Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201400240

Chemoselective Copper-Catalyzed Acylation of Benzothiazoles with Aryl Methyl Ketones

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Received: March 7, 2014; Revised: April 13, 2014; Published online: July 17, 2014

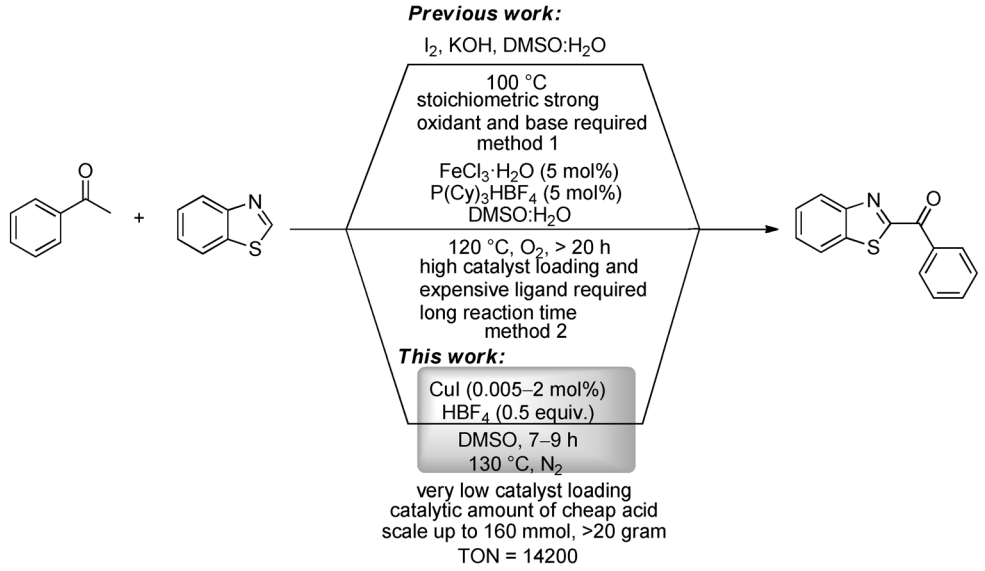
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400240.

Abstract: A copper(I) iodide-catalyzed, highly efficient acylation of benzothiazoles with aryl methyl ketones as carbonyl sources under a nitrogen atmosphere was developed. This is an unprecedented protocol and an extremely efficient method for the selective synthesis of 2-acylbenzothiazoles from commercially available, cheap starting materials with excellent chemoselectivity, good functional group tolerability and high turnover numbers (up to 14,200); also scaling up to 160 mmol without loss of the efficiency is possible. A variety of 2-acylbenzothiazoles was smoothly prepared in good to excellent yields from aryl methyl ketones and benzothiazoles by a one-pot domino protocol of combined sp^3 C–H oxidation, ring opening, and condensation.

Keywords: acylation; 2-acylbenzothiazoles; aryl methyl ketones; benzothiazoles; oxidation

2-Substituted benzothiazoles are ubiquitous scaffolds in pharmaceuticals and have shown many biological activities.[1] Great progress has been achieved for the synthesis of 2-substituted benzothiazoles, especially 2-arylbenzothiazoles.[2] Very recently we developed an efficient method to prepare 2-arylbenzothiazoles from phenylacetic acids and α-hydroxyphenylacetic acids with benzothiazoles under aerobic copper-catalyzed oxidation conditions.[3] Bi et al. reported a novel formation of aldehydes by chemoselective oxidative C(CO)–C(methyl) bond cleavage in aryl methyl ketones catalyzed by CuI and O_2.[4] As part of our continuing interest in prepare 2-arylbenzothiazoles, we speculated that 2-arylbenzothiazoles could be formed from aryl methyl ketones and benzothiazoles in the presence of CuI and O_2 based on our previous research and the above literature report.[4] Aryl methyl ketones as cheap and commercially available starting materials have been widely used in organic and pharmaceutical synthesis. Recently, oxidative functionalization of the sp^3 C–H bond in aryl methyl ketones has become a hot topic and many efficient methods have been developed[5] based on catalytic oxidative functionalization of the sp^3 C–H bond adjacent to the carbonyl group in aryl methyl ketones. For example, α-keto amides were directly synthesized from aryl methyl ketones and amines or DMF under oxidative reaction conditions,[5b,c,6] and MacMillan et al. obtained α-aminoaryl alkyl ketones directly from copper-catalyzed aerobic oxidation of aryl alkyl ketones with secondary amines.[5a] Wu and his co-workers have developed various I_2-mediated methods which functionalize the sp^3 C–H bond in aryl methyl ketones.[7]

Very interestingly, when acetophenone (**1**) and benzothiazole (**2**) were treated with CuI under an O_2 atmosphere, not only 2-arylbenzothiazole (**3**) but also 2-acylbenzothiazole (**4**) were formed and when the catalyst loading was reduced, the ratio of compound **4** to compound **3** increased. Compared to the prevailing synthesis of 2-arylbenzothiazoles, the formation of 2-acylbenzothiazoles is rare due to the difficulties to install an acyl group to the 2-position of benzothiazoles. So we decided to focus on the formation of 2-acylbenzothiazoles. Recently there are two methods for the synthesis of 2-acylbenzothiazoles from aryl methyl ketones and benzothiazoles (Scheme 1, methods 1 and 2).[7a,8,9] Although some significant progress has been achieved, a stoichiometric amount of oxidants (I_2) and strong base (KOH) (method 1)[7a] or expensive ligand, external oxidant and long reaction time (> 20 h) (method 2)[8] were required. These disadvantages seriously limited the utility of such methods in organic synthesis. Thus the development of a highly efficient catalytic system for the synthesis of 2-acylbenzothiazoles is still desirable. Based on the principles of green chemistry, if catalysis loading could be dramatically reduced, no ligands were necessary, no strong



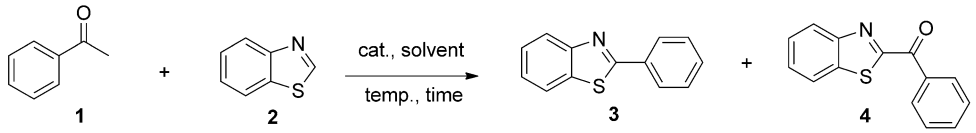
Scheme 1. Methods for the synthesis of 2-acylbenzothiazoles from aryl methyl ketones and benzothiazoles.

oxidant was required and the reaction time was short, it would be an ideal protocol in modern oxidation reactions. To the best of our knowledge, there are no reported examples of the efficient synthesis of 2-acylbenzothiazoles under extremely low catalysis loading in a short reaction time under air, O_2 or N_2 atmospheres as yet. Herein, we report an unprecedented, highly efficient and selective acylation of benzothiazoles from aryl methyl ketones.

In our initial study, acetophenone (**1**) and benzothiazole (**2**) were chosen as model substrates in the presence of $Cu(OAc)_2$ in DMSO at 130 °C under an oxygen atmosphere. Both 2-phenylbenzothiazole (**3**) and 2-acylbenzothiazole (**4**) were formed (Table 1, entry 1). Catalyst screening showed that CuI gave the highest ratio of desired product **4** to by-product **3** (Table 1, entries 1–8). Interestingly, when catalyst loading (CuI) was dropped, the ratios of desired product to by-product were increased (Table 1, entries 8–11). However, due to accurate weighing problems, we could just reduce the catalyst loading to 2 mol% (1.8 mg) based on our standard 0.5 mmol scale. Further investigation indicated that the temperature is very important for this transformation, when the temperature was dropped to 110 °C and 120 °C, no products were obtained (Table 1, entries 12 and 13). Solvent screening exhibited that DMSO is the best solvent and other solvents caused lower ratios of the desired product (Table 1, entries 11, 14–16). Acids as additive were also screened and, notably, HBF_4 could totally suppress the by-product **3** and give a 70% of the desired product **4** (Table 1, entry 20), but other acids gave inferior results (Table 1, entries 17–19). Further fine tuning showed that amounts of HBF_4 and acetophenone were very important for the reaction, when HBF_4 was reduced to 10 mol%, the yield of the desired product dropped to 40% with 5% of by-product **3**; when acetophenone was dropped from 2 equiv. to 1.2 equiv. and 1.5 equiv, the desired product was obtained in 51% and 58% yields, respectively (Table 1, entries 21, 23 and 24). In the absence of CuI, no product was formed at all, which showed that CuI plays a crucial role in the reaction (Table 1, entry 22); Most remarkably, when the reaction was carried out in air or an N_2 atmosphere, the desired product was obtained in 81% and 83% yields, respectively (Table 1, entries 25 and 26), which are much higher than from the reaction under O_2 (70% in entry 20). In order to shorten the reaction time, higher temperatures were applied on the reaction under the optimal conditions at 3 h and 6 h (Table 1, entries 27–30), the best result was obtained with 140 °C after 6 h heating (Table 1, entry 28), but the yield was only 71%, compared to that at 130 °C/9 h, we thus decided to take the latter (Table 1, entry 25) as our optimized conditions.

With the optimal reaction conditions available, the scope of substituted acetophenones was firstly extensively explored (Scheme 2). Both electron-rich and electron-poor aryl methyl ketones readily converted into the desired products (Scheme 2, **5**–**37**). Furthermore, substituents at different positions on the aryl group (*para*-, *meta*-, and *ortho*-positions) did not obviously affect the efficiency (Scheme 2, **5**–**7**, **10**–**21**), only in some cases did substitution at the *ortho*-position give slightly lower yields (Scheme 2, **10**, **13**, **16** and **19**). Halo-substituted aryl methyl ketones survived well leading to halo-substituted products (Scheme 2, **10**–**18**), which could be further transformed into other functionalities. It is noteworthy that

Table 1. Optimization of the reaction conditions.[a]

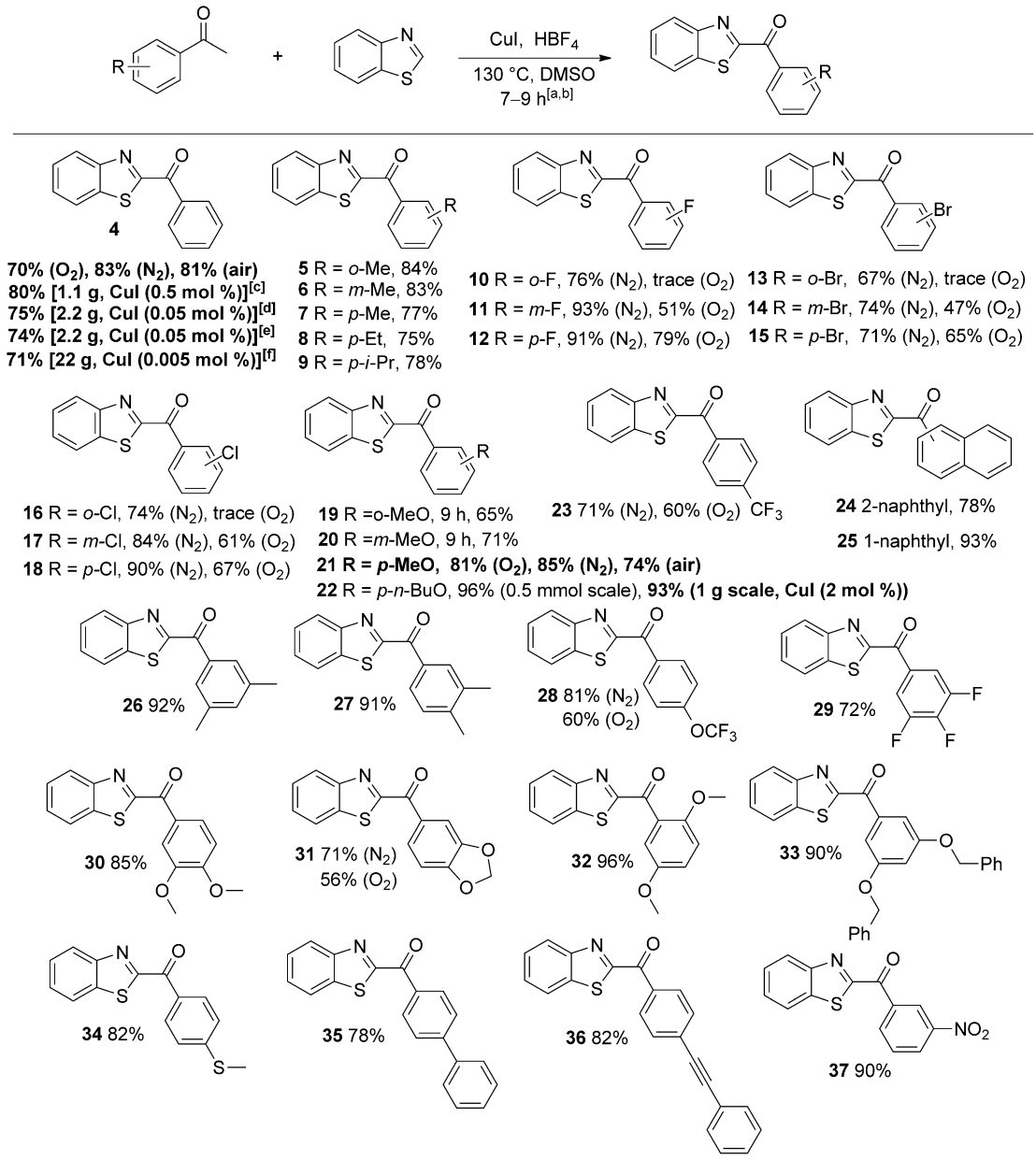


1 + 2 → 3 + 4

Entry	Catalyst	Atmosphere	Additive	Solvent	Temp. [°C]	Time [h]	Yields	
							3 [%][b]	**4** [%][b]
1	$Cu(OAc)_2$ (20 mol%)	O_2		DMSO	130	24	52	25.5
2	$Cu(OTf)_2$ (20 mol%)	O_2		DMSO	130	24	35	37
3	$Cu(TFA)_2$ (20 mol%)	O_2		DMSO	130	24	48	13
4	$CuBr_2$ (20 mol%)	O_2		DMSO	130	24	6	13
5	$CuSO_4$ (20 mol%)	O_2		DMSO	130	24	trace	trace
6	Cu_2O (20 mol%)	O_2		DMSO	130	24	72	7
7	CuCl (20 mol%)	O_2		DMSO	130	24	19.4	5
8	CuI (20 mol%)	O_2		DMSO	130	24	17.5	31
9	CuI (10 mol%)	O_2		DMSO	130	24	8	48
10	CuI (5 mol%)	O_2		DMSO	130	9	3	28
11	CuI (2 mol%)	O_2		DMSO	130	9	2	33
12	CuI (2 mol%)	O_2		DMSO	110	9	0	0
13	CuI (2 mol%)	O_2		DMSO	120	9	0	trace
14	CuI (2 mol%)	O_2		DMF	130	9	0	8
15	CuI (2 mol%)	O_2		toluene	130	9	0	0
16	CuI (2 mol%)	O_2		NMP	130	9	0	trace
17	CuI (2 mol%)	O_2	$BF_3{\cdot}Et_2O$ (1.2 equiv.)	DMSO	130	9	6	32
18	CuI (2 mol%)	O_2	TFA (1.2 equiv.)	DMSO	130	9	4	27
19	CuI (2 mol%)	O_2	AcOH (1.2 equiv.)	DMSO	130	9	0	10
20	**CuI (2 mol%)**	**O_2**	**HBF_4 (0.5 equiv.)**	**DMSO**	**130**	**9**	**trace**	**70[c]**
21	CuI (2 mol%)	O_2	HBF_4 (0.1 equiv.)	DMSO	130	9	5	40
22		O_2	HBF_4 (0.5 equiv.)	DMSO	130	9	0	0
23[d]	CuI (2 mol%)	O_2	HBF_4 (0.5 equiv.)	DMSO	130	9	0	51
24[e]	CuI (2 mol%)	O_2	HBF_4 (0.5 equiv.)	DMSO	130	9	0	58
25	**CuI (2 mol%)**	**N_2**	**HBF_4 (0.5 equiv.)**	**DMSO**	**130**	**9**	**0**	**83[c]**
26	**CuI (2 mol%)**	**air**	**HBF_4 (0.5 equiv.)**	**DMSO**	**130**	**9**	**trace**	**81[c]**
27	CuI (2 mol%)	N_2	HBF_4 (0.5 equiv.)	DMSO	140	3	0	48[c]
28	CuI (2 mol%)	N_2	HBF_4 (0.5 equiv.)	DMSO	140	6	0	71[c]
29	CuI (2 mol%)	N_2	HBF_4 (0.5 equiv.)	DMSO	150	3	0	61[c]
30	CuI (2 mol%)	N_2	HBF_4 (0.5 equiv.)	DMSO	150	6	0	65[c]

[a] *Reaction conditions:* phenylacetic acid (**1a**) (0.5 mmol), benzothiazole (**2a**), catalyst, solvent (0.75 mL) in a sealed tube under the corresponding atmosphere.
[b] GC yield using dodecane as internal standard.
[c] Isolated yields.
[d] With 1.2 equiv. of acetophenone.
[e] With 1.5 equiv. of acetophenone.

reactions under N_2 and O_2 were conducted for all the halo-substituted cases under the standard conditions, in all cases, the reaction under N_2 gave much higher yields of desired product compared with the counterparts under O_2 (average >20% in yields) (Scheme 2, **10**–**18**), which further proved that the N_2 atmosphere is critical for the reaction and that O_2 has some detrimental effect on this reaction. Notably, there were no desired products generated from three *ortho*-halo-substituted aryl methyl ketones under O_2 at all, yet good yields of the corresponding products were obtained under an N_2 atmosphere (Scheme 2, **10**, **13** and **16**), which either could not be achieved by the report-



[a] *Conditions:* benzothiazole (0.5 mmol), acetophenone derivative (1 mmol), CuI (2 mol%), HBF_4 (0.5 equiv.), DMSO, 130 °C, 7–9 h, under corresponding atmosphere, isolated yield.

[b] If not specially labelled, the reactions were conducted under N_2.

[c] 8.0 mmol benzothiazole (1.1 g), 2 equiv. acetophenone and 0.5 mol% CuI in a sealed tube for 9 h.

[d] 16.0 mmol benzothiazole (2.18 g), 2 equiv. acetophenone and 0.05 mol% CuI in a round-bottom flask for 18 h.

[e] 16.0 mmol benzothiazole, 2 equiv. acetophenone and 0.05 mol% CuI in a sealed tube for 9 h.

[f] 160 mmol benzothiazole, 2 equiv. acetophenone and 0.005 mol% CuI in a sealed tube for 32 h.

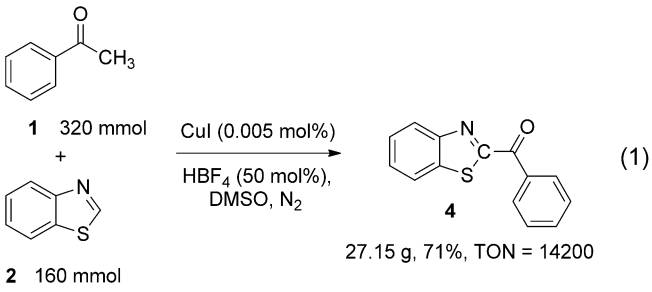
Scheme 2. Reactions of benzothiazole with various aryl methyl ketones.

ed two methods or just obtained in mixture (Scheme 1, methods 1 and 2).

Besides the halo-substituted aryl methyl ketones, 4-CF_3, 4-OCF_3 and 3,4-dioxobenzo-fused aryl methyl ketones were also examined under both N_2 and O_2 atmospheres, in all cases, the former one gave better results than the latter one (average >15% in yield in N_2 than in O_2) (Scheme 2, **23**, **28** and **31**). These results further proved the superiority of N_2 than O_2 in our reactions. Both 1- and 2-naphthyl methyl ketones were tolerated under the standard conditions and gave the corresponding products in excellent yields (Scheme 2,

24 and **25**), methylthiol, phenyl, phenylacetylenyl and nitro groups were also well tolerated under the standard conditions (Scheme 2, **34**–**37**). Besides all these monosubstituted groups, disubstituted or trisubstituted acetophenones were also transformed well to give good to excellent yields of the desired products (Scheme 2, **26**, **27**, **29**–**33**).

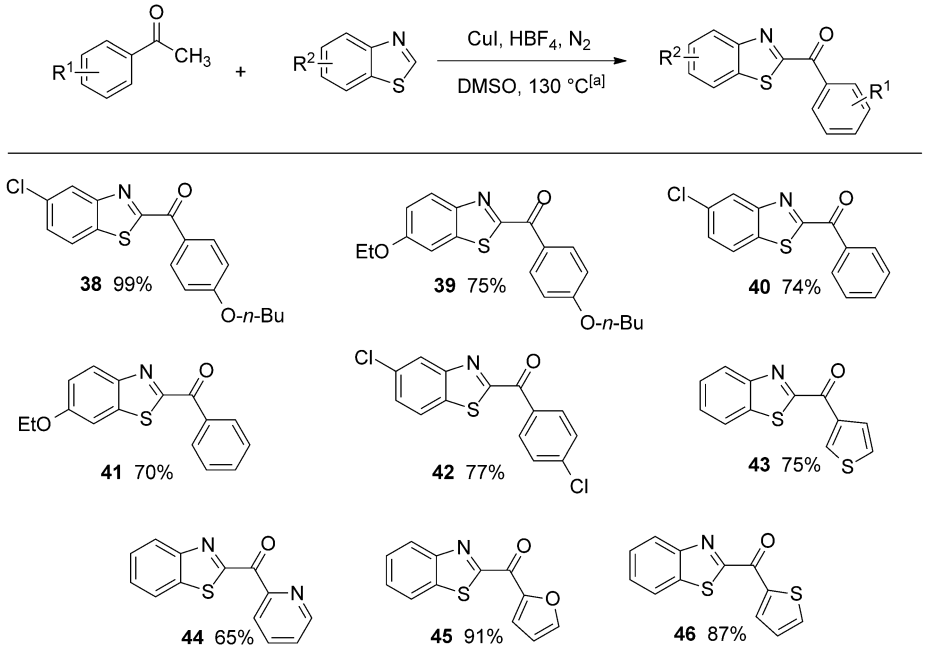
Both 2-benzoylbenzothiazole and 4-methoxybenzoylbenzothiazole (Scheme 2, **4** and **21**) were obtained under all three atmospheres: N_2, air, and O_2, but N_2 always gave the best yields among the three. Significantly, several gram-scale reactions were carried out under the standard conditions, the yields were not dramatically diminished even when the starting material was scaled up to 160 mmol (>20 g of benzothiazole) and the catalyst loading was reduced to 0.005 mol% due to the accurate weighing possible (1.5 mg of CuI, even lower catalyst loadings might be achieved with a larger reaction scale) (Scheme 2, **4** and **22**). This result corresponds to a turnover number of 14,200, which is the highest TON observed among all of sp^3 C–H functionalization of aryl methyl ketone [Eq. (1)]. This is a remarkable progress and it shows the preparative utility of our new CuI-catalyzed acylation of benzothiazoles.



(1)

Next, the scope of heteroaromatic methyl ketones and various benzothiazoles was investigated. As shown in Scheme 3, various heteroaromatic methyl ketones and different functionalities on benzothiazole were tolerated under the standard conditions and the corresponding desired products were obtained in good to excellent yields (Scheme 3, **38**–**46**).

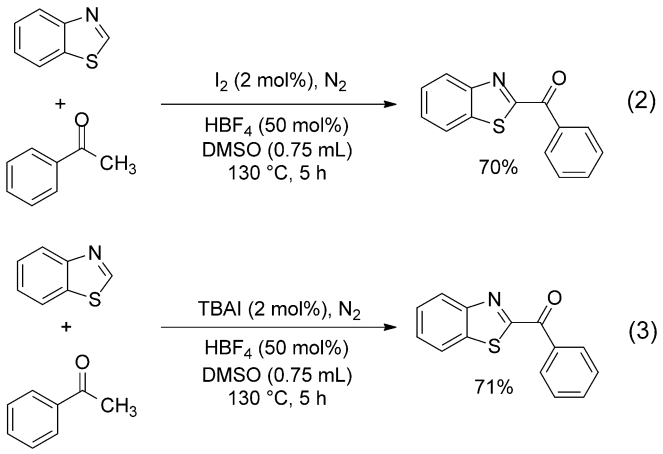
These results astonished us, as far as we know, in all of the reported sp^3 C–H functionalizations of aryl methyl ketone, strong oxidants were always a necessity for the success of these reactions, no one ever reported that the reaction could go smoothly in the absence of an external strong oxidant. Therefore, we carefully explored the reaction: in order to exclude an impurity effect in CuI, we purchased super pure CuI (99.995% purity) and did the reaction under O_2, a 71% yield of the desired product was obtained which was the same result as from 98% purity CuI in O_2, thus it ruled out an impurity effect. In order to rule out effect of a trace amount of O_2 in regular N_2, we also did the same reaction under super pure N_2 (99.995% purity), and it turned out to be just as efficient as under the regular N_2. These results showed that this is an unprecedented protocol. Since O_2 is not necessary for this



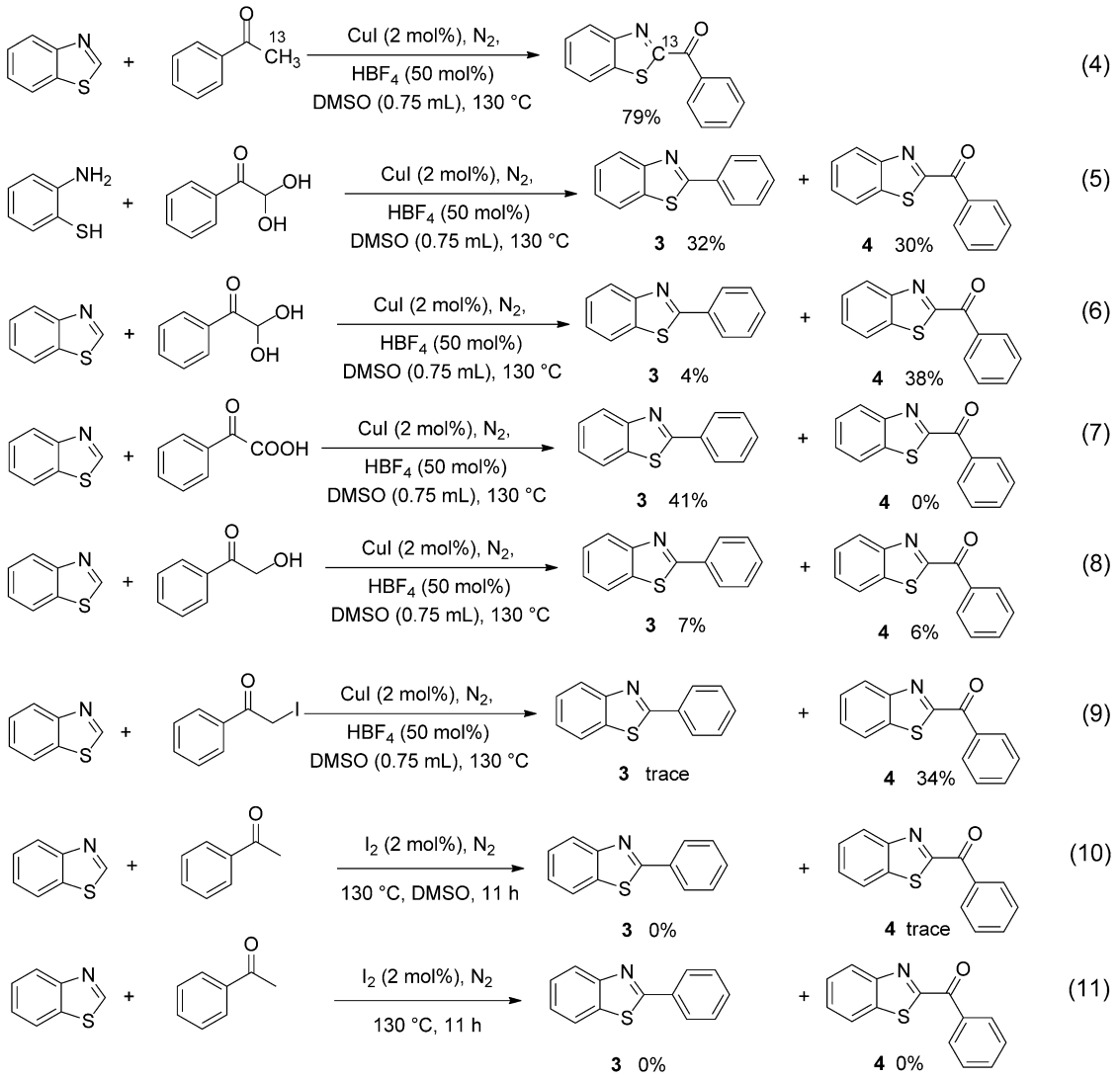
[a] *Conditions:* benzothiazole (0.5 mmol), aryl methyl ketone (1 mmol), CuI (2 mol%), HBF_4 (50 mol%), DMSO (1 mL), 130 °C, 7–9 h, under N_2, isolated yield.

Scheme 3. Reactions of various benzothiazoles and heteroaromatic methyl ketones.

reaction, it makes us realize that the I^- anion, not Cu^+ cation plays the crucial role in this reaction, so we carried out the following experiments: (i) we replaced CuI (2 mol%) with I_2 (2 mol%) under the standard conditions; (ii) we replaced CuI (2 mol%) with TBAI (*tert*-butylammonium iodide, 2 mol%) under the standard conditions, both of the reactions gave similar results and afforded 2-benzoylbenzothiazole in 70% and 71% isolated yields, respectively, after heating at 130 °C for 5 h [Eq. (2) and (3)]! These results clearly indicated that iodide anion is very important and iodine might be the active intermediate in this reaction.



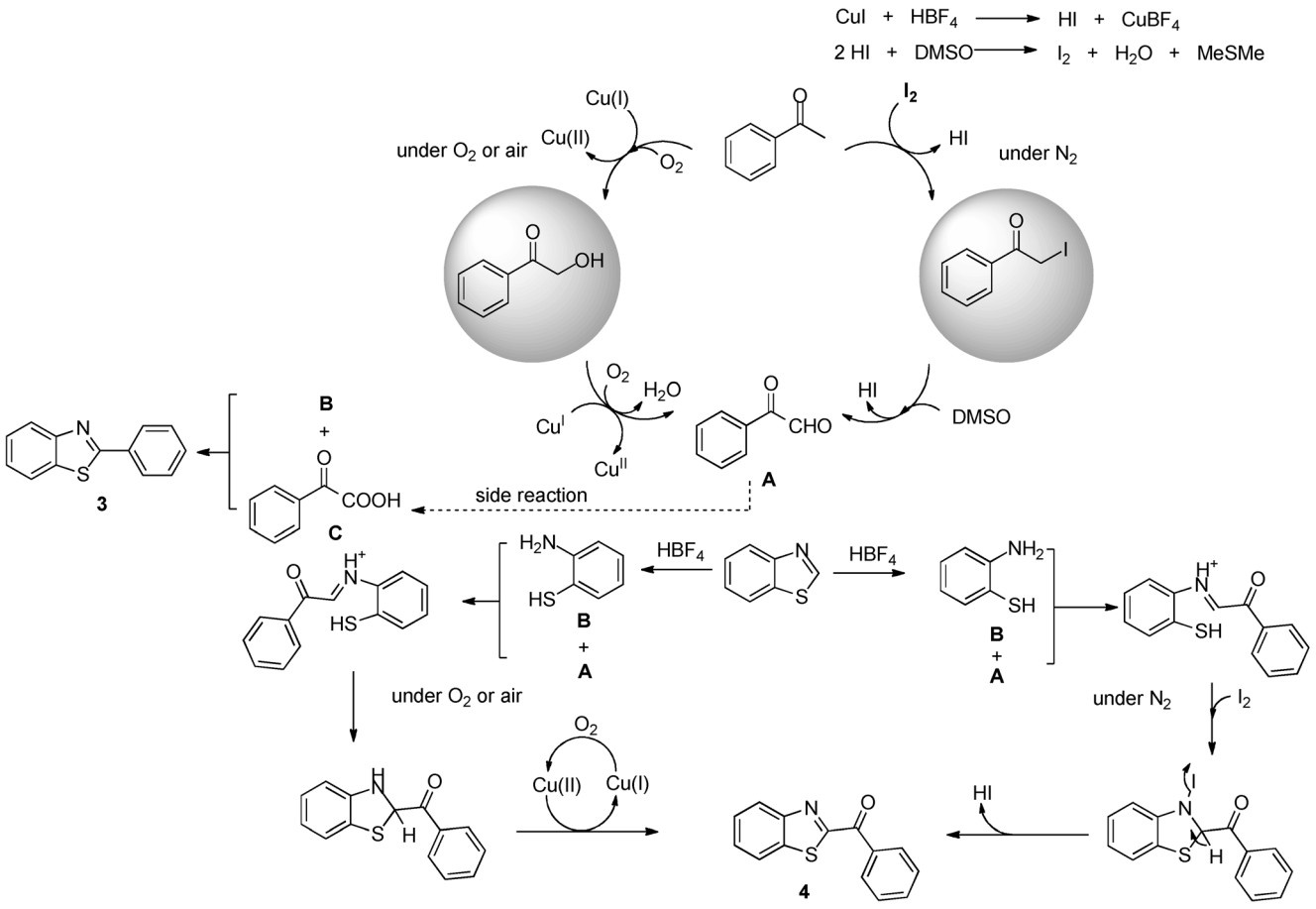
In order to further elucidate the exact pathway of the reaction, several control experiments were carried out. Firstly, the ^{13}C labelled acetophenone was treated with benzothiazole under the standard conditions. NMR showed that the isotopically labelled carbon (^{13}C) was inserted into the benzothiazole ring of the product [Scheme 4, Eq. (4)], which clearly demonstrated that ring opening occurred in the benzothiazole during the course of the reaction. Furthermore,



Scheme 4. Control experiments.

phenylglyoxal monohydrate was treated with 2-aminothiophenol and benzothiazole, respectively, under the standard conditions, in both cases, a mixture of compounds **3** and **4** was obtained [Scheme 4, Eq. (5) and (6)]. When benzothiazole was treated with α-ketophenylacetic acid, only compound **3** was obtained in 41% yield [Scheme 4, Eq. (7)], which might explain the above two results: phenylglyoxal monohydrate was quickly oxidized into α-ketophenylacetic acid under the standard conditions, thus a competitive reaction occurred to give a mixture of compounds **3** and **4**. When 2-hydroxyacetophenone and 2-iodoacetophenone were treated with benzothiazole, respectively, under the standard conditions, the former one gave a lower yield of the mixture of compounds **3** and **4**, yet the latter one mainly generated compound **4** in 34% with a trace amount of compound **3** [Scheme 4, Eq. (8) and Eq. (9)]. Thus 2-hydroxyacetophenone could not be the major intermediate for this reaction, yet 2-iodoacetophenone could not be ruled out as the major intermediate. Meanwhile, acetophenone and benzothiazole were treated with 2 mol% of iodine in additive-free conditions: one is in DMSO, the other one is solvent-free, yet in both conditions, no desired products were detected [Scheme 4, Eq. (10) and Eq. (11)].

On the basis of all the above experiments, we give plausible mechanisms both under O_2 and N_2 atmospheres (Scheme 5): under an O_2 atmosphere, acetophenone was firstly oxidized into 2-hydroxyacetophenone, *via* the activation of oxygen by Cu(I) salt, 2-hydroxyacetophenone further underwent oxidation to give phenylglyoxal (**A**); under an N_2 atmosphere, copper(I) iodide was treated with HBF_4 to afford HI and $CuBF_4$, and HI reacted with DMSO to give I_2 which could active the CH_3 group in acetophenone in the presence of DMSO, to generate 2-iodoacetophenone and further phenylglyoxal (**A**) (Kornblum oxidation). Compound **A** further reacted with the ring-opened benzothiazole (**B**, 2-aminobenzothiol), after heterocyclization, finally, desired product **4** was obtained. Compound **A** could be easily oxidized into α-ketophenylacetic acid which will react with ring-opened 2-aminothiophenol to give 2-phenylbenzothiazole (**3**) as the by-product.



Scheme 5. Plausible mechanism.

In summary, a highly efficient CuI-catalyzed acylation of benzothiazoles with aryl methyl ketones as carbonyl sources has been developed. This reaction could be carried out smoothly with extremely lower catalyst loadings and could tolerate variety of functionality on both benzothiazoles and aryl methyl ketones, to selectively afford 2-acylbenzothiazoles. The superior substrate tolerability and preparative utility (scale-up to 160 mmol in the lab without diminishing the isolated yield) suggested that the reaction is very practical and could be a complementary method for the current reported ones. Later on, I_2 and TBAI also showed great catalytic activity in this reaction. Studies on the mechanism and application of this protocol are ongoing in our laboratory.

Experimental Section

Typical Procedure

A sealed tube was charged with benzothiazole (68 mg, 0.5 mmol), CuI (1.9 mg, 2 mol%), acetophenone (120 mg, 1.0 mmol), HBF_4 (0.25 mmol, 40% aqueous solution) and DMSO (0.75 mL). The resulting solution was purged by N_2 and the tube sealed, then the reaction mixture was stirred at 130 °C under N_2 for 9 h (monitored by TLC and GC). Upon completion of the reaction, ethyl acetate (20 mL) was added, the organic layer was washed with saturated $NaHCO_3$ solution (20 mL × 2), brine (20 mL × 1), the combined aqueous layers were extracted with ethyl acetate (20 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4. The solvents were removed *via* rotary evaporator and the residue was purified by flash chromatography (silica gel, ethyl acetate: petroleum ether = 30:1) to give desired product **4** as a light yellow solid; yield: 98.0 mg (82%).

Acknowledgements

We are grateful for financial support from the National Science Foundation of China (21202049), the Recruitment Program of Global Experts (1000 Talents Plan), Fujian Hundred Talents Program and Research Funds of Huaqiao University. We also thank Prof. Dr. Robert Pascal from Tulane University for helpful mechanism discussion and Prof. Zhenhua Gu from USTC for generous instrumental support.

References

[1] a) L. Zirngibl, *Antifungal Azoles: A Comprehensive Survey of Their Structures and Properties*, Wiley-VCH, Weinheim, **1998**; b) A. R. Katritzky, C. W. Rees, E. F. Scriven, *Comprehensive Heterocyclic Chemistry III*, Pergamon, Oxford, **1999**, Vol. 1; c) A. Katritzky, A. Pozharskii, *Handbook of Heterocyclic Chemistry*, 1st edn., Pergamon, Oxford, **2003**; d) D. A. Horton, G. T. Bourne, M. L. Smythe, *Chem. Rev.* **2003**, *103*, 893–930.

[2] a) Y.-X. Chen, L.-F. Qian, W. Zhang, B. Han, *Angew. Chem.* **2008**, *120*, 9470–9473; *Angew. Chem. Int. Ed.* **2008**, *47*, 9330–9333; b) K. Xie, Z. Yang, X. Zhou, X. Li, S. Wang, Z. Tan, X. An, C.-C. Guo, *Org. Lett.* **2010**, *12*, 1564–1567; c) S. Kirchberg, S. Tani, K. Ueda, J. Yamaguchi, A. Studer, K. Itami, *Angew. Chem.* **2011**, *123*, 2435–2439; *Angew. Chem. Int. Ed.* **2011**, *50*, 2387–2391; d) B. Liu, X. Qin, K. Li, X. Li, Q. Guo, J. Lan, J. You, *Chem. Eur. J.* **2010**, *16*, 11836–11839; e) J. Huang, J. Chan, Y. Chen, C. J. Borths, K. D. Baucom, R. D. Larsen, M. M. Faul, *J. Am. Chem. Soc.* **2010**, *132*, 3674–3675; f) J. C. Lewis, A. M. Berman, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 2493–2500; g) H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2007**, *129*, 12404–12405; h) S. Liu, R. Chen, X. Guo, H. Yang, G. Deng, C.-J. Li, *Green Chem.* **2012**, *14*, 1577; i) Z. Yang, X. Chen, S. Wang, J. Liu, K. Xie, A. Wang, Z. Tan, *J. Org. Chem.* **2012**, *77*, 7086–7091.

[3] Q. Song, Q. Feng, M. Zhou, *Org. Lett.* **2013**, *15*, 5990–5993.

[4] L. Zhang, X. Bi, X. Guan, X. Li, Q. Liu, B.-D. Barry, P. Liao, *Angew. Chem.* **2013**, *125*, 11513–11517; *Angew. Chem. Int. Ed.* **2013**, *52*, 11303–11307.

[5] a) R. W. Evans, J. R. Zbieg, S. Zhu, W. Li, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2013**, *135*, 16074–16077; b) F.-T. Du, J.-X. Ji, *Chem. Sci.* **2012**, *3*, 460–465; c) M. Lamani, K. R. Prabhu, *Chem. Eur. J.* **2012**, *18*, 14638–14642.

[6] J. Zhang, Y. Wei, S. Lin, F. Liang, P. Liu, *Org. Biomol. Chem.* **2012**, *10*, 9237–9242.

[7] a) Q. Gao, X. Wu, F. Jia, M. Liu, Y. Zhu, Q. Cai, A. Wu, *J. Org. Chem.* **2013**, *78*, 2792–2797; b) Y.-P. Zhu, M. Lian, F.-C. Jia, M.-C. Liu, J.-J. Yuan, Q.-H. Gao, A.-X. Wu, *Chem. Commun.* **2012**, *48*, 9086–9088.

[8] S. Liu, R. Chen, H. Chen, G.-J. Deng, *Tetrahedron Lett.* **2013**, *54*, 3838–3841.

[9] During the preparation of this manuscript, another paper which reported the formation of 2-acylbenzothiazoles from aryl methyl ketones and benzothiazoles appeared in *Tetrahedron* (J. Wang, X.-Z. Zhang, S.-Y. Chen, X.-Q. Yu, *Tetrahedron* **2014**, *70*, 245–250). However, the reported methods always gave a mixture of both 2-aryl- and 2-acylbenzothiazole and did not show good chemoselectivity, thus we did not list this reference in Scheme 1.

