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Highly selective oxidation of unsaturated hydrocarbons to carbonyl compounds by two-phase catalysis

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ABSTRACT

An efficient method for selective oxidation of unsaturated hydrocarbons to carbonyl compounds was established by using oxidant [bis(acetoxy)iodo]benene and catalyst ruthenium trichloride (0.1 mol %) in a CH_2Cl_2/H_2O two phase system at 30 °C. Both aromatic and aliphatic olefins could be oxidized via direct carbon–carbon bond cleavage to the corresponding aryl or alkyl aldehydes with good selectivity (up to 100%). Further, diketone could be obtained from alkyne in high yields with this method.

1. Introduction

The oxidation of unsaturated hydrocarbon is a significant reaction in organic chemistry, petrochemical industry as well as conversion of biomass. The aldehyde and ketone are important precursors to acid and alcohol as well as widely used in medicine, agriculture, and fine chemical industry.[1–3] Up to now, the selective transformation of unsaturated hydrocarbon to aldehyde or ketone is still a challenging objective, since the result in most cases is workup conditions dependent.[4,5] The most common method for the direct oxidative cleavage of olefins was ozonolysis,[6] but ozone gas is highly toxic and its generation requires specialized equipment.[7] Other oxidants such as $KMnO_4$,[8] oxone,[9,10] $NaIO_4$,[11] *m*-CPBA,[12,13] and *t*-BuOOH[14,15] were used to this kind of oxidation reaction. However, the problems of long reaction period, low selectivity, and environment unfriendly are still not resolved. In order to improve the selectivity of products, here we used a two-phase CH_2Cl_2/H_2O system for the oxidation reaction of olefin and alkyne to achieve aldehyde or diketone products through using $PhI(OAc)_2$ as an oxidant and $RuCl_3$ as catalyst. The new method is very effective for the selective oxidation of unsaturated hydrocarbons to carbonyl compounds, and the catalyst can be separated easily.

2. Experimental

2.1. Materials

Ruthenium(III) trichloride, dichloromethane, [bis(acetoxy)iodo] benene, sodium periodate, 30% hydrogen peroxide, 1-(3,4-dimethoxyphenyl)ethanone, acetonitrile, ethyl acetate, benzene, acetone, and the substrates of olefins and alkynes were analytical grade and purchased from commercial sources and used with certain purification. The concentration of hydrogen peroxide was examined by titrating a standardized ceric sulfate solution to pale blue endpoint with a ferroin indicator.

2.2. Methods and instrumentations

The typical solution containing 1 mmol of substrates, 0.1 mol % $RuCl_3$, and 3 equiv of $PhI(OAc)_2$, was heated and kept at constant 30 °C. Reaction products were separated and analyzed by GC–MS (Agilent 5973 Network 6890N, Japan) and NMR (Bruker DPX-300FX). The concentrations of reactant and product in the reaction solution were quantitatively analyzed by Gas chromatography (FULI9790, China). NMR data were recorded using $CDCl_3$ as solvent with TMS as an internal standard. Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). GC data was obtained FID gas chromatograph system equipped with a KB-5 capillary column using *p*-nitrotoluene as an internal standard. Electrospray mass spectrometry (ESI-MS) measurements were performed with a TSQ quantum ultra.

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2.3. Synthesis of 1-methoxy-4-vinylbenzene

1-Methoxy-4-vinylbenzene was prepared according to literatures.[16–18] It was characterized by ESI-MS: m/z 135.08 (Calcd for $[M^{+}+1]$: 135.07); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.16–5.19 (dd, J=10.8 8.0 Hz, 1H), 5.64–5.68 (dd, J=17.6 8.0 Hz, 1H), 6.67–6.75 (m, 1H), 6.90–6.92 (m, 2H), 7.38–7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.36, 136.23, 130.42, 127.41, 113.91, 111.60, 55.31. The NMR spectra in the ESI.

3. Results and discussion

3.1. Effect of solvent

Solvent displayed important influence on many oxidation reactions.[19–21] To investigate the solvent effect, styrene, *trans*-stilbene, 1-octene, and 1,2-diphenylethyne were chosen as substrates to carry out oxidation reaction by using oxidant $PhI(OAc)_2$ and catalyst $RuCl_3$ in four kinds of two-phase systems dichloromethane/water, acetonitrile/water, acetone/water, and benzene/water, respectively. The experimental results were listed in Table 1. It can be seen that the oxidation of these substrates afforded small amount of products when acetonitrile/water, acetone/water, and benzene/water were used as solvent systems. Dichloromethane/water was the best solvent system to afford desired product aldehyde or diketone with good yield in relatively short time. It can be further found that the volume ratio of CH_2Cl_2 to H_2O had great influence on the oxidation reaction of styrene (Table S1 in the ESI). From Table S1, it can be observed that the two-phase system of 4:1 ratio of CH_2Cl_2 to H_2O gave the best results of 100% conversion of styrene and 99.8% yield of benzaldehyde.

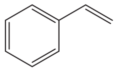
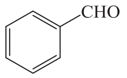
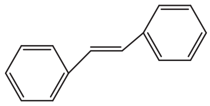
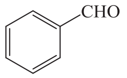
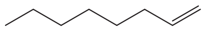
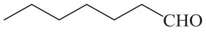
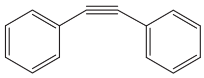
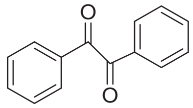
3.2. Effect of oxidant

The chemistry of polyvalent iodine compounds has experienced an unprecedented, explosive development during the past few decades. This increasing interest is mainly due to the very useful oxidizing properties of polyvalent iodine reagents combined with their benign environmental nature and commercial availability.[22,23] $PhI(OAc)_2$ was used as an oxidant for the oxidation of alcohols,[24,25] phenol,[26,27] and olefin aziridination reaction.[28] Although some studies on oxidation of olefins to aldehydes or ketones with $PhI(OAc)_2$ have been reported in the past few years,[22,29] the disadvantages of slow reaction rate, additional oxidants, and low selectivity still exist. In this work, five oxidants were employed to carry out the oxidation reaction. As seen in Table 2, the substrates styrene, *trans*-stilbene, and 1,2-diphenylethyne can't be oxidized by oxidants H_2O_2 and $Fe_2(SO_4)_3$ under the same conditions. However the oxidants *m*-CPBA, $NaIO_4$, and $PhI(OAc)_2$ were efficient, and best results could be achieved with $PhI(OAc)_2$ as oxidant. $RuCl_3$ is one of the commonly used reagent for the oxidation reactions of olefins to aldehydes.[19,30,31] To examine the catalytic activity of catalyst, oxidation cleavage of styrene by $PhI(OAc)_2$ catalyzed by various metal salts was comparatively investigated (Table S2 in the ESI). As seen in Table S2, for $RuCl_3$ catalyzed system, the reaction was satisfactory that the conversion of styrene achieved 100% after 1.5 h, and the yield of benzaldehyde achieved 99.8% at a low catalyst load of 0.1 mol %. It can be observed that other metal halides showed low catalytic activity for both conversion of styrene and yield of benzaldehyde. It should be noted that only 12.7% conversion of styrene and 10.8% yield of benzaldehyde could be obtained after 4 h in the absence of catalyst.

3.3. Oxidative cleavage of terminal olefins

Under the optimum conditions, various aryl- and alkyl-substituted terminal olefins were investigated and the experimental results were listed in Table 3. As observed from Table 3, the $RuCl_3$–$PhI(OAc)_2$–CH_2Cl_2–H_2O system showed excellent catalytic ability for the oxidative cleavage of terminal olefins to aldehydes. The aromatic terminal olefins with electron-rich and electron-poor substituted group in the para position (**2a**–**6a**) were oxidized to the corresponding aldehydes in high yields (76.2–92.1%, Table 3, entries 2–6). Styrene (**1a**) and 2-vinylnaphthalene (**7a**) were converted to benzaldehyde and 2-vinylnaphthaldehyde in 99.8% and 57.5% yields, respectively (Table 3, entries 1 and 7). The GC profiles of styrene oxidation reaction solution were shown in Figs. 1S–2S. However, when aliphatic alkene was employed, this catalysis reaction showed slow reaction rate. For the oxidation of 1-octene (**8a**), although the selectivity of the product heptanal (**8b**) was high (97.5%), only 22.6% yield was obtained after 1.5 h reaction.

Table 1
The yields of carbonyl compounds for the oxidation of unsaturated hydrocarbon in various solvent systems[a]

Substrate	Product	Time (h)	Yield (%)			
			Dichloro-methane[b]	Acetonitrile	Acetone	Benzene
		1.5	99.8	14.5	56.0	52.5
		1.5	99.7	21.4	58.1	31.6
		1.5	22.6	—	7.3	3.2
		2.0	89.6	24.6	63.0	32.5

[a] The reactions were carried out by using oxidant $PhI(OAc)_2$ and catalyst $RuCl_3$ in 5 mL solvent (organic solvent:H_2O=4:1, v/v), GC yields are given. — represent for no reaction.

[b] Isolated yields are given, see ESI for details.

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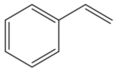
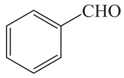
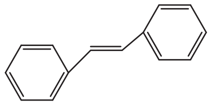
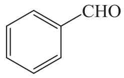
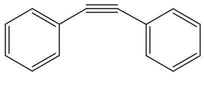
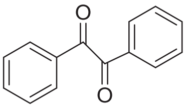
Table 2
Yields of benzaldehyde and diketone for the oxidations of styrene, *trans*-stilbene, and 1,2-diphenylethyne by various oxidants[a]

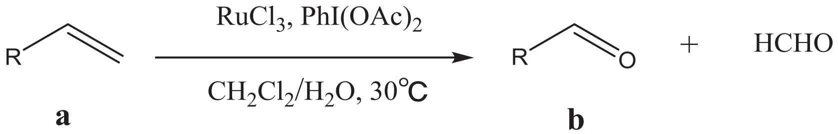
Substrate	Product	Yield (%)				
		H_2O_2 [b]	*m*-CPBA	$PhI(OAc)_2$ [c]	$Fe_2(SO_4)_3$	$NaIO_4$
		—	27.0	99.8	—	76.3
		—	44.5	99.7	—	68.1
		—	67.6	89.6	—	34.5

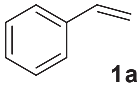
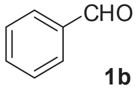
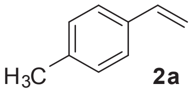
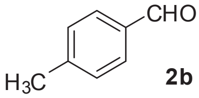
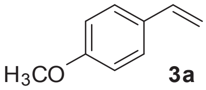
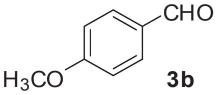
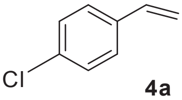
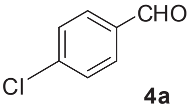
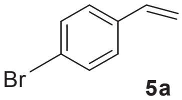
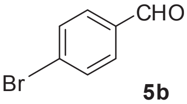
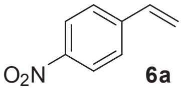
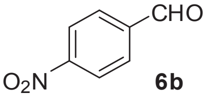
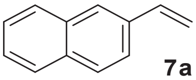
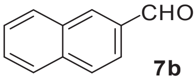
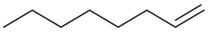
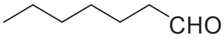
[a] The reactions were performed in 5 mL solvent (CH_2Cl_2:H_2O=4:1, v/v), 0.1 mol % $RuCl_3$, 3 h. GC yields are given.

[b] 5 h.

[c] 1.5 h, Isolated yields are given, see ESI for details.

Table 3
Oxidative cleavage of various terminal olefins to aldehydes[a]



Entry	Substrate	Product	Time (h)	Selectivity (%)	Yield (%)
1	 **1a**	 **1b**	1.5	100	99.8[b]
2	 **2a**	 **2b**	3.0	95.4	76.2[b]
3	 **3a**	 **3b**	2.5	100	92.1[b]
4	 **4a**	 **4a**	3.5	98.0	81.6
5	 **5a**	 **5b**	3.5	99.4	82.0[b]
6	 **6a**	 **6b**	2.5	97.1	83.5[b]
7	 **7a**	 **7b**	4.0	80.7	57.5
8	 **8a**	 **8b**	1.5	97.5	22.6[b]

[a] The reactions were performed in 5 mL solvent (CH_2Cl_2:H_2O=4:1, v/v).

[b] Isolated yields are given, see ESI for details.

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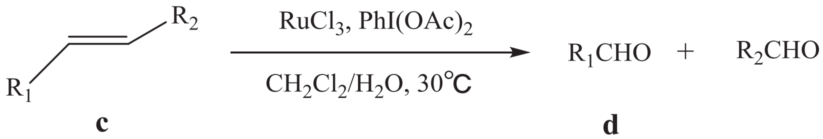
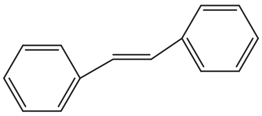
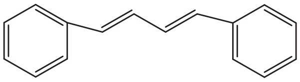
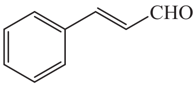
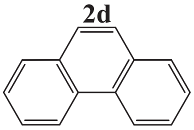
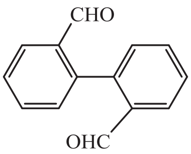
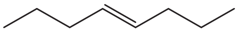
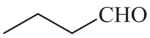
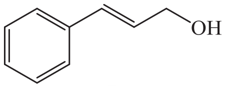
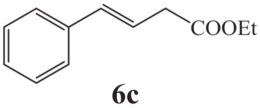
3.4. Oxidative cleavage of internal olefins

Next we focused our attention on the oxidative cleavage of intramolecular alkene since the internal olefins into aldehyde is known to be more difficult than terminal alkene, especially under mild conditions.[32,33] We selected *trans*-stilbene (**1c**), a typical internal olefin, as substrate to carry out the oxidation reaction in two-phase catalysis system. The study showed that benzaldehyde was the sole oxidation product, and the isolated yield arrived 99.7% after 1.5 h reaction. The reduction products acetic acid and iodobenzene derived from $PhI(OAc)_2$ were also detected. The GC–MS profiles of *trans*-stilbene oxidation reaction solution were shown in Figs. 3S–5S. It was also noted that other competing oxidation products, such as diols, phenylacetaldehyde, acetophenone, and styrene oxide, were not observed. Subsequently, the oxidative cleavage of a series of intramolecular alkenes (**2c**–**6c** and **2d**) was investigated and the results were listed in Table 4. As seen in Table 4, the oxidation of aromatic internal dialkene (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**2c**) generated the corresponding product benzaldehyde (**1b**) in 93.7% isolated yield. Meanwhile, the other cleavage product cinnamaldehyde (**2d**) was also detected. And then we employed cinnamaldehyde as substrate to carry out the oxidation reaction under the same reaction conditions. It can be found that the oxidative cleavage product benzaldehyde was 86.8% yield only after 1 h (Table 4, entries 2 and 3). These results strongly implied that the C=C bond of internal olefins was split into two kinds of aldehyde products, and the second step oxidative cleavage reaction rate of cinnamaldehyde was faster than the first step reaction of (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene. In addition, we also concluded that the dialkene was oxidized by cleavaging a carbon–carbon double bond rather than two double bonds. The functional internal olefins (*E*)-3-phenylprop-2-en-1-ol (**5c**) and ethyl cinnamate (**6c**) could be also oxidized to benzaldehyde in highly selectivity (S >95%) with this method (Table 4, entries 6 and 7). Although the oxidation of phenanthrene (**3c**) was slow and only 8.8% yield of aldehyde after 4 h reaction, the selectivity was obtained in 99.1%. It is interesting that linear aliphatic internal olefin *trans*-4-octene (**4c**) could be also transformed to corresponding n-butylaldehyde in very high selectivity (99.6%), although the yield was only 19.3% after 2 h.

Table 4
Oxidative cleavage of various internal olefins to aldehydes[a]



Entry	Substrate	Product	Time (h)	Selectivity (%)	Yield (%)
1	 **1c**	**1b**	1.5	100	99.7[b]
2	 **2c**	**1b**	2.0	98.7	93.7[b]
3	 **2d**	**1b**	1.0	99.4	86.8[b]
4	 **3c**	 **3d**	4.0	99.1	8.8
5	 **4c**	 **4d**	2.0	99.6	19.3
6	 **5c**	**1b**	1.0	95.2	88.5[b]
7	 **6c**	**1b**	1.0	100	98.1[b]

[a] The reactions were performed in 5 mL solvent (CH_2Cl_2:H_2O=4:1, v/v).

[b] Isolated yields are given, see ESI for details.

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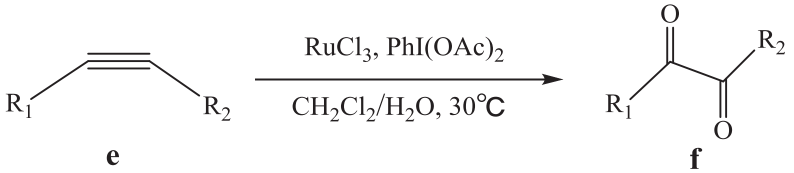
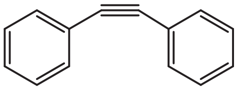
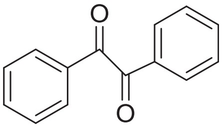
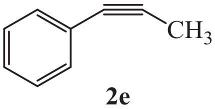
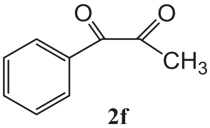
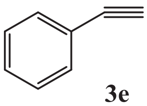
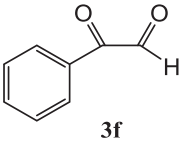
Table 5
The oxidation of various alkynes to diketones[a]



e **f**

Entry	Substrate	Product	Time (h)	Selectivity (%)	Yield (%)
1	 **1e**	 **1f**	2.0	94.5	89.6[b]
2	 **2e**	 **2f**	1.5	100	100
3	 **3e**	 **3f**	1.0	100	100

[a] The reactions were performed in 5 mL solvent (CH_2Cl_2:H_2O=4:1, v/v).

[b] Isolated yields are given, see ESI for details.

3.5. Oxidation of alkynes

Diketones can serve as useful inhibitors of acid corrosion of mild steel, photosensitive agents in photocurable coatings as well as natural compounds.[34,35,40] Diketones are also versatile intermediates in a variety of chemical transformations, especially for the synthesis of biologically active heterocyclic compounds. However, the conventional methods for the preparation of diketone have several drawbacks including severe reaction conditions, long reaction time, and low yield.[36–38] In recent years, there were some new methods to prepare diketone from alkyne by using large amount of oxidant[39,40] or new catalyst.[41,42] Here, we reported a new simple method that oxidize alkyne to diketone with high selectivity and yield in a relatively short time with simple two-phase catalysis method (Table 5). Diphenylacetylene (**1e**) produced 1,2-diphenyl ethanedione (**1f**) in 89.6% isolated yield. Furthermore, 1-phenylpropyne (**2e**) and phenylacetylene (**3e**) can be completely converted to corresponding diketones with 100% selectivity.

3.6. About this method

The proposed method can be applied in the efficient oxidation of unsaturated hydrocarbons to aldehydes and diketones with high yields in a wide range of substrates. The catalyst $RuCl_3$ is only dissolved in aqueous solution phase, while organic substrates and $PhI(OAc)_2$ in CH_2Cl_2 phase. Therefore the catalytic reaction was believed to occur on the interface of two phase. Owing to the relative short contact time with catalyst on the interface, the product aldehyde may rapidly enter organic phase and is difficult to further oxidize to corresponding acid. To detect the opinion, we used dimethyl formamide (DMF) as solvent to carry out the oxidations of styrene and methoxy-4-vinylbenzene by using the same amount of $RuCl_3$ and $PhI(OAc)_2$ at 30 °C. The homogeneous catalysis results showed that the reaction solution contained aldehydes and acids, the selectivity of benzaldehyde and *p*-methoxybenzaldehyde were only 79.7% and 42.0%, respectively. The more products and lower selectivity of aldehyde appeared. This indicated that the aldehyde can be further oxidized in homogeneous catalytic system. The two phases catalysis method avoids the over-oxidation of aldehyde and results in the excellent selectivity. Since only catalyst $RuCl_3$ exists in water phase, the catalyst could be easily separated from the reaction systems and reuse. Moreover, it can be found that the proposed method can be applied in the selective oxidation in wide range of substrates including terminal olefins, internal olefins and alkynes.

4. Conclusions

In summary, we have developed a simple two-phase catalysis method for the generation of aldehydes or diketones from unsaturated hydrocarbon by using a small amount (0.1 mol %) ruthenium trichloride as the catalyst and $PhI(OAc)_2$ as the oxygen donor under mild conditions. In this work's condition, a variety of olefins could be oxidized via direct carbon—carbon bond cleavage to the corresponding aldehydes with good selectivity. Interestingly, this method is also suitable to the oxidation reaction of alkynes to diketones. Moreover, some products of aldehydes and diketones can be isolated in high yield by simple solvent extraction since all oxidation reaction used CH_2Cl_2/H_2O two-phase system. Compared with previous methods about oxidation of unsaturated hydrocarbon to carbonyl compounds, our studies displayed better efficiency and broader range of substrate application.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.09.003.

References and notes

1. Dong, G. B.; Teo, P.; Wickens, Z. K.; Grubbs, R. H. *Science* **2011**, *333*, 1609–1612.
2. Namboodiri, V. V.; Varma, R. S.; Demessie, E. S.; Pillai, U. R. *Green Chem.* **2002**, *4*, 170–173.
3. Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley and Sons: New York, NY, 1994; Vol. 11, pp 1042–1081.
4. Weiner, B.; Baeza, A.; Jerphagnon, T.; Feringa, B. L. *J. Am. Chem. Soc.* **2009**, *131*, 9473–9474.
5. Michel, B. W.; Combs, J. R. M.; Winkler, A.; Sigman, M. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7312–7315.
6. Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745–752.
7. Koike, K.; Inoue, G.; Fukuda, T. *J. Chem. Eng. Jpn.* **1999**, *32*, 295–299.
8. Baskaran, S.; Das, S. J.; Chandrasekaran, S. *J. Org. Chem.* **1989**, *54*, 5182–5184.
9. Travis, B.; Narayan, R. S.; Borhan, B. *J. Am. Chem. Soc.* **2002**, *124*, 3824–3825.
10. Whitehead, D. C.; Travis, B. R.; Borhan, B. *Tetrahedron Lett.* **2006**, *47*, 3797–3800.
11. Hiroshi, O.; Kazuhiro, O.; Shinji, B. *Synlett* **2007**, 3201–3205.
12. Singh, F. V.; Milagre, H. M. S.; Eberlin, M. N.; Stefani, H. A. *Tetrahedron Lett.* **2009**, *50*, 2312–2316.
13. Goulart, M. O. F.; Cioletti, A. G.; de Souza Filho, J. D.; de Simone, C. A.; Castellano, E. E.; Emery, F. S.; de Moura, K. C. G.; Pintod, M. C. F. R.; Pinto, A. V. *Tetrahedron Lett.* **2003**, *44*, 3581–3585.
14. Noh, J. H.; Patala, R.; Meijboom, R. *Appl. Catal., A General* **2016**, *514*, 253–266.
15. Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett.* **2006**, *8*, 693–696.
16. Weinstock, J.; Ladd, D. L.; Wilson, J. W.; Brush, C. K.; Yim, N. C. F. *J. Med. Chem.* **1986**, *29*, 2315–2325.
17. Li, Y.; Hu, Y. Y.; Zhang, S. L. *Chem. Commun.* **2013**, 10635–10637.
18. Svenson, D. R.; Kadla, J. F.; Chang, H. M. *Ind. Eng. Chem. Res.* **2002**, *41*, 5927–5933.
19. Yang, D.; Zhang, C. *J. Org. Chem.* **2001**, *66*, 4814–4818.
20. Yadav, G. D.; Pujari, A. A. *Org. Process Res. Dev.* **2000**, *4*, 88–93.
21. Zimmermann, F.; Meux, E.; Mieloszynski, J. L.; Lecuire, J. M.; Oget, N. *Tetrahedron Lett.* **2005**, *46*, 3201–3203.
22. Chaudhari, D. A.; Fernandes, R. A. *J. Org. Chem.* **2016**, *81*, 2113–2121.
23. Zhdankin, V. V.; Stnag, P. J. *Chem. Rev.* **2002**, *102*, 2523–2584.
24. Hong, Z.; Liu, L.; Sugiyama, M.; Fu, Y.; Wong, C. H. *J. Am. Chem. Soc.* **2009**, *131*, 8352–8353.
25. Adam, W.; Hajra, S.; Herderich, M.; Möller, C. R. S. *Org. Lett.* **2000**, *2*, 2773–2776.
26. Wells, G.; Seaton, A.; Stevens, M. F. G. *J. Med. Chem.* **2000**, *43*, 1550–1562.
27. Braun, N. A.; Ousmer, M.; Bray, J. D.; Bouchu, D.; Peters, K.; Peters, E. M.; Ciufolini, M. A. *J. Org. Chem.* **2000**, *65*, 4397–4408.
28. Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753.
29. Nicolaou, K. C.; Adsool, V. A.; Hale, C. R. H. *Org. Lett.* **2010**, *12*, 1552–1555.
30. Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936–3938.
31. Rup, S.; Sindt, M.; Oget, N. *Tetrahedron Lett.* **2010**, *51*, 3123–3126.
32. Byun, S.; Chung, J.; Jang, Y.; Kwon, J.; Hyeon, T.; Kim, B. M. *RSC Adv.* **2013**, *3*, 16296–16299.
33. Yu, W.; Mei, Y.; Kang, Y.; Hua, Z.; Jin, Z. *Org. Lett.* **2004**, *6*, 3217–3219.
34. Chen, M.; Zhao, Q.; She, D. B.; Yang, M. Y.; Hui, H. H.; Hua, G. S. *J. Chem. Sci.* **2008**, *119*, 347–351.
35. Ita, B. I.; Offiong, O. E. *Mater. Chem. Phys.* **2001**, *70*, 330–335.
36. Mahabusarakama, W.; Deachathaia, S.; Phongpaichitb, S.; Jansakulc, C.; Taylor, W. C. *Phytochemistry* **2004**, *65*, 1185–1191.
37. Yusubov, M. S.; Zholobova, G. A.; Vasilevsky, S. F.; Tretyakov, E. V.; Knight, D. W. *Tetrahedron* **2002**, *58*, 1607–1610.
38. Callahan, J. F.; Burgess, J. L.; Fornwald, J. A.; Gaster, L. M.; Harling, J. D.; Harrington, F. P.; Heer, J.; Kwon, C.; Lehr, R.; Mathur, A.; Olson, B. A.; Weinstock, J.; Laping, N. J. *J. Med. Chem.* **2002**, *45*, 999–1001.
39. Singh, S. K.; Saibaba, V.; Ravikumar, V.; Rudrawar, S. V.; Daga, P.; Rao, C. S.; Akhila, V.; Hegdeb, P.; Raoa, Y. K. *Bioorg. Med. Chem.* **2004**, *12*, 1881–1893.
40. Gao, A.; Yang, F.; Li, J.; Wu, Y. *Tetrahedron* **2012**, *68*, 4950–4954.
41. Xu, Y.; Wan, X. *Tetrahedron Lett.* **2013**, *54*, 642–645.
42. Daw, P.; Petakamsetty, R.; Sarbajna, A.; Laha, S.; Ramapanickerand, R.; Bera, J. K. *J. Am. Chem. Soc.* **2014**, *136*, 13987–13990.

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