941; (g) T. Sawangphon, P. Katrun, K. Chaisiwamongkhol, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram, C. Kuhakarn, *Synth. Commun*. 2013, **43**, 1692; (h) S. Tang, Y. Wu, W. Liao, R. Bai, C. Liu, A. Lei, *Chem. Commun*. 2014, **50**, 4496; (i) N. Zhang, D. Yang, W. Wei, L. Yuan, Y. Cao, H. Wang, *RSC. Adv.* 2015, **5**, 37013; (j) Y.-C. Luo, X.-J. Pan, G.-Q. Yuan, Tetrahedron. 2015, **71**, 2119; (k) Q. Xue, Z. Mao, Y. Shi, H. Mao, Y. Cheng, C. Zhu, *Tetrahedron. Lett.* 2012, **53**, 1851; (l) R. Chawla, R. Kapoor, A. K. Singh, L. D. S. Yadav, *Green Chem*. 2012, **14**, 1308; (m) S. Liang, R.-Y. Zhang, G. Wang, S.-Y. Chen, X.-Q. Yu, *Eur. J. Org. Chem*. 2013, 7050.
10. (a) R. Guo, Q. Gui, D. Wang, Z. Tan, *Catal. Lett*. 2014, **144**, 1377; (b) B. V. Rokade, K. R. Prabhu, *J. Org. Chem.* 2014, **79**, 8110; (c) Q. Jiang, B. Xu, A. Zhao, Y. Zhao, Y. Li, N. He, C. Guo, *J. Org. Chem*. 2014, **79**, 7372; (d) Y. Xu, X. Tang, W. Hu, W. Wu, H. Jiang, *Green Chem*. 2014, **16**, 3720; (e) P. Katrun, S. Hlekhlai, J. Meesin, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram, C. Kuhakarn, *Org. Biomol. Chem.* 2015, **13**, 4785; (f) H. Li, G. Liu, *J. Org. Chem*. 2014, **79**, 509; (g) J. Chen, J. Mao, Y. Zheng, D. Liu, G. Rong, H. Yan, C. Zhang, D. Shi, *Tetrahedron.* 2015, **71**, 5059; (h) J. Gao, J. Lai, G. Yuan, *RSC. Adv*. 2015, **5**, 66723.
11. For selected examples, see: (a) S. Sengupta, H. Duan, W. Lu, J. L. Petersen, X. Shi, *Org. Lett*. 2008, **10**, 1493; (b) B. Quiclet-Sire, S. Z. Zard, *Synthesis*, 2005, 3319; (c) X.-J. Quan, Z.-H. Ren, Y.-Y. Wang, Z.-H. Guan, *Org. Lett*. 2014, **16**, 5728; (d) Y. Chen, G. Nie, Q. Zhang, S. Ma, H. Li, Q. Hu, *Org. Lett.* 2015, **17**, 1118; (e) Q. Hu, Y. Liu, X. Deng, Y. Li , Y. Chen, *Adv. Synth. Catal.* 2016, **358**, 1689.
12. T. Keshari, R. Kapoorr, L. D. S. Yadav, *Eur. J. Org. Chem.* 2016, 2695.
13. For some examples, see: (a) H. Tian, A. Cao, L. Qiao, A. Yu , J. Chang, Y. Wu, *Tetrahedron.* 2014, **70,** 9107; (b) W. Zhang, J. Xie, B. Rao, M. Luo, *J. Org. Chem*. 2015, **80**, 3504; (c) F. Zhao, B. Li, H. Huang ,G.-J. Deng, *RSC. Adv.* 2016, **6**, 13010.
14. (a) Q. Lu, J. Zhang, G. Zhao, Y. Qi , H. Wang, A. Lei, *J. Am. Chem. Soc.* 2013, **135**, 11481; (b) W. Wei, C. Liu, D. Yang, J. Wen, J. You, Y. Suo, H. Wang, *Chem. Comm.* 2013, **49**, 10239; (c) R. Chawla, A. K. Singh, L. D. S. Yadav, *Eur. J. Org. Chem.* 2014, 2032; (d) A. K. Singh, R. Chawla, L. D. S. Yadav, *Tetrahedron. Lett.* 2014, **55**, 4742; (e) W Wei, J. Wen, D. Yang, M. Wu, J You, H. Wang, *Org. Biomol. Chem.* 2014, **12**, 7678; (f) B. Sreedhar V. Rawat, *Synlett*, 2012, 413, (g) A. K. Singh, R. Chawla, L. D. S. Yadav, *Tetrahedron. Letters.* 2014, **55**, 2845; (h) N. Samakkanad, P. Katrun, T. Techajaroonjit, S. Hlekhlai, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram, C. Kuhakarn, *Synthesis*. 2012, **44,** 1693.
15. For some Mn(III)-assisted radical reactions, see: (a) X.-J. Mu, J.-P. Zou, Q.-F. Qian, W. Zhang, *Org. Lett.* 2006, **8**, 5291; (b) W. Xu, J.-P. Zou, W. Zhang, *Tetrahedron. Lett.* 2010, **51**, 2639; (c) J.-F. Xue, S.-F. Zhou, Y.-Y. Liu, X. Pan, J.-P. Zou, O. T. Asekun, *Org. Biomol. Chem*. 2015, **13**, 4896; (d) L. Li, J.-J. Wang, G.-W. Wang, *J. Org. Chem*. 2016, **81**, 5433; (e) T. Kagayama, A. Nakano, S. Sakaguchi, Y. Ishii, *Org. Lett*. 2006, **8**, 407.

View Article Online
DOI: 10.1039/C6RA17842A



A new efficient Mn(III)-mediated coupling reaction of sodium sulfinates with nitro-olefins is described.