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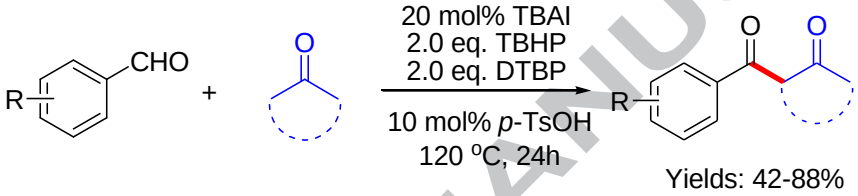

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ABSTRACT

An efficient approach for the synthesis of 1,3-diketones from aldehydes and ketones has been developed using Bu_4NI (TBAI) as the catalyst. In presence of DTBP-TBHP/*p*-TsOH, , aldehydes undergo radical coupling with ketones to provide the desired products in moderate to high yields at 120°C. Although various substituents on the aromatic ring of aldehydes are well tolerable under the standard reaction conditions, the protocol is limited by the scope of ketones. The method exhibits advantages in terms of the easy access of the starting materials, operational simplicity, functional group tolerance and the absence of metal catalyst.

1,3-diketones are very important compounds in synthetic organic chemistry. They are vital building blocks in many pharmaceuticals as well as natural products that exhibit high biological activity, including antioxidant, antitumor, antimicrobial, antiviral, and antifungal activity.[1] They act as important intermediates for accessing various heterocyclic compounds like pyrazoles, isoxazoles, triazoles, and benzopyran-4-ones.[2] 1,3-diketones are also key structural units in many chelating ligands for transition metals and lanthanide.[3] They are used as important intermediates in organic synthesis, including many venerable C-C bond forming reactions, such as Knoevenagel condensation, Tsuji−Trost reaction and the DeMayo reaction.[4] Traditionally, these compounds can be obtained indirectly by the aldol condensation of an enolate and a carbonyl compound followed by oxidation of the resulting 3-hydroxy ketones.[5] Enolate chemistry remains as the common practice for synthesis of 1,3-diketones. The classical procedure involves acylation of a ketone by an ester in the presence of an alkoxide base (Claisen- type condensation). Other acylating agents like acid chlorides, acyl cyanides or 1-acylbenzotriazoles etc. were successfully utilized in C-acylation of enolates (including enamines and silyl enol ether) derived from ketones.[6] However, the formation of lower amount of *O*-acylation product is a drawback in such methods and improvement has been done to avoid its formation.[7] Another method involves C-acylation of acetylacetone or its derivatives by acyl halides or esters followed by base-promoted deacylation. However, this is also suffered from the competition of *O*-acylation.[8] Recently, transition-metal-catalyzed hydroacylation of enones is an alternative direct approach to achieve 1,3-diketones.[9] To date, only a few methods have been developed for the synthesis of 1,3-diketones from aldehydes.[9a,10] Yadav and co-workers developed a protocol involving carbonyl umpolung reactivity of aldehydes, in which the carbonyl carbon attacks nucleophilically on electrophilic α-haloketones to afford 1,3-diketones.[10b] Ryu's protocol was based on formation of a metal enolate from enones *via* hydrometalation strategy which can undergo subsequent cross-aldol reaction with aldehydes and β-hydride elimination to give desired 1,3-diketones.[9a] The development of more suitable protocols to synthesize 1,3-diketones from aldehydes is highly necessary and particularly use of easily available starting material to synthesize such compounds will be able to draw tremendous attention to organic chemist. Here in this paper, we have reported an efficient protocol to synthesize 1,3-diketones *via* radical coupling of aldehydes with ketones under metal-free conditions. Radical synthesis of such compounds is sparse in the literature.[7c]

The most familiar and general strategy for 1,3-diketone functionality is based on disconnection **1** (Figure 1). To the best of our knowledge, disconnection **2**, envisaging the use of the radical synthons has never been explored.

Aldehydes are good source of acyl radicals and can be generated by using oxidants either in presence of metal or metal free conditions.[11] Utility of ketone radical as coupling partner is quite uncommon practices and challenging in synthetic chemistry.[12] We believe that the generation of both acyl radical (Figure 1, **X**) and ketone radical (Figure 1, **Y**) and their subsequent coupling would provide an alternative direct approach to synthesize 1,3-diketones from readily available aldehydes and ketones.

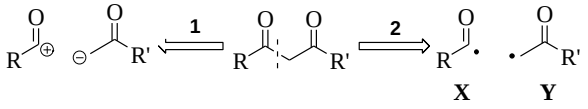
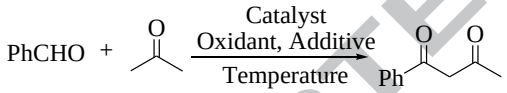


Figure 1. Retrosynthesis analysis of 1,3-diketones

We have initiated our investigation by the reaction of benzaldehyde with acetone (excess) in presence of *tert*-

butylhydroperoxide (TBHP) and *di-tert*-butylhydroperoxide (DTBP) at 120°C without any catalyst (Table1, Entries 1-2), but no desired product was obtained. The reaction even could not occur in presence of a metal catalyst (Table 1, Entries 3-4). It excudes the possibility of formation of acyl radicals from the aldehyde in presence of metal-oxidant system.[11d-e] Iodide/iodine catalytic cycles in presence of TBHP that results in the formation of *tert*-butoxyl or *tert*-butylperoxyl radicals have been reported to be very effective to form acyl radicals.[11b,g,i,12a] Using I_2 as a catalyst, we have observed formation of both 1,2- and 1,3-diketones with former as the major product (Table 1, Entry 5.6:1, *via* ^{1}H NMR). The 1,2-diketone may be formed *via* homocoupling of acyl radical generated from the aldehyde. Replacing iodine with Bu_4NI (TBAI) under similar reaction conditions, only 1,3-diketone was isolated in 49% yield (Table 1, Entry 6). Another iodide equivalent, KI was found inferior (Table 1, Entry 8). Hence, these results suggested TBAI should be the effective catalytic system to synthesize the desired 1,3-diketones. It has been reported that TBHP/*p*-TsOH system can facilitate generation of ketone radical[12b] and using this system we could isolate the desired 1,3-diketone with only 54% yield (Table 1, Entry 9). Recently, we have reported that TBHP-DTBP system can mediate formation of acetone radical during a α-chalocogenation process.[12e] However, its application to current investigation afforded only moderate yield of the desired 1,3-diketone (Table 1, Entry 10). Gratifyingly, addition of catalytic amount of acidic additive to the TBHP-DTBP system provided high yield of the desired product (Table 1, Entries11-12). *p*-TsOH was found to be superior compared to other acidic additive. At lower temperatures, the yields of the product gradually reduced (Table 1, Entries 13-14). Finally, we have optimized the use of TBAI catalyst with TBHP-DTBP system in presence of a catalytic amount of *p*-TsOH at 120°C to be the best reaction conditions.

Table 1. Optimization of the reaction conditions[a]



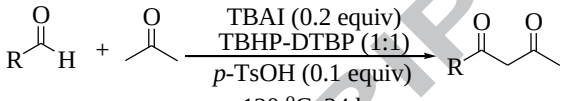
1a **2a** **3a**

Entry	Catalyst (0.2 eq.)	Oxidant (2.0 eq.)	Additive (0.1eq.)	Temp (^{o}C)	Yield (%)[b]
1	-	TBHP	-	120	-
2	-	DTBP	-	120	-
3	CuCl	TBHP	-	120	-
4	$FeCl_3$	TBHP	-	120	-
5	I_2	TBHP	-	120	50[c]
6	TBAI	TBHP	-	120	49
7	TBAI	DTBP	-	120	33
8	KI	TBHP	-	120	37
9	TBAI	TBHP	TsOH	120	54
10	TBAI	TBHP/DTBP	-	120	52
11	TBAI	TBHP/DTBP	TsOH	120	75
12	TBAI	TBHP/DTBP	AcOH	120	68
13	TBAI	TBHP/DTBP	TsOH	100	49
14	TBAI	TBHP/DTBP	TsOH	80	21

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (2 mL), TBHP (2.0 eq.), DTBP (2.0 eq.), *p*-TsOH or AcOH (0.1 eq.), 120 °C , 24h. [b]Isolated yield. [c] Yield of 1,2-diketone and 1,3-diketone mixture.

With the optimized reaction conditions in hand, we have expanded the scope of the method to various aldehydes and ketones. Aromatic aldehydes with various substitution pattern were suitably transformed to the corresponding 1,3-dicarbonyl compounds in high yields (Table 2). Aldehydes bearing electron-withdrawing substituents on the aromatic ring, except fluoro have been found to be superior (Table 2, Entries 6-12). Under the oxidative reaction conditions, the thio-substituents were well tolerated and corresponding products were isolated in high yields (Entries 4-5). Hetero aromatic aldehydes also furnished the desired 1,3-diketones effectively (Table 2, Entries 13-16). However, 4-pyridine carboxaldehyde provided modest yield (Entry 14, 42%).

Table 2. Scope of various aromatic aldehydes [a]



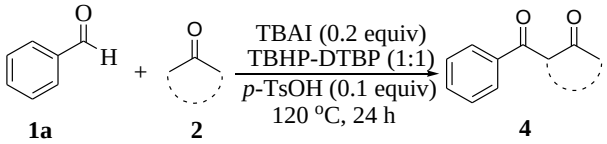
1a-p **2a** **3a-p**

Entry	RCHO(**1a-p**)	Product (**3a-p**)	Yield (%)[b]
1	R= C_6H_5 **1a**	**3a**	75
2	R = 4-Me C_6H_4 **1b**	**3b**	70
3	R =4-*N*,*N*-Me_2 C_6H_4**1c**	**3c**	58
4	R= 2-MeS C_6H_4**1d**	**3d**	77
5	R = 4-PhS C_6H_4**1e**	**3e**	74
6	R = 4-Cl C_6H_4 **1f**	**3f**	83
7	R = 4-Br C_6H_4 **1g**	**3g**	81
8	R = 4-F C_6H_4 **1h**	**3h**	62
9	R = 3-F C_6H_4 **1i**	**3i**	60
10	R = 2-F C_6H_4 **1j**	**3j**	55
11	R = 4-NO_2 C_6H_4 **1k**	**3k**	88
12	R = 4-CN C_6H_4**1l**	**3l**	81
13	R = 1-Naphthyl **1m**	**3m**	76
14	R = 4-Pyridinyl **1n**	**3n**	42
15	R = 2-Thiophyl **1o**	**3o**	61
16	R = 5-Me-2-Furanyl **1p**	**3p**	70

[a] Reaction conditions: **1a-p** (0.3 mmol), **2a** (2 mL), TBHP (2.0 eq.), DTBP (2.0 eq.), *p*-TsOH (0.1 equiv), 120 °C, 24h. [b]Isolated yield.

The scope of ketones is very limited for this protocol (Table 3). Investigation revealed that application of an unsymmetrical ketone, 2-butanone (**2b**) suffers from low regioselectivity and produced a mixture of 1,3-diketones (Table 3, Entry 1). 3,3-dimethylbutan-2-one (**2c**) provided excellent yield of the desired 1,3-diketone. Acetophenone (**2d**) and some symmetrical ketones (**2e-2g**) were also inert under the reaction condition. The reason is not clear at this moment. We have also carried out radical coupling of benzaldehyde with N,N-dimethylacetamide under the standard reaction condition (Table 3, entry 7), but the reaction was unsuccessful.

Table 3. Scope of various ketones[a]

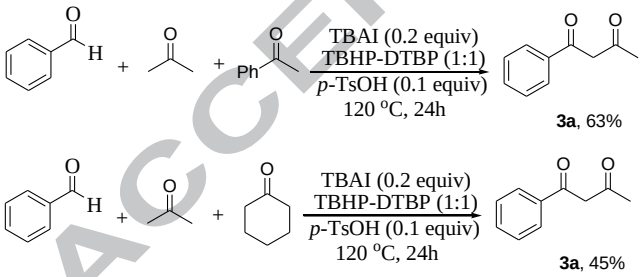


1a **2** **4**

Entry	Ketone	Product	Yield[b]
1	**2b**	**4a** / **4a'**	70 (**4a**/**4a'**= 1:1)
2	**2c**	**4c**	91
3	**2d**	-	-
4	**2e**		
5	**2f**	-	-
6	**2g**	-	-
7	**2h**	-	-

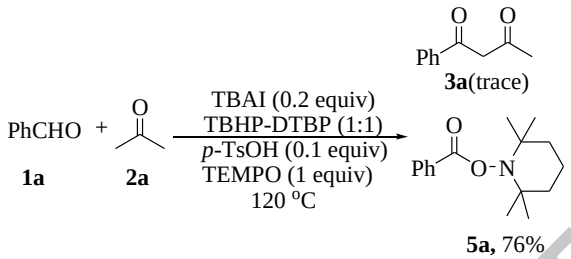
[a] Reaction conditions: **1a** (0.3 mmol), **2b-2c, 2e-2h** (2 mL), **2d** (1.5 eq.), TBHP (2.0 eq.), DTBP (2.0 eq.), *p*-TsOH (0.1 eq.), 120 °C, 24h. [b] Isolated yield. [c] MeCN as solvent.

Additionally, the reactions of benzaldehyde with a mixture of two different ketones have been investigated (Scheme 1), but only acetone can react with benzaldehyde, whereas other ketone remains unreacted.



Scheme 1

To investigate the reaction mechanism, we have performed the radical-trap experiment. When stoichiometric amount of the radical scavenger 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) was added to the reaction mixture under the same reaction conditions, only trace amount of product **3a** was detected. The adduct, **5a** was isolated in 76% yield (Scheme 2). These results suggested that the reaction may indeed undergo a free-radical process.



Scheme 2. Mechanism studies of 1,3-dikeone formation.

On the basis of the above experimental results and literature data,[12b,e] we have proposed a plausible mechanism for this reaction (Figure 2). As previous reported TBHP undergoes better homolytic cleavage in presence of DTBP to furnish the hydroxyl radical.[12e] The *tert*-butylperoxy radical (**A)** would be generated *via* the iodide/iodine catalytic redox process. This active radical species would abstract a hydrogen atom from the aldehyde leading to acyl radical **B**. *Tert*-butylperoxyl radicals (also *tert*-butoxyl) generated from TBHP by iodide/iodine catalytic cycle are proposed as active species to trap H of aldehyde to form acyl radical. [11b,g,i] The ketone radical **C** is formed *via* a alkenyl peroxide in presence of TBHP and *p*-TsOH.[12b] Finally, the coupling of both acyl radical and ketone radical would afford the desired 1,3-diketones.

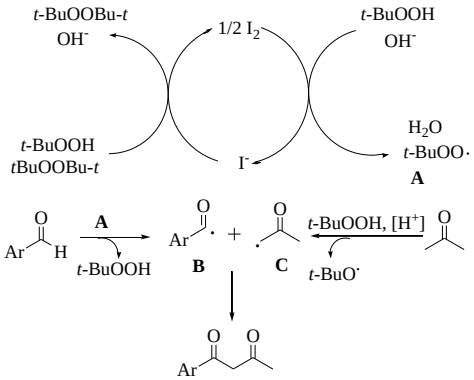


Figure 2. Possible mechanism.

In summary, we have reported an effcetive radical coupling of aldehydes and ketones using TBAI as the suitable catalyst in presence of TBHP-DTBP/*p*-TsOH system. This protocol opens a new direct approach for the synthesis of 1,3-diketone by using readily available starting materials. Various substitution pattern on the aromatic ring of aldehydes are well tolerable under the reaction conditions, providing the desired 1,3-diketone in high yields. However, the scope of ketones is very limited. In addition, the present protocol suffers from poor regioselectivity. Investigations are going on to get a detailed insight into the reaction mechanism and to expand the scope of the radical coupling of aldehydes with various ketones.

Experimental Section

Typical procedure for radical coupling of aldehydes with ketones:

Under air atmosphere, aldehydes (0.3 mmol), TBAI (0.2 eq.), TBHP (2.0 eq.), DTBP (2.0 eq.), *p*-TsOH (0.1 eq.) and acetone or other ketones (2 mL) were added to a screw-capped vial. The

reaction vial was placed in a temperature-controlled aluminum-heating block set at 120 °C. The reaction progress was monitored by TLC. After the completion of the reaction, the vial was removed from the heating block and was left to cool to the ambient temperature. The solution was filtered though a short column of silica gel and washed with EtOAc. The filtrate was concentrated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel with Petroleum ether/EtOAc as an eluent to give the desired product.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.xxx.

References and notes

† These authors contributed equally.

1. (a) Kel'in, A. V. *Curr. Org. Chem*. **2003**, *7*, 1691; (b) Kel'in, A. V.; Maioli, A. *Curr. Org. Chem*. **2003**, *7*, 1855.
2. (a) Raston, C. L.; Salem, G. *J. Chem. Soc., Chem. Commun*. **1984**, 1702; (b) Alekseev, V. V.; Zelinin, K. N.; Yakimovich, S. I. *Russ. J. Org. Chem*. **1995**, *31*, 705; (c) Simoni, D.; Invidiata, F. P.; Rondanin, R.; Grimaudo, S.; Cannizzo, G.; Barbusca, E.; Porretto, F.; D'Alessandro, N.; Tolomeo, M. *J. Med. Chem*. **1999**, *42*, 4961; (d) Nagpal, A.; Unny, R.; Joshi, Y. C. *Heterocycl. Commun*. **2001**, *32*, 589.
3. Garnovskii, A. D.; Kharixov, B. I.; Blanco, L. M.; Garnovskii, D. A.; Burlov, A. S.; Vasilchenko, I. S.; Bondarenko, G. I. *J. Coord. Chem*. **1999**, *46*, 365.
4. (a) Tietze, L. F.; Beifuss, U. In *Comparative Organic Synthesis*; B. Trost, M.; Fleming, I. Eds.; Elsevier: Oxford, **1991**; Vol. *2*, pp 341; (b) Crimmins, M. T.; Reinhold, T. L. *Org. React.* **1993**, *44*, 297; (c) Tsuji, J. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I. Ed.; Wiley-Interscience: New York, **2002**; Vol. *2*, pp 1689; Selected examples: (d) Gao, M.; Yang, Y.; Wu, Y.-D.; Deng, C.; Shu, W.-M.; Zhang, D.-X.; Cao, L.-P.; She, N.-F.; Wu, A.-X. *Org. Lett*. **2010**, *12*, 4026; (e) Biswas, A.; De Sarkar, S.; Fröhlich, R.; Studer, A. *Org. Lett*. **2011**, *13*, 4966; (f) Zhao, J.; Zhao, Y.; Fu, H. *Org. Lett*. **2012**, *14*, 2710; (g) Liu, Y.; Sun, J.-W. *J. Org. Chem*. **2012**, *77*, 1191; (h) Yang, K.; Song, Q. *Org. Lett*. **2015**, *17*, 548.
5. Selected examples: (a) Iii, A. B. S.; Levenberg, P. A. *Synthesis*, **1981**, 567; (b) Katayama, S.; Fukuda, K.; Watanabe, T.; Yamauchi, M. *Synthesis* **1988**, 178; (c) Bartlett, S. L.; Beaudry, C. M.. *J. Org. Chem*. **2011**, *76*, 9852.
6. (a) House, H. O.; Auerbach, R. A.; Gall, M. ; Peet, N. P. *J. Org. Chem*. ***1973***, *38*, 514; (b) Beck, A. K.; Hoekstra, M. S.; Seebach, D. *Tetrahedron Lett*. **1977**, *18*, 1187; (c) Howard, A. S.; Meerholz, C. A.; Michael, J. P. *Tetrahedron Lett*. **1979**, *15*, 1339; (d) Q. Tang and S. E. Sen, *Tetrahedron Lett*., 1998, **39**, 2249; (e) Katritzky, A. R.; Pastor, A. *J. Org. Chem*. **2000**, *65*, 3679; (f) Hopka, I.; Rathke, M. W. *J. Org. Chem*. **1981**, *46*, 3771; (g) Tirpak, R. E.; Rathke, M. W. *J. Org. Chem*., **1982**, *47*, 5099; (h) Linn, B. O.; Hauser, C. R. *J. Am. Chem. Soc*. **1956**, *78*, 6066; (i) Le Roux, C.; Mandrou, S.; Dubac, J. *J. Org. Chem*. **1996**, *61*, 3885; for acylation of enamine: (j) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc*. **1963**, *85*, 207; (k) Park, K. -H.; Cox, L. J. *Tetrahedron Lett*. **2003**, *44*, 1067.
7. (a) Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Tetrahedron Lett*. **2002**, *43*, 2945; (b) Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Chem. Commun.* **2002**, *10*, 1034; (c) Miura, K.; Tojoni, M.; Fujisawa, N.; Hosomi, A.; Ryu, I. *Angew. Chem. Int. Ed*. **2004**, *43*, 2423; (d) Nishimura, Y.; Miyake, Y.; Amemiya, R.; Yamaguchi, M. *Org. Lett*. **2006**, *8*, 5077; (e) Ikeda, Z.; Hirayama, T.; Matsubara, S. *Angew. Chem., Int. Ed*. **2006**, *45*, 8200; (f) Lim, D.; Fang, F.; Zhou, G.; Coltart, D. M. *Org. Lett.* **2007**, *9*, 4139; (g) Sada, M.; Matsubara, S. *J. Am. Chem. Soc*. **2010**, *132*, 432; (h) Gøgsig, T. M.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. *Angew. Chem. Int. Ed*. **2012**, *51*, 798; (i) He, Z.; Qi, X.; Li, S.; Zhao, Y.; Gao, G.; Lan, Y.; Wu, Y.; Lan, J.; You, J. *Angew. Chem. Int. Ed*. **2015**, *54*, 855.
8. (a) Karnik, A. V.; Rane, J. P. *Indian J. Chem., Sect. B*, **1998**, *37*, 1191; (b) Katritzky, A. R.; Wang, Z.; Wang, M.; Wilkerson, C. R.; Hall, C. D.; Akhmedov, N. G. *J. Org. Chem*. **2004**, *69*, 6617.
9. (a) Fukuyama, T.; Doi, T.; Minamino, S.; Omura, S.; Ryu, I. *Angew. Chem. Int. Ed*. **2007**, *46*, 5559; (b) Sato, K.; Yamazoe, S.; Yamamoto, R.; Ohata, S.; Tarui, A.; Omote, M.; Kumadaki, I.; Ando, A. *Org. Lett*. **2008**, *10*, 2405.
10. (a) Padwa, A.; Hornbuckle, S. F.; Zhang, Z.; Zhi, L. *J. Org. Chem*. **1990**, *55*, 5297; (b) Singh, S.; Singh, P.; Rai, V. K.; Kapoor, R.; Yadav, L. D. S. *Tetrahedron Lett*. **2011**, *52* , 125.
11. For review see: (a) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev*. **1999**, *99*, 1992; representative examples: (b) Wei, W. ; Zhang, C.; Xu, Y.; Wan, X. *Chem. Commun.* **2011,** *47*, 10827; (c) Zhou, M. -B.; Song, R.-J.; Ouyang, X.-H.; Liu, Y.; Wei, W. -T.; Deng, G. -B.; Li, J.-H. *Chem. Sci*. **2013**, *4*, 2690; (d) Leifert, D.; Daniliuc, C. G.; Studer, A. *Org. Lett*. **2013**, *15*, 6286; (e) Wang, Q.; Zheng, H.; Chai, W.; Chen, D.; Zeng, X.; Fu, R.; Yuan, R. *Org. Biomol. Chem*. **2014**, *12*, 6549; (f) Cheng, P.; Qing, Z.; Liu, S.; Liu, W.; Xie, H.; Zeng, J. *Tetrahedron Lett*. **2014**, *55*, 6647; (g) Qin, W. -J.; Li, Y.; Yu, X.; Deng, W. -P. *Tetrahedron* **2015**, *71*, 1182; (h) Wei, W.-T.; Yang, X.-H.; Li, H.-B.; Li, J.-H. *Adv. Synth. Catal*. **2015**, *357*, 59; (i) Achar, T. K.; Mal, P. *J. Org. Chem.* **2015**, *80*, 666.
12. a) 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; (b) Schweitzer-Chaput, B.; Demaerel, J.; Engler, H.; Klussmann, M. *Angew.Chem. Int. Ed*. **2014**, *53*, 8737; (c) Chu, X.-Q.; Meng, H.; Zi, Y.; Xu, X.-P.; Ji, S.-J. *Chem. Eur. J*. **2014**, *20*, 17198; (d) Jiang, Q. ; Xu, B.; Zhao, A.; Jia, J.; Liu, T.; Guo, C. *J. Org. Chem*. **2014**, *79*, 8750; (e) Yan, G.; Borah, A. J.; Wang, L.; Pan, Z.; Chen, S.; Shen, X.; Wu, X. *Tetrahedron Lett*., **2015**, *56*, 4305.