Advanced Synthesis & Catalysis

Accepted Article

Title: Nickel-Catalyzed Sulfonylation of C(sp2)–H Bonds with Sodium Sulfinates

Authors: Shuang-Liang Liu, Xue-Hong Li, Shu-Sheng Zhang, Sheng-Kai Hou, Guang-Chao Yang, and Jun-Fang Gong

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201700290

Link to VoR: http://dx.doi.org/10.1002/adsc.201700290

10.1002/adsc.201700290

COMMUNICATION

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

Nickel-Catalyzed Sulfonylation of C(sp^2)–H Bonds with Sodium Sulfinates

Shuang-Liang Liu,[a] Xue-Hong Li,[a] Shu-Sheng Zhang,[a] Sheng-Kai Hou,[a] Guang-Chao Yang,[a] Jun-Fang Gong,[a,*] and Mao-Ping Song [a,*]

[a] College of Chemistry and Molecular Engineering, Henan Key laboratory of Chemical Biology and Organic Chemistry, Zhengzhou University, Zhengzhou 450001, P. R. China
E-mail: mpsong@zzu.edu.cn or gongjf@zzu.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. The first Ni-catalyzed *ortho*-sulfonylation of C(sp^2)–H bonds with sodium sulfinates directed by (pyridin-2-yl)isopropylamine (PIP-amine) is described. This strategy exhibits a broad substrate scope and good functional group tolerance with high monosulfonylation selectivity. Besides arenes and heteroarenes, the reaction can also be extended to alkenes, providing diverse diaryl and alkyl-aryl sulfones in high yields. Furthermore, a plausible Ni(I)/Ni(III) mechanism is outlined based on our experimental results and related precedents.

Keywords: sulfonylation; C–H activation; nickel; sodium sulfinates; (pyridin-2-yl)isopropylamine (PIP-amine)

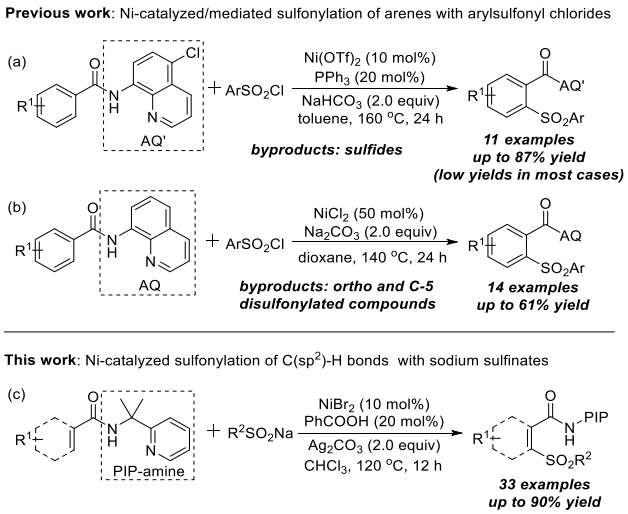
The sulfone moiety is one of the common structural units in organic molecules and widely found in pharmaceutical compounds and functional materials.[1] Sulfones also play important roles in synthetic chemistry such as in the classical Ramberg–Backlund reaction[2] and Julia olefination.[3] Consequently, the synthesis of sulfones has been extensively explored.[4] Traditional approaches mainly include oxidation of sulfides or sulfoxides, sulfonylation of arenes in the presence of strong acids, addition of sulfonyl radical precursors to alkenes and alkynes, or cross-coupling reaction of sulfinates with prefunctionalized coupling partners such as halides, triflates, aryl boronic acids, and diaryliodonium salts.[4a] However, these methods generally face problems of multi-step prefunctionalization, poor regioselectivity and functional group compatibility.

In recent years, transition metal catalyzed C-H activation has emerged as a simple and efficient tool in organic synthesis.[5] During which, nickel has exhibited its priority in terms of abundance, low-cost and good catalytic performance.[6,7] Especially, since the first report of Ni-catalyzed 2-pyridinylmethyl-amine-assisted transformation of *ortho* C-H bonds by Chatani and coworkers,[7a] this type of chelation assisted C-H functionalizations has emerged as a hotspot in chemical research.[7b-f]

In 2009, Dong and coworkers reported the first example of direct C(sp^2)-H bond sulfonylation with arylsulfonyl chlorides promoted by pyridine under Pd catalysis.[8] Since then, extensive efforts have been devoted to the selective sulfonylation of C–H bonds with sulfonyl chlorides or sulfinate salts catalyzed or mediated by various transition metals including Pd,[8,9] Rh,[10] Cu[11] and Ru.[12] Despite the impressive progress, particularly the use of inexpensive Cu salt as the catalyst,[11a,b,d,f-j] C-H sulfonylation catalyzed or mediated by the same inexpensive nickel remains much less explored. To the best of our knowledge, there are only two reports on this subject up to now.[13] Furthermore, the achieved results were quite unsatisfying with regard to the substrate scope, selectivity, and reaction efficiency. As for the two reports, one is disclosed by Chatani in 2015 which concerned Ni-catalyzed *ortho*-sulfonylation of C–H bonds in aromatic amides with arylsulfonyl chlorides employing 5-chloro-8-aminoquinoline as the directing group (Scheme 1a).[13a] The utilization of 5-chloro-8-aminoquinoline instead of 8-aminoquinoline successfully avoided the formation of the C-5 sulfonylated quinolines. However, the narrow substrate scope and low reactivity (11 examples, 21-46% yields except the α-naphthalyl substrate), the formation of sulfides byproducts (up to 10%) due to the use of PPh_3 in the catalytic system as well as high reaction temperature (160 °C) limited the application of this method. The other is reported by Kambe and coworkers almost simultaneously which described a similar sulfonylation in the presence of 50 mol% of Ni with the assistance of 8-aminoquinoline at 140 °C (Scheme 1b).[13b] Unfortunately, this methodology also gave unsatisfying results: the desired *ortho*-sulfonylated products were obtained in only 33-61% yields (14 examples), always along with the *ortho*- and C-5 disulfonylated byproducts (<2%). Therefore, the development of highly regioselective and efficient nickel protocols would still be highly desirable. To this

10.1002/adsc.201700290

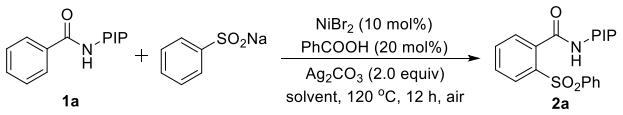
end and also as a continuation of our interest in cheap metal-catalyzed bidentate directing group-assisted C-H functionalization reactions,[14] herein we disclose the first nickel-catalyzed *ortho*-sulfonylation of C(sp^2)–H bonds with the non-toxic and stable sodium sulfinates accelerated by the 2-(pyridine-2-yl)isopropylamine (PIP-amine) (Scheme 1c). The PIP-amine has been developed by Shi and demonstrated as a powerful directing group for diverse C-H functionalizations.[15] Compared with the above two methods based on Ni catalyst,[13] it is noteworthy that our method exhibits good functional group tolerance and high regioselectivity, providing a milder approach to diverse diaryl and alkyl-aryl sulfones in modest to excellent yields (33 examples, up to 90% yields).



Scheme 1. Ni-Catalyzed/Mediated Direct Sulfonylation of C(sp^2)−H Bonds.

We commenced our investigation by choosing the reaction of benzamide derivative **1a** with $PhSO_2Na$ as a model. First, nickel catalysts were extensively screened (see Table S1 in the Supporting Information for details). It was found that $NiBr_2$ could afford a better yield and the desired monosulfonylated product **2a** was obtained in 35% yield under 10 mol% of $NiBr_2$ and 2.0 equiv of Ag_2CO_3 in 1,2-dichloroethane (DCE) at 120 °C for 12 h under air (Table 1, entry 1). The effect of oxidants was then examined (Table S2 in the Supporting Information). Notably, the use of Ag_2CO_3 as an oxidant was crucial for this transformation: without oxidant or other oxidants such as AgOAc, AgTFA, Ag_2O, O_2, $PhI(OAc)_2$, $K_2S_2O_8$, BQ, $Mn(OAc)_3{\cdot}2H_2O$, and NMO, led to obviously low reactivity. To our delight, the addition of 20 mol% PhCOOH significantly improved the yield to 73% (entry 2). Encouraged by this, various carboxylate ligands were tested but unfortunately, no improvement was observed. Other ligands, such as BINOL, BINAP, $(BnO)_2POOH$, Xphos, PCy_3, and 2,2'-dipyridyl, were less effective or totally ineffective (Table S3 in the Supporting Information). Finally, a thorough screening of solvents (entries 3-

Table 1. Optimization of the Reaction Conditions[a]



1a 2a

Entry	Solvent	Yield (%)
1	DCE	35[b]
2	DCE	73
3	MTBE	28
4	DME	trace
5	THF	24
6	toluene	trace
7	CH_3CN	24
8	1,4-dioxane	12
9[c]	**$CHCl_3$**	**80**
10	*n*-BuOH	0
11	DMAc	trace
12	DMSO	0
13	DMF	0

[a] Reaction conditions: **1a** (0.2 mmol), $PhSO_2Na$ (0.4 mmol), $NiBr_2$ (10 mol%), PhCOOH (20 mol%) and Ag_2CO_3 (0.4 mmol) in solvent (1.0 mL) at 120 °C for 12 h under air. Isolated yields.

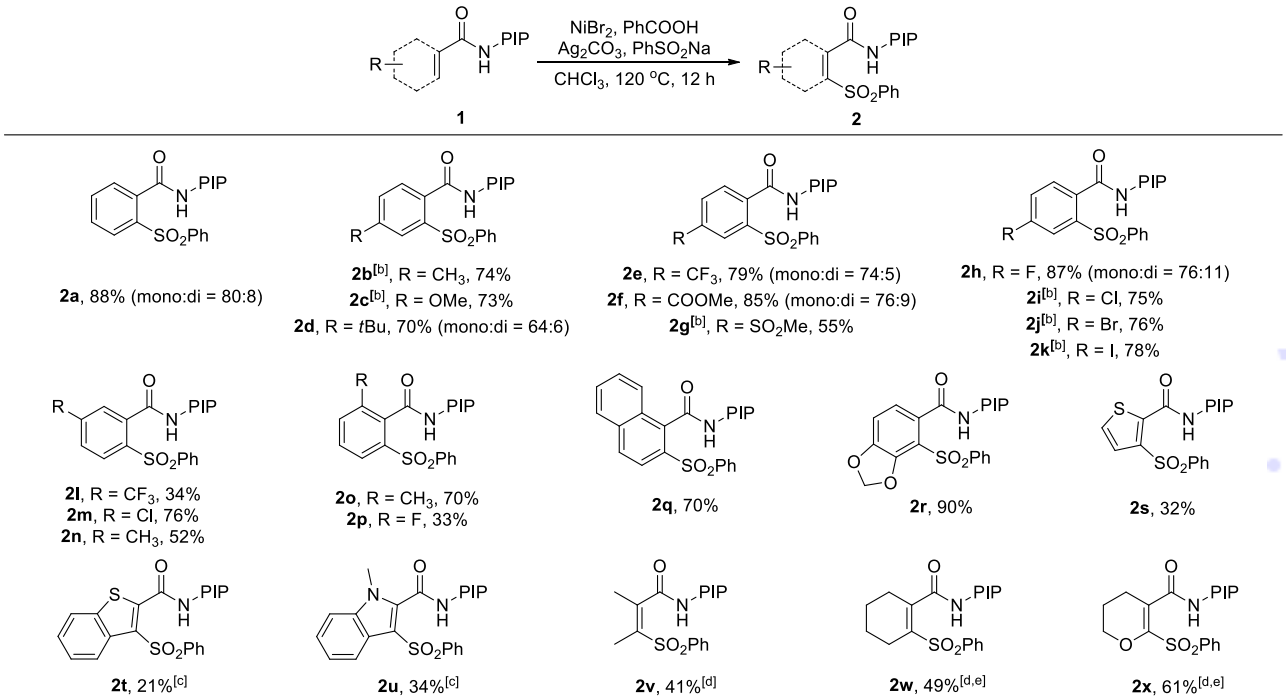
[b] Without PhCOOH.

[c] With 8% disulfonylated product **2a'**.

13) revealed that $CHCl_3$ provided **2a** in a maximum yield of 80%, along with 8% of the disulfonylated product **2a'** (entry 9).

With the optimized conditions in hand, we proceeded to investigate the scope of amides (Table 2). Generally, both electron-rich (R = Me, OMe and *t*-Bu) and electron-poor (R = CF_3, COOMe and SO_2Me) substituents in the *para*-position of benzamides were well tolerated, giving the corresponding products **2b-g** in moderate to high yields (55-85%). Reactions of benzamides bearing halides including fluoride, chloride, bromide and iodide on the *para*-position of the benzene ring with $PhSO_2Na$ went quite well (**2h-k**, 75-87%), thus making further functionalization possible. When *meta*-substituted benzamides were reacted with $PhSO_2Na$, sulfonylation occurred at the less sterically hindered position, affording the monosulfonylated products **2l-n** exclusively (34-76%). In the case of *ortho*-substituted substrates including a 1-naphth-amide, the desired products were obtained in 33-70% yields (**2o-q**). Interestingly, piperonylic acid amide participated in this transformation with much high efficiency, producing the 2-sulfonylated benzamide **2r** as the sole product (90%). This was presumably due to the potential coordination property of the dioxole, which may stabilize the arylnickel interme- diates during the catalytic process. Heteroaromatic amides such as thiophene and indole derivatives were also feasible, albeit with lower yields (**2s-u**, 21-34%). To our delight, the amide scope could be extended to alkene substrates to produce the alkyl-aryl sulfones, although higher temperature and catalyst loading

Table 2. Scope of Amides[a]

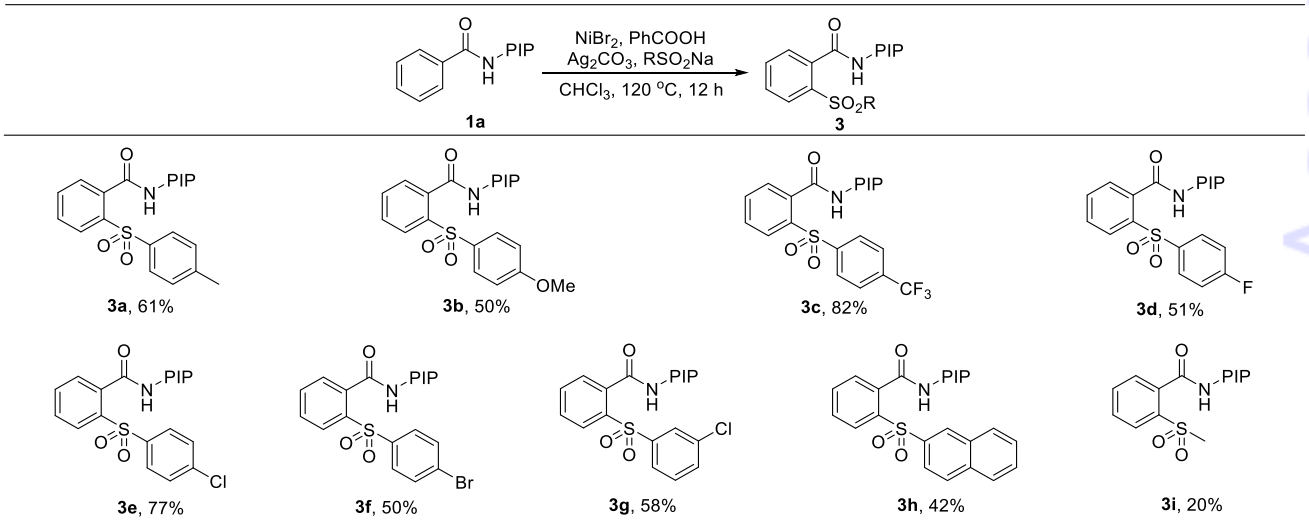


[a] Reaction conditions: **1** (0.2 mmol), $PhSO_2Na$ (0.4 mmol), $NiBr_2$ (10 mol%), PhCOOH (20 mol%) and Ag_2CO_3 (0.4 mmol) in $CHCl_3$ (1.0 mL) at 120 °C for 12 h under air. Isolated yields.
[b] To these examples, disulfonylated products were trace or not detected.
[c] $NiBr_2$ (20 mol%), PhCOOH (40 mol%).
[d] $NiBr_2$ (30 mol%), PhCOOH (60 mol%).
[e] 140 °C.

were required to achieve satisfactory conversion rates (**2v-x**, 41-61%).

The results for sulfonylation of benzamide **1a** with various sodium sulfinates were summarized in Table 3. It was found that arylsulfinates bearing both electron-donating and -withdrawing group could react smoothly with **1a** to afford the corresponding 2-arylsulfonyl benzamides in moderate to good yields (**3a-g**, 50-82%). Halides (F, Cl and Br) were well tolerated in the reactions (**3d-g**), which could be used for further elaboration. In addition, coupling of 2-naphthylsulfinic acid sodium salt proceeded well,

Table 3. Scope of Sodium Sulfinates[a]

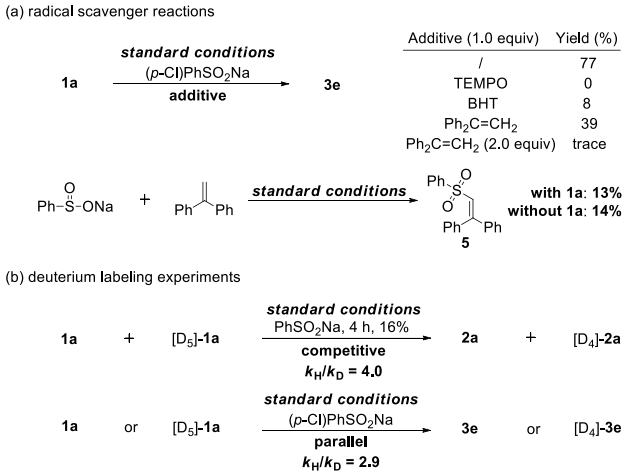


[a] Reaction conditions: **1a** (0.2 mmol), RSO_2Na (0.4 mmol), $NiBr_2$ (10 mol%), PhCOOH (20 mol%) and Ag_2CO_3 (0.4 mmol) in $CHCl_3$ (1.0 mL) at 120 °C for 12 h under air. Isolated yields. Disulfonylated products were not detected.

furnishing the desired product **3h** in 42% yield. Finally, we were pleased to find that aliphatic sodium sulfinate such as sodium methanesulfinate was also reactive to give the desired alkyl-aryl sulfone product **3i**, albeit in only 20% yield (see Table S5 in the Supporting Information for additional results on this reaction). The outcome was probably due to the low reactivity of sodium methanesulfinate or the thermal instability of the methylsulfonyl radical under the stated reaction conditions.[11d,13b,16]

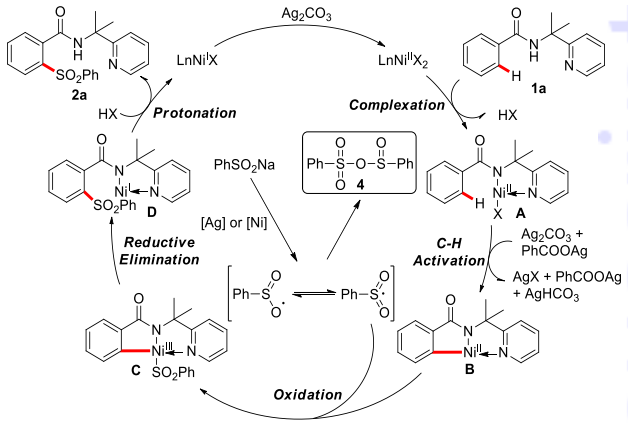
Finally, the PIP directing group can be removed efficiently via the known three-step sequence,[11d] affording the corresponding sulfonylated carboxylic acids.

To shed light on the plausible reaction mechanism, various control experiments were performed (Scheme 2). Firstly, we noted that benzenesulfinic benzenesulfonic anhydride **4** was formed in the reaction of amide **1a** and $PhSO_2Na$, which could also be observed in the absence of either Ag_2CO_3 or $NiBr_2$ under standard conditions (see the Supporting Information). In addition, the reaction of **1a** and (*p*-Cl)$PhSO_2Na$ was completely inhibited when TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was added. The addition of BHT (2,6-di-*tert*-butyl-4-methyl-phenol) and 1,1-diphenylethylene also decreased the yield significantly (Scheme 2a). More importantly, a sulfonyl radical was trapped by 1,1-diphenylethylene in the presence or absence of amide **1a** (Scheme 2a). The results suggested the probable involvement of radicals in the reaction. Furthermore, kinetic isotope effect (KIE) experiments were conducted (Scheme 2b). The reaction of **1a** and [D_5]-**1a** with $PhSO_2Na$ gave a significant KIE of 4.0. Likewise, the KIE value of two parallel reactions was calculated to be 2.9. These results indicated that C-H cleavage of benzamide was involved in the rate-determining step.



Scheme 2. Control Experiments.

On the basis of the observations above and literature precedents,[7c-e,17] especially the related work of Chatani and Ge,[7c-e] a plausible Ni(I)/Ni(III) mechanism was proposed in Scheme 3. First complexation of benzamide **1a** with a Ni^{II} species affords the Ni^{II} intermediate **A**. Next C–H bond activation occurs to form the Ar-Ni^{II} intermediate **B**.[17a] Simultaneously, the single-electron oxidation of sodium sulfinate leads to the formation of sulfonyl radical,[17b,c] which reacts with **B** to generate the Ni^{III} complex **C**.[17d,e] Subsequent C−SO_2Ph reductive elimination of **C** leads to the formation of the Ni^{I} species **D**. The sulfonylated product **2a** can be obtained after protonation of **D**. Finally, the generated Ni^{I} species is re-oxidized into the Ni^{II} species by Ag_2CO_3 to complete the catalytic cycle. However, at the current stage, the Ni(II)/Ni(IV) pathway could not be excluded.



Scheme 3. Proposed Mechanism.

In summary, we have developed a Ni-catalyzed auxiliary-assisted sulfonylation of C(sp^2)–H bonds with sodium sulfinates to afford various diaryl and alkyl-aryl sulfones in modest to excellent yields. This strategy has the advantages of using inexpensive Ni as the catalyst and safe, air and moisture stable sodium sulfinates as the sulfonylating agent, high regioselectivity as well as broad substrate scope. What's more, based on our experimental results and related precedents, a plausible mechanism for the current sulfonylation is proposed.

Experimental Section

Typical Procedure

To a 35 mL pressure Schlenk tube were added **1a** (48.1 mg, 0.2 mmol), $NiBr_2$ (4.4 mg, 0.02 mmol), PhCOOH (4.9 mg, 0.04 mmol), $PhSO_2Na$ (65.7 mg, 0.4 mmol), Ag_2CO_3 (110.3 mg, 0.4 mmol) and $CHCl_3$ (1.0 mL). The reaction was stirred at 120 °C for 12 hours under air. Then the mixture was cooled to room temperature, diluted with EtOAc and filtered through a pad of celite, which was washed with EtOAc. Evaporation of the organic solvent and purified by preparative TLC on silica gel plates using petroleum ether/EtOAc = 3:1 as the eluent to give the desired product **2a** as a white foam (60.9 mg) in 80% yield.

Acknowledgements

Financial support from the National Natural Science Foundation of China (Nos. 21672192 and 21472176) is gratefully acknowledged.

References

[1] a) S. Patai, Z. Rappoport, C. J. M. Stirling, *The Chemistry of Sulfones and Sulfoxides*, Wiley, New York, **1988**; b) Q. A. Acton, *Sulfones-Advances in Research and Application*, ScholarlyEditions, Atlanta, **2013**.

[2] a) L. Ramberg, B. Bäcklund, *Ark. Chim., Mineral Geol.* **1940**, *27*, 1-50; b) S. C. Söderman, A. L. Schwan, *J. Org. Chem*. **2012**, *77*, 10978-10984.

[3] M. Julia, J.-M. Paris, *Tetrahedron Lett*. **1973**, *14*, 4833-4836.

[4] For recent reviews, see: a) N.-W. Liu, S. Liang, G. Manolikakes, *Synthesis* **2016**, *48*, 1939-1973; b) S. Shaaban, S. Liang, N.-W. Liu, G. Manolikakes, *Org. Biomol. Chem*. **2017**, *15*, 1947-1955. For recent examples, see: c) X.-S. Wu, Y. Chen, M.-B. Li, M.-G. Zhou, S.-K. Tian, *J. Am. Chem. Soc*. **2012**, *134*, 14694-14697; d) Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu, A. Lei, *Angew. Chem.* **2013**, *125*, 7297-7300; *Angew. Chem. Int. Ed*. **2013**, *52*, 7156-7159; e) X. Tang, L. Huang, Y. Xu, J. Yang, W. Wu, H. Jiang, *Angew. Chem.* **2014**, *126*, 4289-4292; *Angew. Chem. Int. Ed*. **2014**, *53*, 4205-4208; f) Y. Xi, B. Dong, E. J. McClain, Q. Wang, T. L. Gregg, N. G. Akhmedov, J. L. Petersen, X. Shi, *Angew. Chem.* **2014**, *126*, 4745-4749; *Angew. Chem. Int. Ed*. **2014**, *53*, 4657-4661.

[5] Selected reviews: a) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196-5217; *Angew. Chem. Int. Ed*. **2009**, *48*, 5094-5115; b) T. W. Lyons, M. S. Sanford, *Chem. Rev*. **2010**, *110*, 1147-1169; c) X.-X. Guo, D.-W. Gu, Z. Wu, W. Zhang, *Chem. Rev*. **2015**, *115*, 1622-1651; d) C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. Andy Hor, X. Liu, *Chem. Soc. Rev*. **2015**, *44*, 291-314.

[6] Selected recent reviews: a) G. Rouquet, N. Chatani, *Angew. Chem.* **2013**, *125*, 11942-11959; *Angew. Chem. Int. Ed*. **2013**, *52*, 11726-11743; b) S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature*, **2014**, *509*, 299-309; c) L. C. Misal Castro, N. Chatani, *Chem. Lett*. **2015**, *44*, 410-421; d) B.-B. Zhan, B. Liu, F. Hu, B.-F. Shi, *Chin. Sci. Bull.* **2015**, *60*, 2907-2917.

[7] Selected examples: a) H. Shiota, Y. Ano, Y. Aihara, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc*. **2011**, *133*, 14952-14955; b) K. Muto, J. Yamaguchi, K. Itami, *J. Am. Chem. Soc*. **2012**, *134*, 169-172; c) Y. Aihara, N. Chatani, *J. Am. Chem. Soc*. **2013**, *135*, 5308-5311; d) Y. Aihara, N. Chatani, *J. Am. Chem. Soc*. **2014**, *136*, 898-901; e) X. Wu, Y. Zhao, H. Ge, *J. Am. Chem. Soc*. **2014**, *136*, 1789-1792; f) W. Song, S. Lackner, L. Ackermann, *Angew. Chem.* **2014**, *126*, 2510-2513; *Angew. Chem. Int. Ed*. **2014**, *53*, 2477-2480.

[8] X. Zhao, E. Dimitrijević, V. M. Dong, *J. Am. Chem. Soc*. **2009**, *131*, 3466-3467. For review on the synthesis of sulfones via C-H functionalization, see ref. 4b.

[9] a) Y.-H. Xu, M. Wang, P. Lu, T.-P. Loh, *Tetrahedron* **2013**, *69*, 4403-4407; b) B. Ge, D. Wang, W. Dong, P. Ma, Y. Li, Y. Ding, *Tetrahedron Lett*. **2014**, *55*, 5443-5446; c) Y. Xu, P. Liu, S.-L. Li, P. Sun, *J. Org. Chem*. **2015**, *80*, 1269-1274; d) D. Zhang, X. Cui, Q. Zhang, Y. Wu, *J. Org. Chem*. **2015**, *80*, 1517-1522; e) W.-H. Rao, B.-B. Zhan, K. Chen, P.-X. Ling, Z.-Z. Zhang, B.-F. Shi, *Org. Lett*. **2015**, *17*, 3552-3555.

[10] F. Wang, X. Yu, Z. Qi, X. Li, *Chem. Eur. J*. **2016**, *22*, 511-516.

[11] Selected examples: a) Z. Wu, H. Song, X. Cui, C. Pi, W. Du, Y. Wu, *Org. Lett*. **2013**, *15*, 1270-1273; b) H.-W. Liang, K. Jiang, W. Ding, Y. Yuan, L. Shuai, Y.-C. Chen, Y. Wei, *Chem. Commun*. **2015**, *51*, 16928-16931; c) J. Liu, L. Yu, S. Zhuang, Q. Gui, X. Chen, W. Wang, Z. Tan, *Chem. Commun*. **2015**, *51*, 6418-6421; d) W.-H. Rao, B.-F. Shi, *Org. Lett*. **2015**, *17*, 2784-2787; e) S. Liang, N.-W. Liu, G. Manolikakes, *Adv. Synth. Catal*. **2016**, *358*, 159-163; f) S. Liang, G. Manolikakes, *Adv. Synth. Catal*. **2016**, *358*, 2371-2378; g) Y. Yang, W. Li, C. Xia, B. Ying, C. Shen, P. Zhang, *ChemCatChem* **2016**, *8*, 304-307; h) J. Wei, J. Jiang, X. Xiao, D. Lin, Y. Deng, Z. Ke, H. Jiang, W. Zeng, *J. Org. Chem*. **2016**, *81*, 946-955; i) B. Du, P. Qian, Y. Wang, H. Mei, J. Han, Y. Pan, *Org. Lett*. **2016**, *18*, 4144-4147; j) S. Liang, M. Bolte, G. Manolikakes, *Chem. Eur. J*. **2017**, *23*, 96-100.

[12] O. Saidi, J. Marafie, A. E. W. Ledger, P. M. Liu, M. F. Mahon, G. Kociok-Köhn, M. K. Whittlesey, C. G. Frost, *J. Am. Chem. Soc*. **2011**, *133*, 19298-19301.

[13] a) A. Yokota, N. Chatani, *Chem. Lett*. **2015**, *44*, 902-904; b) V. P. Reddy, R. Qiu, T. Iwasaki, N. Kambe, *Org. Biomol. Chem*. **2015**, *13*, 6803-6813.

[14] Selected recent publications: a) L.-B. Zhang, X.-Q. Hao, S.-K. Zhang, Z.-J. Liu, X.-X. Zheng, J.-F. Gong, J.-L. Niu, M.-P. Song, *Angew. Chem.* **2015**, *127*, 274-277; *Angew. Chem. Int. Ed*. **2015**, *54*, 272-275; b) X.-X. Zheng, C. Du, X.-M. Zhao, X. Zhu, J.-F. Suo, X.-Q. Hao, J.-L. Niu, M.-P. Song, *J. Org. Chem.* **2016**, *81*, 4002-4011; c) S.-L. Liu, X.-H. Li, T.-H. Shi, G.-C. Yang, H.-L. Wang, J.-F. Gong, M.-P. Song, *Eur. J. Org. Chem*. DOI: 10.1002/ejoc.201700147.

[15] Selected examples: a) Q. Zhang, K. Chen, W. Rao, Y. Zhang, F.-J. Chen, B.-F. Shi, *Angew. Chem.* **2013**, *125*, 13833-13837; *Angew. Chem. Int. Ed*. **2013**, *52*, 13588-13592; b) F.-J. Chen, S. Zhao, F. Hu, K. Chen, Q. Zhang, S.-Q. Zhang, B.-F. Shi, *Chem. Sci*. **2013**, *4*, 4187-4192; c) Y.-H. Liu, Y.-J. Liu, S.-Y. Yan, B.-F. Shi, *Chem. Commun.* **2015**, *51*, 11650-11653; d) Y.-J. Liu, Y.-H. Liu, X.-S. Yin, W.-J. Gu, B.-F. Shi, *Chem. Eur. J*. **2015**, *21*, 205-209.

[16] H. H. Thoi, M. Iino, M. Matsuda, *Macromolecules* **1979**, *12*, 338-339.

[17] a) K. Yang, Y. Wang, X. Chen, A. A. Kadi, H.-K. Fun, H. Sun, Y. Zhang, H. Lu, *Chem. Commun.*, **2015**, *51*, 3582-3585; b) H.-S. Li, G. Liu, *J. Org. Chem.* **2014**, *79*, 509-516; c) N. Taniguchi, *J. Org. Chem.* **2015**, *80*, 7797-7802; d) S. Biswas, D. J. Weix, *J. Am. Chem. Soc*. **2013**, *135*, 16192-16197; e) J. Breitenfeld, J. Ruiz, M. D. Wodrich, X. Hu, *J. Am. Chem. Soc*. **2013**, *135*, 12004-12012.

10.1002/adsc.201700290

COMMUNICATION

Nickel-Catalyzed Sulfonylation of C(sp^2)–H Bonds with Sodium Sulfinates

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

Shuang-Liang Liu,[a] Xue-Hong Li,[a] Shu-Sheng Zhang,[a] Sheng-Kai Hou,[a] Guang-Chao Yang,[a] Jun-Fang Gong,[a,*] and Mao-Ping Song [a,*]