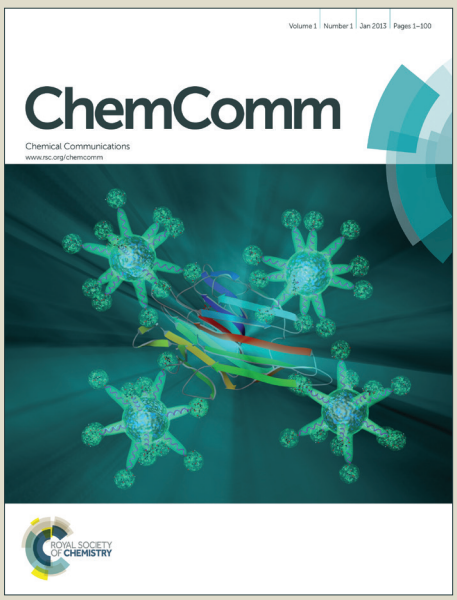
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ChemComm

COMMUNICATION

Transition Metal-free Aroylation of *NH*-Sulfoximines with Methyl Arenes

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

DOI: 10.1039/x0xx00000x

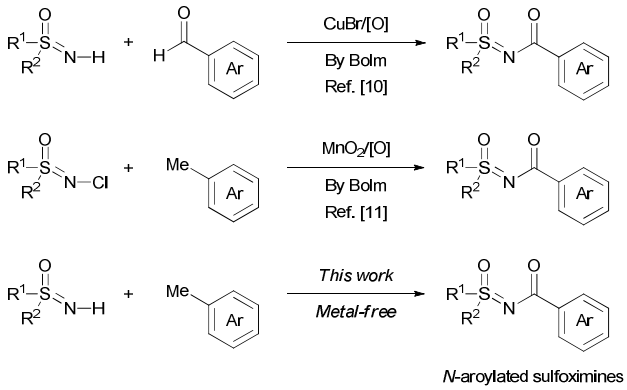
www.rsc.org/chemcomm

Ya Zou,[†] Jing Xiao,[†] Zhihong Peng[†] Wanrong Dong[†,]*and Delie An[†,]*

A novel protocol towards *N*-aroylated sulfoximines from *NH*-sulfoximines and methyl arenes was herein demonstrated. The reaction took place in the presence of elemental iodine, requiring for no external organic solvents, transition metal-catalysts or ligands. The aroylated products were obtained from the oxidative transformation in moderate to excellent yields (up to 94% yields) with a broad substrate scope (up to 35 examples) through a radical pathway.

Recently, sulfoximine chemistry has attracted more and more attention due to the extensive utilizations in the pharmaceutical and agricultural applications,[1] as well as for being chiral precursors or ligands in asymmetric synthesis.[2] What's more, sulfoximines also served as pivotal intermediates for the construction of other heterocyclic compounds.[3] *NH*-sulfoximines undertook various transformations such as arylation,[4] alkylation,[5] vinylation,[6] alkynylation[7] *etc al*.[8] easily due to the fickleness of the *NH* group. Amongst, aroylation of *NH*-sulfoximines has been well-established with benzoyl chlorides, aromatic carboxylic acids.[9] However, the traditional methods for the *N*-aroylated sulfoximines still suffer from the limitations like toxic reagents, harsh conditions and low conversions. To solve the above-mentioned issues, great attempt has been devoted over the topic. For example, Bolm has disclosed a copper(I)-catalyzed *N*-aroylation method from *NH*-sulfoximines and benzaldehydes under the oxidative conditions through a dual C-H/N-H activations pathway.[10] Then, another aroylation protocol of *N*-chloro sulfoximines with methyl arenes was described from the same group, using MnO_2 as the catalyst.[11] Meanwhile, it is noteworthy that methyl arenes have been applied successfully for the formation of carbon-heteroatom bonds through the C-H activation and successive oxidative functionalization pathway.[12] The metallic catalysts like Pd, Cu and Mn salts were proved necessary to the transformations.[12] However, to rule out the transition metal-catalysts, contributions have been made to seek the possibilities for utilization of methyl arenes as aroylation coupling partners towards *N*-aroylated sulfoximines in the presence of non-metal-catalysts. Thus, we wish to demonstrate a novel protocol for the combination of the two nucleophilic reagents catalysed by elemental iodine howbeit the inertness of the benzylic C(sp^3)-H bonds on methyl arenes.[13]

Scheme 1 *N*-Aroylation of Sulfoximines

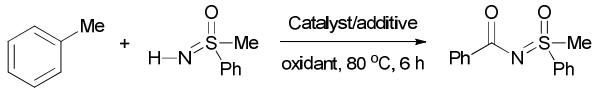


With this in mind, reactions were embarked for the optimal conditions with toluene (**1a**) and *NH*-sulfoximine (**2a**) as model substrates (Table 1). In the presence of a catalytic amount of I_2 (20 mol%) and *tert*-butyl hydroperoxide (TBHP), *N*-benzoyl sulfoximine **3aa** was obtained in moderate yield (58% for entry 1). Disappointingly, other oxidants like DTBP (Di-*tert*-butyl peroxide), oxone, $K_2S_2O_8$ and H_2O_2 were proved totally ineffective to the transformation for no product was detected after 6 h (entries 2 - 5). However, the participation of the oxidant TBHP was significant to the reaction. The yield decreased dramatically to 28% when the reaction took place in the absence of TBHP (entry 6). Surprisingly, the addition of Na_2CO_3 (50 mol%) improved the yield greatly up to 91% under the air atmosphere, and **3aa** was obtained in 89% yield when the reaction was conducted under the nitrogen atmosphere (entry 7). However, no reaction was detected by replacement of Na_2CO_3 with triethyl amine (TEA) (entry 8). Other iodine sources,

[†] *State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China.*
Email-Address for the correspondence authors: wanrongdong@hnu.edu.cn, deliean@hnu.edu.cn.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

which were able to offer elemental iodine when combined with external oxidant,[13] were also checked. Pleasingly, KI, *t*Bu_4NI and NIS afforded the desired product **3aa** successfully, but in lower yields, from 38% to 68% (entries 9 – 11).

Table 1 Selected results for optimization of conditions[a]



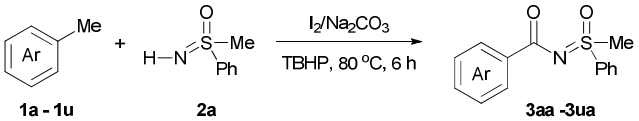
1a **2a** **3aa**

Entry	catalysts	additives	oxidants	Yields (%)[b]
1	I_2	--	TBHP	58
2	I_2	--	DTBP	n.d.[c]
3	I_2	--	oxone	n.d.
4	I_2	--	$K_2S_2O_8$	n.d.
5	I_2	--	H_2O_2	n.d.
6	I_2	--	--	28[d]
7	I_2	Na_2CO_3	TBHP	91 (89[e])
8	I_2	Et_3N	TBHP	n.d.
9	KI	Na_2CO_3	TBHP	42
10	*n*Bu_4NI	Na_2CO_3	TBHP	n.d. (38[f])
11	NIS	Na_2CO_3	TBHP	68

[a] Reaction conditions: **1a** (6 mmol, 20 equiv.), **2a** (0.3 mmol), catalyst (0.06 mmol, 20 mol%), additive (0.15 mmol, 50 mol%), oxidant (1.2 mmol, 4.0 equiv.) at 80 °C for 6 h. [b] Isolated yields. [c] n.d. for not detected. [d] I_2 (0.3 mmol) was used instead of I_2 (0.06 mmol)/TBHP (0.6 mmol). [e] N_2 (1 atm) atmosphere was used instead of air (1 atm). [f] The yield was obtained in the absence of Na_2CO_3.

With the optimal conditions in hand, the limitations and scope of the substrates were evaluated (Table 2). Firstly, the functional groups on the *para*- position of the methyl arenes were tested. Both electron-donating and electron-withdrawing functional groups were well-tolerated in the system. For example, 4-methyl- (**1b**), 4-*n*-butyl- (**1c**) and 4-methoxy- (**1d**) toluenes exhibited negative effect to the reaction for the desired products **3ba** – **3da** were obtained in lower yields, 79%, 81% and 82%, respectively (entries 2 – 4). While 4-fluoro- (**1e**), 4-chloro- (**1f**), 4-bromo- (**1g**) and 4-iodo- (**1h**) toluenes reacted with **2a** smoothly, furnishing the desired products **3ea** – **3ha** in yields ranging from 68% to 94% (entries 5 – 8). Other electron-withdrawing groups as ester (**1i**), cyano (**1j**), trifluoromethyl (**1k**) and nitro (**1l**) on the *para*- positions of the substrates were surprisingly compatible in the transformation, producing the expected compounds **3ia** – **3la** in 58% to 89% yields (entries 9 – 12). In a similar manner, various functional groups on the *meta*- position of toluenes were also checked in the protocol. *N*-(3-methylbenzoyl) sulfoximine (**3ma**), *N*-(3-fluorobenzoyl) sulfoximine (**3na**), *N*-(3-chlorobenzoyl) sulfoximine (**3oa**), *N*-(3-bromobenzoyl) sulfoximine (**3pa**), *N*-(3-iodobenzoyl) sulfoximine (**3qa**) and *N*-(3-nitrobenzoyl) sulfoximine (**3ra**) were successfully obtained, however, generally in lower yields, ranging from 59% to 80% (entries 13 -18). But *N*-(3,5-dimethylbenzoyl) sulfoximine (**3sa**) was smoothly produced in good yield (91% for entry 19). When 1,2-dimethylbenzene (**1t**) reacted with *NH*-sulfoximine (**2a**), offering the *N*-(2-methylbenzoyl) sulfoximine **3ta** in a moderate yield probably due to the steric hindrance (entry 20). It is noteworthy that 2-methyl naphthalene (**1u**) reacted with *NH*-sulfoximine (**2a**) towards the corresponding product **3ua** in 85% yield (entry 21). Howbeit, methyl-(hetero)arenes **1v** – **1x** failed to react with *NH*-sulfoximine **2a** (entries 22 – 24) for unclarified reasons.

Table 2 Evaluation of scope of methylarenes[a]



1a - 1u **2a** **3aa -3ua**

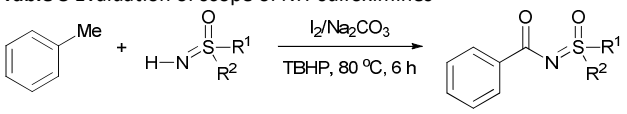
Entry	Ar	**3**	Yield (%)[b]
1	Ph	**3aa**	91
2	4-$CH_3C_6H_4$	**3ba**	79
3	4-*t*BuC_6H_4	**3ca**	81
4	4-$MeOC_6H_4$	**3da**	82
5	4-FC_6H_4	**3ea**	74
6	4-ClC_6H_4	**3fa**	94
7	4-BrC_6H_4	**3ga**	88
8	4-IC_6H_4	**3ha**	68
9	4-MeO(O)CC_6H_4	**3ia**	86
10	4-NCC_6H_4	**3ja**	87
11	4-$CF_3C_6H_4$	**3ka**	58
12	4-$NO_2C_6H_4$	**3la**	69
13	3-MeC_6H_4	**3ma**	80
14	3-FC_6H_4	**3na**	63
15	3-ClC_6H_4	**3oa**	68
16	3-BrC_6H_4	**3pa**	68
17	3-IC_6H_4	**3qa**	60
18	3-$NO_2C_6H_4$	**3ra**	59
19	3,5-$Me_2C_6H_3$	**3sa**	91
20	2-MeC_6H_4	**3ta**	58
21	2-Naphthyl	**3ua**	85
22	2-Furyl	**3va**	n.d.[c]
23	2-Thienyl	**3wa**	n.d.[c]
24	2-Pyridinyl	**3xa**	n.d.[c]

Note: [a] Reaction conditions: **1** (10 mmol, 20 equiv.), **2a** (0.5 mmol), I_2 (0.1 mmol), Na_2CO_3 (0.25 mmol), TBHP (2.0 mmol) at 80 °C for 6 h. [b] Isolated yields. [c] n.d. for not detected.

In the same manner, the limitations and scope of the substrates on *NH*-sulfoximines were checked in the reaction (Table 3). *S*-methyl-*S*-(4-methylphenyl)- (**2b**) and *S*-methyl-*S*-(4-methoxyphenyl)- (**2c**) *NH*-sulfoximines underwent the aroylation reaction with toluene (**1a**) smoothly, furnishing the corresponding products **3ab** and **3ac** in 85% and 89% yields, respectively (entries 1 and 2). Gratifyingly, *S*-methyl-*S*-halophenyl *NH*-sulfoximines such as *S*-methyl-*S*-(4-fluorophenyl)- (**2d**), *S*-methyl-*S*-(4-chlorophenyl)- (**2e**), *S*-methyl-*S*-(4-bromophenyl)- (**2f**) *NH*-sulfoximines reacted with toluene (**1a**) successfully, offering the desired products **3ad** – **3af** in moderate to good yields, from 67% to 82% (entries 3 - 5). Meantime, the activities of *S*-(3-substituted phenyl) or *S*-(2-substituted phenyl) like *S*-methyl-*S*-(3-methylphenyl)- (**2g**), *S*-methyl-*S*-(2-methylphenyl)- (**2h**) and *S*-methyl-*S*-(2-chlorophenyl)- (**2i**) *NH*-sulfoximines were transformed into the corresponding compounds **3ag** – **3ai** in yields ranging from 69% to 84% (entries 6 – 8). In contrast, hetero-

aromatic bearing *NH*-sulfoximine such as *S*-pyridinyl-*S*-methyl *NH*-sulfoximine (**2j**) furnished the corresponding *N*-benzoyl-*S*-pyridinyl-*S*-methyl sulfoximine (**3aj**) in a medium yield under the optimal conditions (62% for entry 9). Moreover, *S*-ethyl-*S*-phenyl (**2k**), *S*-isopropyl-*S*-phenyl (**2l**), *S*,*S*-diphenyl (**2m**) *NH*-sulfoximines exhibited good compatibility in the approach, affording the *N*-aroylated products **3ak** – **3am** in 78% to 92% yields (entries 10 - 12). Similarly, *N*-benzoyl-*S*,*S*-dimethyl sulfoximine (**3an**) and *N*-benzoyl-*S*,*S*-tetramethylene sulfoximine (**3ao**) were successfully produced in 78% and 80% yields, respectively (entries 13 and 14).

Table 3 Evaluation of scope of *NH*-sulfoximines[a]



1a **2b - 2o** **3ab - 3ao**

Entry	R^1	R^2	**3**	Yield (%)[b]
1	4-$CH_3C_6H_4$	Me	**3ab**	85
2	4-$CH_3OC_6H_4$	Me	**3ac**	89
3	4-FC_6H_4	Me	**3ad**	67
4	4-ClC_6H_4	Me	**3ae**	78
5	4-BrC_6H_4	Me	**3af**	82
6	3-$CH_3C_6H_4$	Me	**3ag**	84
7	2-$CH_3C_6H_4$	Me	**3ah**	79
8	2-ClC_6H_4	Me	**3ai**	69
9	Pyridinyl	Me	**3aj**	62
10	Ph	Et	**3ak**	78
11	Ph	*i*-Pr	**3al**	88
12	Ph	Ph	**3am**	92
13	Me	Me	**3an**	78
14	—$(CH_2)_4$—	(R^1R^2)	**3ao**	80

Note: [a] Reaction conditions: **1a** (10 mmol, 20 equiv.), **2** (0.5 mmol), I_2 (0.1 mmol), Na_2CO_3 (0.25 mmol), TBHP (2.0 mmol) at 80 °C for 6 h. [b] Isolated yields.

Nevertheless, the mechanism of the newly developed aroylation protocol remained blurry. According to the report from Bolm[10], it was considered the reaction might take place *via* the acyl-radical intermediate. Therefore, control reactions were conducted for clarification (Figure 1). When benzaldehyde was applied as the aroylation reagent, **3aa** was obtained in 62% yield from the iodine-catalysed protocol.

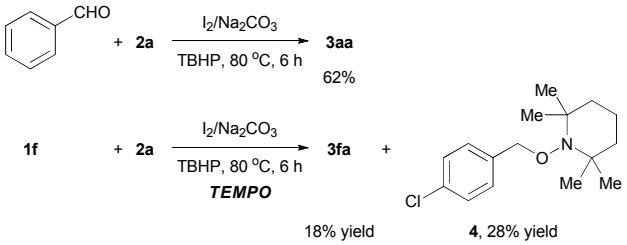


Figure 1 Control reactions with benzaldehyde and addition of TEMPO

However, with the addition of the radical scavenger TEMPO (2,2,6,6-tetramethylpiperidinooxy) into the reaction between **1f** and **2a**, the yield of **3fa** decreased sharply to 18%, and benzyl-TEMPO adduct **4** other than the acyl-TEMPO adduct was successfully isolated in 28% yield.[14] The result proved that the reaction likely took place *via* a benzyl radical intermediate.

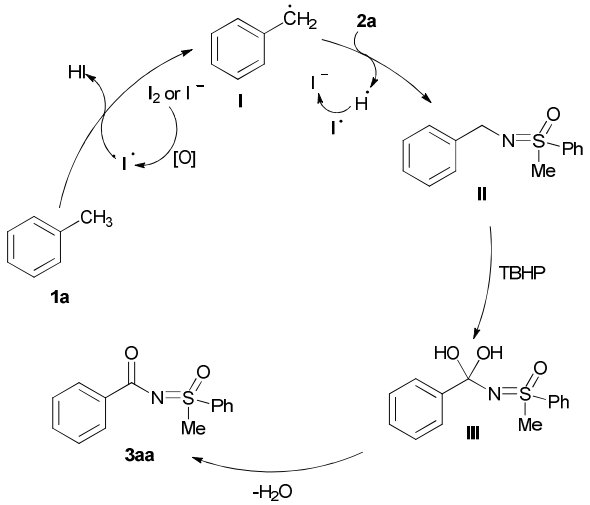
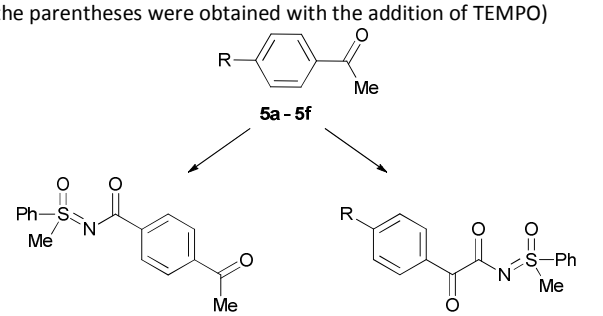


Figure 2 Proposed mechanism

Thus, possible mechanism of the transition metal-free protocol was proposed as shown in Figure 2. Firstly, iodine radical particle was generated from elemental iodine with the assistance of the oxidant TBHP. Then, another key radical intermediate **I** was formed in the presence of *in-situ* generated iodine radical, releasing a molecular of HI. Successively, the newly-formed intermediate **I** coupled with the substrate **2a** with a release of an H radical, forming another key intermediate *N*-benzyl sulfoximine **II**. The H radical was captured by another iodine radical to form a HI, which was easily neutralized with Na_2CO_3. Meanwhile, the newly-generated intermediate **II** underwent another fast oxidation step to furnish a diol intermediate **III** in the presence of TBHP, which afforded the desired product **3aa** after dehydration.

Scheme 2 Reactions between acetopheones **5** and **2a** (The yields in the parentheses were obtained with the addition of TEMPO)



6b: R = H, 43%; **6c**: R = MeO, 46%; **6d**: R = F, 45%; **6e**: R = Cl, 55%; **6f**: R = Br, 52%; **6g**: R = NO_2, 41%.

It is noteworthy that 4-methyl acetopheone (**5a**) reacted with *NH*-sulfoximine **2a** under the metal-free conditions smoothly (scheme

2). Different products **3ya**, **6a** were isolated successfully, in 38% and 42% yields, respectively. The product **3ya** was formed by the radical procedure, while the compound **6a** was generated through a C-H/N-H dual activations pathway.[15] As expected, with the addition of TEMPO, the yield of **3ya** was depressed significantly and only trace was isolated while the yield of the product **6a** arose to 48% (shown in the parentheses). Furthermore, the compatibilities of the substituents on the acetophenone were checked in the system, and the corresponding *N*-(2-oxo-2-arylacetyl)-sulfoximines **6b** – **6g** were furnished in yields ranging from 41% - 55% as shown in scheme 2.

Conclusions

In summary, a new protocol towards *N*-aroylated sulfoximines from methyl arenes and *NH*-sulfoximines was disclosed. The simple and benign method feathers for free of transition metal -catalysts, and no extra organic solvents are required. The transformation offers a practical and facile synthetic tool for the useful compounds.

Acknowledgement

The authors are grateful for the financial support from the National Natural Science Foundation of China (NSFC) (grant number 21072052), the National Basic Research Program of China (grant number 2009CB421601), and the Hunan Provincial Science and Technology Department Program (grant number 2011WK4007, 06FJ4115) and The Fundamental Research Funds for the Central Universities, Hunan University (grant number 531107040840).

References

1 For selected reviews, see a) C. R. Johnson, *Acc. Chem. Res.,* 1973, **6**, 341; b) M. Reggelin and C. Zur, *Synthesis,* **2000**, 1; c) U. Lucking, *Angew. Chem. Int. Ed.,* 2013, **52**, 9399; d) V. Bizet, R. Kowalczyk and C. Bolm, *Chem. Soc. Rev.,* 2014, **43**, 2426; for selected papers, see d) Y. Zhu, M. R. Loso, G. B. Watson, T. C. Sparks, R. B. Rogers, J. X. Huang, B. C. Gerwick, J. M. Babcock, D. Kelley, V. B. Hegde, B. M. Nugent, J. M. Renga, I. Denholm, K. Gorman, G. J. DeBoer, J. Hasler, T. Meade, J. D. Thomas, *J. Agric. Food Chem.,* 2011, **59**, 2950; e) S. J. Park, H. Buschmann, C. Bolm, *Bioorg. Med. Chem. Lett.,* 2011, **21**, 4888; f) X. Y. Chen, S. J. Park, H. Buschmann, M. De Rosa, C. Bolm, *Bioorg. Med. Chem. Lett.,* 2012, **22**, 4307; g) S. J. Park, H. Baars, S. Mersmann, H. Buschmann, J. M. Baron, P. M. Amann, K. Czaja, H. Hollert, K. Bluhm, R. Redelstein, C. Bolm, *ChemMedChem,* 2013, **8**, 217.

2 For book chapter, see a) C. Worch, A. C. Mayer, C. Bolm, in: *Organosulfur Chemistry in Asymmetric Synthesis* (Eds.: T. Toru, C. Bolm), Wiley-VCH, Weinheim, Germany, **2008**, pp 209–232; for selected reviews, see b) H. Okamura and C. Bolm, *Chem. Lett.,* 2004, **33**, 482; c) H.-J. Gais, *Heteroat. Chem.,* 2007, **18**, 472; for selected papers, see d) M. Frings, I. Atodiresei, Y. Wang, J. Runsink, G. Raabe, C. Bolm, *Chem. Eur. J.,* 2010, **16**, 4577; e) M. Frings, D. Goedert, C. Bolm, *Chem. Commun.,* 2010, **46**, 5497; f) E. B. Benetskiy, C. Bolm, *Tetrahedron: Asymmetry,* 2011, **22**, 373.

3 a) M. Harmata and S. K. Ghosh, *Org. Lett.,* 2001, **3**, 3321; b) M. Harmata and X. Hong, *Org. Lett.*, 2005, **7**, 3581; c) M. Harmata, N. L. Calkins, R. G. Banghman and C. L. Barnes, *J. Org. Chem*., 2006, **71**, 3650; d)M. Harmata and X. Hong, *J. Am. Chem. Soc*., 2003, **125**, 5754; e) W. Dong, L. Wang, K. Parthasarathy, F. Pan and C. Bolm, *Angew. Chem. Int. Ed.* 2013, **52**, 11573; f) W. Dong, K. Parthasarathy, Y. Cheng, F. Pan and C. Bolm, *Chem. Eur. J.* , 2014, **20**, 15732; g) D. G. Yu, F. de Azambuja and F. Glorius, *Angew. Chem. Int. Ed.*, 2014, **53**, 2754.

4 a) C. Bolm and J. P. Hildebrand, *Tetrahedron Lett.*, 1998, **39**, 5731; b) C. Bolm and J. P. Hildebrand, *J. Org. Chem.*, 2000, **65**, 169; c) J. Sedelmeier and C. Bolm, *J. Org. Chem.*, 2005, **70**, 6904; d) G. Y. Cho, P. Remy, J. Jansson, C. Moessner and C. Bolm, *Org. Lett.*, 2004, **6**, 3293; e) J. Sedelmeier and C. Bolm, *J. Org. Chem.*, 2005, **70**, 6904; f) C. Moessner and C. Bolm, *Org. Lett.*, 2005, **7**, 2667; g) M. Harmata, X. Hong and S. K. Ghosh, *Tetrahedron Lett.*, 2004, **45**, 5233; h) N. Yongpruksa, N. L. Calkins and M. Harmata, *Chem. Commun.*, 2011, **47**, 7665; i) M. Miyasaka, K. Hirano, T. Satoh, R. Kowalczyk, C. Bolm and M. Miura, *Org. Lett.*, 2011, **13**, 359; j) L. Wang, D. L. Priebbenow, W. Dong and C. Bolm, *Org. Lett*., 2014, **16**, 2661.

5 a) C. R. Johnson and O. M. Lavergne, *J. Org. Chem.*, 1993, **58**, 1922; b) Y. Cheng, W. Dong, L. Wang, K. Parthasarathy and C. Bolm, *Org. Lett.*, 2014, **16**, 2000 and references therein; c) C. M. M. Hendriks, R. A. Bohmann, M. Bohlem and C. Bolm, *Adv. Synth. Catal.*, 2014, **356**, 1847.

6 J. R. Dehli and C. Bolm, *J. Org. Chem.*, 2004, **69**, 8518 and references therein.

7 a) L. Wang, H. Huang, D. L. Priebbenow, F. F. Pan and C. Bolm, *Angew. Chem. Int. Ed.*, 2013, **52**, 3478; b) D. L. Priebbenow, P. Becker and C. Bolm, *Org. Lett.*, 2013, **15**, 6155; c) X. Y. Chen, L. Wang, M. Frings and C. Bolm, *Org. Lett.* , 2014, **16**, 3796.

8 a) Rit, R. K.; Yadav, M. R.; Sahoo, A. K. *Org. Lett.* **2012**, *14*, 3724; b) Yadav, M. R.; Rit, R. K.; Sahoo, A. K. *Org. Lett.* **2013**, *15*, 1638; c) Yadav, M. R.; Rit, R. K.; Shankar, M.; Sahoo, A. K. *J. Org. Chem.* **2014**, *79*, 6123; d) Rit, R. K.; Yadav, M. R.; Ghosh, K.; Shankar, M.; Sahoo, A. K. *Org. Lett.* **2014**, *16*, 5258; e) F. Teng, J. Cheng and C. Bolm, *Org. Lett.*, 2015, **17**, 3166 and references therein; f) C. Bohnen and C. Bolm, *Org. Lett.*, 2015, **17**, 3011 and references therein; g) Chen, X. Y.; Bohmann, R. A.; Wang, L.; Dong, S.; Rauber, C.; Bolm, C. *Chem. Eur. J.* **2015**, *21*, 10330 and references therein.

9 a) G. Y. Cho and C. Bolm, *Org. Lett.*, 2005, **7**, 1351; b) M. R. Yadav, R. K. Rit and A. K. Sahoo, *Chem. Eur. J.*, 2012, **18**, 5541; c) M. R. Yadav, M. Shankar, E. Ramesh, K. Ghosh and A. K. Sahoo, *Org. Lett.*, 2015, **17**, 1886.

10 L. Wang, D. L. Priebbenow, L.-H. Zou and C. Bolm, *Adv. Synth. Catal.*, 2013, **355**, 1490.

11 D. L. Priebbenow and C. Bolm, *Org. Lett.*, 2014, **16**, 1650.

12 a) W. Zhou, L. Zhang and N. Jiao, *Angew. Chem. Int. Ed.*, 2009, **48**, 7094; b) S. K. Rout, S. Guin, K. K. Ghara, A. Banerjee and B. K. Patel, *Org. Lett.*, 2012, **14**, 3982; c) Y. Wang, K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2012, **51**, 7250; d) S. Guin, S. K. Rout, A. Banerjee, S. Nandi and B. K. Patel, *Org. Lett.*, 2012, **14**, 5294; e) T. Wang, L. Yuan, Z. Zhao, A. Shao, M. Gao, Y. Huang, F. Xiong, H. Zhang and J. Zhao, *Green Chemistry*, 2015, **17**, 2741; f) H. Xie, Y. Liao, S. Chen, Y. Chen and G.-J. Deng, *Org. Biomol. Chem.*, 2015, **13**, 6944.

13 K. Azizi, M. Karimi and A. Heydari, *RSC Advances*, 2014, **4**, 31817.

14 J. Xu, P. Zhang, X. Li, Y. Gao, J. Wu, G. Tang and Y. Zhao, *Adv. Synth. Catal.*, 2014, **356**, 3331.

15 Zou, Y.; Peng, Z.; Dong, W.; An, D. *Eur. J. Org. Chem.* **2015**, *2015*, 4913.

