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Iodine Promoted Regioselective α-Sulfenylation of Carbonyl Compounds using Dimethyl Sulfoxide as an Oxidant

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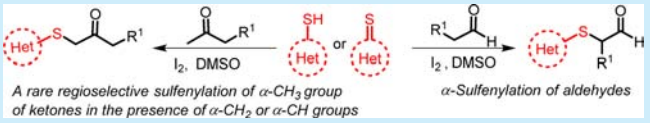
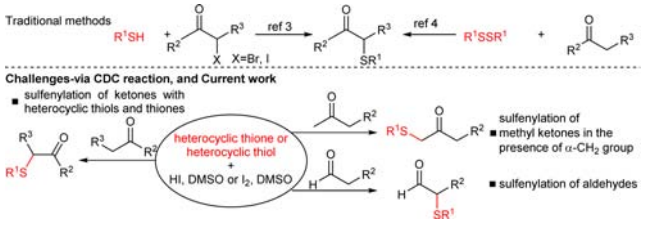
Supporting Information

ABSTRACT: A metal-free regioselective sulfenylation of the α-CH_3 group of ketones has been achieved in the presence of the α-CH_2 or α-CH group using the cross dehydrogenative (CDC) strategy. Aldehydes also exhibit good selectivity forming the corresponding α-sulfenylated products. This efficient sulfenylation of ketones or aldehydes with thiones or heterocyclic thiols utilizes dimethyl sulfoxide (DMSO) as an oxidant in the presence of iodine. This eco-friendly method uses readily available and inexpensive I_2 and DMSO. The application of this methodology has been demonstrated by synthesizing precursors for Julia− Kocienski olefination intermediates.



The cross dehydrogenative (CDC) reactions for α-sulfenylation of ketones with nonheterocylcic thiols are facile,[1a−d] whereas a similar reaction with heterocyclic thiols is a challenge.[1e] The CDC strategy is becoming more attractive for C−C bond forming reactions, as it provides short, atom economical, and environmentally benign protocols.[2] Sulfenylation methods using a broad range of either heterocyclic thiols or heterocyclic thiones are very limited.[1] Regioselective α-sulfenylation of methyl ketones in the presence of α-CH_2 or α-CH groups and α-sulfenylation of aldehydes are unaddressed problems through the CDC method. Typically, α-sulfenylation of ketones has been achieved by the reaction of α-halo ketones with thiols (Scheme 1),[3] and the reaction of ketones with

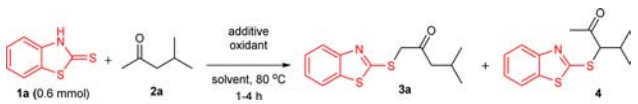
Scheme 1. Sulfenylation Methods



disulfides,[4] *N*-(phenylthio)imides,[5] and phenyl benzenethiosulfonate.[6] Diazo ketones,[7] olefins,[8] or active methylene compounds[9] are known to react with thiols to provide sulfenylated products. Heterocyclic thiols and thiones serve as building blocks for synthesizing a variety of pharmaceutically and medicinally active sulfur containing compounds.[10] Dimethyl sulfoxide (DMSO) as an oxidant is gaining importance in organic synthesis owing to its low cost, high abundance, low toxicity, and environmentally benignity.[11] In continuation of our efforts on the reactions promoted by the I_2−DMSO combination[11h] and metal-free reactions,[1e,12] herein we report a rare regioselective sulfenylation of the α-CH_3 of ketones in the presence of the α-CH_2 group, α-sulfenylation of aldehydes, and α-sulfenylation of aromatic ketones.

We began the screening experiments by reacting benzo[*d*]-thiazole-2(3*H*)-thione (**1a**) with 4-methylpentan-2-one (**2a**) using DMSO as an oxidant (Table 1). Thus, the reaction of thione **1a** with ketone **2a** in DMSO (3 equiv) and HI (55% solution in water, 1 equiv, as an additive) in dichloroethane

Table 1. Optimization Studies[a]



entry	additive (equiv)	oxidant (equiv)	solvent (mL)	yield[b] **3a:4**
1	HI 55% (1)	DMSO (3)	DCE	85 (1:0)
2	HI 55% (1)	DMSO (3)	EtOAc	82 (1:0)
3	HI 55% (1)	none	DMSO	78 (1:0)
4	HBr 55% (1)	none	DMSO	nd
5	**I_2 (1)**	**none**	**DMSO**	**84 (1:0)**
6	NIS (1)	none	DMSO	76 (1:0)
7	NBS(1)	none	DMSO	trace
8	NCS (1)	none	DMSO	36 (1:2)
9	I_2 (1)	none	DMSO	72 (1:0)[c]
10	I_2 (1)	none	DMSO	56 (1:0)[d]
11	I_2 (1)	none	DMSO	18 (1:0)[e]
12	I_2 (0.5)	none	DMSO	58 (1:0)
13	I_2 (0.2)	none	DMSO	28 (1:0)
14	I_2 (1)	none	DMSO	nd[f]
15	I_2 (1)	none	none	nd
16	none	none	DMSO	nd

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (2.4 mmol), additive (0.6 mmol), oxidant (1.8 mmol, 3 equiv) in 1 mL of solvent at 80 °C. [b]Isolated yield. [c]3 equiv of **2a**. [d]2 equiv of **2a**. [e]1 equiv of **2a** and 3 equiv **1a**. [f]Na_2CO_3 (1 equiv), nd = Not determined.

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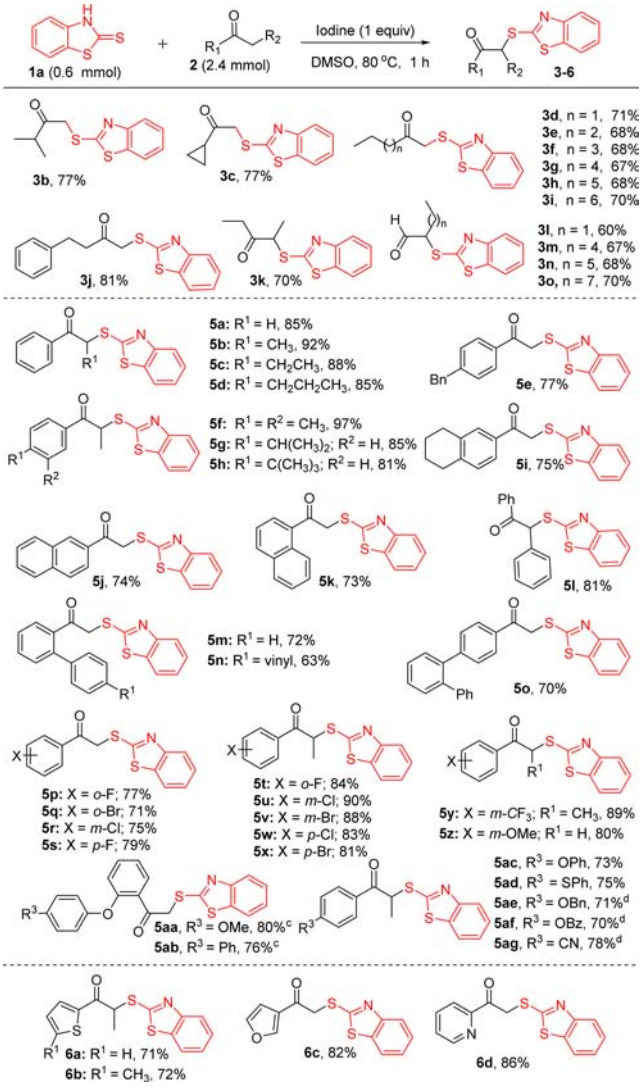
resulted in the selective formation of **3a** in 85% yield, in which a rare regioselective sulfenyaltion of the α-CH_3 of ketone in the presence of the more reactive α-CH_2 group has taken place (entry 1, Table 1). The solvent screening studies revealed that a similar reaction in EtOAc in DMSO (3 equiv) or DMSO (1 mL) led to the product **3a** in 82 and 78% yields, respectively (entries 2 and 3, Table 1; see the Supporting Information for more details). Our attempts on using aq. HBr instead of aq. HI did not afford the expected products (entry 4, Table 1). The reaction of **1a** with **2a** using iodine was highly successful, which furnished the product **3a** in 84% yield (entry 5). Using NIS as a halogen source led to the formation of **3a** in 76% yield (entry 6), whereas the reaction of **1a** and **2a** with NBS failed to provide the product **3a** (entry 7). Surprisingly, the reaction of thione **1a** with ketone **2a** using NCS afforded a mixture of products **3a** and **4** in 36% in a 1:2 ratio (entry 8). This is the only example which has furnished a mixture of α- and α'-sulfenylated products, **3a** and **4**, respectively, whereas the remaining experiments afforded α-sulfenylated product **3a** as the sole product. Further screening was performed using iodine (entries 9−15). As can be seen, varying the amount of **1a** or **2a** was not helpful in enhancing the yield of **3a** (entries 9−11). Decreasing the amount of iodine to 0.5 or 0.2 equiv resulted in decreasing the yield of the product (entries 12 and 13, Table 1). A reaction of **1a** with **2a** in Na_2CO_3 was performed, which did not yield the expected product **3a** (entry 14, Table 1). The reactions in the absence of either iodine or DMSO were not successful, and the formation of **3a** was not observed (entries 15−16, Table 1; for an elobarate screening study, see the Supporting Information). With these screening studies, entry 5 of Table 1 has been chosen as the optimal conditions, as iodine is easier to handle and DMSO is a green solvent over a halogenated solvent.[2a] It is also noteworthy that most of the heterocyclic thiols used are stable crystalline solids and do not possess a bad odor.

With the optimal conditions in hand, sulfenylation reactions using heterocyclic thione with a variety of ketones have been performed (Scheme 2). As can be seen in the scheme, the reactions of aliphatic ketones that contain α-CH_2 or α-CH groups were highly regioselective and exhibited a novel, and hitherto unknown, regioselectivity. Thus, the reaction of thione (**1a**) with 3-methylbuta-2-one and 1-cyclopropylethan-1-one led to α-sulfenylation at the α-CH_3 group of the ketones in the presence of the more reactive α-CH group and furnished the products **3b** and **3c** in excellent yields (Scheme 2). Indeed this remarkable selectivity observed was found to be general, and the reaction of 4-phenylbutan-2-one, and a few other aliphatic ketones with thione (**1a**), furnished their sulfenylated products **3d−3j**, in good yields. We believe that the reason for this selectivity is due to the thermodynamic stability of the terminal enolate that leads to the sulfenylation at the α-CH_3 group of the ketone. To the best of our knowledge, this is the first report of the highly regioselective sulfenylation of ketones at α-CH_3 in the presence of the more reactive α-CH_2 or α-CH group using heterocyclic thiones under CDC methods, and these compounds are difficult to synthesize. Similarly, the reaction of 3-pentanone with thione **1a** afforded the product **3k** in 70% yield. Interestingly, in the sulfenylation reactions of aldehydes with thione (**1a**) it was found that the aldehyde functionality was unaffected, and the corresponding α-sulfenylated aldehydes (**3l−3o**) were obtained in good yields. In these reactions, a highly oxidative prone aldehyde functionality survived under the reaction conditions, and this is also the first report on an efficient α-sulfenylation of aldehydes using CDC methodology.

Scheme 2. Reactions of Thiones with Ketones and Aldehydes[a,b]



[a]Reaction conditions: **1a** (0.6 mmol), **2** (2.4 mmol), I_2 (0.6 mmol) in DMSO (1 mL) at 80 °C for 1 h. [b]Isolated yield, [c]3 equiv of ketone used. [d]2 equiv of ketone used.

Furthermore, this sulfenylation reaction was found to be versatile and a variety of aromatic ketones were successfully sulfenylated with benzo[*d*]thiazole-2(3*H*)-thione (**1a**) (Scheme 2). It is noteworthy that the thio-derivatives obtained in the reaction of **1a** with aromatic ketones are highly useful compounds.[13] Thus, the thione **1a** underwent a smooth coupling reaction with acetophenone, propiophenone, 1-phenylbutan-1-one, and 1-phenylpentan-1-one affording the corresponding α-sulfenylated products **5a−5d**, respectively, in good to excellent yields (85−92%, respectively, Scheme 2). Benzyl and alkyl substituents on the phenyl ring were well tolerated under the reaction conditions furnishing their corresponding sulfenylated products **5e−5i**, in good to excellent yields (77−97%). The reaction of thione **1a** with naphthyl ketones, 1,2-diphenylethan-1-one derivatives, and biphenyl ketone derivatives afforded their corresponding sulfenylated products **5j−5o** in good yields. The halogen substituted acetophenone and propiophenone derivatives furnished their corresponding α-sulfenylated products in good to excellent yields (**5p−5x**, Scheme 2), which are useful

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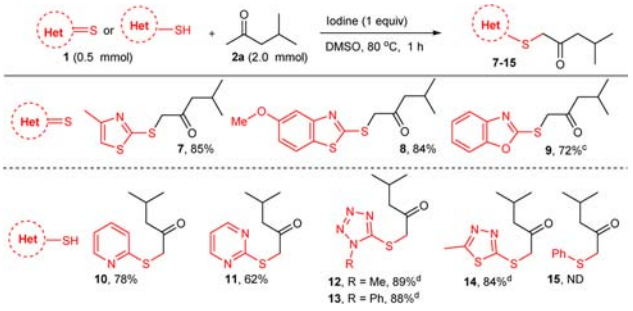
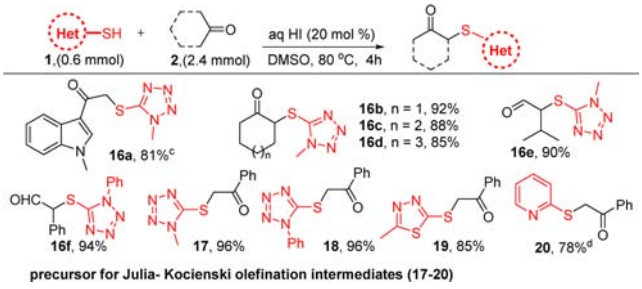
Scheme 3. Regioselective Sulfenylation of 4-Methylpentan-2-one with Thione or Thiols[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2a** (2.0 mmol), iodine (0.5 mmol) in 1 mL of DMSO at 80 °C, 1 h. [b]Isolated yield. [c]1 equiv of NIS used. [d]20 mol % of iodine used in 1 mL of DMSO at 80 °C, 4 h.

Scheme 4. Reaction of Heterocyclic Thiols with Ketones and Aldehydes[a,b]



[a]Reaction conditions: **1** (0.6 mmol), **2** (2.4 mmol), aq HI (55% in water, 20 mol %) in 1 mL of DMSO at 80 °C, 4 h. [b]Isolated yield. [c]2 equiv of ketone used. [d]1 equiv of I_2 used.

precursors for metal-catalyzed cross-coupling reactions.[14] The reaction of 1-(4-(trifluoromethyl)phenyl)propan-1-one and 1-(3-methoxyphenyl)ethan-1-one with thione **1a** furnished the sulfenylated product **5y** and **5z** in 89% and 80% yields, respectively.[15] Sulfenyaltion of a variety of aromatic ketones that contain both electron-releasing and -withdrawing substituents on the phenyl ring was highly facile and proceeded smoothy furnishing the products **5aa**−**5ag** in good yields.

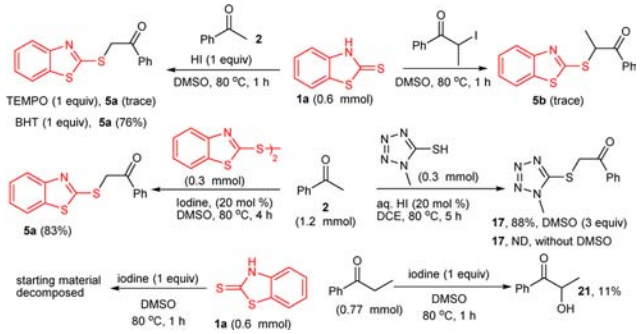
Further investigation revealed that several heterocyclic ketones such as 1-(thiophen-2-yl)propan-1-one, 1-(5-methylthiophen-2-yl)propan-1-one, 1-(furan-3-yl)ethan-1-one, and 1-(pyridin-2 yl)ethan-1-one underwent a facile reaction with thione (**1a**) furnishing their corresponding α-sulfenylated products **6a**−**6d**, in good to excellent yields (Scheme 2).

Next, it was found that sulfenylation of 4-methylpentan-2-one (**2a**) with a variety of heterocyclic thiones or thiols were also regioselective and led to the sulfenylation of the α-CH_3 group of ketones in the presence of more reactive α-CH_2 groups. Thus, the reaction of 4-methyl-2-pentanone (**2a**) with 4-methylthiazole-2(3*H*)-thione, 5-methoxybenzo[*d*]thiazole-2(3*H*)-thione, and benzo[*d*]oxazole-2(3*H*)-thione furnished the corresponding sulfenylated products **7**, **8**, and **9** in excellent yields (85%, 84%, and 72%, respectively, Scheme 3). The reaction of heterocyclic thiols with ketone **2a** was also regioselective yielding the sulfenylated products **10**−**14** in good to excellent yields (Scheme 3). However, the reaction of thiophenol with ketone **2a** failed to afford the expected product **15**. Similarly, 2-mercaptobenzimidazole failed to undergo a sulfenyaltion reaction with **2a**.

Further exploration of this versatile sulfenylation reaction revealed that the reactions of a variety of carbonyl compounds with heterocyclic thiols were also facile (Scheme 4). However, these reactions furnished better yields using HI, instead of iodine, and thus further exploration has been performed using HI (see Table 11 of the Supporting Information for more details). As expected, the reaction of 1-methyl-1*H*-tetrazole-5-thiol with ketones such as 1-(1-methyl-1*H*-indol-3-yl)ethan-1-one, cyclohexanone, cycloheptanone, and cyclooctanone proceeded smoothly furnishing sulfenylated products **16a**−**16d** in good to excellent yields (Scheme 4). Similarly, the aldehydes 3-methylbutanal and 2-phenylacetaldehyde reacted well with 1-methyl-1*H*-tetrazole-5-thiol and 1-phenyl-1*H*-tetrazole-5-thiol respectively, furnishing the sulfenylated products **16e** and **16f**, respectively, in excellent yields. In these α-sulfenylation reactions, the aldehyde functional group was unaffected. The application of this selective sulfenylation reaction has been demonstrated by synthesizing a host of sulfenylated products, which are useful intermediates in the Julia−Kocienski olefination reaction. Thus, the reaction of thiols such as 1-methyl-1*H*-tetrazole-5-thiol, 1-phenyl-1*H*-tetrazole-5-thiol, 5-methyl-1,3,4-thiadiazole-2-thiol, and pyridine-2-thiol with acetophenone furnished the corresponding sulfenylated products **17**, **18**, **19**, and **20**, respectively, in excellent yields.[13c,e]

To understand the mechanism of this reaction, a few control experiments were performed. First, the reaction of acetophenone (**2**) with benzo[*d*]thiazole-2(3*H*)-thione (**1a**) under the optimal conditions in the presence of TEMPO furnished a trace amount of sulfenylated product **5a**, while the same reaction in the presence of a radical inhibitor such as BHT proceeded well to form **5a** in 76% yield (Scheme 5). This observation indicates that

Scheme 5. Control Experiments



the reaction does not proceed through a radical pathway. To find whether 2-iodo-1-phenylpropan-1-one is an intermediate, a reaction was performed with 2-iodo-1-phenylpropan-1-one, which failed to furnish the expected product **5b**. The reaction of 1,2-bis(benzo[*d*]thiazol-2-yl)disulfane with acetophenone in the presence of a catalytic amount of iodine (20 mol %), furnishing **5a** in 83% yield. This experiment supports the intermediacy of disulfide in the reaction. To confirm the role of DMSO as an oxidant and iodine as a catalyst, a reaction was performed with 1-methyl-1*H*-tetrazole-5-thiol with 20 mol % of aq. HI and DMSO (3 equiv) in DCE as solvent, which proceeded well to form **17** in 88% yield (Scheme 5). The same reaction, in the absence of DMSO, failed to furnish the product **17**. These experiments clearly support the role of iodine as a catalyst and DMSO as an oxidant. Further, the reaction of thione **1a** with iodine and DMSO resulted in complete decomposition of thione (**1a**). However, the reaction of propiophenone with iodine and

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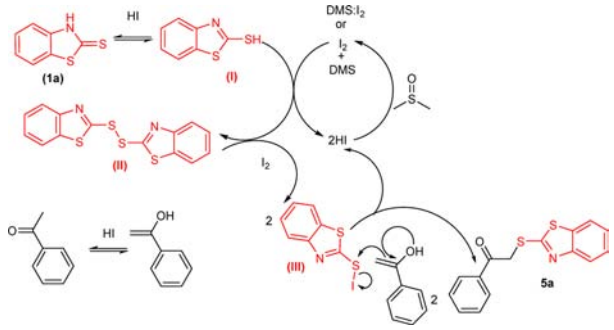
DMSO, in the absence of thione or thiol, furnished 2-hydroxy-1-phenylpropan-1-one (**21**) in 11% yield along with unreacted propiophenone.

Based on these experiments and the literature precedence,[11d−h] a tentative mechanism is proposed (Scheme 6).

Scheme 6. Tentative Mechanism



Benzo[*d*]thiazole-2(3*H*)-thione (**1a**) requires a strong acidic condition to exist in benzo[*d*]thiazole-2-thiol (**I**).[1e,12d,e] Iodine reacts with benzo[*d*]thiazole-2-thiol (**I**) furnishing 1,2-bis-(benzo[*d*]thiazol-2-yl)disulfane (**II**). Disulfane (**II**) further reacts with iodine to form an intermediate (**III**), which contains a S−I bond. Nucleophilic displacement of the iodo group from intermediate **III** from the enolate of ketone or aldehyde furnishes an α-sulfenylated product. DMSO reacts with HI to regenerate an active species I_2 or $[DMSI^+]I^-$ (Scheme 6).[11g]

In summary, a rare regioselective C−H sulfenylation of carbonyl compounds with heterocyclic thiones and thiols has been described by employing an iodine and DMSO combination. To the best of our knowledge, this is the first report of the regioselective sulfenylation of (i) methyl ketones in the presence of α-CH_2 or α-CH groups and (ii) aldehydes. This ecofriendly protocol uses readily available and inexpensive I_2 and DMSO. A broad substrate scope has been demonstrated, and target products were obtained in good to excellent yields. The application of this methodology has been demonstrated by synthesizing highly useful precursors for Julia−Kocienski olefination intermediates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03084.

Experimental procedures, characterization data and spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Sasaki, T.; Hayakawa, K.; Nishida, S. *Tetrahedron* **1982**, *38*, 75. (b) Sasaki, T.; Hayakawa, K.; Nishida, S. *Tetrahedron Lett.* **1980**, *21*, 3903. (c) Bordwell, F. G.; Zhang, X.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7623. (d) Yadav, J. S.; Subba Reddy, B. V.; Jain, R.; Baishya, G. *Tetrahedron Lett.* **2008**, *49*, 3015. (e) Varun, B. V.; Gadde, K.; Prabhu, K. R. *Org. Biomol. Chem.* **2016**, *14*, 7665.

(2) (a) Wu, X.-F.; Natte, K. *Adv. Synth. Catal.* **2016**, *358*, 336. (b) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, *2013*, 5769. (c) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (d) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (e) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095.

(3) (a) Prüger, B.; Hofmeister, G. E.; Jacobsen, C. B.; Alberg, D. G.; Nielsen, M.; Jørgensen, K. A. *Chem. - Eur. J.* **2010**, *16*, 3783. (b) Ranu, B. C.; Jana, R. *Adv. Synth. Catal.* **2005**, *347*, 1811. (c) Huang, X.; Zheng, W.-X. *Synth. Commun.* **1999**, *29*, 1297.

(4) (a) Yadav, V. K.; Babu, K. G.; Parvez, M. *J. Org. Chem.* **2004**, *69*, 3866. (b) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887. (c) Groenewegen, P.; Kallenberg, H.; van der Gen, A. *Tetrahedron Lett.* **1979**, *20*, 2817.

(5) Wang, W.; Li, H.; Wang, J.; Liao, L. *Tetrahedron Lett.* **2004**, *45*, 8229.

(6) Trost, B. M.; Massiot, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4405.

(7) (a) Sengupta, S.; Mondal, S. *Tetrahedron Lett.* **1999**, *40*, 8685. (b) Anthony McKervey, M.; Ratananukul, P. *Tetrahedron Lett.* **1982**, *23*, 2509. (c) Sellars, J. D.; Steel, P. G. *Chem. Soc. Rev.* **2011**, *40*, 5170.

(8) Lu, Q.; Wang, H.; Peng, P.; Liu, C.; Huang, Z.; Luo, Y.; Lei, A. *Org. Chem. Front.* **2015**, *2*, 908.

(9) Zou, L.-H.; Priebbenow, D. L.; Wang, L.; Mottweiler, J.; Bolm, C. *Adv. Synth. Catal.* **2013**, *355*, 2558.

(10) (a) Dumas, J.; Brittelli, D.; Chen, J.; Dixon, B.; Hatoum-Mokdad, H.; König, G.; Sibley, R.; Witowsky, J.; Wong, S. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2531. (b) Kočí, J.; Klimešová, V.; Waisser, K.; Kaustová, J.; Dahse, H.-M.; Möllmann, U. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3275. (c) Huang, W.; Yang, G.-F. *Bioorg. Med. Chem.* **2006**, *14*, 8280. (d) Shanmugapriya, J.; Rajaguru, K.; Muthusubramanian, S.; Bhuvanesh, N. *Eur. J. Org. Chem.* **2016**, *2016*, 1963.

(11) (a) Song, S.; Huang, X.; Liang, Y.-F.; Tang, C.; Li, X.; Jiao, N. *Green Chem.* **2015**, *17*, 2727. (b) Song, S.; Li, X.; Sun, X.; Yuan, Y.; Jiao, N. *Green Chem.* **2015**, *17*, 3285. (c) Xu, Y.; Tang, X.; Hu, W.; Wu, W.; Jiang, H. *Green Chem.* **2014**, *16*, 3720. (d) Ge, W.; Wei, Y. *Green Chem.* **2012**, *14*, 2066. (e) Saba, S.; Rafique, J.; Braga, A. L. *Catal. Sci. Technol.* **2016**, *6*, 3087. (f) Rafique, J.; Saba, S.; Rosário, A. R.; Braga, A. L. *Chem. - Eur. J.* **2016**, *22*, 11854. (g) Song, S.; Sun, X.; Li, X.; Yuan, Y.; Jiao, N. *Org. Lett.* **2015**, *17*, 2886. (h) Siddaraju, Y.; Prabhu, K. R. *J. Org. Chem.* **2016**, *81*, 7838.

(12) (a) Siddaraju, Y.; Lamani, M.; Prabhu, K. R. *J. Org. Chem.* **2014**, *79*, 3856. (b) Siddaraju, Y.; Prabhu, K. R. *Org. Biomol. Chem.* **2015**, *13*, 6749. (c) Siddaraju, Y.; Prabhu, K. R. *Org. Biomol. Chem.* **2015**, *13*, 11651. (d) Varun, B. V.; Gadde, K.; Prabhu, K. R. *Org. Lett.* **2015**, *17*, 2944. (e) Varun, B. V.; Prabhu, K. R. *J. Org. Chem.* **2014**, *79*, 9655.

(13) (a) Nielsen, M.; Jacobsen, C. B.; Paixão, M. W.; Holub, N.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2009**, *131*, 10581. (b) Wang, Q.-G.; Zhou, Q.-Q.; Deng, J.-G.; Chen, Y.-C. *Org. Lett.* **2013**, *15*, 4786. (c) Kumar, A.; Sharma, S.; Tripathi, V. D.; Srivastava, S. *Tetrahedron* **2010**, *66*, 9445. (d) Chai, H.; Guo, R.; Yin, W.; Cheng, L.; Liu, R.; Chu, C. *ACS Comb. Sci.* **2015**, *17*, 147. (e) Billard, F.; Robiette, R.; Pospíšil, J. *J. Org. Chem.* **2012**, *77*, 6358.

(14) Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062 and references cited therein.

(15) The reaction with propiophenone derivatives led to a minor amount of α-hydroxylation along with α-sulfenylation whereas no side products were observed with acetophenone derivatives.

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