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Dual Roles of Sulfonyl Hydrazides: A Three-Component Reaction To Construct Fully Substituted Pyrazoles Using TBAI/TBHP

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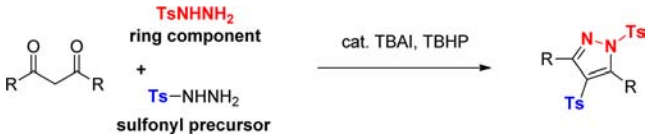
Supporting Information

ABSTRACT: A mild and rapid approach has been developed for the construction of fully substituted pyrazoles using TBAI as a catalyst and TBHP as an oxidant, in which tosylhydrazide functions as the ring component and sulfonyl precursor. This protocol features a wide substrate scope with a broad range of functional group tolerance, utilizes easily available starting materials, can be scaled-up, and is operationally simple.

Pyrazoles and their derivatives have attracted considerable attention because of their wide applications in the pharmaceutical and agrochemical sciences.[1] For example, Celebrex,[2] employed as a selective COX-2 inhibitor, is one of the top 200 brand name drugs by total US prescriptions in 2012.[3] Additionally, pyrazoles serve as ligands in coordination chemistry,[4] precursors to *N*-heterocyclic carbenes (NHCs),[5] and directing groups for C−H activations.[6] As a result, a variety of methods have been elegantly developed for the synthesis of pyrazoles.[7−10] Among the various pyrazoles, fully substituted pyrazoles are notably prevalent in many bioactive molecules.[11] The most popular approaches toward them consist of the cyclocondensation of a monosubstituted hydrazine with a substituted 1,3-dielectrophile,[12] the [3 + 2] cycloaddition,[13] and the functionalization of preformed trisubstituted pyrazoles.[14] In 2010, Glorius et al. reported a new method for the synthesis of fully substituted pyrazoles from enamines and nitriles via an oxidative N−N bond formation.[15] However, in the majority of these methods, complex prefunctionalized starting materials or multistep sequences were usually required. Therefore, a simple and rapid protocol is still highly desirable for the construction of fully substituted pyrazoles.

The sulfonyl group, a strong electron-withdrawing group, is of great interest due to its importance in medical chemistry, photovoltaic materials, nonlinear optics, and synthetic chemistry.[16] Therefore, it is valuable to develop new strategies to introduce sulfonyl groups to the designated molecular frameworks. Recently, sulfonylation via sulfonyl radicals generated *in situ* from sulfonyl hydrazides[17a−e] using tetrabutylammonium iodide (TBAI) and *tert*-butyl hydroperoxide (TBHP) has been well developed by several groups. As an outgrowth of these studies, we postulated that tosylhydrazide might play dual roles as the ring component as well as a sulfonyl precursor to construct a novel fully substituted pyrazole in one step. As a result, we herein described the successful execution of this ideal and fully substituted pyrazoles were prepared efficiently without isolating or purifying any intermediates (Scheme 1).

Scheme 1. Our Strategy for the Synthesis of Fully Substituted Pyrazoles



Initially, the reaction of acetylacetone **1a** and tosylhydrazide **2a** using TBAI/TBHP[18] afforded the desired 3,5-dimethyl-1,4-ditosyl-1*H*-pyrazole **3a** in moderate yield (Table 1, entry 1). Gratifyingly, the desired product **3a** was isolated in 72% and 80% yields using 30 mol % pyridine or 20 mol % $Co(OAc)_2 \cdot 4H_2O$ as an additive, respectively (Table 1, entries 2−3). When both of them were added, the yield increased slightly to 85% (Table 1, entry 4). The reaction could not proceed in the absence of TBAI (Table 1, entries 5). Other oxidants such as air, di-*tert*-butyl peroxide (DTBP), and 30% aqueous H_2O_2 were also examined and were found to be less effective than TBHP (Table 1, entries 6−8).

With optimized conditions identified, a series of sulfonyl hydrazides were evaluated, as shown in Scheme 2. Sulfonyl

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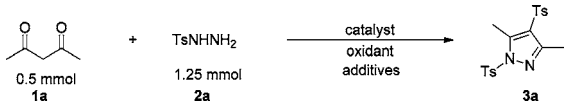
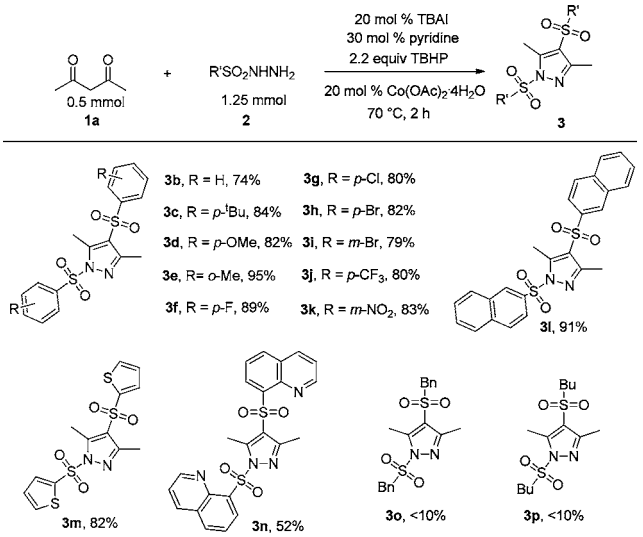
Table 1. Optimization Studies[a]



entry	oxidant	catalyst	additives	yield (%)[b]
1	TBHP	TBAI	–	58
2	TBHP	TBAI	pyrdine	72
3	TBHP	TBAI	$Co(OAc)_2{\cdot}4H_2O$	80
4	**TBHP**	**TBAI**	**$Co(OAc)_2{\cdot}4H_2O$/pyridine**	**85**
5	TBHP	–	$Co(OAc)_2{\cdot}4H_2O$/pyridine	N.D.[c]
6	air	TBAI	$Co(OAc)_2{\cdot}4H_2O$/pyridine	31
7	DTBP	TBAI	$Co(OAc)_2{\cdot}4H_2O$/pyridine	18
8	H_2O_2	TBAI	$Co(OAc)_2{\cdot}4H_2O$/pyridine	38

[a]0.5 mmol of **1a**, 1.25 mmol of **2a**, 0.1 mmol of TBAI, 0.1 mmol of $Co(OAc)_2{\cdot}4H_2O$, 0.15 mmol of pyridine, 1.1 mmol of oxidant, 2.0 mL of ethyl acetate (EA) under air, at 70 °C for 2 h. [b]Isolated yield. [c]Not detected.

Scheme 2. Scope of Sulfonyl Hydrazides[a]

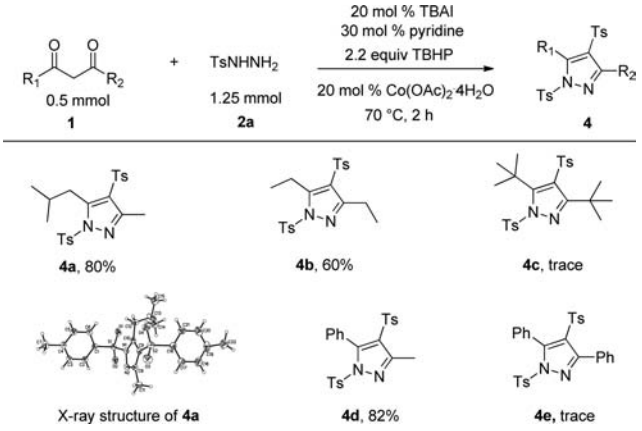


[a]0.5 mmol of **1a**, 1.25 mmol of **2**, 0.1 mmol of TBAI, 0.1 mmol of $Co(OAc)_2{\cdot}4H_2O$, 0.15 mmol of pyridine, 1.1 mmol of TBHP, 2.0 mL of EA under air, at 70 °C for 2 h.

hydrazides with *ortho*, *meta*, or *para* substitutents on the phenyl group could be converted to corresponding pyrazoles in good to excellent yields. Both electron-donating and -withdrawing groups hardly influenced the reactivity of this transformation. It is noteworthy that the presence of halide substituents (**3f**, **3g**, **3h**, **3i**) on the aromatic groups had no significant effect on the efficiency, which could be used for further functionalization through transition-metal-catalyzed cross-coupling. To our delight, some heteroaryl sulfonyl hydrazides such as thiophene and quinolone resulted in smooth reactions and the corresponding products **3m** and **3n** were furnished in satisfactory yields. Unfortunately, aliphatic sulfonyl hydrazides (**3o**, **3p**) were not adaptable substrates for this protocol, presumably owing to the relative instability of the sulfonyl radicals generated *in situ* from aliphatic sulfonyl hydrazides.

Next, we set out to survey the reactivity of symmetrical and nonsymmetrical 1,3-diketones in this reaction, and the results are summarized in Scheme 3. When 6-methyl-2,4-heptanedione was used as the substrate, the corresponding product **4a** was

Scheme 3. Scope of 1,3-Diketones[a]

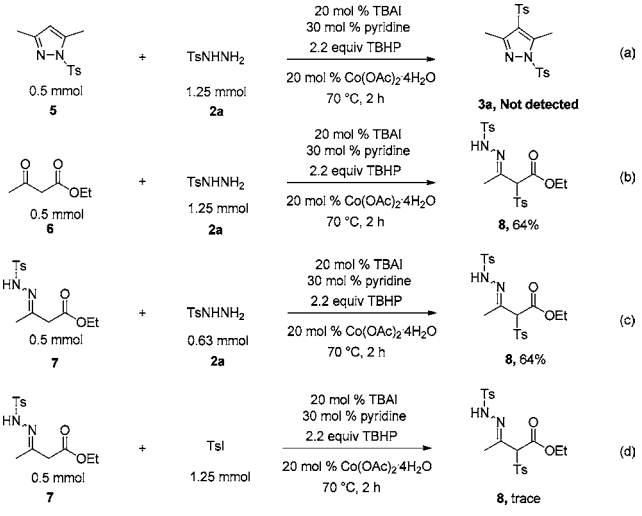


[a]0.5 mmol of **1**, 1.25 mmol of **2a**, 0.1 mmol of TBAI, 0.1 mmol of $Co(OAc)_2{\cdot}4H_2O$, 0.15 mmol of pyridine, 1.1 mmol of TBHP, 2.0 mL of EA under air, at 70 °C for 2 h.

obtained with excellent regioselectivity and high yield, and the exact structure was unequivocally confirmed by single-crystal X-ray analysis. However, the bulk steric effects related to 1,3-diketones almost canceled this catalytic behavior, leading to a trace amount of product **4c** and **4e**. Again, 1-phenylbutane-1,3-dione could also participate in the reaction smoothly (product **4d**).

To explore the reaction mechanism for this transformation, some control experiments were conducted. When pyrazole **5** was subjected to the standard conditions, no desired product **3a** was detected (Scheme 4a). The use of ethyl 3-oxobutanoate **6**

Scheme 4. Probe for Possible Mechanism



or ethyl 3-(2-tosylhydrazono)butanoate **7** lead to the desired product **8** in good yields (Scheme 4b, 4c). Based upon the above-mentioned results, we suspected that sequential condensation of tosylhydrazide with 1,3-diketone, sulfonylation, and cyclization were involved in this pyrazole formation reaction. Notably, reaction of TsI and **7** only afforded a trace amount of **8** (Scheme 4d), thus excluding the possibility of TsI as the reaction intermediate.

On the basis of the above-mentioned findings and literature, a tentative mechanism is depicted in Scheme 5. Initially, I^- promotes the decomposition of TBHP to generate ^{t}BuO$^\bullet$ radical **A** and ^{t}BuOO$^\bullet$ radical **B** (step 5a). The sulfonyl radical

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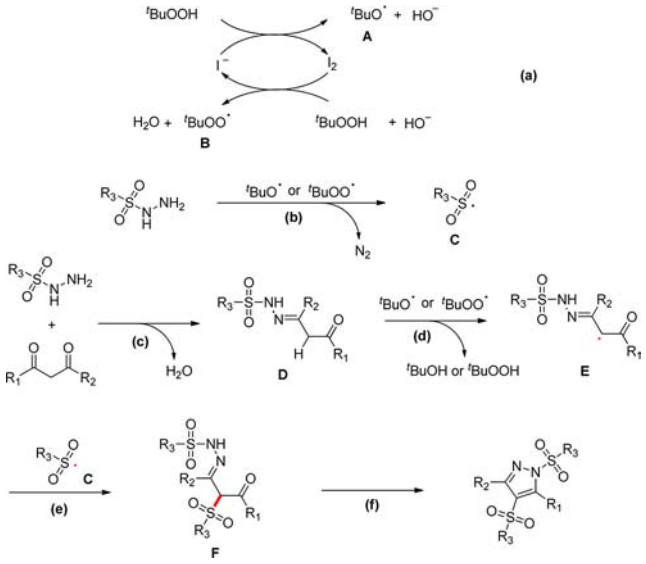
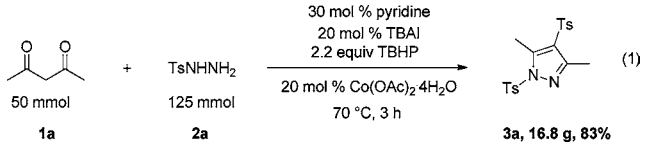
Scheme 5. Proposed Reaction Mechanism



C was also generated *in situ* from sulfonyl hydrazides under the oxidative conditions with the release of N_2 (step 5b).[17] The condensation of sulfonyl hydrazides and 1,3-diketones afforded imine **D** (step 5c), which undergoes H-abstraction by $^tBuO^•$ radical **A** or $^tBuOO^•$ radical **B** to form radical **E** (step 5d). Then, **E** was trapped by sulfonyl radical **C** to afford intermediate **F** (step 5e). Finally, the desired pyrazole was delivered through the intramolecular condensation of intermediate **F** (step 5f).

To showcase the practicality of our method, the reaction of acetylacetone **1a** and tosylhydrazide **2a** was scaled up to 50 mmol and the desired product **3a** was obtained without a significant loss in yield (16.8 g, 83%, eq 1).



In summary, we have successfully disclosed a facile and efficient approach for the installation of fully substituted pyrazoles in one step. This transformation allows a broad substrate scope, including aromatic and heteroaromatic sulfonyl hydrazides bearing a wide range of functional groups, utilizes easily available starting materials, and offers operational simplicity. Synthetically, the simple catalytic system was found to be highly effective even on a 50 mmol scale. Currently, studies to expand the scope to other hydrazines and to uncover further mechanisms are in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Terrett, N. K.; Bell, A. S.; Brown, D.; Ellis, P. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1819. (b) Elguero, J.; Goya, P.; Jagerovic, N.; Silva, A. M. S. *Targets Heterocycl. Syst.* **2002**, *6*, 52. (c) Tracey, W. R.; Allen, M. C.; Frazier, D. E.; Fossa, A. A.; Johnson, C. G.; Marala, R. B.; Knight, D. R.; Guzman-Perez, A. *Cardiovasc. Drug Rev.* **2003**, *21*, 17. (d) Keter, F. K.; Darkwa, J. *BioMetals* **2012**, *25*, 9. (e) Havrylyuk, D.; Zimenkovsky, B.; Vasylenko, O.; Gzella, A.; Lesyk, R. *J. Med. Chem.* **2012**, *55*, 8630.

(2) Yang, C. Y.; Meng, C. L.; Liao, C. L.; Wong, P. Y.-K. *Prostaglandins & Other Lipid Mediators* **2003**, *72*, 115.

(3) (a) McGrath, N. A.; Brichacek, M.; Njardarson, J. T. *J. Chem. Educ.* **2010**, *87*, 1348. (b) Ilardi, E. A.; Vitaku, E.; Njardarson, J. T. *J. Chem. Educ.* **2013**, *90*, 1403.

(4) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Halcrow, M. A. *Dalton Trans.* **2009**, 2059. (c) Viciano-Chumillas, M.; Tanase, S.; de Jongh, L. J.; Reedijk, J. *Eur. J. Inorg. Chem.* **2010**, 3403.

(5) Schmidt, A.; Dreger, A. *Curr. Org. Chem.* **2011**, *15*, 2897.

(6) (a) Thirunavukkarasu, V. S.; Raghuvanshi, K.; Ackermann, L. *Org. Lett.* **2013**, *15*, 3286. (b) Liu, P. M.; Frost, C. G. *Org. Lett.* **2013**, *15*, 5862.

(7) (a) Makino, K.; Kim, H. S.; Kurasawa, Y. *J. Heterocycl. Chem.* **1998**, *35*, 489. (b) Svete, J. *ARKIVOC* **2006**, *7*, 35. (c) Fustero, S.; Simón-Fuentes, A.; Sanz-Cervera, J. F. *Org. Prep. Proced. Int.* **2009**, *41*, 253. (d) Fustero, S.; Sánchez-Roselló, M.; Barrio, P.; Simón-Fuentes, A. *Chem. Rev.* **2011**, *111*, 6984. (e) Janin, Y. L. *Chem. Rev.* **2012**, *112*, 3924.

(8) (a) Norris, T.; Colon-Cruz, R.; Ripin, D. H. B. *Org. Biomol. Chem.* **2005**, *3*, 1844. (b) Xie, F.; Cheng, G.; Hu, Y. *J. Comb. Chem.* **2006**, *8*, 286. (c) Heller, S. T.; Natarajan, S. R. *Org. Lett.* **2006**, *8*, 2675. (d) Surmont, R.; Verniest, G.; Kimpe, N. D. *Org. Lett.* **2010**, *12*, 4648. (e) Guo, S.; Wang, J.; Guo, D.; Zhang, X.; Fan, X. *RSC Adv.* **2012**, *2*, 3772. (f) Kirkham, J. D.; Edeson, S. J.; Stokes, S.; Harrity, J. P. A. *Org. Lett.* **2012**, *14*, 5354.

(9) (a) Qi, X.; Ready, J. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3242. (b) Browne, D. L.; Helm, M. D.; Plant, A.; Harrity, J. P. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8656. (c) Kawai, H.; Yuan, Z.; Tokunaga, E.; Shibata, N. *Org. Lett.* **2012**, *14*, 5330. (d) Foster, R. S.; Adams, H.; Jakobi, H.; Harrity, J. P. A. *J. Org. Chem.* **2013**, *78*, 4049. (e) Pérez-Aguilar, M. C.; Valdés, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 7219. (f) Zhang, G.; Ni, H.; Chen, W.; Shao, J.; Liu, H.; Chen, B.; Yu, Y. *Org. Lett.* **2013**, *15*, 5967.

(10) (a) Gérard, A.-L.; Mahatsekake, C.; Collot, V.; Rault, S. *Tetrahedron Lett.* **2007**, *48*, 4123. (b) McLaughlin, M.; Marcantonio, K.; Chen, C.; Davies, I. W. *J. Org. Chem.* **2008**, *73*, 4309. (c) Mateos, C.; Mendiola, J.; Carpintero, M.; Mínguez, J. M. *Org. Lett.* **2010**, *12*, 4924. (d) Pandey, G.; Bhowmik, S.; Batra, S. *Org. Lett.* **2013**, *15*, 5044.

(11) (a) Sliskovic, D. R.; Roth, B. D.; Wilson, M. W.; Hoefle, M. L.; Newton, R. S. *J. Med. Chem.* **1990**, *33*, 31. (b) Genin, M. J.; Biles, C.; Keiser, B. J.; Poppe, S. M.; Swaney, S. M.; Tarpley, W. G.; Yagi, Y.; Romero, D. L. *J. Med. Chem.* **2000**, *43*, 1034. (c) Gupta, G. K.; Kumar, A. *Acta Poloniae Pharmaceutica - Drug Research* **2012**, *69*, 763.

(12) (a) Lee, K. Y.; Kim, J. M.; Kim, J. N. *Tetrahedron Lett.* **2003**, *44*, 6737. (b) Gerstenberger, B. S.; Rauckhorst, M. R.; Starr, J. T. *Org. Lett.* **2009**, *11*, 2097. (c) Okitsu, T.; Sato, K.; Wada, A. *Org. Lett.* **2010**, *12*, 3506. (d) Zora, M.; Kivrak, A.; Yazici, C. *J. Org. Chem.* **2011**, *76*, 6726. (e) Qian, J.; Liu, Y.; Zhu, J.; Jiang, B.; Xu, Z. *Org. Lett.* **2011**, *13*, 4220.

(13) (a) Deng, X.; Mani, N. S. *J. Org. Chem.* **2008**, *73*, 2412. (b) Browne, D. L.; Vivat, J. F.; Plant, A.; Gomez-Bengoa, E.; Harrity, J. P. A. *J. Am. Chem. Soc.* **2009**, *131*, 7762. (c) Browne, D. L.; Taylor, J.

B.; Plant, A.; Harrity, J. P. A. *J. Org. Chem.* **2009**, *74*, 396. (d) Foster, R. S.; Jakobi, H.; Harrity, J. P. A. *Org. Lett.* **2012**, *14*, 4858.
(14) (a) Goikhman, R.; Jacques, T. L.; Sames, D. *J. Am. Chem. Soc.* **2009**, *131*, 3042. (b) Willy, B.; Müller, T. J. J. *Org. Lett.* **2011**, *13*, 2082. (c) Ye, M.; Edmunds, A. J. F.; Morris, J. A.; Sale, D.; Zhang, Y.; Yu, J.-Q. *Chem. Sci.* **2013**, *4*, 2374.
(15) Neumann, J. J.; Suri, M.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 7790.
(16) For select examples of applications of the sulfonyl group: (a) Ivachtchenko, A. V.; Dmitriev, D. E.; Golovina, E. S.; Kadieva, M. G.; Koryakova, A. G.; Kysil, V. M.; Mitkin, O. D.; Okun, I. M.; Tkachenko, S. E.; Vorobiev, A. A. *J. Med. Chem.* **2010**, *53*, 5186. (b) Ivachtchenko, A. V.; Golovina, E. S.; Kadieva, M. G.; Kysil, V. M.; Mitkin, O. D.; Tkachenko, S. E.; Okun, I. M. *J. Med. Chem.* **2011**, *54*, 8161. (c) Huang, Y.; Huo, L.; Zhang, S.; Guo, X.; Han, C. C.; Li, Y.; Hou, J. *Chem. Commun.* **2011**, *47*, 8904. (d) Ulman, A.; Willand, C. S.; Köhler, W.; Robello, D. R.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc.* **1990**, *112*, 7083. (e) Hardinger, S. A.; Bayne, C.; Kantorowski, E.; McClellan, R.; Larres, L.; Nuesse, M.-A. *J. Org. Chem.* **1995**, *60*, 1104. (f) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189. (g) Ruano, J. L. G.; de Diego, S. A. A.; Martín, M. R.; Torrente, E.; Castro, A. M. M. *Org. Lett.* **2004**, *6*, 4945.
(17) For sulfonyl radicals generated *in situ* from sulfonyl hydrazides, see: (a) Li, X.; Xu, X.; Zhou, C. *Chem. Commun.* **2012**, *48*, 12240. (b) Li, X.; Xu, X.; Tang, Y. *Org. Biomol. Chem.* **2013**, *11*, 1739. (c) Li, X.; Xu, X.; Shi, X. *Tetrahedron Lett.* **2013**, *54*, 3071. (d) Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 4496. (e) Li, X.; Fang, M.; Hu, P.; Hong, G.; Tang, Y.; Xu, X. *Adv. Synth. Catal.* **2014**, DOI: 10.1002/adsc.201301158. (f) Taniguchi, T.; Sugiura, Y.; Zaimoku, H.; Ishibashi, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 10154. (g) Taniguchi, T.; Idota, A.; Ishibashi, H. *Org. Biomol. Chem.* **2011**, *9*, 3151. (h) Li, X.; Shi, X.; Fang, M.; Xu, X. *J. Org. Chem.* **2013**, *78*, 9499.
(18) Recently, we and others developed reactions using TBAI/TBHP; see: (a) Chen, L.; Shi, E.; Liu, Z.; Chen, S.; Wei, W.; Li, H.; Xu, K.; Wan, X. *Chem.—Eur. J.* **2011**, *17*, 4085. (b) Wei, W.; Zhang, C.; Xu, Y.; Wan, X. *Chem. Commun.* **2011**, *47*, 10827. (c) Chen, S.; Xu, Y.; Wan, X. *Org. Lett.* **2011**, *13*, 6152. (d) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 3231. (e) Shi, E.; Shao, Y.; Chen, S.; Hu, H.; Liu, Z.; Zhang, J.; Wan, X. *Org. Lett.* **2012**, *14*, 3384. (f) Zhang, J.; Jiang, J.; Li, Y.; Zhao, Y.; Wan, X. *Org. Lett.* **2013**, *15*, 3222. (g) Zhang, J.; Jiang, J.; Li, Y.; Wan, X. *J. Org. Chem.* **2013**, *78*, 11366. (h) Zhang, C.; Liu, C.; Shao, Y.; Bao, X.; Wan, X. *Chem.—Eur. J.* **2013**, *19*, 17917. (i) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331. (j) Ma, L.; Wang, X.; Yu, W.; Han, B. *Chem. Commun.* **2011**, *47*, 11333. (k) Froehr, T.; Sindlinger, C. P.; Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *Org. Lett.* **2011**, *13*, 3754. (l) Li, L.-T.; Huang, J.; Li, H.-Y.; Wen, L.-J.; Wang, P.; Wang, B. *Chem. Commun.* **2012**, *48*, 5187. (m) Wong, Y.-C.; Tseng, C.-T.; Kao, T.-T.; Yeh, Y.-C.; Shia, K.-S. *Org. Lett.* **2012**, *14*, 6024. (n) Mai, W.-P.; Wang, H.-H.; Li, Z.-C.; Yuan, J.-W.; Xiao, Y.-M.; Yang, L.-R.; Mao, P.; Qu, L.-B. *Chem. Commun.* **2012**, *48*, 10117. (o) Xie, J.; Jiang, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2012**, *48*, 979. (p) Tan, B.; Toda, N.; Barbas, C. F., III. *Angew. Chem., Int. Ed.* **2012**, *51*, 12538. (q) Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* **2013**, *49*, 3031. For selected examples of transition metal catalytic systems using TBHP, see: (r) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 11810. (s) Pan, S.; Liu, J.; Li, H.; Wang, Z.; Guo, X.; Li, Z. *Org. Lett.* **2010**, *12*, 1932. (t) Boess, E.; Schmitz, C.; Klussmann, M. *J. Am. Chem. Soc.* **2012**, *134*, 5317. (u) Ratnikov, M. O.; Doyle, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 1549. (v) Li, H.; Li, P.; Wang, L. *Org. Lett.* **2013**, *15*, 620. (w) Wei, W.-T.; Zhou, M.-B.; Fan, J.-H.; Liu, W.; Song, R.-J.; Liu, Y.; Hu, M.; Xie, P.; Li, J.-H. *Angew. Chem., Int. Ed.* **2013**, *52*, 3638. (x) Priebbenow, D. L.; Bolm, C. *Org. Lett.* **2014**, *16*, 1650. (y) Zhao, J.; Fang, H.; Han, J.; Pan, Y. *Org. Lett.* **2014**, *16*, 2530. (z) Zhang, F.; Du, P.; Chen, J.; Wang, H.; Luo, Q.; Wan, X. *Org. Lett.* **2014**, *16*, 1932.