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Metal-free amidation of ether sp³ C–H bonds with sulfonamides using PhI(OAc)₂ \dagger

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A selective protocol for the metal-free α -C–H amidation of ethers using sulfonamides and hypervalent iodine oxidants has been developed. The absence of precious metals and the conditions employed make the method environmentally attractive. A number of cyclic and acyclic, linear and branched ethers have been successfully amidated, and a broad sulfonamide scope has been demonstrated. Two unusual reactions, namely the amidation of an unactivated *tert*-butyl group and a tandem C–C coupling reaction, are also described.

Introduction

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Direct amidation of sp³ C–H bonds remains an important and challenging task with applications ranging from production of valuable organic targets to enhancing the utility of readily available but inert aliphatic substrates. The classical strategy for these atom-economical transformations involves transition metal catalysts that are able to mediate nitrene insertion into C–H bonds.^{1–11} The many pharmaceutical applications for oxidative coupling of C–H and N–H bonds require rigorous removal of trace amounts of these catalysts, which are often based on toxic and expensive precious metals. Eliminating the need for the metal catalysts is thus desirable from a standpoint of simplification and economy.^{12–14}

A variety of amine and oxidant combinations have been used for metal-free amination, amidation and imidation of C–H bonds. The oxidants in these systems include peroxides (*tert*butyl hydroperoxide,^{15–18} di-*tert*-butyl peroxide,¹⁹ H₂O₂²⁰, benzoquinones,²¹ chloramine-T,²² and hypervalent halogen species.^{23–35} Additional organic catalysts (*e.g.*, I₂ ^{15,24,29} and *n*-Bu₄NI)^{17,18} and stoichiometric additives (*e.g.*, I₂, ^{16,22,35–37} *N*-iodosuccinimide,^{16,20} ^{*n*}Bu₄NI,¹⁶ KI,^{16,28} TsOH¹⁹ and AcOH^{15,20}) are often involved and perform various functions. Hypervalent iodine species, particularly iodosobenzene derivatives such as PhI(OAc)₂, are prevalent in both metal-catalyzed and metal-free processes for C–H amidation.^{1–10,23–32,35} Owing to their high oxidation potential, these species are documented to activate

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While a majority of the metal-free processes for C-H amidation and amination have been applied to oxidative coupling of N-H bonds to sp and sp² C-H bonds of unsaturated alkynes,³⁸ arenes,^{23,35,37,39,40} alkenes,^{25-27,41} and azoles,^{20,31,32,42,43} several examples of sp³ C-H amidation of benzylic^{16-19,22-24,41} and allylic^{18,21,30} bonds have also been reported. In addition, Muñiz and coworkers described the amidation of an α-methyl group of a ketone.²⁵ Metal-free amidation is rare for sp³ C-H bonds unactivated by adjacent double bonds. The I2-catalyzed oxidative coupling of purines with tetrahydrofuran (THF) oxidized by PhI(OAc)₂ is known,²⁹ and a similar system utilizing PhI(OAc)₂ as oxidant but involving stoichiometric I₂ has been reported for intramolecular amidation of alkyl sulfonamides.36 Most prominently, Ochiai and coworkers discovered a highly active hypervalent bromine reagent, p-(CF₃)(Ph)BrNTf (Tf = CF₃SO₂), for α -C-H amidation of alkyl ethers (eqn (1))³⁴ and also, in a striking example, for regioselective amidation of unfunctionalized alkanes.33





Scheme 1 In situ formation of an iminoiodinane from a hypervalent iodine oxidant.

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The present work began with an initial finding that reaction of 2,2,2-trichloroethoxysulfonamide in neat THF in the presence of $PhI(OAc)_2$ selectively produces the α -C-H amidation product (eqn (2)). The simple sulfonamide/PhI(OAc)₂ system offers some advantages over the specialized p-(CF₃)(Ph)BrNTf reagent reported for amidation of alkyl ethers with sulfonamides.34 The air- and moisture-stable and commercially available PhI(OAc)₂ is more convenient than p-(CF₃)(Ph)BrNTf, which must be handled under inert atmosphere and whose twostep synthesis involves BrF₃ and liberates HF.^{41,44} Additionally, extending the reaction scope to new sulfonamides while using preformed reagents is limited by the necessity to synthesize a different reagent for each case. In this work, we sought to explore the potentially broader amide substrate scope offered for direct α -C-H amidation of alkyl ethers using the simple sulfonamide/PhI(OAc)₂ system.



Results and discussion

We first optimized the experimental conditions for the α -CH amidation of THF using PhI(OAc)₂/2,2,2-trichloroethoxysulfonamide (**1a**) (Table 1). Although amidation takes place even at room temperature (entry 1), mild heating (60 °C, entry 4) leads to faster

reactions and near-quantitative conversion of the sulfonamide to the functionalized compound 2a. The first step in our screening was to test different oxidants. Whereas the hypervalent iodine oxidants PhI(OAc)₂ and PhI(OPiv)₂ (OPiv = pivalate) worked equally well and led to almost quantitative formation of 2a (entry 6), the fluorinated $PhI(TFA)_2$ (TFA = trifluoroacetate) yielded poor results (entry 7). We focused on PhI(OAc)₂ due to its lower price and higher stability compared to its pivalate analogue. Although chloramine-T has been shown to be an excellent nitrene source for the α -CH amidation of ethers using a copper catalyst,45 product formation was barely detected under our metal-free conditions (entry 8). Acetoxylation of activated C-H bonds has been previously identified as an undesired side reaction in the amidation of C-H bonds using PhI(OR)₂/sulfonamide systems.^{24,46} With the aim of avoiding this deleterious pathway and, at the same time, looking for cheaper and greener alternatives,47,48 we tested a series of iodine-containing salts^{49,50} (entries 9-12), although with unsuccessful results. In addition, the same product selectivity was achieved using this method in several common organic solvents but with diminished reaction rates (entries 13-16).

In terms of the sulfonamide scope, we obtained excellent yields with both aromatic and aliphatic sulfonamides (Table 2). This constitutes an important benefit compared to the previous metal-free amidation of ethers reported by Ochiai, which, despite its excellent activity, was limited to the highly reactive p-(CF₃)(Ph)BrNTf reagent.³⁴ In our system, α -CH amidation of THF takes place with excellent yields for substituted and unsubstituted aromatic sulfonamides (entries 1–5), although no conversion was detected in the case of the –OMe and –NH₂



Entry	Oxidant	Solvent	T (°C)	<i>t</i> (h)	$\operatorname{Yield}^{b}(\%)$
1	$PhI(OAc)_2$	Neat	25	10	53
2	$PhI(OAc)_2^c$	Neat	60	2	77
3	$PhI(OAc)_2^d$	Neat	60	2	89
4	$PhI(OAc)_2$	Neat	60	2	91
5	$PhI(OAc)_2^e$	Neat	60	2	94
6	$PhI(OPiv)_2$	Neat	60	2	93
7	PhI(TFA) ₂	Neat	60	2	23
8	Chloramine-T ^f	Neat	60	2	3^g
9	NH_4IO_3	Neat	60	2	<1
10	KIO ₃	Neat	60	2	<1
11	KIO ₄	Neat	60	2	<1
12	$^{n}\mathrm{Bu}_{4}\mathrm{NIO}_{4}$	Neat	60	2	<1
13	$PhI(OAc)_2$	DCE/THF(1:1)	60	4	71
14	$PhI(OAc)_2$	MeCN/THF(1:1)	60	4	83
15	$PhI(OAc)_2$	Toluene/THF (1:1)	60	4	42
16	$PhI(OAc)_2$	Cyclohexane/THF (1:1)	60	4	56

^{*a*} Conditions: **1a** (0.2 mmol, 46 mg), oxidant (0.4 mmol, 2 equiv.), THF or mixed solvent (2 mL), reactions carried out under N₂ atmosphere. ^{*b*} Yields determined by ¹H NMR spectroscopy using trimethoxybenzene as internal standard. ^{*c*} 1 Equiv. of PhI(OAc)₂. ^{*d*} 1.5 Equiv. of PhI(OAc)₂. ^{*e*} 3 Equiv. of PhI(OAc)₂. ^{*f*} Chloramine-T was used instead of the pair **1a**/PhI(OAc)₂. ^{*g*} The -NTs adduct was detected in this case.

Table 2 Sulfonamide scope on the α -CH amidation of THF^a



^{*a*} Conditions: **1b–k** (0.2 mmol), oxidant (0.3 mmol, 1.5 equiv.), neat THF (2 mL), 60 $^{\circ}$ C, 2 h, reactions carried out under N₂ atmosphere. ^{*b*} Yields were determined by ¹H NMR spectroscopy using trimethoxybenzene as internal standard.

derivatives (entries 6 and 7). Aliphatic sulfonamides also gave excellent conversions and high selectivity for the α -CH position (entries 8–10). The broad sulfonamide scope exhibited by our method is especially significant considering the useful biological and pharmacological properties of molecules based on the *N*-(methoxoalkyl)sulfonamide framework.^{51–54}

The new functionalized THF compounds **2a–k** were characterized by ¹H and ¹³C{¹H} NMR spectroscopy as well as highresolution mass spectrometry (see ESI†). A characteristic ¹H NMR resonance in the range from 5.20 to 5.42 ppm is assigned to the O–CH–NH proton and is common to all compounds **2a–k**; the corresponding ¹³C{¹H} signal appears at *ca.* 85 ppm. The molecular structures of two of these species (**2a** and **2d**) were further confirmed by X-ray diffraction studies (Fig. 1). Their C–N bond distances are identical within the experimental error, with values of 1.472(8) Å and 1.470(4) Å for **2a** and **2d**, respectively, which are consistent with single bond character. Different rotameric orientations of the THF ring are present in each structure, likely due to packing forces.



Fig. 1 ORTEPs of compounds 2a and 2d. 50% Thermal ellipsoids are shown. Most hydrogen atoms have been omitted for clarity.

Under our optimized conditions (60 °C, 2 h, 1.5-2 equiv. PhI(OAc)₂), a series of aliphatic and aromatic, cyclic and acyclic ethers were tested as substrates for amidation with 1a/PhI(OAc)₂; however, the results were unsatisfactory in terms of yields (from 5 to 10%) and selectivity, except for the cyclic tetrahydropyran (THP, 50% yield). Both the less polar character of acyclic ethers compared to THF and their slightly higher α-C-H bond dissociation energies⁵⁵ might contribute to the decreased activity. Further optimization of reaction conditions for diethyl ether (Table S1 in the ESI[†]) resulted in a maximum yield of 35% for the desired amidated product, but its formation was accompanied by a number of other unidentified species (60% overall sulfonamide conversion). Interestingly, we observed improved activity and considerably enhanced selectivity under microwave irradiation (MW, 120 °C, 10 min) in the neat ethers (Table 3, entries 4, 5; and Table S2[†]). We carried out the same reactions in pressurized microwave vials but heated in a conventional oil bath (Table 3, yields in parentheses).56-58 The results were almost identical, suggesting a thermal origin for the improved yields and selectivity under microwave irradiation. For the sake of comparison, we undertook the α-CH amidation of THF under MW conditions and obtained yields comparable to those observed under mild thermal heating.

The addition of iodine in catalytic or stoichiometric amounts in conjunction with hypervalent iodine oxidants has been widely and successfully employed in other C-H amidation reactions.^{24,29,35-37} We observed an interesting effect with the addition of variable amounts of iodine. In the presence of catalytic amounts (2 mol% I2 relative to sulfonamide) the yields for linear acyclic ethers increased considerably. For instance, the yield for di-n-butyl ether increased from 12 to 54% (entries 9 and 10), whereas that of di-*n*-propyl ether increased from 27 to 68% (entries 6 and 7). However, amidation of cyclic ethers (THF and THP) was not affected by the presence of trace amounts of iodine, which even had a deleterious effect in the case of *tert*-butyl ethers. In all cases, higher amounts of iodine (0.5 equiv.) greatly suppressed product formation. In contrast, 0.5 equiv. of I2 was previously found to be the optimal loading for benzylic amidations by Fan and coworkers who obtained lower yields at both 1 equiv. of I2 and 0.05 to 0.2 equiv. of I2.24 These results highlight the importance of testing a wide range of I₂ concentrations in optimizing this type of reaction.

While linear cyclic and acyclic ethers gave the expected α amidated products, both aromatic and branched aliphatic ethers exhibited a different reactivity. The branched di-isopropyl ether could not be amidated under our experimental conditions; instead we observed the formation of isopropyl acetate (7) as the major product, due to direct acetoxylation, determined by ¹H NMR after addition of an authentic sample of 7. In contrast, acetoxylation was barely detected with the other ether substrates. Surprisingly, reaction of *tert*-butyl methyl ether and *tert*-butyl ethyl ether gave completely different outcomes. The former yielded compound **8** where the *O*-methyl fragment is doubly functionalized and the *tert*butoxy groups released. The molecular structure of **8** is

Table 3 α -CH amidation of ethers^{*a*}

		$\begin{array}{c} R_{0} \\ R_{0} \\ R_{0} \\ R_{1} \\$	HI(OAc) ₂ 20 °C, 10 min R. O R, 3-11		
Entry	Substrate	Product	Additive (equiv.)	$\mathrm{Yield}^{b}\left(\%\right)$	Selectivity ^c
1 2 3 4 5	Et_0-Et	$ \begin{array}{c} $	$\begin{array}{c}\\ I_2 \ (0.02)\\ I_2 \ (0.5)\\\\ I_2 \ (0.02) \end{array}$	62 (56) 59 3 60 (51) 70	0.82 (0.79) 0.76 0.20 0.83 (0.78) 0.89
6 7 8	ⁿ Pr _O ⁿ Pr		$\begin{array}{c}\\ I_2 \ (0.02)\\ I_2 \ (0.5) \end{array}$	27 (27) 68 <1	0.49 (0.44) 0.84 0.10
9 10	″Bu _{∖O} ∕″Bu		I_2 (0.02)	12 (12) 54	0.21 (0.24) 0.86
11 12	ⁱ Pr ₀ ⁱ Pr	0 7 7	-I ₂ (0.02)	14 26	_
13 14 15	^t Bu _{\O} ,Me		$\begin{array}{c} - \\ I_2 (0.02) \\ I_2 (0.5) \end{array}$	79 (85) 60 15	0.98 (0.94) 0.83 0.30
16 17	^ℓ Bu _{∖O} ∕Et		 I ₂ (0.02)	14 (13) 3	0.61 (0.54) 0.10
18	Bz _{∖Ó} Me	ОН 10 + ОН 11	_	$10, 1.5^d, 11, 1.9^d$	_
19	Bz _{\O} Bz	С Н + С ОН 10 + 11	_	10, 5.6 ^{d} , 11, 3.5 ^{d}	_

^{*a*} Conditions: **1a** (0.5 mmol), PhIO(Ac)₂ (0.55 mmol, 1.1 equiv.), neat ether (2 mL), microwave radiation (MW): 120 °C, 10 min. Reactions carried out under N₂ atmosphere. ^{*b*} Yields were determined by ¹H NMR spectroscopy using trimethoxybenzene as internal standard. Values between parentheses correspond to yields obtained under identical conditions as for MW experiments but heating in conventional oil bath. ^{*c*} Selectivities were calculated for sulfonamide as the limiting reagent. ^{*d*} These yields are calculated based on the ether (instead of the sulfonamide) as the limiting reagent, since the reaction also proceeds in the absence of **1a**.

consistent with the reduced number of resonances appearing in its ¹H and ¹³C{¹H} NMR spectra and was confirmed by Xray diffraction (Fig. 2). On the other hand, *tert*-butyl ethyl ether was converted into compound **9** after α -CH amidation of the ethyl group and unexpected β -CH amidation of the *tert*butyl fragment. This species was unambiguously characterized by ¹H and ¹³C{¹H} NMR spectroscopy, as well as HRMS (FT-ICR). It constitutes a rare example of amidation of unactivated primary C–H bonds. A somewhat related reaction has been recently reported by Che and coworkers, where the C–H bond of a *tert*-butyl fragment was also aminated, although in low yield as a result of competition with the more reactive benzylic C–H bond.⁵⁹ Finally, and in contrast to the related copper-catalyzed process,⁶⁰ we observed that benzylic ethers cannot be amidated using the present method; instead they experience C–O cleavage and further oxidation to yield benzaldehyde and benzoic acid. The same transformation has previously been reported under related conditions and mainly investigated as a protocol for the synthesis of aldehydes from benzylic ethers.^{61–63} Although these reactions were accelerated by the addition of the sulfonamide and especially by the presence of the hypervalent iodine oxidant, they proceed even in the absence of these additives (see ESI for more details, Table S3[†]).

Purification of the functionalized ethers reported in this work proved difficult. In most cases extensive decomposition occurred during attempted column chromatography on both silica gel and alumina. In some cases degradation of the



Fig. 2 ORTEPs of compounds 8 and 12. 50% Thermal ellipsoids are shown. Most hydrogen atoms have been omitted for clarity.

amidated compounds was observed after mild work-up or even upon standing in air for several days. The intrinsic reactivity of these species gave rise to an interesting derivative (12, Scheme 2), which is formed from Friedel-Crafts alkylation of electron-rich trimethoxybenzene (employed as an internal standard for¹ H NMR spectroscopy analysis). The Friedel-Crafts coupling of sulfonamides with aromatic compounds typically employs N-sulfonyl aldimines,64-67 but the direct use of N,O-acetals has been less explored. In an elegant study, Du Bois and co-workers developed a related rhodium-catalyzed one-pot amidation/nucleophilic addition process using ethers, sulfonamides and nucleophiles such as allylsilanes, silyl enol ethers, and ketene acetals.68 Another interesting related process for the synthesis of 3-oxyindoles via tandem amidation/acetoxylation/Friedel-Crafts reaction has been recently described.69 The molecular structure of 12 was elucidated by Xray diffraction studies of suitable crystals grown by slow diffusion of pentane into a dichloromethane solution of the compound (Fig. 2). The length of the new C-C bond, 1.512(3) Å, and that of the adjacent C-N bond, 1.490(3) Å, are both indicative of single bonds.

Attempts to perform amination reactions of primary and secondary alkyl amines with THF using PhI(OAc)₂ led to



Scheme 2 Formation of compound 12 by C–C coupling between 6 and trimethoxybenzene.



Scheme 3 Amidation of THF with methyl tosylamide.

acetoxylation product (compound **14** in Scheme 3) as evidenced by¹ H and ¹³C{¹H} NMR spectroscopy in comparison with literature data.⁷⁰ This reaction is presumably base-mediated as the yields were dependent on the amount of amine present, and the same product could be formed using inorganic base K_2CO_3 in place of the amine.

To investigate the feasibility of the classic mechanism for *in situ* nitrene formation (Scheme 1), which requires a primary sulfonamide,^{6,10,11} we tested the reactivity of methyl tosylamide with THF. Interestingly, we found that amidated product is formed in 14% yield along with 17% of the acetoxylation product (Scheme 3). Compound 13 displays ¹H and ¹³C{¹H} NMR spectra similar to a previously reported and related product derived from cyclohexyl tosylamide.⁷¹ This result suggests that *in situ* nitrene formation is not the only available pathway in the present system, and there is at least one other mechanism implicated that would account for the amidation using secondary sulfonamides.

The amidation of THF by sulfonamide 1a was completely shut down by addition of the radical trap TEMPO, suggesting a mechanism involving radicals. Two distinct radical-based mechanisms for PhI(OAc)2-based systems have been proposed in the literature for oxidative C-N functionalization of sp³ benzylic C-H bonds. In an account by Cho and Chang involving imidation of benzylic C-H bonds using PhI(OAc)₂ alone, a carbon-centered radical R¹('CH)R² at the benzylic position was proposed from a single-electron transfer (SET) reaction between the benzylic substrate $R^{1}(CH_{2})R^{2}$ ($R^{1} = Ar$) and $PhI(OAc)_{2}$ (Scheme 4, pathway A).²³ A second SET to form a carbocation $R^{1}(^{+}CH)R^{2}$; followed by attack by a sulfonimide nitrogen and removal of a proton would then produce the final amidation product. Accounts describing amidation and amination of sp³ carbons using PhI(OAc)₂/I₂ systems are in general agreement in proposing mechanisms involving formation of a nitrogencentered R³R⁴N' radical resulting from reaction of the oxidant/I₂ combination with substrate either thermally or by photoactivation.24,29,36,37 Subsequent hydrogen atom transfer (HAT) produces a carbon-centered radical $R^{1}(CH)R^{2}$, which abstracts iodine from R³R⁴NI to propagate the production of the R³R⁴N' radical. Substitution of the R¹(CH)R² I species with either R³R⁴NH or AcOH can lead to formation of amination/ amidation product or the undesired acetoxylation byproduct.

In our system, a substantial KIE of $k_{\rm H/D} = 9.3$ is observed for the reaction of **1a** in a 1 : 1 mixture of THF and THF- d_8 with 2 equiv. of PhI(OAc)₂. Under identical conditions after addition of 2 mol% I₂, the $k_{\rm H/D}$ is decreased to 2.2. The large difference in KIE between these two cases implies a change in mechanism which may involve a shift from pathway A operative with PhI(OAc)₂ alone to pathway B upon addition of I₂ (Scheme 4). Future studies will focus on further elucidating the reaction



Scheme 4 Possible radical-based pathways for the amidation reaction based on literature reports.

mechanism(s) implicated and understanding the dependence of the role of I_2 on the identity of the ether substrate.

Conclusions

In summary, we have developed a metal-free protocol for the selective amidation of sp³ C-H bonds in ethers using inexpensive and commercially available reagents. The resulting functionalized ethers are valuable nitrogen-containing compounds with potential biological and pharmacological properties. The reactions proceed without the need of precious-metal catalysts, with minimal use of organic solvents and under mild conditions. Higher reaction temperatures, achieved most conveniently by microwave irradiation, allow for reaction times in the scale of several minutes, thus reducing energetic costs and making the process environmentally attractive. Preliminary studies suggest several radical mechanistic pathways in competition.

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Notes and references

- 1 R. T. Gephart and T. H. Warren, *Organometallics*, 2012, **31**, 7728.
- 2 J. L. Roizen, M. E. Harvey and J. Du Bois, Acc. Chem. Res., 2012, 45, 911.
- 3 T. A. Ramirez, B. Zhao and Y. Shi, *Chem. Soc. Rev.*, 2012, **41**, 931.
- 4 F. Collet, R. H. Dodd and P. Dauban, *Chem. Commun.*, 2009, 2009, 5061.
- 5 H. M. L. Davies and M. S. Long, *Angew. Chem., Int. Ed.*, 2005, 44, 3518.
- 6 C. M. Che, V. K. Lo, C. Y. Zhou and J. S. Huang, *Chem. Soc. Rev.*, 2011, **40**, 1950.
- P. Dauban, C. Lescot, M. M. Diaz-Requejo and P. J. Perez, in Innovative Catalysis in Organic Synthesis, Wiley-VCH Verlag GmbH & Co. KGaA, 2012, p. 257, DOI: 10.1002/ 9783527646586.ch12.
- 8 H. Lebel, in *Catalyzed Carbon-Heteroatom Bond Formation*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, p. 137, DOI: 10.1002/9783527633388.ch5.
- 9 P. Dauban and R. H. Dodd, in *Amino Group Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2008, p. 55, DOI: 10.1002/ 9783527621262.ch2.
- 10 K. W. Fiori, C. G. Espino, B. H. Brodsky and J. Du Bois, *Tetrahedron*, 2009, **65**, 3042.
- 11 S.-M. Au, J.-S. Huang, C.-M. Che and W.-Y. Yu, *J. Org. Chem.*, 2000, **65**, 7858.
- 12 R. Samanta, K. Matcha and A. P. Antonchick, *Eur. J. Org. Chem.*, 2013, **2013**, 5769.
- 13 V. P. Mehta and B. Punji, RCS Adv., 2013, 3, 11957.
- 14 R. Samanta and A. P. Antonchick, Synlett, 2012, 23, 809.
- 15 M. Lamani and K. R. Prabhu, J. Org. Chem., 2011, 76, 7938.
- 16 Y. Yan, Y. Zhang, Z. Zha and Z. Wang, Org. Lett., 2013, 15, 2274.
- 17 Q. Xue, J. Xie, H. Li, Y. Cheng and C. Zhu, *Chem. Commun.*, 2013, **49**, 3700.
- 18 X. Zhang, M. Wang, P. Li and L. Wang, *Chem. Commun.*, 2014, **50**, 8006.
- 19 D. Zhao, T. Wang and J. X. Li, *Chem. Commun.*, 2014, **50**, 6471.
- 20 Y. S. Wagh, D. N. Sawant and B. M. Bhanage, *Tetrahedron Lett.*, 2012, **53**, 3482.
- 21 Y. Wu, F. Y. Kwong, P. Li and A. S. C. Chan, *Synlett*, 2013, 24, 2009.
- 22 Y. Takeda, J. Hayakawa, K. Yano and S. Minakata, *Chem. Lett.*, 2012, **41**, 1672.
- 23 H. J. Kim, J. Kim, S. H. Cho and S. Chang, J. Am. Chem. Soc., 2011, 133, 16382.
- 24 R. Fan, W. Li, D. Pu and L. Zhang, Org. Lett., 2009, 11, 1425.
- 25 J. A. Souto, C. Martínez, I. Velilla and K. Muñiz, Angew. Chem., Int. Ed., 2013, **52**, 1324.
- 26 J. A. Souto, Y. Gonzalez, A. Iglesias, D. Zian, A. Lishchynskyi and K. Muniz, *Chem. - Asian J.*, 2012, 7, 1103.
- 27 C. Röben, J. A. Souto, Y. González, A. Lishchynskyi and K. Muñiz, *Angew. Chem., Int. Ed.*, 2011, **50**, 9478.

- 28 H. J. Kim, S. H. Cho and S. Chang, Org. Lett., 2012, 14, 1424.
- 29 H.-M. Guo, C. Xia, H.-Y. Niu, X.-T. Zhang, S.-N. Kong, D.-C. Wang and G.-R. Qu, *Adv. Synth. Catal.*, 2011, **353**, 53.
- 30 J. A. Souto, D. Zian and K. Muñiz, J. Am. Chem. Soc., 2012, 134, 7242.
- 31 J. Joseph, J. Y. Kim and S. Chang, *Chem. Eur. J.*, 2011, **17**, 8294.
- 32 Y. S. Wagh, N. J. Tiwari and B. M. Bhanage, *Tetrahedron Lett.*, 2013, 54, 1290.
- 33 M. Ochiai, K. Miyamoto, T. Kaneaki, S. Hayashi and W. Nakanishi, *Science*, 2011, **332**, 448.
- 34 M. Ochiai, S. Yamane, M. M. Hoque, M. Saito and K. Miyamoto, *Chem. Commun.*, 2012, **48**, 5280.
- 35 Y. Li, Q. Ding, G. Qiu and J. Wu, *Org. Biomol. Chem.*, 2014, **12**, 149.
- 36 R. Fan, D. Pu, F. Wen and J. Wu, J. Org. Chem., 2007, 72, 8994.
- 37 H. Togo, Y. Hoshina, T. Muraki, H. Nakayama and M. Yokoyama, *J. Org. Chem.*, 1998, 63, 5193.
- 38 J. A. Souto, P. Becker, Á. Iglesias and K. Muñiz, J. Am. Chem. Soc., 2012, 134, 15505.
- 39 A. A. Kantak, S. Potavathri, R. A. Barham, K. M. Romano and
 B. DeBoef, J. Am. Chem. Soc., 2011, 133, 19960.
- 40 A. P. Antonchick, R. Samanta, K. Kulikov and J. Lategahn, Angew. Chem., Int. Ed., 2011, 50, 8605.
- 41 M. Ochiai, T. Kaneaki, N. Tada, K. Miyamoto, H. Chuman, M. Shiro, S. Hayashi and W. Nakanishi, *J. Am. Chem. Soc.*, 2007, **129**, 12938.
- 42 M. Zhang, Synthesis, 2011, 2011, 3408.
- 43 A. Armstrong and J. C. Collins, *Angew. Chem., Int. Ed.*, 2010, 49, 2282.
- 44 M. Ochiai, Y. Nishi, S. Goto, M. Shiro and H. J. Frohn, *J. Am. Chem. Soc.*, 2003, **125**, 15304.
- 45 D. P. Albone, S. Challenger, A. M. Derrick, S. M. Fillery, J. L. Irwin, C. M. Parsons, H. Takada, P. C. Taylor and D. J. Wilson, *Org. Biomol. Chem.*, 2005, 3, 107.
- 46 H. Liu, X. Wang and Y. Gu, Org. Biomol. Chem., 2011, 9, 1614.
- 47 H. Lebel, K. Huard and S. Lectard, *J. Am. Chem. Soc.*, 2005, 127, 14198.
- 48 K. Huard and H. Lebel, Chem. Eur. J., 2008, 14, 6222.
- 49 G. C. Fortman, N. C. Boaz, D. Munz, M. M. Konnick, R. A. Periana, J. T. Groves and T. B. Gunnoe, *J. Am. Chem. Soc.*, 2014, **136**, 8393.

- 50 A. R. Parent, T. P. Brewster, W. De Wolf, R. H. Crabtree and G. W. Brudvig, *Inorg. Chem.*, 2012, **51**, 6147.
- 51 P. A. Colinas and R. D. Bravo, *Tetrahedron Lett.*, 2005, 46, 1687.
- 52 P. A. Colinas and R. D. Bravo, Org. Lett., 2003, 5, 4509.
- 53 R. Crespo, M. G. de Bravo, P. A. Colinas and R. D. Bravo, *Bioorg. Med. Chem. Lett.*, 2010, 20, 6469.
- 54 C. Wu, E. R. Decker, N. Blok, H. Bui, T. J. You, J. Wang, A. R. Bourgoyne, V. Knowles, K. L. Berens, G. W. Holland, T. A. Brock and R. A. F. Dixon, *J. Med. Chem.*, 2004, 47, 1969.
- 55 Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, 2003.
- 56 C. O. Kappe, B. Pieber and D. Dallinger, *Angew. Chem., Int. Ed.*, 2013, **52**, 1088.
- 57 A. de la Hoz, A. Diaz-Ortiz and A. Moreno, *Chem. Soc. Rev.*, 2005, **34**, 164.
- 58 C. O. Kappe, Acc. Chem. Res., 2013, 46, 1579.
- 59 Y. Liu, X. Guan, E. L. Wong, P. Liu, J. S. Huang and C. M. Che, *J. Am. Chem. Soc.*, 2013, **135**, 7194.
- 60 L. He, J. Yu, J. Zhang and X.-Q. Yu, Org. Lett., 2007, 9, 2277.
- 61 S. R. Joshi, S. B. Sawant and J. B. Joshi, *Org. Process Res. Dev.*, 2001, 5, 152.
- 62 M. Sasidharan and A. Bhaumik, J. Mol. Catal. A: Chem., 2011, 338, 105.
- 63 P. Strazzolini and A. Runcio, *Eur. J. Org. Chem.*, 2003, **2003**, 526.
- 64 P. Thirupathi and S. Soo Kim, J. Org. Chem., 2010, 75, 5240.
- 65 J. Esquivias, R. Gómez Arrayás and J. C. Carretero, *Angew. Chem., Int. Ed.*, 2006, **45**, 629.
- 66 P. N. Chatterjee, A. K. Maity, S. S. Mohapatra and S. Roy, *Tetrahedron*, 2013, **69**, 2816.
- 67 T. Terada, T. Kurahashi and S. Matsubara, *Heterocycles*, 2012, **85**, 2415.
- 68 K. W. Fiori, J. J. Fleming and J. Du Bois, *Angew. Chem., Int. Ed.*, 2004, **43**, 4349.
- 69 Y. Sun and R. Fan, Chem. Commun., 2010, 46, 6834.
- N. P. Dolman, J. C. A. More, A. Alt, J. L. Knauss, H. M. Troop,
 D. Bleakman, G. L. Collingridge and D. E. Jane, *J. Med. Chem.*, 2006, 49, 2579.
- 71 K. S. Feldman, M. M. Bruendl, K. Schildknegt and A. C. Bohnstedt, *J. Org. Chem.*, 1996, **61**, 5440.