Copper- and Cobalt-Catalyzed Direct Coupling of sp³ α-Carbon of Alcohols with Alkenes and Hydroperoxides

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Ⓢ *Supporting Information*

ABSTRACT: A zerovalent copper- and cobalt-catalyzed direct coupling of the sp³ α-carbon of alcohols with alkenes and hydroperoxides was developed in which the hydroperoxides acted as radical initiator and then coupling partner. 1,3-Enynes and vinylarenes underwent alkylation−peroxidation to give β-peroxy alcohols and β-hydroxyketones correspondingly with excellent functional group tolerance. The resulting β-peroxy alcohols could be further transformed into β-hydroxyynones and propargylic 1,3-diols.

The direct sp³ α-C−H bond activation and functionalization of alcohols and ethers will provide one of the most efficient entries to more functionalized alcohols and ethers.[1−6] Particularly, the ability to construct new a C−C bond with the α-carbon of alcohols with concomitant retention of the active hydroxyl group in the final products renders this synthetic approach more attractive than the classical methods which utilized the corresponding carbonyl compounds (Scheme 1a,b).[7−9] Furthermore, alcohols are expedient coupling partners as they are readily available, more stable, less toxic, and easier to handle than the corresponding aldehydes. Accordingly, there has been much interest in the generation of α-hydroxy carbon radicals and the subsequent addition to radical acceptors.[5,6] Elegant work by Tu and co-workers has shown the possibility

of coupling the α-carbon of alcohols with a series of alkenes catalyzed by Rh, Ru, Pd, or Fe catalyst, generating the hydroalkylation products.[4] On the other hand, Liu and co-workers have demonstrated the coupling of alcohols with alkynes, cinnamic acids, and isocyanides under metal-free conditions or employing Cu catalysts.[5] However, the direct coupling of the α-carbon of alcohols with simple alkenes and peroxides to yield 1,3-dioxygenated compounds has been difficult.

Inspired by these elegant works and our interest in developing an atom-economical method for the synthesis of 1,3-dioxygenated propargylic compounds, we were especially interested in the reaction of alcohols with simple alkenes and peroxides. To the best of our knowledge, there is no report on the oxyalkylation of simple alkenes such as 1,3-enynes with alcohols to assemble the synthetically versatile alkynyl β-peroxy alcohols. Notably, Li and co-workers developed the relevant chemistry to synthesize peroxy compounds from aldehydes and 1,3-dicarbonyl compounds.[10] Klussmann et al. later demonstrated the preparation of γ-peroxyketones from unactivated ketones.[11] Herein, we report an efficient method for three-component coupling of α-carbon alcohols with alkenes and hydroperoxides catalyzed by zerovalent copper or cobalt. Hydroperoxides played a dual role as an initiator for the radical reaction and also as a coupling partner.

Initial studies were focused on investigating the coupling reaction of silylated 1,3-enyne **1a**, 3.0 equiv of *tert*-butyl hydroperoxide (in decane solution) **2**, and 2-butanol **3a** using 10 mol% of zerovalent copper in neat conditions, which gave 23% of desired oxyalkylated enyne. Switching the solvent to DMSO enhanced the reaction efficiency to furnish 48% of the oxylalkylated enyne in 6 h (Supporting Information). Other copper catalysts exhibited inferior catalytic activity and the reaction in the absence of any metal catalyst was sluggish to give 28% of β-peroxy alcohol. After investigating the effect of amount of alcohol substrate and TBHP to our model reaction, we found that 12 equiv of alcohol and 4 equiv of TBHP gave the optimal product yields (Supporting Information).

It was observed that using 4 or 5 equiv of TBHP gave similar yields for some alcohols, but this was not general across all alcohols. Hence, an excess of 5 equiv of TBHP was used to study the alcohol substrate scope. Performing the reaction with strict exclusion of oxygen proved to be beneficial, giving 68% of

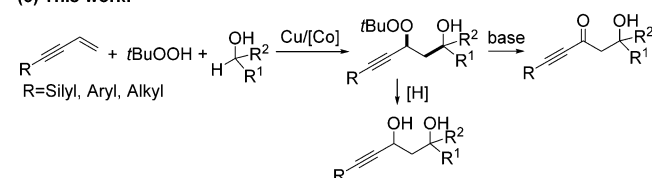**Scheme 1. Conventional and Current Approaches To Synthesize Alcohols**

(a) Classical Method to Synthesize Alcohol (Nucleophilic Attack on Carbonyl Compound)
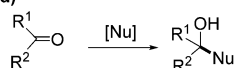
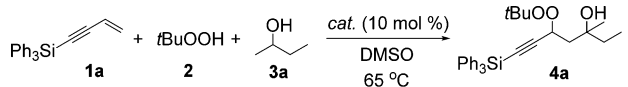**(b) Direct sp³ α-C-H Functionalization of Alcohol**
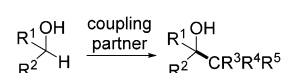
(c) This work:

the desired product after 2 h. With this optimized condition, we proceeded to investigate other metal catalysts and were delighted to observe augmented reaction efficiency with cobalt(II) acetate, while other cobalt salts were shown to be nonactive (Table 1, entries 14−17).

Table 1. Optimization of Reaction Condition[a,b]

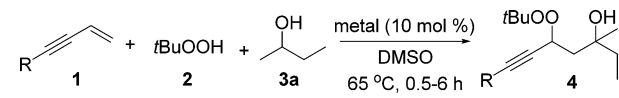| entry	ROH, equiv	TBHP, equiv	catalyst, 10 mol%	time, h	yield, %[c]
1[d]	–	3	Cu	24	23
2	14	3	Cu	6	48
3	14	3	CuCl	4	36
4	14	3	Cu₂O	6	37
5	14	3	CuI	4	39
6	14	3	CuO	24	18
7	14	3	–	10	28
8	12	4	Cu	5	59
9[e]	12	4	Cu	2	68
10[e]	12	4	FeBr₂	3	30
11[e]	12	4	FeCl₂	8	<10
12[e]	12	4	FeBr₃	3	38
13[e]	12	4	Fe	24	trace
14[e]	12	4	CoCl₂	8	–
15[e]	12	4	Co(acac)₃	8	–
16[e]	12	4	CoBr₂	8	–
17[e]	12	4	Co(OAc)₂	0.5	73

[a]Unless otherwise noted, typical reaction conditions: **1a** (0.15 mmol), **2** (5.5 M in decane), DMSO (0.9 mL), 65 °C, air. [b]dr was approximated as 1:1. [c]Isolated yields of inseparable diastereomers. [d]**3a** (0.9 mL). [e]Under nitrogen atmosphere.

Using copper and cobalt catalysts under the optimal reaction conditions, we then probed the reaction generality of enyne substrates using 2-butanol as the standard coupling partner. Pleasingly, 1,3-enynes bearing different silyl protecting groups such as TES, TIPS, TBDMS, and TPS were well accommodated to yield the corresponding products in 33−68% isolated yields with Cu (**4a−d**, Table 2), whereas reactions with Co(OAc)₂ afforded the respective products in better yields (51−73%). Phenyl-substituted enyne was compatible with our reaction protocol to give β-peroxy alcohol **4e** in 58% isolated yield with Cu catalyst. Notably, when halogen substituents were present on the phenyl ring, the reactions also proceeded smoothly, giving rise to **4f−i** in 51%, 58%, 51%, and 43% yield, respectively. The presence of these halides would render these substrates amenable for further functionalization.

Cyclic (**4j,k**) and linear (**4l,m**) aliphatic enynes were also effective substrates for this transformation to furnish the peroxidation−alkylation products in moderate to good yields. In particular, aryl-substituted aliphatic enyne **4m** showed good applicability for this reaction with Cu to give the β-peroxy alcohols in 63%. With these substrates, both Cu and Co(OAc)₂ showed comparable catalytic competence, except for **4g**, **4i**, **4l**, and **4m**.

The generality of this reaction protocol with respect to **1a** was then examined against aliphatic primary and secondary alcohols. Generally, both primary and secondary alcohols were effective substrates for this transformation. Reactions of primary alcohols gave moderate yields of the desired products (**5a−c**) with both catalysts (Table 3). Isopropanol furnished the
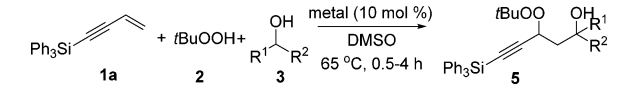
Table 2. Reaction Scope of 1,3-Enynes with 3a[a,b,c,e]

4a[d]: Si = Ph₃Si, 68% (73%)	**4e**, R¹=4-H, 58% (52%)	
4b, = i-Pr₃Si, 36% (66%)	**4f**, =4-Cl, 51% (47%)	
4c, = Me₂tBuSi, 50% (56%)	**4g**, =4-Br, 58% (44%)	
4d, = Et₃Si, 33% (51%)	**4h**, =4-F, 51% (52%)	
	4i, =2-F, 43% (61%)	

4j, n=0, R=cyclopentyl, 35% (39%)
4k, n=0, =cyclohexyl, 38% (41%)
4l, n=1, =cyclohexyl, 42% (33%)
4m, n=2, =phenyl, 63% (42%)

[a]Unless otherwise noted, typical reaction conditions 1: **1** (0.3 mmol), **2** (1.2 mmol, 5.5 M in decane), **3a** (3.6 mmol), Cu (0.03 mmol), DMSO (1.8 mL), 65 °C, under nitrogen atmosphere. [b]Isolated yields of inseparable diastereomers. [c]dr was approximated as 1:1. [d]Performed with **1a** (0.15 mmol), **2** (0.6 mmol, 5.5 M in decane), **3a** (1.8 mmol), Cu (0.015 mmol), DMSO (0.9 mL), 65 °C, under nitrogen atmosphere. [e]Yields in parentheses refer to isolated yields of reactions performed with Co(OAc)₂ instead of Cu under typical reaction conditions.
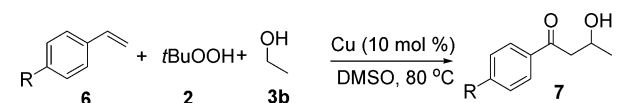
Table 3. Reaction Scope of Alcohols with 1a[a,b,c]

5a[d], n=0, 26% (44%)   **5d**, n=0, 62% (69%)   **5f**, 35% (58%)
5b[d], n=1, 55% (42%)   **5e**[d], n=3, 40% (55%)
5c[d], n=2, 40% (35%)

5g[e], R¹=Me, R²=Me, 46% (61%)   **5i**[d], n=0, 55% (50%)   **5k**, n=1, 48% (60%)
5h[d], R¹=H, R²=Ph, 57% (57%)   **5j**[d], n=1, 39% (32%)   **5l**, n=2, 33% (70%)
                                                                    5m, n=4, 30% (61%)

[a]Reaction conditions: **1a** (0.15 mmol), **2** (0.75 mmol, 5.5 M in decane), **3** (1.8 mmol), Cu (0.015 mmol), DMSO (0.9 mL), 65 °C, under nitrogen atmosphere. [b]Isolated yields of inseparable diastereomers. [c]Yields in parentheses refer to isolated yields of reactions performed with Co(OAc)₂ instead of Cu under typical reaction conditions. [d]dr was approximated as 1:1. [e]dr was approximated as 1:1:1:1.

corresponding peroxy alcohol **5d** in good yield, and other secondary alcohols tested were found to be well suited to generate the products in moderate to good yields (**5e−j**). Remarkably, Co(OAc)₂ acted as better catalyst with most substrates, albeit the reaction efficiency decreased when alcohols with increasing chain length were tested (**5d**, **5e**, **5i**, and **5j**). Reactions of cyclic alcohols with Cu gave peroxy alcohols **5k−m** in moderate yields. Complementarily, these products could be accessed using Co(OAc)₂ with significantly better chemical yields (60−70%).

We next turned our attention to the oxyalkylation of aryl alkenes, the commercially available substrates. Styrenes with diversified functionalities were well tolerated, granting entry for further functionalization. Styrene with halogen substituents provided the products in moderate yields of 32–50% (**7b–d**, Table 4). Other functional motifs such as methyl ester, cyano,

**Table 4. Reaction Scope of Styrene Derivatives with 3b**[a,b]

product	R	yield, % (time, h)	product	R	yield, % (time, h)
7a	H	48 (24)	**7f**	CN	40 (7)
7b	Br	32 (24)	**7g**	OCOMe	31 (15)
7c	Cl	50 (24)	**7h**	CF$_3$	53 (5)
7d	F	45 (12)	**7i**	C(Me)$_3$	50 (22)
7e	COOMe	39 (8)			

[a]Reaction conditions: **6** (0.50 mmol), **2** (1.5 mmol, 5.5 M in decane), **3b** (4.0 mmol), DMSO (3.0 mL), 80 °C, air. [b]Isolated yields.

and acetoxy groups on styrene remained intact, and the corresponding aldol products were isolated in 39%, 40%, and 31% yields (**7e–g**). Notably, substrates with the strongly electron-withdrawing CF$_3$ group (**7h**) as well as alkyl substituents were suitable for this transformation to deliver the corresponding product in moderate yields (**7i**).

Subsequently, transformation on the β-peroxy alcohol was studied with **4a** as model substrate. The respective aldol product **8** was furnished in the presence of a catalytic amount of base (Kornblum−DelaMare rearrangement).[12] Additionally, 1,3-diol **9** was obtained when **4a** was subjected to reduction conditions (Scheme 2).[13]

Scheme 2. Transformation of 4a
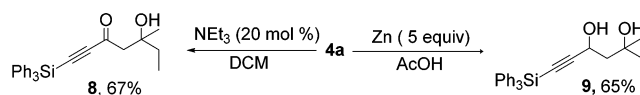
On the basis of our experimental observation and precedent reports, we have devised the mechanistic pathway as depicted in Scheme 3. Copper/cobalt is thought to facilitate the generation of *tert*-butyloxy and *tert*-butylperoxy radicals.[14] Subsequent hydrogen abstraction by the *tert*-butoxy radical generated the α-hydroxy carbon radical which added to the double bond. This was followed by radical coupling with *tert*-butylperoxy radical. This observed selectivity of this radical coupling was steered by the persistent radical effect.[15] For the styrene substrates, the peroxy group is cleaved to give the carbonyl group in situ owing to the reactivity of the benzylic proton. This speculation could be supported by the peroxy intermediate **10** isolated. When further subjected under the standard reaction condition, **10** converted facilely to **7f** (Scheme 4).

It is worth noting that the isolability of the peroxy intermediate differed for different styrene derivatives, and this intermediate could not be observed for some substrates.

In conclusion, we have developed a novel copper- and cobalt-catalyzed three-component oxidative coupling of olefins with hydroperoxides and alcohols which involved the α-C−H activation of alcohols. Various aliphatic, silylated, and aryl 1,3-enynes underwent alkylation–peroxidation to assemble β-

Scheme 3. Proposed Mechanism
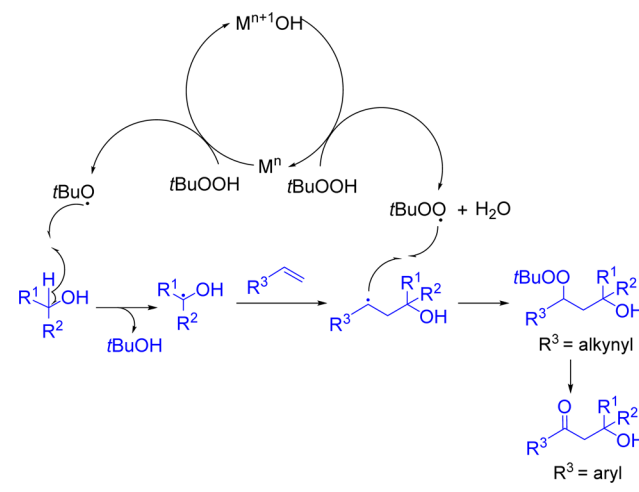
Scheme 4. Mechanistic Study
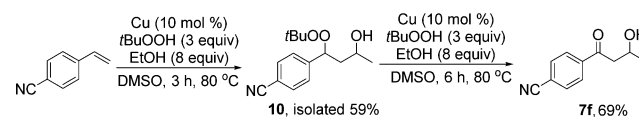
peroxy alcohols, which further allowed access to propargylic 1,3-diols and β-hydroxyynones. Further studies directed toward the synthetic utilization of enynes are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experiment procedures and compound characterization data. 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.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) For a comprehensive review on sp^3 α-C−H activation of alcohols, see: Zhang, S.-Y.; Zhang, F.-M.; Tu, Y.-Q. *Chem. Soc. Rev.* **2011**, *40*, 1937.
(2) For selected recent papers on sp^3 α-C−H activation of ethers, see: (a) Meng, Z.; Sun, S.; Yuan, H.; Lou, H.; Liu, L. *Angew. Chem., Int. Ed.* **2013**, *53*, 543. (b) Zhang, Y.; Li, C.-J. *Angew. Chem., Int. Ed.* **2006**, *45*, 1949. (c) Muramatsu, W.; Nakano, K.; Li, C.-J. *Org. Lett.* **2013**, *15*, 3650. (d) Zhang, Y.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 4242. (e) Pan, S.; Liu, J.; Li, H.; Wang, Z.; Guo, X.; Li, Z. *Org. Lett.* **2010**, *12*, 1932. (f) Kumar, G. S.; Pieber, B.; Reddy, K. R.; Kappe, C. O. *Chem.—Eur. J.* **2012**, *18*, 6124. (g) Liu, D.; Liu, C.; Li, H.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 4453. (h) Liu, D.; Liu, C.; Li, H.; Lei, A. *Chem.*

Commun. **2014**, *50*, 3623. (i) Zhou, L.; Tang, S.; Qi, X.; Lin, C.; Liu, K.; Liu, C.; Lan, Y.; Lei, A. *Org. Lett.* **2014**, *16*, 3404. (j) Xie, Z.; Cai, Y.; Hu, H.; Lin, C.; Jiang, J.; Chen, Z.; Wang, L.; Pan, Y. *Org. Lett.* **2013**, *15*, 4600. (k) Guo, X.; Pan, S.; Liu, J.; Li, Z. *J. Org. Chem.* **2009**, *74*, 8848. (l) Kamijo, S.; Hoshikawa, T.; Inoue, M. *Org. Lett.* **2011**, *13*, 5928. (m) Liu, C.; Liu, D.; Lei, A. *Acc. Chem. Res.* **2014**, *47*, 3459. (n) Rout, S. K.; Guin, S.; Ali, W.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2014**, *16*, 3086. (o) Chu, X.-Q.; Meng, H.; Zi, Y.; Xu, X.-P.; Ji, S.-J. *Chem. Commun.* **2014**, *50*, 9718. (p) Wan, M.; Meng, Z.; Lou, H.; Liu, L. *Angew. Chem., Int. Ed.* **2014**, *53*, 13845. (q) Guo, S.-R.; Yuan, Y.-Q.; Xiang, J.-N. *Org. Lett.* **2013**, *15*, 4654.

(3) For selected papers on sp^3 α-C−H activation of alcohols, see: (a) Zbieg, J. R.; Yamaguchi, E.; McInturff, E. L.; Krische, M. J. *Science* **2012**, *336*, 324. (b) Chen, T.-Y.; Krische, M. J. *Org. Lett.* **2013**, *15*, 2994. (c) Leung, J. C.; Geary, L. M.; Chen, T.-Y.; Zbieg, J. R.; Krische, M. J. *J. Am. Chem. Soc.* **2012**, *134*, 15700. (d) Geary, L. M.; Woo, S. K.; Leung, J. C.; Krische, M. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 7830. (e) Ketcham, J. M.; Shin, I.; Montgomery, T. P.; Krische, M. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 9142. (f) Zhao, Z.; Xue, W.; Gao, Y.; Tang, G.; Zhao, Y. *Chem.—Asian J.* **2013**, *8*, 713. (g) Xu, Q.; Chen, J.; Liu, Q. *Adv. Synth. Catal.* **2013**, *355*, 697. (h) Pandit, R. P.; Lee, Y. R. *Adv. Synth. Catal.* **2014**, *356*, 3171.

(4) (a) Shi, L.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M.; Fan, C.-A.; Zhao, Y.-M.; Xia, W.-J. *J. Am. Chem. Soc.* **2005**, *127*, 10836. (b) Jiang, Y.-J.; Tu, Y.-Q.; Zhang, E.; Zhang, S.-Y.; Cao, K.; Shi, L. *Adv. Synth. Catal.* **2008**, *350*, 552. (c) Zhang, S.-Y.; Tu, Y.-Q.; Fan, C.-A.; Jiang, Y.-J.; Shi, L.; Cao, K.; Zhang, E. *Chem.—Eur. J.* **2008**, *14*, 10201. (d) Zhang, S.-Y.; Tu, Y.-Q.; Fan, C.-A.; Zhang, F.-M.; Shi, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 8761.

(5) (a) Liu, Z.-Q.; Sun, L.; Wang, J.-G.; Han, J.; Zhao, Y.-K.; Zhou, B. *Org. Lett.* **2009**, *11*, 1437. (b) Cui, Z.; Shang, X.; Shao, X.-F.; Liu, Z.-Q. *Chem. Sci.* **2012**, *3*, 2853. (c) Li, Z.; Fan, F.; Yang, J.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 3396.

(6) (a) Correia, C. A.; Yang, L.; Li, C.-J. *Org. Lett.* **2011**, *13*, 4581. (b) He, T.; Yu, L.; Zhang, L.; Wang, L.; Wang, M. *Org. Lett.* **2011**, *13*, 5016. (c) Meng, Y.; Guo, L.-N.; Wang, H.; Duan, X.-H. *Chem. Commun.* **2013**, *49*, 7540. (d) Zhou, Z.-Z.; Hua, H.-L.; Luo, J.-Y.; Chen, Z.-S.; Zhou, P.-X.; Liu, X.-Y.; Liang, Y.-M. *Tetrahedron* **2013**, *69*, 10030.

(7) For selected examples on nucleophilic attack of organometallic reagents, see: (a) Abdel-Magid, A. F. Reduction of C═O to CHOH by Metal Hydrides. In *Comprehensive Organic Synthesis*; Knochel, P., Molander, G. A., Eds.; Elsevier: Oxford, 2014; Vol. *8*, pp 1−84. (b) Zong, H.; Huang, H.; Liu, J.; Bian, G.; Song, L. *J. Org. Chem.* **2012**, *77*, 4645. (c) Luderer, M. R.; Bailey, W. F.; Luderer, M. R.; Fair, J. D.; Dancer, R. J.; Sommer, M. B. *Tetrahedron: Asymmetry* **2009**, *20*, 981. (d) Hatano, M.; Ishihara, K. *Synthesis* **2008**, *11*, 1647. (e) Hatano, M.; Ito, O.; Suzuki, S.; Ishihara, K. *J. Org. Chem.* **2010**, *75*, 5008. (f) Miller, J. J.; Sigman, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 2752. (g) Kang, J. Y.; Connell, B. T. *J. Am. Chem. Soc.* **2010**, *132*, 7826. (h) Osorio-Planes, L.; Rodríguez-Escrich, C.; Pericàs, M. A. *Org. Lett.* **2012**, *14*, 1816. (i) Hatano, M.; Mizuno, T.; Ishihara, K. *Synlett* **2010**, *2010*, 2024. (j) Fernández-Mateos, E.; Maciá, B.; Yus, M. *Tetrahedron: Asymmetry* **2012**, *23*, 789. (k) Fernández-Mateos, E.; Maciá, B.; Yus, M. *Eur. J. Org. Chem.* **2012**, *2012*, 3732. (l) Blinder, C. M.; Bautista, A.; Zaidlewicz, M.; Krzemiński, M. P.; Oliver, A.; Singaram, B. *J. Org. Chem.* **2009**, *74*, 2337. (m) Song, T.; Zheng, L.-S.; Ye, F.; Deng, W.-H.; Wei, Y.-L.; Jiang, K.-Z.; Xu, L.-W. *Adv. Synth. Catal.* **2014**, *356*, 1708. (n) Hirose, T.; Kodama, K. Recent Advances in Organozinc Reagents. In *Comprehensive Organic Synthesis*; Knochel, P., Molander, G. A., Eds.; Elsevier: Oxford, 2014; Vol. *1*, pp 204−266. (o) Madduri, A. V. R.; Minnaard, A. J.; Harutyunyan, S. R. *Org. Biomol. Chem.* **2012**, *10*, 2878. (p) Kotani, S.; Kukita, K.; Tanaka, K.; Ichibakase, T.; Nakajima, M. *J. Org. Chem.* **2014**, *79*, 4817.

(8) Recent reviews on aldol reaction: (a) Murakami, M.; Matsuo, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 9109. (b) Trost, B. M.; Brindle, C. S. *Chem. Soc. Rev.* **2010**, *39*, 1600. (c) Mahrwald, R. *Modern Aldol Reactions*; Wiley-VCH: Weinhem, 2008. (d) Mahrwald, R. *Modern Methods in Stereoselective Aldol Reactions*; Wiley-VCH: Weinhem, 2013.

(9) Other selected examples: (a) Wang, F.-F.; Luo, C.-P.; Wang, Y.; Deng, G.; Luo, Y. *Org. Biomol. Chem.* **2012**, *10*, 8605. (b) Jin, W.; Li, X.; Wan, B. *J. Org. Chem.* **2011**, *76*, 484. (c) White, J. D.; Shaw, S. *Org. Lett.* **2012**, *14*, 6270. (d) Soengas, R. G.; Silva, A. M. S. *Synlett* **2012**, *23*, 873. (e) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 732. (f) Scharnagel, D.; Prause, F.; Kaldun, J.; Haase, R. G.; Breuning, M. *Chem. Commun.* **2014**, *50*, 6623. (g) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986. (h) Magano, J.; Dunetz, J. R. *Org. Process Res. Dev.* **2012**, *16*, 1156.

(10) (a) Liu, W.; Li, Y.; Liu, K.; Li, Z. *J. Am. Chem. Soc.* **2011**, *133*, 10756. (b) Zheng, X.; Lu, S.; Li, Z. *Org. Lett.* **2013**, *15*, 5432. (c) Lv, L.; Shen, B.; Li, Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 4164. (d) Zheng, X.; Lv, L.; Lu, S.; Wang, W.; Li, Z. *Org. Lett.* **2014**, *16*, 5156. (e) Liu, K.; Li, Y.; Zheng, X.; Liu, W.; Li, Z. *Tetrahedron* **2012**, *68*, 10333.

(11) Schweitzer-Chaput, B.; Demaerel, J.; Engler, H.; Klussmann, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 8737.

(12) (a) Kornblum, N.; DeLaMare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 880. (b) Kelly, D. R.; Bansal, H.; Morgan, J. J. G. *Tetrahedron Lett.* **2002**, *43*, 9331.

(13) (a) Kropf, H. In *Houben-Weyl Methoden der Organischen Chemie, Peroxo-Verbndugen*; Kropf, H., Ed.; Thieme: Stuttgart, 1988; p 1102−1116. (b) Dai, P.; Dussault, P. H.; Trullinger, T. K. *J. Org. Chem.* **2004**, *69*, 2851.

(14) (a) Zhang, F.; Du, P.; Chen, J.; Wang, H.; Luo, Q.; Wan, X. *Org. Lett.* **2014**, *16*, 1932. (b) Turrà, N.; Neuenschwander, U.; Baiker, A.; Peeters, J.; Hermans, I. *Chem.—Eur. J.* **2010**, *16*, 13226. (c) Spier, E.; Neuenschwander, U.; Hermans, I. *Angew. Chem., Int. Ed.* **2013**, *52*, 1581. (d) Zhang, J.; Jiang, J.; Xu, D.; Luo, Q.; Wang, H.; Chen, J.; Li, H.; Wang, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2014**, DOI: 10.1002/anie.201408874.

(15) (a) Studer, A. *Chem.—Eur. J.* **2001**, *7*, 1159. (b) Studer, A. *Chem. Soc. Rev.* **2004**, *33*, 267. (c) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13. (d) Chenier, J. H. B.; Tong, S. B.; Howard, J. A. *Can. J. Chem.* **1978**, *56*, 3047. (e) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581. (f) Focsaneanu, K.-S.; Scaiano, J. C. *Helv. Chim. Acta* **2006**, *89*, 2473.