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ARTICLE

TBAI-catalyzed selective synthesis of sulfonamides and β-aryl sulfonyl Enamines: coupling of arenesulfonyl chlorides and sodium sulfinates with tert-amines

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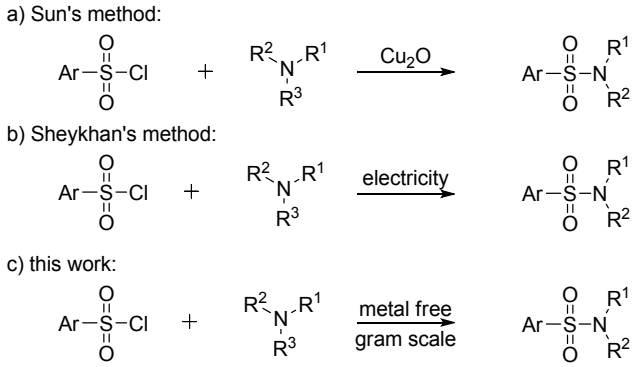
A simple, practical and metal-free method has been developed for synthesis of sulfonamides and β-arylsulfonyl enamines via a selective cleavage of C-N and C-H bonds through an iodine-catalyzed oxidation of arenesulfonyl chlorides and sodium sulfinates with *tert*- amines. The method uses commercially available, inexpensive catalysts and oxidants, actually has a wide substrate scope and operational simplicity.

Introduction

The C-N bond is one of the most abundant chemical bonds and widely exists in the natural products, which is also found in the many pharmaceuticals, dyes and functional molecules. A mild and convenient approach to formation and transformation of C-N bond is among a hot topic in organic chemistry.[1] Transformation of C-N bond is generally hard, due to the high C-N bond dissociation energy as well as the stability of unactivated *N*-containing compounds.[2] Over the past few decades, transition-metal catalysis processes have been proved a powerful tool for this transformation.[3] However, it is worth pointing out that the use of transition metals has some inherent drawbacks, including cost and toxicity. Transition metal-free catalysis for the cleavage of C-N bond, on the other hand, has been rarely discovered. Only a few such catalysis methods have been reported, and stoichiometric bond breaking agents are usually required.[4] Therefore, development of a new and efficient transition metal-free method to induce cleavage of C-N bond under mild conditions is still a challenge.

Sulfonamides and arylsulfonyl enamines occur widely in biologically active compounds and pharmaceutical interesting molecules, due to their well-known biological activities such as anticancer, antibacterial, anti-inflammatory, antitumor and HIV protease inhibitory activities.[5] In addition, sulfonamides are a type of amine protecting group, owing to their easy removability.[6] Consequently, various methods have been developed for the synthesis of sulfonamindes. Traditionally, sulfonamides are prepared through the nucleophilic attack of a primary or secondary amines to sulfonyl chlorides in the presence of additional base.[7] Subsequently, transition metal catalysis processes were developed, including cross-coupling of primary sulfonamides and aryl halide or boronic acids,[8] a Chan-Lam type coupling using sulfonyl azides with boronic acids,[9] and an oxidative coupling reaction of sulfinate salts with amines.[10] Recently, Sun et al. has developed an elegant work for Cu_2O-catalyzed oxidative synthesis of sulfonamides by coupling of commercial available arenesulfonyl chlorides with tertiary amines (**Scheme 1**, **a**).[11] Although these methods are available and can be used to easily build the S-N bond,[12] the reactions produce a large quantity of toxic waste, and need a long reaction time and transition metal usage. Therefore, an alternative and facile catalytic method is needed to synthesize sulfonamides efficiently.



Scheme 1. Methods for the synthesis of sulphonamides

During the past few years, molecular iodine and its salts have emerged as efficient catalysts in synthetic chemistry.[13] As a non-metallic element, iodine has diverse valence states as well as moderate redox potentials, which make it easy to gain or lose electrons like transition metal. In addition, iodine is cheap, readily available, water tolerable and eco-friendly element. As a result, iodine-mediated or iodine-catalyzed coupling reactions have been widely developed. Recently, various green and efficient methods for

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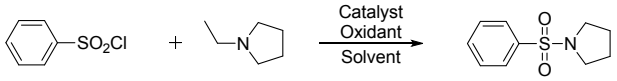
synthesis of sulfonamides using sulfinates or sulfonyl hydrazides to react with amines have been built up via I_2-mediated approach.[14] However, most of them suffer from the lack of commercially available starting materials and the poor functional group tolerability (primary and secondary amines).[15] Moreover, high reactivity of primary or secondary amines may be destructive for some amine-sensitive functional groups. In 2017, Sheykhan et al. described a green electro-oxidative reaction of sulfonyl chlorides with tertiary amines respectively (**Scheme 1**, **b**).[16] Herein, we have reported a novel TBAI (tetrabutylammonium iodide) -catalyzed process to synthesize sulfonamide and β-arylsulfonyl enamines via a selective cleavage of C-N and C-H bonds of tertiary amines (**Scheme 1**, **c**).

Results and discussion

We first investigated the S-N formation reaction between benzenesulfonyl chloride (**1a**) and1-ethylpyrrolidine (**2a**). A series of reaction conditions were investigated (Table 1). As shown in Table 1, $PhI(OAc)_2$ was not an effective catalyst when using TBHP as the oxidant (**Table 1**, **entry 1**). Further catalyst screening revealed that TBAI was the best catalyst to KI, I_2 (**Table 1**, **entries 2-4**). Other oxidants such as H_2O_2, Oxone, m-CPBA and O_2 were also tested, but the reactions did not proceed smoothly (**Table 1**, **entries 5-8**). In addition to THF, other solvents including DMSO, DMF, CH_3CN, toluene, DCM and EtOAc were tested, and the results indicated that THF was the best choice (**Table 1**, **entries 9-14**). The reactions were conducted with a 1:1 (**1a**:**2a**) ratio of substrates to obtain benzenesulfonamide **3a** in a modest yield. When the amount of **1a** or **2a** increased, the reaction showed lower activation under the same conditions (**Table 1**, **entries 15-16**). Both TBAI and TBHP were essential for efficient conversion (**Table 1**, **entries 17-18**).

Table 1. Optimization of reaction conditions[a]



1a **2a** **3a**

Entry	Catalyst (5 mol%)	Oxidant (2.0 eq)	Solvent	Yield (%)[b]
1	$PhI(OAc)_2$	TBHP	THF	trace
2	KI	TBHP	THF	42
3	I_2	TBHP	THF	<10
4	TBAI	TBHP	THF	90
5	TBAI	H_2O_2	THF	0
6	TBAI	Oxone	THF	0
7	TBAI	m-CPBA	THF	0
8	TBAI	O_2	THF	0
9	TBAI	TBHP	DMSO	trace
10	TBAI	TBHP	DMF	0
11	TBAI	TBHP	CH_3CN	22
12	TBAI	TBHP	toluene	15
13	TBAI	TBHP	DCM	25
14	TBAI	TBHP	EtOAc	trace
15[c]	TBAI	TBHP	THF	78
16[d]	TBAI	TBHP	THF	81
17	—	TBHP	THF	trace

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), THF (3.0 mL), 4 h, 80 °C. TBHP: tert-butyl hydroperoxide, 5.0-6.0 M in decane, H_2O_2 30%wt in water. [b]Isolated yield. [c]**1a**:**2a** = 1:1.5. [d]**1a**:**2a** = 1.5:1.

In general, the reactions were carried out by TBAI in THF and then adding 1-ethylpyrrolidine followed by the addition of arylsulfonyl chloride at 80 °C. Under this mild conditions, a 90% isolated yield of *N*,*N*-diethyl benzenesulfonamide **3a** was obtained. Encouraged by the preliminary results, we explored the functional group tolerance for the synthesis of various sulfonamides under the standard conditions. Both electron-donating and electron-withdrawing groups were well tolerated in this reaction. For example, arylsulfonyl chloride containing electron-withdrawing groups such as chloro, cyano groups transformed into the desired products in 65-88% yield (**3b-3g**). On the other hand, coupling of 1-ethylpyrrolidine with electron-rich arylsulfonyl chlorides afforded the sulfonamide in even better yields (**3h-3j**). Because of the steric hindrance, *ortho*- and *meta*- substituent groups gave a slightly lower reaction yield (**3l-3m**). Moreover, coupling with 1- or 2-Naphthalenesulfonyl chloride also proceeded uneventfully, albeit in moderate yields, and did not significantly affect the catalytic efficiency (**3n-3o**). Heteroaromatic sulfonyl chlorides could be tolerated in this reaction as well, achieving the desired product in better yields (**3q-3r**). It should be noted this reaction could be scaled up to gram sacle effectively under the standard conditions (**Table 2**, **3p**). Thus, this simple protocol can be considered as a practical and efficient method to access various sulfonamides.

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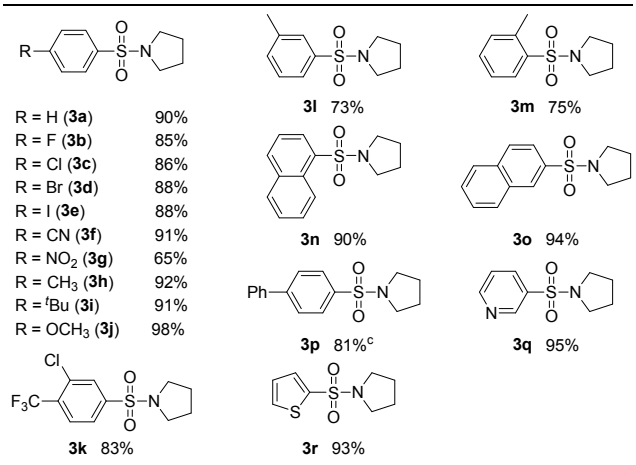
Table 2. Scope of arylsulfonyl chloride[ab]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), TBAI (5 mol%), THF (3.0 mL), 4 h, 80 °C. TBHP: tert-butyl hydroperoxide, 5.0-6.0 M in decane. [b]Isolated yield. [c]**1p** (5 mmol), **2a** (5 mmol).

We next set out to explore the substrate scope of tertiary amines, which could be applicable to this reaction process. Various tertiary amines were investigated under the optimized conditions. As shown in **Table 3**, both aliphatic and aromatic tertiary amines reacted smoothly with 4-Methoxybenzenesulfonyl chloride to get the target products with a yield from 88% to 97%. When the tertiary amine with two different substituent groups such as *N*,*N*-Dipropylethylamine, Dimethyl-*N*-propylamine, *N*,*N*-Diethylaniline and *N*,*N*-Dimethylaniline were involved, the final products were also obtained with a high selectivity and a yield of over 89% (**4b-4e)**. It was found that tribenzylamine reacted smoothly with 4-methoxybenzenesulfonyl chloride to afford the target product in 88% yield (**4f**). Other cyclic and heterocyclic tertiary amines, such as 1-

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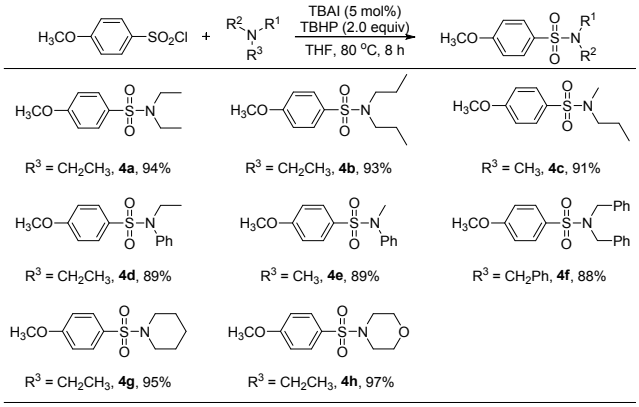
ethylpiperidine and 4-ethyl morpholine, were used as the starting materials, and the corresponding sulfonamides were obtained with a yield of over 95% (**4g-4h**). Using *N*-methyl-*N*-ethyl aniline as the substrate, the reaction of 4-methoxybenzenesulfonyl chloride with *N*-methyl-*N*-ethyl aniline gave a mixture of sulfonamides in THF (see the Supplementary Information).

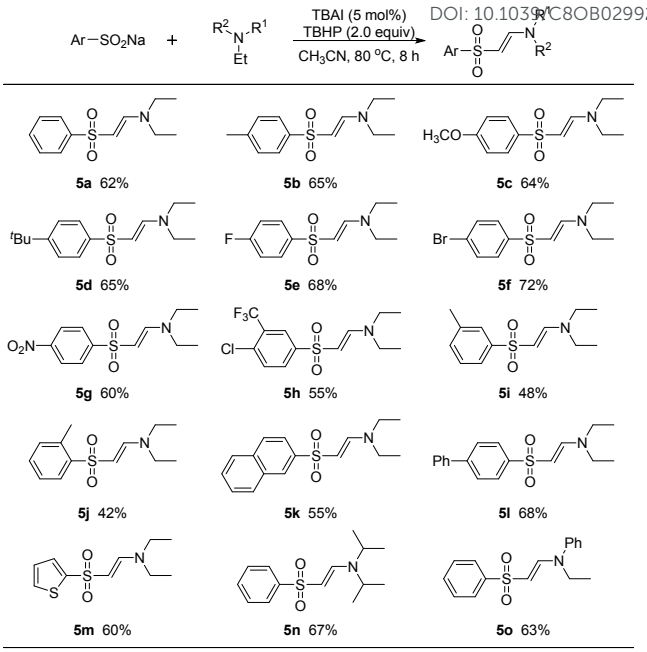
Table 3. Scope of tertiary amines[ab]



[a]Reaction conditions: **1j** (0.3 mmol), **2** (0.3 mmol), TBAI (5 mol%), THF (3.0 mL), 8 h, 80 °C. TBHP: tert-butyl hydroperoxide, 5.0-6.0 M in decane. [b]Isolated yield.

On the other hand, β-functionalization of unactivated substrates is always a challenging target, such as transition metal catalysts or strong oxidants are often need. When we investigated the reaction of sodium arylsulfinates with triethylamine under the standard condition, we surprisingly found trimethylamine β-arylsulfonyl enamines in the products. Good to excellent yields of β-arylsulfonyl enamines were obtained in most cases. The sulfonylation showed excellent functional group tolerance, and sodium arylsulfinates bearing both electron-donating and electron-withdrawing group were explored. Sodium arylsulfinates possessing an fluoro-, bromo-, nitro- group on the para of benzene ring would generate the products in good yields (**5e-5g**). Some of these functional groups are useful for further synthetic transformation. Generally, the sodium arylsulfinates bearing an meta-CF_3 or Methyl-, ortho-methyl groups lead to evident decrease of reaction yield (**5h-5j**). Moreover, 2-naphthyl， 4-phenyl, and 2-thiophen containing substituents were particularly reactive, expanding the synthetic utility of the protocol in this work significantly (**5k-5m**). In addition, other tertiary amines were efficiently transformed into their corresponding β-arylsulfonyl enamines as well (**5n-5o**).

Table 4. Synthesis β-arylsulfonyl enamines[ab]



[a]Reaction conditions: **sodium arylsulfinates** (0.3 mmol), **tertiary amines** (0.3 mmol), TBAI (5 mol%), TBHP (2.0 eq.), CH_3CN (3.0 mL), 8 h, 80 °C. TBHP: tert-butyl hydroperoxide, 5.0-6.0 M in decane. [b]Isolated yield.

Control experiments were further conducted to investigate the reaction mechanism. When a radical scavenger was added to the reaction system, yield of the desired product decreased. The yields of sulfonamide **4a** were 30%, 11%, and less than 1%, respectively, in the presence of TEMPO, BHT, and hydroquninone. The results indicated that the reaction was inhibited by theradical scavenger. Moreover, the reaction did not proceed smoothly in the presence of iodine alone, implying that I_2 did not react with substrates during this transformation. Therefore, we could reasonably deduce that the formation of sulfonamide might involve the conversion of tertiary amine to secondary amine. As shown in **Scheme 2c**, diethylamine with 4-methoxybenzenesulfonyl chloride could be converted to sulfonamide **4a** with a yield of 98%. When powdered molecular sieves were added to the reaction mixture, the yield dropped exceedingly. This experimental result indicates that H_2O have an effect on the C-N bond cleavage (**Scheme 2d**). β-arylsulfonyl enamines **5c** was obtained in CH_3CN solvent, which indicates that *N*,*N*-diethylethenamine may be the intermediate product (**Scheme 2e**).

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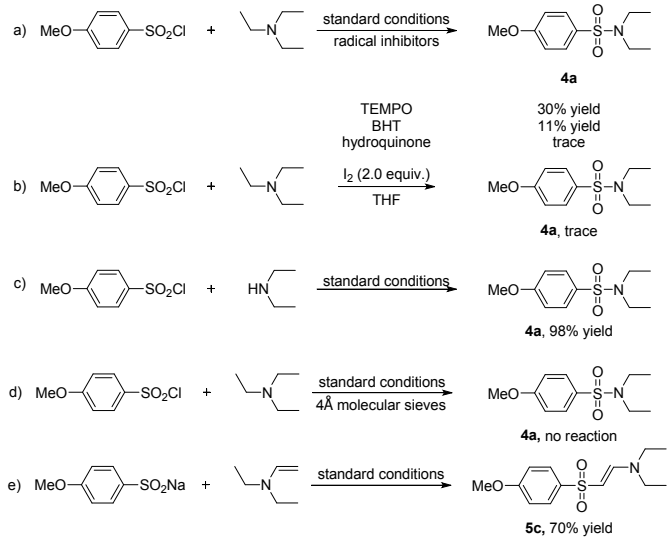
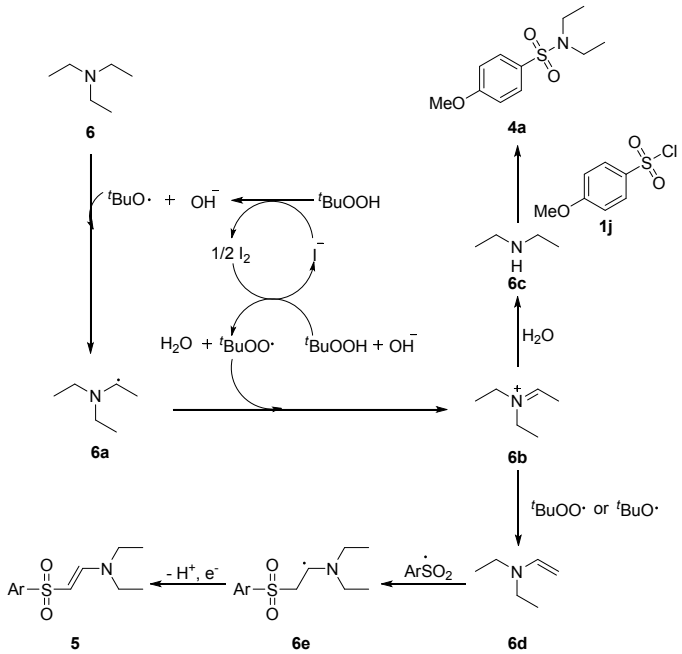


Scheme 2. Control experiment

Based on the findings in this study and reports from previous studies,[11,14-17] we proposed a tentative mechanism for the oxidative amidation of arylsulfonyl chloride with tertiary amines as nitrogen sources (**Scheme 3**). In first step, tert-butoxyl or tert-butylperoxy radicals were produced from the decomposition of TBHP in an iodide (I^-) ion catalytic system. The radicals produced in the first step will abstract a hydrogen atom from the C-H bond adjacent to a nitrogen atom to form a radical **6a**, which will be oxidized to form aminium ion **6b**. The ion **6b** was an intermediate product and will be quickly hydrolyzed and form a diethylamine **6c**. Finally, **6c** reacted with **1j** to form the target product **4a**. However, the aminium ion **6b** was converted into enamine **6d** in CH_3CN. Subsequently **6d** reacted with a sulfonyl radical to give **6e**. Finally, β-hydride elimination of **6e** provided the β-arylsulfonyl enamines **5**.



Scheme 3. Proposed catalytic cycle

Conclusions

In conclusion, we herein report a novel method to synthesize sulfonamides and β-arylsulfonyl enamines through a metal-free catalyzed selective cleavage of tertiary amines. The method is simple and easy to operate, and has been demonstrated tobe possibly applied to synthesis of multifarious sulfonamides, β-arylsulfonyl enamines and related compounds.

Experimental Section

General experimental procedures for sulfonamides

A mixture of benzenesulfonyl chloride **1a** (0.3 mmol), 1-ethylpyrrolidine **2a** (0.3 mmol), TBAI (5 mol%), *tert*-Butyl hydroperoxide (0.6 mmol) and THF (3.0 mL) was sealed in a 25 mL tube with a Teflon lined cap. The tube was then placed in an oil bath, stirred and heated at 80 °C for 4 h. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (25 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified over a column of silica gel (eluent: hexane/ethyl acetate = 8: 1) to afford the desired product **3a**.

General experimental procedures for β-arylsulfonyl enamines

A mixture of sodium benzenesulfinates (0.3 mmol), tertiary amines (0.3 mmol), TBAI (5 mol%), *tert*-Butyl hydroperoxide (0.6 mmol) and CH_3CN (3.0 mL) was sealed in a 25 mL tube with a Teflon lined cap. The tube was then placed in an oil bath, stirred and heated at 80 °C for 8 h. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (25 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified over a column of silica gel (eluent: hexane/ethyl acetate = 2: 1) to afford the desired product.

A gram-scale synthesis of 1-(biphenyl-4-ylsulfonyl)pyrrolidine (3p)

A solution of 4-biphenylsulfonyl chloride (5.0 mmol, 1.26 g), 1-ethylpyrrolidine **2a** (5.0 mmol, 0.50 g), TBAI (5 mol%, 0.092 g), *tert*-Butyl hydroperoxide (10 mmol, 2.0-2.4 mL) in THF (50 mL) was stirred and heated at 80 °C for 4 h. After cooling to room temperature, the reaction mixture was quenched with water (200 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified over a column of silica gel (eluent: hexane/ethyl acetate = 8: 1) to afford the desired product **3p** (81% yield, 1.42 g).

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 For selected examples: (a) J. F. Hartwig, *Acc. Chem. Res.,* 1998, **31**, 852; (b) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev*., 2007, **107**, 5318; (c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.,* 2012, **41**, 3651; (d) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.,* 2011, **40**, 5068; (e) T. Wang, N. Jiao, *Acc. Chem. Res.,* 2014, **47**, 1137; (f) Q. Yang, Q. Wang, Z. Yu, *Chem. Soc. Rev.,* 2015, **44**, 2305; (g) N. J. Turner, *Chem. Rev*., 2011, **111**, 4073.

2 S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res*., 2003, **36**, 255.

3 For selected examples: (a) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.,* 2006, **106**, 4622; (b) S. R. Golisz, N. Hazari, J. A. Labinger, J. E. Bercaw, *J. Org. Chem*., 2009, **74**, 8441; (c) A. Wang, H. Jiang, X. Li, *J. Org. Chem.,* 2011, **76**, 6958; (d) X. Zhao, D. Liu, H. Guo, Y. Liu, W. Zhang, *J. Am. Chem. Soc.,* 2011, **133**,19354; (e) M.-B. Li, Y. Wang, S.-K. Tian, *Angew. Chem. Int. Ed*., 2012, **51**, 2968; (f) D. Hollmann, S. Bahn, A. Tillack, M. Beller, *Angew. Chem. Int. Ed.,* 2007, **46**, 8291; (g) S. Ueno, N. Chatani, F. Kakiuchi, *J. Am. Chem. Soc.,* 2007, **129**, 6098; (h) T. Koreeda, T. Kochi, F. Kakiuchi, *J. Am. Chem. Soc.,* 2009, **131**, 7238; (i) W. Wu, W. Su, *J. Am. Chem. Soc.,* 2011, **133**, 11924; (j) P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem. Int. Ed*., 2011, **50**, 519; (k) S. Guo, B. Qian, Y. Xie, C. Xia, H. Huang, *Org. Lett.,* 2011, **13**, 522; (l) L. Zhang, C. Peng, D. Zhao, Y. Wang, H.-J. Fu, Q. Shen, J.-X. Li, *Chem. Commun*., 2012, **48**, 5928; (m) J. Zhang, J. Chen, M. Liu, X. Zheng, J. Ding, H. Wu, *Green Chem*., 2012, **14**, 912; (n) Y. Kuninobu, M. Nishi, K. Takai, *Chem. Commun.,* 2010, **46**, 8860; (o) C.-R. Liu, F.-L. Yang, Y.-Z. Jin, X.-T. Ma, D.-J. Cheng, N. Li, S.-K. Tian, *Org. Lett*., 2010, **12**, 3832; (p) L.-Y. Xie, S. Peng, L.-L. Jiang, X. Peng, W. Xia, X. Yu, X.-X. Wang, Z. Cao, W.-M. He, *Org. Chem. Front.*, 2019, **6** , 167; (q) S. B. Blakey, D. W. C. MacMillan, *J. Am. Chem. Soc*., 2003, **125**, 6046; (r) J. Liu, M. J. Robins, *Org. Lett*., 2004, **6**, 3421; (s) T. S. Kleckley, J. L. Bennett, P. T. Wolczanski, E. B. Lobkovsky, *J. Am. Chem. Soc.,* 1997, **119**, 247; (t) J. B. Bonanno, T. P. Henry, D. R. Neithamer, P. T. Wolczanski, E. B. Lobkovsky, *J. Am. Chem. Soc.,* 1996, **118**, 5132; (u) H. Shen, H.-S. Chan, Z. Xie, *J. Am. Chem. Soc*., 2007, **129**, 12934; (v) T. M. Cameron, K. A. Abboud, J. M. Boncella, *Chem. Commun*., 2001, 1224.

4 (a) K. Q. Lao, E. Jensen, P. W. Kash, L. J. Butler, *J. Chem. Phys*., 1990, **93**, 3958; (b) H. Inui, S. Murata, *J. Am. Chem. Soc.,* 2005, **127**,2628; (c) R. F. Klima, A. V. Jadhav, P. N. D. Singh, M. Chang, C. Vanos, J. Sankaranarayanan, M. Vu, N. Ibrahim, E. Ross, S. McCloskey, R. S. Murthy, J. A. Krause, B. S. Ault, A. D. Gudmundsdottir, *J. Org. Chem*., 2007, **72**, 6372; (d) X.-S. Wu, S.-K. Tian, *Chem. Commun*., 2012, **48**, 898; (e) D.-J. Dong, H.-H. Li, S.-K. Tian, *J. Am. Chem. Soc.,* 2010, **132**, 5018; (f) D.-J. Dong, Y. Li, J.-Q. Wang, S.-K. Tian, *Chem. Commun*., 2011, **47**, 2158; (g) Y. Wang, Y. Chi, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.,* 2012, **134**, 2926; (h) D. H. R. Barton, W. B. Motherwell, S. Z. Zard, *Tetrahedron Lett*., 1983, **24**, 5227; (i) R. Ballini, M. Petrini, *Tetrahedron,* 2004, **60**, 1017; (j) H. K. Potturi, R. K. Gurung, Y. Hou, *J. Org. Chem*., 2012, **77**, 626; (k) J. Bures, J. Vilarrasa, *Tetrahedron Lett*., 2008, **49**, 441; (l) Z. Liu, R. C. Larock, *J. Am. Chem. Soc.,* 2005, **127**, 13112.

5 For selected examples: (a) C. Hansch, P. G. Sammes, J. B. Taylor, in Comprehensive Medicinal Chemistry, Pergamon Press, Oxford, 1990, vol. 2, ch. 7.1; (b) A. Kleemann, J. Eagel, B. Kutscher, D. Reichert, in Pharmaceutical Substances, Synthesis, Patents, Applications, Thieme, Stuttgart, 1999, Guide 2nd ed; (c) Z. Huang, Z. Lin, J. Huang, *Eur. J. Med. Chem*., 2001, **36**, 863; (d) B. Masereel, S. Rolin, F. Abbate, A. Scozzafava, C. T. Supuran, *J. Med. Chem*., 2002, **45**, 312; (e) A. M. Gilbert, S. Caltabiano, F. E. Koehn, Z. J. Chen, G. D. Francisco, J. W. Ellingboe, Y. Kharode, A. M. Mangine, R. Francis, M. T. Smith, D. Gralnick, *J. Med. Chem.,* 2002, **45**, 2342; (f) A. Scozzafava, T. Owa, A. Mastrolorenzo, C. T. Supuran, *Curr. Med. Chem*., 2003, **10**, 925; (g) C. T. Supuran, A. Casini, A. Scozzafava, *Med. Res. Rev*., 2003, **23**, 535; (h) M. Banerjee, A. Poddar, G. Mitra, A. Surolia, T. Owa, B. Bhattacharyya, *J. Med. Chem*., 2005, **48**, 547; (i) N. Siddiqui, S. N. Pandeya, S. A. Khan, J. Stables, A. Rana, M. Alam, M. F. Arshad, M. A. Bhat, *Bioorg. Med. Chem. Lett*., 2007, **17**, 255; (j) S. Bano, K. Javed, S. Ahmad, I. G. Rathish, S. Singh, M. S. Alam, *Eur. J. Med. Chem*., 2011, **46**, 5763; (k) A. K. Ganguly, S. S. Alluri, D. Caroccia, D. Biswas, C.-H. Wang, E. Kang, Y. Zhang, A. T. McPhail, S. S. Carroll, C. Burlein, V. Munshi, P. Orth, C. Strickland, *J. Med. Chem*., 2011, **54**, 7176; (l) M. Basanagouda, K. Shivashankar, M. V. Kulkarni, V. P. Rasal, H. Patel, S. S. Mutha, A. A. Mohite, *Eur. J. Med. Chem*., 2010, **45**, 1151.

6 (a) T. W. Green, P. G. M. Wuts, in Protecting Groups in Organic Synthesis, Wiley-Inter science, *New York*, 1999; (b) W. Yuan, K. Fearon, M. H. Gelb. *J. Org. Chem*., 1989, **54**, 906; (c) S. Chandrasekhar, S. Mohapatra, *Tetrahedron Lett.,* 1998, **39**, 695; (d) S. P. Fritz, A. Mumtaz, M. Yar, E. M. McGarrigle, V. K. Aggarwal, *Eur. J. Org. Chem*., 2011, **17**,3156.

7 (a) T. J. De Boer, H. J. Backer, *Org. Synth*., 1954, **34**, 96; (b) K. K. Anderson, in Comprehensive Organic Chemistry, ed. D. N. Jones, Pergamon Press, Oxford, 1979, vol. 3; (c) G. Burton, P. Cao, G. Li, R. Rivero, *Org. Lett*., 2003, **5**, 4373; (d) M. Harmata, P. Zheng, C. Huang, M. G. Gomes, W. Jing, K. Ranyanil, G. Balan, N. L. Calkins, *J. Org. Chem*., 2007, **72**,683; (e) R. Sridhar, B. Srinivas, V. P. Kumar, M. Narender, K. R. Rao, *Adv. Synth. Catal*., 2007, **349**, 1873.

8 (a) J. Yin, S. L. Buchwald, *Org. Lett*., 2000, **2**, 1101; (b) J. Yin, S. L. Buchwald, *J. Am. Chem. Soc*., 2002, **124**, 6043; (c) H. He, Y.-J. Wu, *Tetrahedron Lett*., 2003, **44**, 3385; (d) J. Baffoe, M. Y. Hoe, B. B. Toure, *Org. Lett*., 2010, **12**, 1532; (e) B. R. Rosen, J. C. Ruble, T. J. Beauchamp, A. Navarro, *Org. Lett*., 2011, **13**, 2564; (f) D. Audisio, S. Messaoudi, J. F. Peyrat, J. D. Brion, M. Alami, *J. Org. Chem*., 2011, **76**, 4995; (g) K. S. Rao, T.- S. Wu, *Tetrahedron,* 2012, **68**, 7735; (h) J.-B. Lan, G.-L. Zhang, X.-Q. Yu, J.-S. You, L. Chen, M. Yan, R.-G. Xie, *Synlett,* 2004, 1095.

9 S.-Y. Moon, J. Nam, K. Rathwell, W.-S. Kim, *Org. Lett*., 2014, **16**, 338.

10 For selected examples: (a) X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun*., 2013, **49**, 6102; (b) W. Wei, C. Liu, D. Yang, J. Wen, J. You, H. Wang, *Adv. Synth. Catal*., 2015, **357**, 987; (c) H. Zhu, Y. Shen, Q. Deng, T. Tu, *Chem. Commun*., 2015, **51**, 16573.

11 J. Ji, Z. Liu, P. Liu, P. Sun, *Org. Biomol. Chem*., 2016, **14**, 7018.

12 For selected examples: (a) F. A. H. Nasab, L. Z. Fekri, A. Monfared, A. Hosseinian, E. Vessally, *RSC Adv*., 2018, **8**, 18456; (b) O. M. Mulina, A. I. Ilovaisky, A. O. Terent'ev, Eur. *J. Org. Chem*., 2018, 4648; (c) N. Taniguchi, *Eur. J. Org. Chem*., 2010, 2670; (d) K. Bahrami, M. M. Khodaei, M. Soheilizad, *Tetrahedron Lett*., 2010, **51**, 4843; (e) A. R. Massah, S. Sayadi, S. Ebrahimi, *RSC Adv*., 2012, **2**, 6606; (f) X. Huang, J. Wang, Z. Ni, S. Wang, Y. Pan, *Chem. Commun*., 2014, **50**, 4582; (g) J.-B. Feng, X.-F. Wu, *Org. Biomol. Chem*., 2016, **14**, 6951; (h) M. Zhu, W. Wei, D. Yang, D. Cui, L. Wang, G. Meng, H. Wang, *Org. Biomol. Chem.,* 2017, **15**, 4789; (i) A. O. Terent'ev, O. M. Mulina, D. A. Pirgach, M. A. Syroeshin, A. P. Glinushkin, G. I. Nikishin, *Mendeleev Commun*., 2016, **26**, 538.

13 (a) M. S. Yusubov, V. V. Zhdankin, *Resource-Efficient Technologies*, 2015, **1**, 49; (b) V. V. Zhdankin Hypervalent

View Article Online
DOI: 10.1039/C8OB02992J

Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds. Wiley, Chichester, UK (2013).

14 For selected examples: (a) J. Lai, L. Chang, G. Yuan, *Org. Lett.,* 2016, **18**, 3194; (b) C. Buathongjan, D. Beukeaw, S. Yotphan, *Eur. J. Org. Chem*., 2015, 1575; (c) K. Yang, M. Ke, Y. Lin, Q. Song, *Green Chem*., 2015, **17**, 1395; (d) S.-X. Wu, Y.-K. Zhang, H.-W. Shi, J. Yan, *Chin. Chem. Lett.,* 2016, **27**, 1519; (e) X. Pan, J. Gao, J. Liu, J. Lai, H. Jiang, G. Yuan, *Green. Chem*., 2015, **17**, 1400; (f) S. K. R. Parumala, R. K. Peddinti, *Tetrahedron Lett*., 2016, **57**, 1232; (g) S. Yotphan, L. Sumunnee, D. Beukeaw, C. Buathongjan, V. Reutrakul, *Org. Biomol. Chem*., 2016, **14**, 590; (h) W.-H. Bao, C. Wu, J.-T. Wang, P. Chen, Z. Tang, W.-M. He, *Org. Biomol. Chem.* 2018, **16**, 7025.

15 sodium arenesulfinates were prepared from their corresponding sulfonyl chlorides.

16 M. Sheykhan, S. Hkani, M. Abbsania, S. Shaabanzadeh, M. Joafshan, *Green Chem*., 2017, **19**, 5940.

17 (a) X.-F. Wu, J.-L. Gong, X. Qi, *Org. Biomol. Chem*., 2014, **12**, 5807; (b) J. Zhao, J. Xu, J. Chen, X. Wang, M, He, *RSC Adv*., 2014, **4**, 64698.