View Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 2141

www.rsc.org/greenchem

COMMUNICATION

TBHP/I_2-promoted oxidative coupling of acetophenones with amines at room temperature under metal-free and solvent-free conditions for the synthesis of α-ketoamides†

Xiaobin Zhang[a] **and Lei Wang***[a,b]

Received 2nd April 2012, Accepted 25th May 2012
DOI: 10.1039/c2gc35489f

Published on 28 May 2012 on http://pubs.rsc.org | doi:10.1039/C2GC35489F
Downloaded by Pennsylvania State University on 31 July 2012

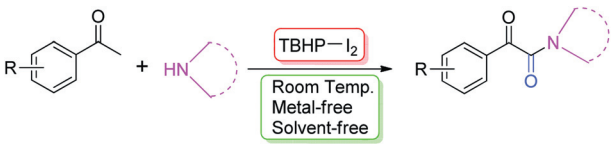
A novel and efficient TBHP/I_2-promoted oxidative coupling reaction of acetophenones with amines for the synthesis of α-ketoamides has been developed. The reactions proceeded smoothly at room temperature under metal-free and solvent-free conditions and generated the corresponding products in good yields.

The α-ketoamides, as the key structural skeletal framework of many natural products and pharmaceuticals, have attracted considerable interest because of their important biologically active properties.[1] They are also the important synthetic intermediates for the further transformation to Na-channel blocker GW 356194, 5-HT_6 binding ligands, α-diones and β-lactams, *etc.*[2] The traditional method for the synthesis of α-ketoamides is based on the condensation of α-keto acids with amines in the presence of dicyclohexylcarbodiimide or other activating agents, however, the preparation of α-keto acids is impractical.[3] Although a number of modifications on the synthesis of α-ketoamides were developed,[4] the drawbacks are the use of hazardous reagents, harsh reaction conditions, multi-step processes, and low yields in the most of the cases.

Transition-metal-catalyzed organic reactions for the construction of carbon–carbon and carbon–heteroatom bonds have received much attention in modern organic synthesis.[5] To synthesize α-ketoamides, Pd-, and Cu-catalyzed double carbonylation of aryl iodides with amines,[6] Pd-catalyzed aerobic oxidative cleavage of preformed α-arylamino amides,[7] and Cu-catalyzed aerobic oxidative amidation–diketonization of terminal alkynes,[8] Cu-catalyzed oxidative coupling of aryl acetaldehydes with anilines[9] and Cu-catalyzed oxidative coupling of aryl methyl ketones with amines[10] have been developed in recent years.

Most recently, organic reactions carried out under metal-free conditions have also received much attention because it can overcome the drawbacks of the expensive, poisonous, and air-sensitive properties of metals or organometallics.[11] A variety of metal-free systems, such as TBHP (*tert*-butyl hydroperoxide)/I_2,[12] TBPB (*tert*-butyl peroxybenzoate),[13] TBHP,[14] TBAF (tetra-*n*-butylammonium fluoride),[15] I_2,[16] I_2/NBS (*N*-bromosuccinimide),[17] and O_2,[18] have been reported for the organic transformations. For example, Jiang *et al.* reported a TBHP/I_2-mediated domino oxidative cyclization for the one-pot synthesis of polysubstituted oxazoles in 2010.[12a] Meanwhile, Wang and his co-workers developed a series of TBHP/I_2-promoted organic reactions, such as a tandem oxidative cyclization of 2-amino-1-phenylethanone with aromatic aldehydes for the preparation of 2,5-disubstituted oxazoles,[12b] a tandem reaction of 2-aminobenzophenones and benzylic amines for the synthesis of 2-phenylquinazolines,[12c] a decarboxylative cyclization from natural α-amino acids to construct pyridine derivatives,[12d] an oxidative decarboxylative coupling of primary α-amino acids with 2-aminobenzoketones for the synthesis of quinazolines,[12e] and an oxidation of benzylic methylenes to ketones and primary amines to nitriles.[12f] Herein, we wish to report a TBHP/I_2-promoted tandem direct oxidative coupling of acetophenones with amine at room temperature under metal-free and solvent-free conditions. The reactions proceeded smoothly and generated the corresponding α-ketoamide products in good yields under mild reaction conditions (Scheme 1).

At the beginning of our investigation, the optimization of reaction conditions was focused on a variety of reaction parameters by using a model reaction of acetophenone (**1a**) with piperidine (**2a**). As listed in Table 1, the oxidant plays an important role in the reaction. When the model reaction was performed in the presence of I_2 (30 mol%) in toluene at room temperature (20–25 °C), *tert*-butyl hydroperoxide (TBHP) exhibited the highest reactivity to the reaction, and 78% yield of the desired oxidative coupling product **3a** was isolated (Table 1, entry 1). Di-*tert*-butyl peroxide, H_2O_2, *tert*-butyl perbenzoate (TBPB),



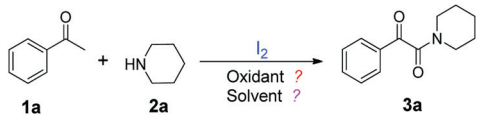
Scheme 1 The direct oxidative coupling of acetophenones with amines.

[a]*Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P.R. China. E-mail: leiwang@chnu.edu.cn; Fax: +86-561-309-0518; Tel: +86-561-380-2069*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P.R. China*

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c2gc35489f

Published on 28 May 2012 on http://pubs.rsc.org | doi:10.1039/C2GC35489F
Downloaded by Pennsylvania State University on 31 July 2012

Table 1 Optimization of the reaction conditions[a]



Entry	Solvent	Oxidant	Yield of **3a**[b] (%)
1	Toluene	*tert*-Butyl hydroperoxide (TBHP)	78
2	Toluene	Di-*tert*-butyl peroxide	59
3	Toluene	H_2O_2	43
4	Toluene	*tert*-Butyl perbenzoate (TBPB)	32
5	Toluene	$PhI(OAc)_2$	24
6	Toluene	Cumyl hydroperoxide	20
7	Toluene	O_2	18
8	Toluene	$(C_6H_5COO)_2$	14
9	Toluene	*tert*-Butyl hydroperoxide (TBHP)	0[c]
10	DMF	*tert*-Butyl hydroperoxide (TBHP)	30
11	CH_3CN	*tert*-Butyl hydroperoxide (TBHP)	43
12	THF	*tert*-Butyl hydroperoxide (TBHP)	51
13	Dioxane	*tert*-Butyl hydroperoxide (TBHP)	62
14	Dichloromethane	*tert*-Butyl hydroperoxide (TBHP)	65
15	Neat	*tert*-Butyl hydroperoxide (TBHP)	91
16	Neat	*tert*-Butyl hydroperoxide (TBHP)	76[d]
17	Neat	*tert*-Butyl hydroperoxide (TBHP)	50[e]
18	Neat	*tert*-Butyl hydroperoxide (TBHP)	92[f]
19	Neat	*tert*-Butyl hydroperoxide (TBHP)	45[g]
20	Neat	*tert*-Butyl hydroperoxide (TBHP)	76[h]
21	Neat	*tert*-Butyl hydroperoxide (TBHP)	92[i]
22	Neat	—	Trace
23	Neat	—	Trace[j]

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (0.60 mL, 6.07 mmol), I_2 (0.30 mmol), oxidant (3.0 mmol), solvent (2.0 mL) if needed at room temperature (20–25 °C) for 8 h. [b] Isolated yields. [c] In the absence of I_2. [d] TBHP (2.0 mmol). [e] TBHP (1.0 mmol). [f] TBHP (4.0 mmol). [h] I_2 (0.10 mmol). [h] I_2 (0.20 mmol). [i] I_2 (0.40 mmol). [j] I_2 (1.0 mmol).

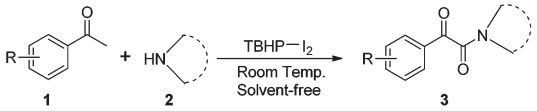
$PhI(OAc)_2$, cumyl hydroperoxide, O_2, and $(C_6H_5COO)_2$ were subsequently inferior, and only 14–59% yields of **3a** were obtained (Table 1, entries 2–8). However, no desired product **3a** was observed when the model reaction was carried out in the presence of *tert*-butyl hydroperoxide (TBHP) without I_2 in toluene (Table 1, entry 9). Subsequently, the effect of solvent on the model reaction was also examined and a significant solvent effect was observed. When the model reaction was performed in toluene, 78% yield of **3a** was obtained, and 30–65% yields of **3a** was obtained when the reaction was performed in DMF, CH_3CN, THF, dioxane, or dichloromethane (Table 1, entries 10–14). To our delight, 91% yield of **3a** was isolated, representing the best results, when the model reaction was carried out in the presence of I_2 and *tert*-butyl hydroperoxide (TBHP) at room temperature without additional solvent (Table 1, entry 15). For the optimization of the amount of I_2 and *tert*-butyl hydroperoxide (TBHP) used in the model reaction, less than 30 mol% of I_2 and 3 equiv. of TBHP led to the incompletion of the reaction (Table 1, entries 16, 17, 19 and 20). Meanwhile, up to 40 mol% of I_2 and 4 equiv. of TBHP did not increase the yield of **3a** significantly (Table 1, entries 18 and 21). However, when the model reaction was carried out in the presence of 0.30 equiv. or 1.0 equiv. of I_2 in the absence of TBHP, only trace amounts of **3a** was observed (Table 1, entries 22 and 23). The optimized reaction conditions for the model reaction were I_2 (30 mol%), TBHP (3.0 equiv.) at room temperature (20–25 °C) for 8 h without additional solvent.

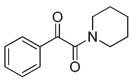
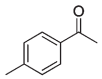
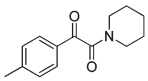
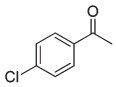
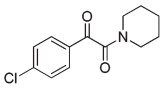
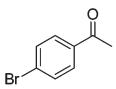
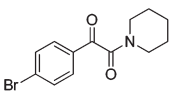
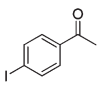
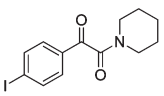
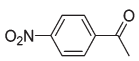
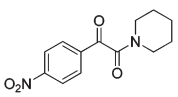
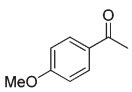
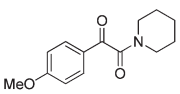
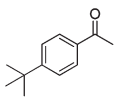
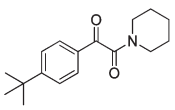
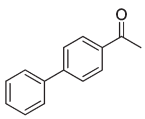
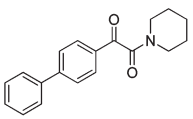
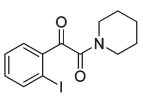
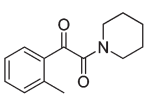
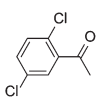
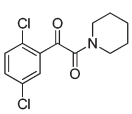
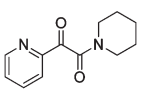
Under the optimized reaction conditions, the scope of substituted acetophenones and amines in the direct oxidative coupling reactions was investigated. The results were shown in Table 2. A variety of acetophenones bearing substituents on the benzene rings were examined for the direct coupling with piperidine. The results indicated that a variety of functional groups, including electron-donating groups and electron-withdrawing ones were tolerated, and the oxidative coupling reactions produced the corresponding products in good to excellent yields (Table 2, entries 1–12). Acetophenones with electron-withdrawing groups on the *para*-positions of acetophenone, such as Cl, Br, I, and NO_2, generated the corresponding oxidative coupling products in 88–94% yields (Table 2, entries 3–6). On the other hand, acetophenones with electron-donating groups, such as Me, MeO, and *t*-Bu on the *para*-positions of their benzene rings, gave the desired products in 85–89% yields (Table 2, entries 2, 7 and 8). It is important to note that the reaction of 4-phenylacetophenone with piperidine generated the corresponding product in 65% yield (Table 2, entry 9). Meanwhile, the *ortho*-effect is not obvious for methyl, and iodo groups on the *ortho*-positions of the acetophenones in the reactions (Table 2, entries 10 and 11). Disubstituted acetophenone, such as 2,4-dichloroacetophenone, also underwent the tandem reaction with piperidine under the present reaction conditions and afforded the corresponding product in 92% yield (Table 2, entry 12). However, the reaction of 2-acetylpyridine with piperidine only gave 68% yield of the product (Table 2, entry 13). Under the recommended reaction conditions, 1-acetylnaphthalene also preceded the reaction smoothly to generate the corresponding product in 85% yield (Table 2, entry 14). The present reaction conditions were also suitable for the reactions of acetophenone with other secondary amines, such as diethylamine, dibenzylamine, 1-methylpiperazine and morpholine, and the corresponding products were isolated in 58–87% yields (Table 2, entries 15–18). Finally, the reactions of substituted acetophenones having *p*-Cl and *p*-Me groups, with morpholine generated the desired products in 83 and 80% yields, respectively (Table 2, entries 19 and 20).

Although the exact mechanism of this reaction is not clear up till now, a possible cascade pathway was proposed and shown in Scheme 2. The reaction occurs involving an iodination of acetophenone, subsequently intermolecular nucleophilic substitution with amine, and finally oxidation of methylene unit. When the reaction was carried out in the presence of a radical scavenger, such as TEMPO (2,2,6,6-tetramethyl-piperidyl-1-oxyl) and ascorbic acid up to 2.0 equiv., the oxidative coupling reaction did not occur and the starting material was recovered.[19] On the other hand, when the reaction of **1a** without **2a** was performed under the present reaction conditions, it also did not occur and the starting material was recovered, suggesting that **2a** was essential for the formation of 2-iodo-1-phenylethanone. Initially, acetophenone reacted with piperidine (a secondary amine) to afford enamine **I**.[20] Then obtained enamine **I** reacted with I^+, which was generated from the reaction of I_2 with an oxidant TBHP,[17] *via* a iodocyclization of the enamine C=C double bond, forming a three-membered iodonium intermediate **II**, followed by an intramolecular ring opening to give **III**, followed

This journal is © The Royal Society of Chemistry 2012

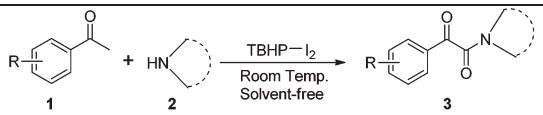
Table 2 The direct oxidative coupling of acetophenones and amines[a]



Entry	Ketone	Amine	Product	3	Yield[b] (%)
1				**3a**	91
2				**3b**	89
3				**3c**	94
4				**3d**	92
5				**3e**	90
6				**3f**	88
7				**3g**	85
8				**3h**	89
9				**3i**	65
10				**3j**	87
11				**3k**	82
12				**3l**	92
13				**3m**	68
14				**3n**	85
15				**3o**	58

Published on 28 May 2012 on http://pubs.rsc.org | doi:10.1039/C2GC35489F
Downloaded by Pennsylvania State University on 31 July 2012

Table 2 *(Contd.)*

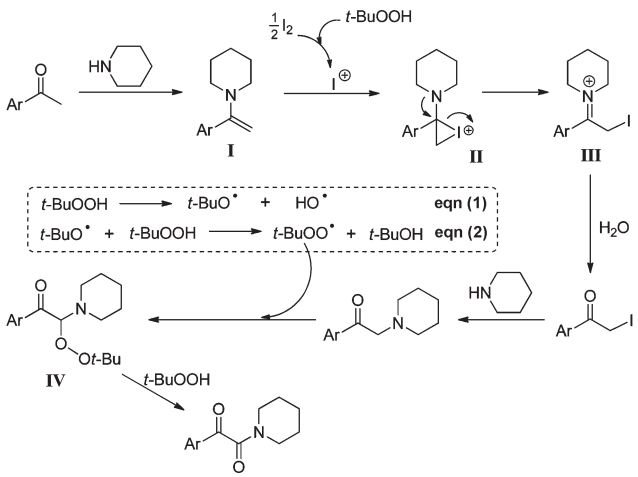


1 2 3

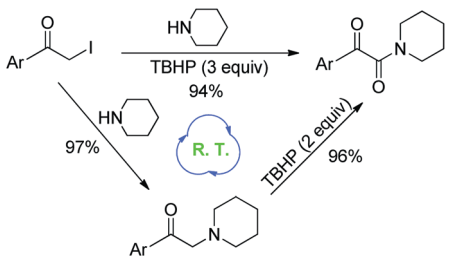
Entry	Ketone	Amine	Product	3	Yield[b] (%)
16				**3p**	87
17				**3q**	66
18				**3r**	81
19				**3s**	83
20				**3t**	80

[a] Reaction conditions: ketone (**1**, 1.0 mmol), amine (**2**, 0.60 mL), TBHP (3.0 mmol), I_2 (0.30 mmol) at room temperature (20–25 °C) without additional solvent for 8 h. [b] Isolated yields.

Published on 28 May 2012 on http://pubs.rsc.org | doi:10.1039/C2GC35489F
Downloaded by Pennsylvania State University on 31 July 2012



Scheme 2 Possible reaction mechanism.



Scheme 3 The transformation of 2-iodo-1-phenylethanone and 2-cyclohexyl-1-phenylethanone in the presence of TBHP.

by hydrolysis to give 2-iodo-1-phenylethanone.[16a] The generated 2-iodo-1-phenylethanone then underwent a nucleophilic substitution with piperidine to form the key intermediate 2-cyclohexyl-1-phenylethanone. The obtained 2-cyclohexyl-1-phenylethanone proceeded free radical substitution of its methylene with a *tert*-butylperoxy free radical generated from the reactions of eqn (1) and (2)[21] in Scheme 2 *via* homolytic cleavage of *tert*-butyl hydroperoxide to generate intermediate **IV**,[12f] which underwent further oxidation by TBHP to afford the final product 1-cyclohexyl-2-phenylethane-1,2-dione.

To verify the formation of the key intermediates 2-iodo-1-phenylethanone and 2-cyclohexyl-1-phenylethanone in the reaction, the prepared 2-iodo-1-phenylethanone was reacted with piperidine in the presence of TBHP (3 equiv.) to generate the desired product 1-cyclohexyl-2-phenylethane-1,2-dione in 94% yield (Scheme 3). On the other hand, the reaction of 2-iodo-1-phenylethanone with piperidine generated 2-cyclohexyl-1-phenylethanone in 97% yield. The obtained 2-cyclohexyl-1-phenylethanone was oxidized in the presence of TBHP (2 equiv.) to give the final product 1-cyclohexyl-2-phenylethane-1,2-dione in 96% yield.

Conclusion

In conclusion, a highly efficient synthetic method for the preparation of α-ketoamides has been developed. In the presence of I_2 and *tert*-butyl hydroperoxide (TBHP), the direct oxidative coupling reactions of acetophenones and amines proceeded smoothly at room temperature under metal-free and solvent-free conditions to generate the corresponding products in good

 This journal is © The Royal Society of Chemistry 2012

Published on 28 May 2012 on http://pubs.rsc.org | doi:10.1039/C2GC35489F
Downloaded by Pennsylvania State University on 31 July 2012

yields. A detailed reaction mechanism and further investigation on the application of this kind of oxidative system under metal-free and solvent-free conditions are currently underway in our laboratory.

Experimental section

All the direct oxidative coupling reactions of acetophenones with amines were carried out under an air atmosphere. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz NMR spectrometer with $CDCl_3$ as solvent and recorded in ppm relative to an internal tetramethylsilane standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT or a Bruker Apex IV FTMS instrument. General chemicals were purchased from commercial suppliers and used without further purification.

Typical procedure for the metal-free and solvent-free reaction

A sealable reaction tube equipped with a magnetic stirrer bar was charged with acetophenone (1.0 mmol), piperidine (0.60 mL), I_2 (0.30 mmol), *tert*-butyl hydroperoxide (TBHP, 3.0 mmol). The reaction vessel was carried out at room temperature (20–25 °C). After stirring the mixture for 8 h, it was diluted with ethyl acetate, washed with water and brine, dried with Mg_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (eluant: hexane–ethyl acetate 5 : 1) to afford the corresponding product.

Acknowledgements

This work was financially supported by the National Science Foundation of China (nos. 21172092 and 20102039).

Notes and references

1 (*a*) N. Fusetani, S. Matsunaga, H. Matsumoto and Y. Takebayashi, *J. Am. Chem. Soc.*, 1990, **112**, 7053; (*b*) M. Hagihara and S. L. Schreiber, *J. Am. Chem. Soc.*, 1992, **114**, 6570; (*c*) B. E. Maryanoff, M. N. Greco, H.-C. Zhang, P. Andrade-Gordon, J. A. Kauffman, K. C. Nicolaou, A. Liu and P. H. Brungs, *J. Am. Chem. Soc.*, 1995, **117**, 1225; (*d*) D. H. Slee, K. L. Laslo, J. H. Elder, I. R. Ollmann, A. Gustchina, J. Kervinen, A. Zdanov, A. Wlodawer and C.-H. Wong, *J. Am. Chem. Soc.*, 1995, **117**, 11867; (*e*) Z. Li, A.-C. Ortega-Vilain, G. S. Patil, D.-L. Chu, J. E. Foreman, D. D. Eveleth and J. C. Powers, *J. Med. Chem.*, 1996, **39**, 4089; (*f*) S. Chatterjee, D. Dunn, M. Tao, G. Wells, Z.-Q. Gu, R. Bihovsky, M. A. Ator, R. Siman and J. P. Mallamo, *Bioorg. Med. Chem. Lett.*, 1999, **9**, 2371; (*g*) M. M. Sheha, N. M. Mahfouz, H. Y. Hassan, A. F. Youssef, T. Mimoto and Y. Kiso, *Eur. J. Med. Chem.*, 2000, **35**, 887; (*h*) Y.-H. Chen, Y.-H. Zhang, H.-J. Zhang, D.-Z. Liu, M. Gu, J.-Y. Li, F. Wu, X.-Z. Zhu, J. Li and F.-J. Nan, *J. Med. Chem.*, 2006, **49**, 1613.

2 (*a*) I. L. Jones, D. J. Schofield, R. R. Strevens, P. N. Horton, B. M. Hursthouse and N. C. O. Tomkinson, *Tetrahedron Lett.*, 2007, **48**, 521; (*b*) J. Holenz, R. Mercè, J. L. Díaz, X. Guitart, X. Codony, A. Dordal, G. Romero, A. Torrens, J. Mas, B. Andaluz, S. Hernández, X. Monroy, E. Sánchez, E. Hernández, R. Pérez, R. Cubí, O. Sanfeliu and H. Buschmann, *J. Med. Chem.*, 2005, **48**, 1781; (*c*) A. Natarajan, K. Wang, V. Ramamurthy, J. Scheffer and B. Patrick, *Org. Lett.*, 2002, **4**, 1443; (*d*) U. T. Mueller-Westerhoff and M. Zhou, *Tetrahedron Lett.*, 1993, **34**, 571; (*e*) Y. Inoue, *Chem. Rev.*, 1992, **92**, 741.

3 For selected examples, see: (*a*) I. Ojima, N. Yoda, M. Yatabe, T. Tanaka and T. Kogure, *Tetrahedron*, 1984, **40**, 1255; (*b*) A. Chiou, T. Markidis, V. C. Kokotou, R. Verger and G. Kokotos, *Org. Lett.*, 2000, **2**, 347; (*c*) G. M. Dubowchik, J. L. Ditta, M. V. Vrudhula, B. DasGupta, J. Ditta, T. Chen, S. Sheriff, K. Sipman, M. Witmer, J. Tredup, D. M. Vyas, T. A. Verdoorn, S. Bollini and A. Vinitsky, *Org. Lett.*, 2001, **3**, 3987.

4 For selected examples, see: (*a*) J. E. Semple, T. D. Owens, K. Nguyen and O. E. Levy, *Org. Lett.*, 2000, **2**, 2769; (*b*) M. Nakamura, J. Inoue and T. Yamada, *Bioorg. Med. Chem. Lett.*, 2000, **10**, 2807; (*c*) Z. Yang, Z. Zhang, N. A. Meanwell, J. F. Kadow and T. Wang, *Org. Lett.*, 2002, **4**, 1103; (*d*) A. J. Burton, K. S. Cardwell, J. M. Fuchter, M. K. Lindvall, R. Patel, T. W. Packham, J. C. Prodger, M. B. Schilling and D. M. Walker, *Tetrahedron Lett.*, 2003, **44**, 5653; (*e*) N. Tsukada, Y. Ohba and Y. Inoue, *J. Organomet. Chem.*, 2003, **687**, 436; (*f*) R. P. Singh and J. M. Shreeve, *J. Org. Chem.*, 2003, **68**, 6063; (*g*) B. Song, S. Wang, C. Sun, H. Deng and B. Xu, *Tetrahedron Lett.*, 2007, **48**, 8982; (*h*) Z. F. Al-Rashid, W. L. Johnson, R. P. Hsung, Y. Wei, P.-Y. Yao, R. Liu and K. Zhao, *J. Org. Chem.*, 2008, **73**, 8780; (*i*) J.-M. Grassot, G. Masson and J. Zhu, *Angew. Chem., Int. Ed.*, 2008, **47**, 947; (*j*) M. Bouma, G. Masson and J. Zhu, *J. Org. Chem.*, 2010, **75**, 2748.

5 (*a*) J. Tsuji, *Palladium Reagents and Catalysis*, Wiley, Chichester, 1995; (*b*) R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, London, 1985.

6 For recent examples, see: (*a*) Y. Uozumi, T. Arii and T. Watanabe, *J. Org. Chem.*, 2001, **66**, 5272; (*b*) M. Iizuka and Y. Kondo, *Chem. Commun.*, 2006, 1739; (*c*) J. Liu, R. Zhang, S. Wang, W. Sun and C. Xia, *Org. Lett.*, 2009, **11**, 1321.

7 L. El Kaïm, R. Gamez-Montaño, L. Grimaud and T. Ibarra-Rivera, *Chem. Commun.*, 2008, 1350.

8 C. Zhang and N. Jiao, *J. Am. Chem. Soc.*, 2010, **132**, 28.

9 C. Zhang, Z. Xu, L. Zhang and N. Jiao, *Angew. Chem., Int. Ed.*, 2011, **50**, 11088.

10 F.-T. Du and J.-X. Ji, *Chem. Sci.*, 2012, **3**, 460.

11 (*a*) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li and Z.-J. Shi, *Nat. Chem.*, 2010, **2**, 1044; (*b*) E. Shirakawa, K. Itoh, T. Higashino and T. Hayashi, *J. Am. Chem. Soc.*, 2010, **132**, 15537; (*c*) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong and A. Lei, *J. Am. Chem. Soc.*, 2010, **132**, 16737.

12 (*a*) H. Jiang, H. Huang, H. Cao and C. Qi, *Org. Lett.*, 2010, **12**, 5561; (*b*) C. Wan, L. Gao, Q. Wang, J. Zhang and Z. Wang, *Org. Lett.*, 2010, **12**, 3902; (*c*) J. Zhang, D. Zhu, C. Yu, C. Wan and Z. Wang, *Org. Lett.*, 2010, **12**, 2841; (*d*) Q. Wang, C. Wan, Y. Gu, J. Zhang, L. Gao and Z. Wang, *Green Chem.*, 2011, **13**, 578; (*e*) Y. Yan and Z. Wang, *Chem. Commun.*, 2011, **47**, 9513; (*f*) J. Zhang, Z. Wang, Y. Wang, C. Wan, X. Zheng and Z. Wang, *Green Chem.*, 2009, **11**, 1973; (*g*) M. Lamani and K. R. Prabhu, *J. Org. Chem.*, 2011, **76**, 7938.

13 T. He, H. Li, P. Li and L. Wang, *Chem. Commun.*, 2011, **47**, 8946.

14 T. He, L. Yu, L. Zhang, L. Wang and M. Wang, *Org. Lett.*, 2011, **13**, 5016.

15 W. Chen, Y. Zhang, L. Zhang, M. Wang and L. Wang, *Chem. Commun.*, 2011, **47**, 10476.

16 (*a*) Z. He, H. Li and Z. Li, *J. Org. Chem.*, 2010, **75**, 4636; (*b*) A. A. Lamar and K. M. Nicholas, *J. Org. Chem.*, 2010, **75**, 7644; (*c*) C.-B. Miao, M. Zhang, Z.-Y. Tian, H.-T. Xi, X.-Q. Sun and H.-T. Yang, *J. Org. Chem.*, 2011, **76**, 9809.

17 Z. He, W. Liu and Z. Li, *Chem.–Asian J.*, 2011, **6**, 1340.

18 D. Shanmugapriya, R. Shankar, G. Satyanarayana, V. H. Dahanukar, U. K. Syam Kumar and N. Vembu, *Synlett*, 2008, 2945.

19 (*a*) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong and A. Lei, *J. Am. Chem. Soc.*, 2010, **132**, 16737; (*b*) J. J. Warren and J. M. Mayer, *J. Am. Chem. Soc.*, 2010, **132**, 7784; (*c*) C.-W. Chan, Z. Zhou, A. S. C. Chan and W.-Y. Yu, *Org. Lett.*, 2010, **12**, 3926.

20 G. Stork, R. Terrell and J. Szmuszkovicz, *J. Am. Chem. Soc.*, 1954, **76**, 2029.

21 E. Boess, C. Schmitz and M. Klussmann, *J. Am. Chem. Soc.*, 2012, **134**, 5317.