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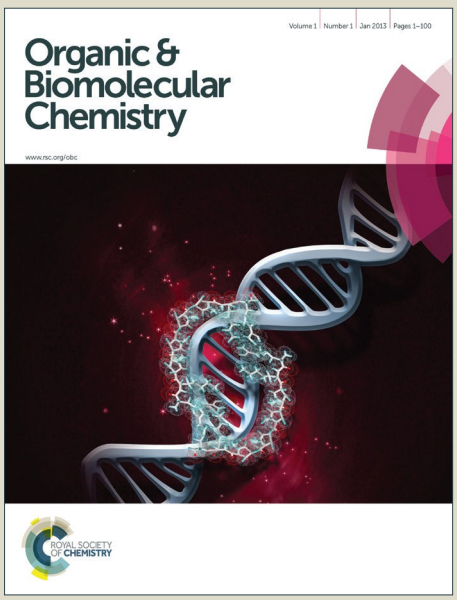

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Sequential Michael addition/retro-Claisen condensation of aromatic β-diketones with α, β-unsaturated esters: an approach to 1, 5-ketoesters

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Gui-Xin Cai[a,b,*], Jing Wen[a], Ting-Ting Lai[a], Xie Dan[a], Cheng-He Zhou[a,*]

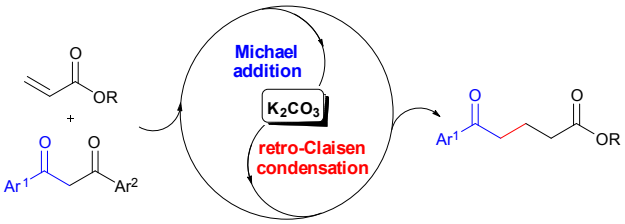
K_2CO_3-catalyzed one-pot protocol involving sequential C-C bond formation and cleavage of aromatic β-diketones with α, β-unsaturated esters is developed to obtain 1,5-ketoesters. The sequential reaction via Michael addition and retro-Claisen condensation proceeds smoothly under mild conditions up to 98% isolated yield. The mechanism study disclosed that the cascade process involved C-C bond cleavage of aromatic β-diketone as a phenacyl donor under alcoholic alkalescent conditions.

Introduction

Michael sequential reactions such as double Michael, Michael/Aldol, Michael/Henry and Michael/Conia−Ene improve the elegance of synthesis[1-2]. However, sequential Michael/retro-Claisen condensation reaction which makes C-C bond formation and cleavage in one pot is hardly reported. Herein, we presented sequential Michael/retro-Claisen condensation reaction involving C-C bond cleavage of β-diketones under mild conditions to obtain 1, 5-dicarbonyl compounds, as useful building blocks[3], which were generally prepared under harsh conditions[4-7].

Although selective C-C bond cleavage possesses both kinetic and thermodynamic challenges, significant achievements have been made in the field[8]. Cook[9] firstly reported C-C bond cleavage of β-diketones, that is, retro-Claisen condensation which subsequently was also developed via 6-oxocamphor hydrolase[10a], $In(OTf)_3$[10b], $Fe(OTf)_3$[10c], $FeCl_3$[10d], H_2O_2[10e] along with *t*-BuONa[10f], individually. In particular, C-C bond cleavage of aromatic β-diketones, compared with that of aliphatic β-diketones[11-14], is a greater challenge. Jiao[15] and Song[16] reported copper-catalyzed C-C bond cleavage of aromatic β-diketones giving α-ketoesters and azole amides, respectively. Rodriguez and Quintard[17] also disclosed the enantioselective synthesis of 3-alkylpentanols concerning C-C bond cleavage of aromatic β-diketones via dual iron-amine catalysis. In comparison with transition metal catalyzed C-C bond cleavage, the C-C bond cleavage without transition metal catalyst is in its infancy[18]. We now demonstrate K_2CO_3-catalyzed sequential Michael addition/retro-Claisen condensation of aromatic β-diketones with α, β-unsaturated esters leading to 1, 5-ketoesters (Scheme 1).

Scheme 1. Catalytic sequential Michael addition/retro-Claisen condensation of aromatic β-diketones with α, β-unsaturated esters.



Results and discussion

First of all, treatment of 1, 3-diphenylpropane-1, 3-dione (**1a**) with ethyl acrylate (**2a**) was chosen as a model reaction (Table 1). K_2CO_3 exhibiting excellent catalytic activity in ethanol at 85 °C for 2 h, astonishingly, afforded ethyl 5-oxo-5-phenylpentanoate (**4a**) in 98% isolated yield and a trace of Michael addition product **3a** as well as ethyl benzoate as a side product (Table 1, entry 1). Moreover, the reaction temperature played an important role in promoting the transformation (Table 1, entries 2-3). Experimental results showed that increasing temperature obviously decreased the energy barrier of **4a** thus promoting the transformation of **3a** into **4a**. K_2CO_3 as base catalyst is crucial for this catalytic transformation (Table 1, entries 4-12). No product was detected in the absence of the catalyst (Table 1, entry 4). Furthermore, other carbonates replacing K_2CO_3 as the catalyst showed poorer catalytic activities (Table 1, entries 5-7). This reaction also proceeded smoothly with $KHCO_3$ and KOH (Table 1, entries 8-9), nevertheless NEt_3 as organic base could not promote this process (Table 1, entry 10). Besides, the effect of K^+ ion was evaluated in the presence of KCl and an equivalent amount additive of 18-crown-6, respectively, which showed the proper basicity was necessary (Table 1, entries 11-12). In addition, no product was generated using HOAc or $PdCl_2$; and even the copper catalyst, which usually worked well in C-C bond cleavage of 1, 3-diketones[11,15], showed inferior efficiency for this process (Table 1, entries 13-15).

[a]*Key Laboratory of Applied Chemistry of Chongqing Municipality, Institute of Bioorganic & Medicinal Chemistry, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China.*
[b]*Beijing National Laboratory for Molecular Sciences, Beijing 100190, China*
E-mail: gxcai@swu.edu.cn; zhouch@swu.edu.cn.
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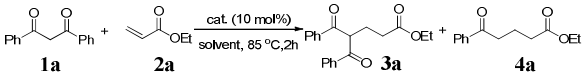
Further screening of solvents displayed the production of **4a** only in ethanol, which indicated that ethanol played a key role in the transformation (Table 1, entries 16-19). Moreover, the pressure in sealed tube and the inhibitor in commercial acrylates were evaluated, and experimental results showed that both factors had little effect on this transformation (Table 1, entry 20). Above systematic studies indicated that several factors including the proper basicity, alcohol and the reaction temperature corporately controlled this transformation.

Table 1. Optimization of reaction conditions[a]

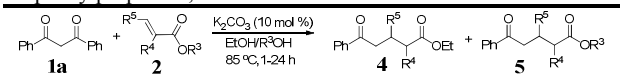


Entry	Catalyst	Solvent	Yield of **3a**(%)[b]	Yield of **4a**(%)[b]
1	K_2CO_3	EtOH	trace	98
2[d]	K_2CO_3	EtOH	43	NP[c]
3[e]	K_2CO_3	EtOH	20	40
4	-	EtOH	NP	NP
5	Li_2CO_3	EtOH	trace	NP
6	Na_2CO_3	EtOH	29	16
7	Cs_2CO_3	EtOH	trace	86
8	$KHCO_3$	EtOH	trace	93
9	KOH	EtOH	trace	92
10	NEt_3	EtOH	trace	NP
11	KCl	EtOH	trace	NP
12[f]	K_2CO_3	EtOH	trace	96
13	HOAc	EtOH	NP	NP
14	$PdCl_2$	EtOH	NP	NP
15	$CuBr_2$	EtOH	NP	15
16	K_2CO_3	CH_3CN	42	NP
17	K_2CO_3	Toluene	10	NP
18	K_2CO_3	DCE	11	NP
19	K_2CO_3	H_2O	trace	NP
20	K_2CO_3	EtOH	trace	96[g](97)[h]

[a]**1a** (0.5 mmol), **2a** (1 mmol), catalyst (0.05 mmol) and solvent (2 mL) in a sealed tube at 85 °C for 2 h; [b]Isolated yields; [c]NP = no product; [d]25 °C; [e]60 °C; [f]18-crown-6 (0.5 mmol) as an additive; [g]Atmospheric pressure in refluxing ethanol; [h]Fresh distilled ethyl acrylate (1 mmol).

With optimal conditions in hand, the scope of acrylate was investigated in EtOH and the corresponding alcohol, respectively (Table 2). Firstly, methyl acrylate (**2b**) replacing **2a** in EtOH gave the complete transesterification product **4a** in 90% isolated yield, while methyl 5-oxo-5-phenylpentanoate (**5a**) was also obtained in corresponding MeOH in 75% isolated yield (Table 2, entry 2). Besides, long-chain aliphatic acrylates (**2c, 2d**) in EtOH led to both the product **4a** in moderate yields and a little amount of corresponding products (**5b**, **5c**), while **5b** and **5c** was provided in corresponding *n*BuOH and hexylalcohol in 80% and 75% isolated yields, respectively (Table 2, entries 3-4). Those results illustrated that the transesterification process in EtOH preferred short-chain aliphatic acrylates. Moreover, benzyl acrylate (**2e**) in EtOH and corresponding BnOH was well-behaved with the products of **4a** and **5d** in 87% and 49% yields, respectively (Table2, entry 5). It is noteworthy that, due to steric hindrance, *tert*-butyl acrylate (**2f**) did not undergo transesterification

Table 2. K_2CO_3-Catalyzed sequential reactions of acrylates **2** with 1, 3-diphenylpropane-1, 3-dione **1a** [a]



Entry	2	Yield of **4** (%)[b]	Yield of **5** (%)[b]
1	**2a**	**4a** 98	–
2	**2b**	**4a** 90	**5a** NP (75)
3	**2c**	**4a** 75	**5b** 4 (80)
4	**2d**	**4a** 62	**5c** 10 (75)
5	**2e**	**4a** 87	**5d** NP (49)
6[c]	**2f**	**4a** NP	**5e** 90
7	**2g**	**4a** 94	**5f** NP
8[d]	**2h**	**4a** 95	**5g** NP (80)
9[d]	**2i**	**4a** 91	**5h** NP (91)
10[d]	**2j**	**4a** 95	**5i** NP (16)
11[e]	**2k**	**4a** trace	**5j** <10
12[e]	**2l**	**4b** 30	–
13[e]	**2m**	**4c** 10	–
14[e]	**2n**	**4b** 57	**5k** trace (45)
15[e]	**2o**	**4b** 72	**5l** <10
16[e]	**2p**	**4b** 35	**5m** trace
17[e]	**2q**	**4b** trace	**5n** <10
18[e]	**2r**	NP	NP

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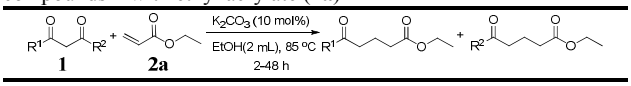
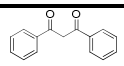
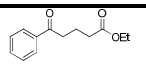
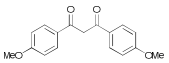
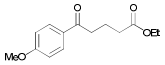
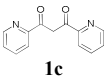
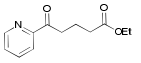
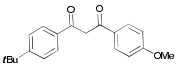
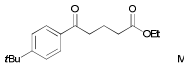
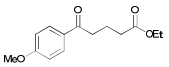
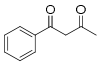
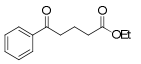
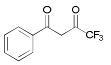
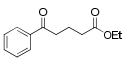
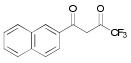
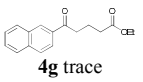
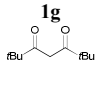
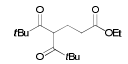
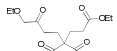
[a]**1a** (0.5 mmol), **2** (1 mmol), K_2CO_3 (0.05 mmol), EtOH (2 mL), at 85 °C, 1-24 h; [b]Isolated yields. Yields from corresponding alcohol solutions were reported in parentheses; [c]EtOH (0.5 mL); [d] EtOH (2 mL), R^3OH (0.5 mL); [e] EtOH (0.5 mL), R^3OH (0.5 mL).

in EtOH and completely transferred to the corresponding product **5e** in 90% isolated yield (Table 2, entry 6). Other acrylates (**2g-2j**) with functional groups, such as CH_2CH_2OH, CH_2CH_2OMe, tetrahydrofurfuryl and CH_2CF_3, in EtOH afforded the complete transesterification product **4a** in excellent yields, while those in corresponding alcohol solutions gave products **5g-5h** in moderate to excellent yields, expect for **5i** (Table 2, entries 7-10). Owing to the poor nucleophilicity of trifluoroethanol, trifluoroethyl acrylate (**2j**) in trifluoroethanol might be limited in the step of retro-Claisen condensation and thus led to desired product **5i** in poor yield. Additionally, cyclohexyl acrylate (**2k**), due to steric factor, provided the trace product **5j** in EtOH or cyclohexanol (Table 2, entry 11). Furthermore, it was found that steric hindrance of alkenes obviously depressed this cascade process. The methyl group presenting at α- and β-position of ethyl acrylate (**2l, 2m**, respectively) afforded corresponding products in low to moderate yields along with a great deal of acetophenone, which illustrated that steric hindrance of alkene had the side effect on the step of Michael addition (Table 2, entries 12-13, 18). Other methacrylates (**2n-2p**) containing functional groups, such as benzyl, trifluoroethyl and glycol, in EtOH and corresponding alcohol solutions provided the product **4a** and the corresponding products (**5k, 5l**) in moderate and poor yields, respectively (Table 2,

Table 3 K_2CO_3-catalyzed cascade reactions of 1,3-dicarbonyl compounds **1** with ethyl acrylate (**2a**)[a]



1 **2a**

Entry	1	Yield (%)[b]		
1	 **1a**	 **4a** 98		
2	 **1b**	 **4d** 70		
3	 **1c**	 **4e** 75		
4	 **1d**	 **4f** 40	 **4d** 57	
5	 **1e**	 **4a** 89		
6	 **1f**	 **4a** trace	 **7a** 65	
7	 **1g**	 **4g** trace	 **7b** 54	
8	 **1h**	 **6a** 62		
9	 **1i**	 **6b** 25		

[a]**1** (0.5 mmol), **2a** (1 mmol), K_2CO_3 (0.05 mmol), EtOH (2 mL), at 85 °C, 2-48 h; [b]Isolated yields.

entries 14-16). The results of **2q** being similar to those of **2k** showed that steric hindrance of the cyclohexyl group played a leading role in the cascade process compared with that of α-position methyl group (Table 2, entry 17).

Subsequently, the reactions of various 1, 3-diketones **1** with ethyl acrylate (**2a**) were explored under optimal conditions and the screening results were displayed in Table 3. To our delight, symmetrically aromatic β-diketones (**1a-1c**) containing the methoxyl group and the pyridyl group were well tolerant under the optimal conditions affording corresponding products (**4a**, **4d** and **4e**) in moderate to excellent yields (Table 3, entries 1-3). However, in the case of asymmetrically aromatic β-diketone **1d**, two desired products both **4f** and **4d** were obtained in 40% and 57% isolated yields, respectively, which illustrated that the substituents on the aromatic rings had a slight effect on the transformation (Table 3, entry 4). Regarding asymmetrical 1-phenyl-1, 3-butanedione (**1e**), **4a** was selectively afforded in 89% isolated yield (Table 3, entry 5), which illustrated that the acetyl group compared with the benzoyl group was a better leaving group in this transformation. Besides, tested asymmetrical 1,3-diketones containing the trifluoromethyl group (**1f** and **1g**) showed that the trifluoromethyl group made retro-Claisen condensation precede Michael addition and thus the products of C-C bond cleavage **7a** and **7b** were prior obtained in moderate yields, respectively (Table 3, entries 6-7). Furthermore, aliphatic 1, 3-diketone **1h**, owing to steric hindrance, only afforded Michael addition product **6a** without further C-C bond cleavage process (Table 3, entry 8). Whereas cyclohexane-1,3-dione (**1i**) behaved differently giving *bis*-addition product **6b**, which successfully made the formation of two C-C bonds in one step (Table 3, entry 9).

Control experiments were conducted in Scheme 2. Treatment of **1a** with 2-methoxyethyl acrylate (**2h**) under standard conditions for 8 minutes gave a mixture of **6c**, **5g** and **3a** as well as the desired product **4a** in 41%, 25%, 8% and trace isolated yields, respectively (Scheme 2, Eq. 1). However, extending reaction time provided the desired product **4a** in 95% isolated yield (Scheme 2, Eq. 2). The control experiment without **2h** under standard conditions only obtained a trace of acetophenone (Scheme 2, Eq. 3). Moreover, the reaction of acetophenone and **2h** under standard conditions resulted in no product formation (Scheme 2, Eq. 4). Furthermore, **6c** smoothly transferred to **4a** in 91% isolated yield under optimal conditions (Scheme 2, Eq. 5). Above results showed that the Michael addition product as the key intermediate participated in the catalytic cycle, which illustrated that the reaction might firstly occur through Michael addition and then undergo close two steps concerning C-C bond cleavage and transesterification. Single retro-Claisen process certainly existed in the reaction system to lead to trace amounts of byproduct.

Scheme 2. Control experiments

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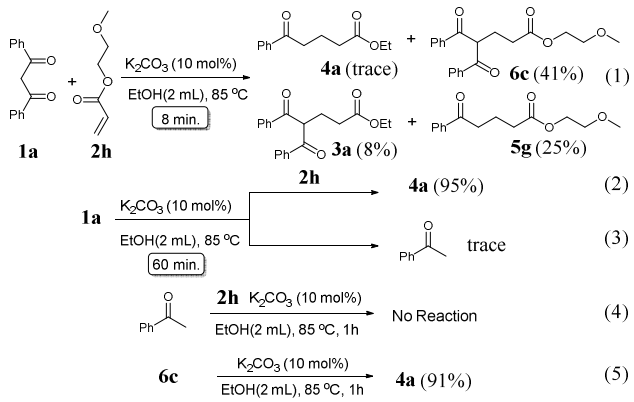
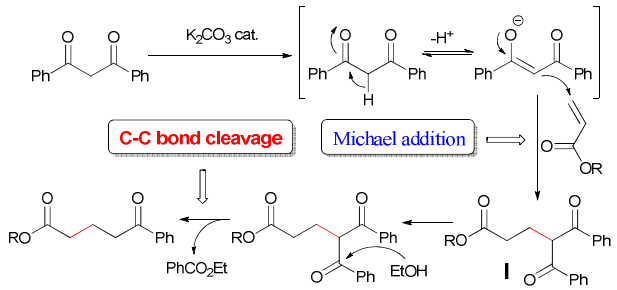


The proposed mechanism of K_2CO_3-catalyzed a pot strategy for synthesis of 1, 5-ketoesters was listed in Scheme 3. In the presence of K_2CO_3, Michael addition between aromatic *β*-diketones and *α, β*-unsaturated carbonyl compounds occurred, which realized the formation of intermediate **I**. Subsequently, the C-C bond cleavage, namely retro-Claisen condensation, as a key step came true as followed by releasing ethyl benzoate in the presence of ethanol. Importantly, the C-C bond cleavage and transesterification occurred almost at the same time regarding to the formation of 1, 5-ketoesters. Besides, alcohol had an unusual part to play in concurrently cleaving C-C and C-O bonds.

Scheme 3. Proposed mechanism



Conclusions

In summary, we have disclosed a cascade process involving Michael addition and retro-Claisen condensation in one pot. Aromatic *β*-diketones with *α, β*-unsaturated carbonyl compounds could smoothly access to 1, 5-ketoesters in the presence of K_2CO_3 in alcohol solutions. Especially, the C-C bond cleavage of aromatic *β*-diketones supplying the phenacyl group differentiated from reported 1, 3-diketones as an acylation reagent. Further mechanical studies showed that EtOH played an unprecedented role, which assisted the cleavages of both C-C and C-O bonds in one pot. This method provides a convenient and practical alternative to 1, 5-dicarbonyl compounds. The synthetic applications in medicinal candidates are now in progress in our group.

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Notes and references

1. (a) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993-3099. (b) Grondal, C.; Jeanty, M.; Enders, D. *Nature Chem.* **2010**, *2*, 167-178.
2. (a) Zeng, X. M. *Chem.Rev.* **2013**, *113*, 6864-6900. (b) Cichowicz, N. R.; Kaplan, W.; Khomutnyk, Y.; Bhattarai, B.; Sun, Z.; Nagorny, P. *J. Am. Chem. Soc.* **2015**, *137*, 14341-14348.
3. (a) Donohoe, T. J.; Basutto, J. A.; Bower, J. F.; Rathi, A. *Org. Lett.* **2011**, *13*, 1036-1039. (b) Yang, X. H.; Xie, J. H.; Liu, W. P.; Zhou, Q. L. *Angew. Chem. Int. Ed.* **2013**, *52*, 7833-7836. (c) Periasamy, M.; Gurubrahamam, R.; Muthukumaragopal, G. P. *Tetrahedron: Asymmetry* **2013**, *24*, 568-574. (d) Goh, K. K. K.; Kim, S.; Zard, S. Z. *Org. Lett.* **2013**, *15*, 4818-4821. (e) Tatton, M. R.; Simpson, I.; Donohoe, T. J. *Org. Lett.* **2014**, *16*, 1920-1923.
4. (a) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1973**, *95*, 6152-6153. (b) Yasuda, M.; Ohigashi, N.; Shibata, I.; Baba, A. *J. Org. Chem.* **1999**, *64*, 2180-2181. (c) Yasuda, M.; Chiba, K.; Ohigashi, N.; Katoh, Y.; Baba, A. *J. Am. Chem. Soc.* **2003**, *125*, 7291-7300. (d) Ratnikov, M. O.; Tumanov, V. V.; Smit, W. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 9739-9742.
5. (a) Lin, K. W.; Chen, C. Y.; Chen, W. F.; Yan T. H. *J. Org. Chem.* **2008**, *73*, 4759-4761. (b) Suzuki, H.; Sato, I.; Yamashita, Y.; Kobayashi, S. *J. Am. Chem. Soc.* **2015**, *137*, 4336-4339.
6. (a) Ono, N.; Miyake, H.; Kaji, A. *J. Chem. Soc., Chem.Commun.*, **1983**, 875-876. (b) Kumar, T. P.; Sattar, M. A.; Sarma, V. U. M. *Tetrahedron: Asymmetry* **2013**, *24*, 1615-1619.
7. (a) Stork, G.; Jung M. E. *J. Am. Chem. Soc.* **1974**, *96*, 3682-3684. (b) Li, L. Z.; Xiao, B.; Guo, Q. X.; Xue, S. *Tetrahedron* **2006**, *62*, 7762-7771. (c) Gowrisankar, S.; Kim, K. H.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 6241-6244. (d) Tang, X. Y.; Shi, M. *Tetrahedron* **2009**, *65*, 8863-8868.
8. (a) Rybtchinski, B.; Milstein, D. *Angew. Chem. Int. Ed.* **1999**, *38*, 870-883. (b) Jun, C. H. *Chem. Soc. Rev.* **2004**, *33*, 610-618. (c) Miura, T. S. M. *Top. Organomet. Chem.* **2005**, *14*, 1-20. (d) Chen, F.; Wang, T.; Jiao, N. *Chem. Rev.* **2014**, *114*, 8613-8661. (e) Dermenci, A.; Coe, J. W.; Dong, G. *Org. Chem. Front.* **2014**, *1*, 567-581. (f) Marek, I.; Masarwa, A.; Delaye, P. O.; Leibeling, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 414-429.
9. Han, W. C.; Takahashi, K.; Cook, J. M.; Weiss, U.; Silverton, J. V. *J. Am. Chem. Soc.* **1982**, *104*, 318-321.
10. (a) Grogan, G.; Graf, J.; Jones, A.; Parsons, S.; Turner, N. J.; Flitsch, S. L. *Angew. Chem. Int. Ed.* **2001**, *40*, 1111-1114. (b) Kawata, A.; Takata, K.; Kuninobu, Y.; Takai, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 7793-7795. (c) Biswas, S.; Maiti, S.; Jana, U. *Eur. J. Org. Chem.* **2010**, 2861-2866. (d) Rao, C. B.; Rao, D. C.; Babu, D. C.; Venkateswarlu, Y. *Eur. J. Org. Chem.* **2010**, 2855-2859. (e) Sun, X.; Wang, M.; Li, P.; Zhang, X. L.; Wang, L. *Green Chem.* **2013**, *15*, 3289-3294. (f) Xie, F.; Yan, F. X.; Chen, M. M.; Zhang, M. *RSC Adv.* **2014**, *4*, 29502-29508.
11. He, C.; Guo, S.; Huang, L.; Lei, A. W. *J. Am. Chem. Soc.* **2010**, *132*, 8273-8275.
12. Li, Z. W.; Dong, J. Y.; Chen, X. L.; Li, Q.; Zhou, Y. B.; Yin, S. F. *J. Org. Chem.* **2015**, *80*, 9392-9413.
13. (a) Shrout, D. P.; Lightner, D. A. *Synthesis* **1990**, 1062-1065. (b) Pierre, M. R.; Markus, M. W.; Dirk, S. L.; Dietmar, F. B.K.; Andreas, B. B. U.S. Patent 20080242857 (A1), 2008-8-2.

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14. (a) Ayed, T. B.; Amri, H. *Synth. Commun.* **1995**, *25*, 3813-3819. (b) Chamakh, A.; Amri, H. *Tetrahedron Lett.* **1998**, *39*, 375-378. (c) Im, Y. J.; Lee, C. G.; Kimb, H. R.; Kim, J. N. *Tetrahedron Lett.* **2003**, *44*, 2987-2990. (d) Clark, J. H.; Farmer, T. J.; Macquarrie, D. J. *ChemSusChem*. **2009**, *2*, 1025-1027.
15. Zhang, C.; Feng, P.; Jiao, N. *J. Am. Chem. Soc*. **2013**, *135*, 15257-15262.
16. Ding, W.; Song, Q. L. *Org. Chem. Front.* **2015**, *2*, 765-770.
17. Roudier, M.; Constantieux, T.; Quintard, A.; Rodriguez, J. *Org. Lett.* **2014**, *16*, 2802-2805.
18. (a) Liu, H.; Dong, C.; Zhang, Z. G.; Wu, P. Y.; Jiang, X. F. *Angew. Chem. Int. Ed.* **2012**, *51*, 12570-12574. (b) Liu, H.; Jiang, X. F. *Synlett* **2013**, *24*, 1311-1315. (c) Mayo, M. S.; Yu, X. Q.; Zhou, X. Y.; Feng, X. J.; Yamamoto, Y.; Bao, M. *Org. Lett.* **2014**, *16*, 764-767.