Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c8ob02539h

Efficient synthesis of esters through oxone-catalyzed dehydrogenation of carboxylic acids and alcohols†

Fei Hou,[a,b] Xi-Cun Wang [a,b] and Zheng-Jun Quan *[a,b]

Received 13th October 2018,
Accepted 26th November 2018

DOI: 10.1039/c8ob02539h

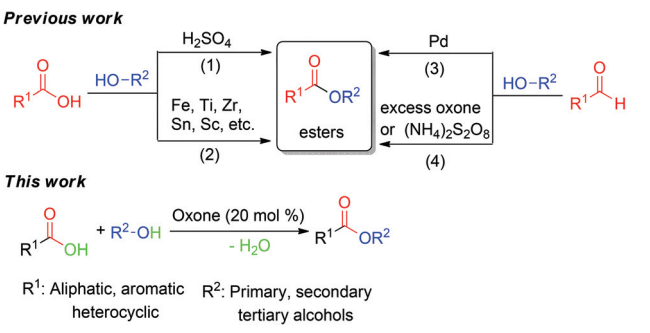
rsc.li/obc

Since esters are important organic synthesis intermediates, an environmentally friendly oxone catalyzed-esterification of carboxylic acids with alcohols has been developed. A series of carboxylic acid esters are obtained in high yield. This strategy requires mild reaction conditions, providing an attractive alternative for the construction of valuable carbonyl esters. Electron-rich and electron-deficient groups are compatible with the standard conditions and a variety of substrates are demonstrated. Moreover, the reaction could easily be adapted to typical prodrugs, drugs and gram-scale synthesis.

Introduction

The ester is one of the most common functional groups in natural products and one which causes many of the sweet smells of fruits and flowers. It is also used as a key intermediate for drug synthesis; for instance, ester linkages can be found in Tamiflu, Methylphenidate and Fenofibrate.[1] Esters are also widely used in industry, accounting for 25% of all the chemical operations involved in drug synthesis.[2] In particular, benzoate compounds have antitrypsin and antithrombin activities, and low toxicity. They can also be used as medicaments for treating pancreatic diseases.[1d] Thus, the synthesis of esters has attracted a great deal of attention from many researchers, and many effective methods have been developed.[3] Therefore, the direct condensation of carboxylic acids with alcohols is one of the simplest ways.

Initially, synthesis of carboxylic acid esters was achieved through preactivation of the carboxylic acid (mostly as the acyl chloride, *i.e.*, X = Cl) and coupling agents,[4] or the use of concentrated sulfuric acid as a catalyst (Scheme 1, eqn (1)).[5] However, this method seriously corrodes equipment and is not suitable for large-scale industrial production. From a green aspect, a method that avoids using sulfuric acid would be highly desirable. In that regard, the use of Lewis acid catalysis with a Dean–Stark apparatus (Scheme 1, eqn (2)) and syntheses through the use of new catalysis have been described.[3f,6–12] However, in the former case, Lewis acids have limited use due to their poor tolerance to functional groups, and complicated experimental operation. The Mitsunobu reaction, which uses triphenylphosphine (Ph_3P) or a related phosphine activated by an oxidant, has become an extremely useful tool for the esterification of acids with alcohols.[13] But, it has limited utility in process chemistry and industrial applications due to poor atom economy and the generation of stoichiometric phosphine oxide and hydrazine by-products that complicate purification.[14] Since then, a great deal of efforts have been made to identify effective and practical oxidative esterification methods, and several possible methods have been reported.[15] Direct preparation of the esters of aldehydes and alcohols has also been reported.[16] Nevertheless, in terms of atom economy, the direct conversion of aldehydes and alcohols to esters (oxidative esterification) was attractive. Despite indisputable advances, these oxidative esterifications of aldehydes and alcohols were yet limited to requiring transition-metal catalysts (Scheme 1, eqn (3))[17] or stoichiometric amounts of



Scheme 1 Previous work and the current method.

[a]College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, People's Republic of China
[b]Gansu International Scientific and Technological Cooperation Base of Water-Retention Chemical Functional Materials, Lanzhou, Gansu 730070, People's Republic of China. E-mail: quanzhengjun@hotmail.com; Fax: +86-931-7972626

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ob02539h

oxidants,[18–21] harsh reaction conditions and limited substrate scopes (Scheme 1, eqn (4)). Aldehydes are more unstable than carboxylic acids and the market price is several times higher compared with carboxylic acids. What's more, aldehydes are more difficult to prepare than carboxylic acids.[22] Besides, the substrate scope of aldehydes is not as broad as that of carboxylic acids. Therefore, the evolvement of a novel, non-metallic, green method of ester synthesis still has some research value.

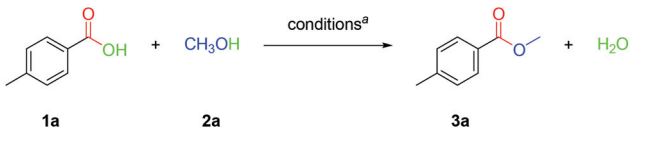
In recent years, reactions promoted by oxone have been widely reported. Oxone (2 $KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) is easy to handle, non-toxic, and soluble in water. In addition, it is incredibly cheap, which can compete with the cost of bleach and H_2O_2.[23] The active oxidizing reagent is $KHSO_5$, and peroxymonosulfate anions (HSO_5^-) have been extensively studied in various fields.[24] Herein, we report the general catalytic direct esterification of carboxylic acids with alcohols catalyzed by oxone (20 mol%). Moreover, the reaction could easily be adapted to two prodrugs, drugs and gram-scale synthesis.

Results and discussion

We started by using simple, commercially available $Na_2S_2O_8$ as the catalyst for the esterification of a carboxylic acid and an alcohol. We were pleased that the target product **3a** was obtained in 83% yield when using methanol as the solvent and *p*-methylbenzoic acid as the substrate at 60 °C for 48 h. Therefore, *p*-methylbenzoic acid (**1a**) and methanol (**2a**) were selected as the model substrates to optimize the reaction conditions. At the outset, several oxidants were screened. Oxone was used as an oxidant, which gave the desired carboxylic ester product **3a** in excellent yield (Table 1, entries 1–6). In sharp contrast, **3a** was obtained in only 10% yield in the case of $K_2S_2O_8$ as the oxidant. This might be attributed to differences between the solubilities of the oxidants as reported.[19,25] In an effort to further improve the yield of **3a**, we tested various reaction conditions *via* testing the amount of oxone, temperature and various solvents. Reducing the amount of oxone has little impact on the yield of **3a** (Table 1, entries 6–10). When comparing the use of 1.5 equiv. and 0.2 equiv. of oxone (Table 1, entries 6 and 9), **3a** was obtained in yields of 96% and 88%. Taking into account the economic benefits and green policy, 0.2 equiv. oxone can be used as the catalytic amount. We finally chose 0.2 equiv. oxone as the best quantity (Table 1, entry 9). The screening of temperature suggested that 60 °C was the best choice for the transformation (Table 1, entry 9 and entries 11–12). Finally, the solvent was screened and it was found that the reaction was successful only when the alcohol was used as the solvent (Table 1, entries 13–16). After various reaction parameters were optimized, the best result was found under the following conditions: oxone (0.2 equiv.) at 60 °C in MeOH. Under these reaction conditions, an 88% yield of **3a** was obtained after 48 h (Table 1, entry 9).

With the optimized reaction conditions in hand, we investigated the activity of a variety of carboxylic acids with methanol in the reaction. Various carboxylic acids including aromatic, aliphatic and heteroaromatic acids provided the desired esters in moderate to excellent yields (Scheme 2). Aryl rings with electron-donating groups or electron-withdrawing groups at the *para*-, *meta*-, and *ortho*-positions could furnish the desired car-

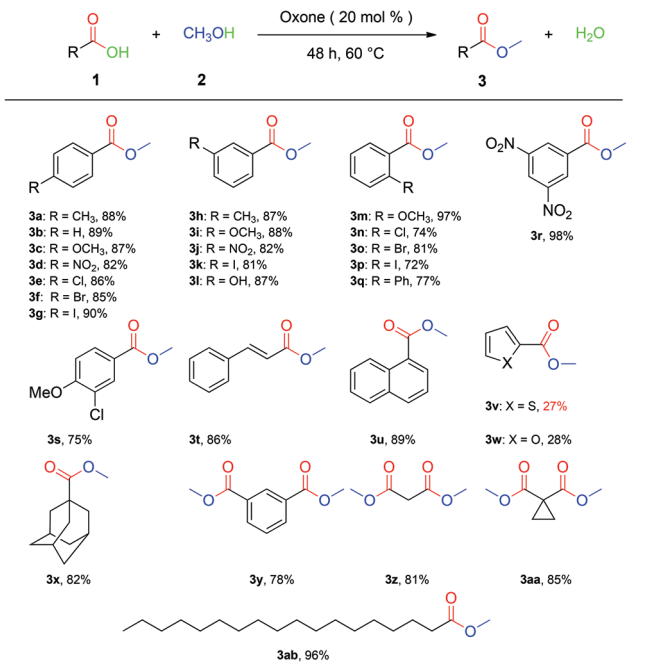
Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	Catalyst (equiv.)	Solvent (mL)	Temp. (°C)	Time (h)	Yield[c] (%)
1	$Na_2S_2O_8$ (1.5)	CH_3OH	60	48	83
2	$K_2S_2O_8$ (1.5)	CH_3OH	60	48	10
3	$(NH_4)_2S_2O_8$ (1.5)	CH_3OH	60	48	22
4	$PhI(OAc)_2$ (1.5)	CH_3OH	60	48	N.R
5	mCPBA (1.5)	CH_3OH	60	48	N.R
6	Oxone (1.5)	CH_3OH	60	48	96
7	Oxone (1)	CH_3OH	60	48	94
8	Oxone (0.5)	CH_3OH	60	48	90
9	**Oxone (0.2)**	**CH_3OH**	**60**	**48**	**88**
10	Oxone (0.15)	CH_3OH	60	48	75
11	Oxone (0.2)	CH_3OH	40	48	30
12	Oxone (0.2)	CH_3OH	80	48	85
13[b]	Oxone (0.2)	DMF	60/80	48	N.R
14[b]	Oxone (0.2)	Dioxane	60/80	48	N.R
15[b]	Oxone (0.2)	CH_3CN	60	48	N.R
16[b]	Oxone (0.2)	Toluene	60	48	32

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3.0 mL), oxone (0.2 equiv., equal to 40 mol% $KHSO_5$). [b] Reaction conditions: **1a** (0.5 mmol), **2a** (1.2 equiv.), oxone (0.2 equiv.), under air atmosphere for 48 h. [c] Isolated yields.



Scheme 2 Reactions of different carboxylic acids and methanol.

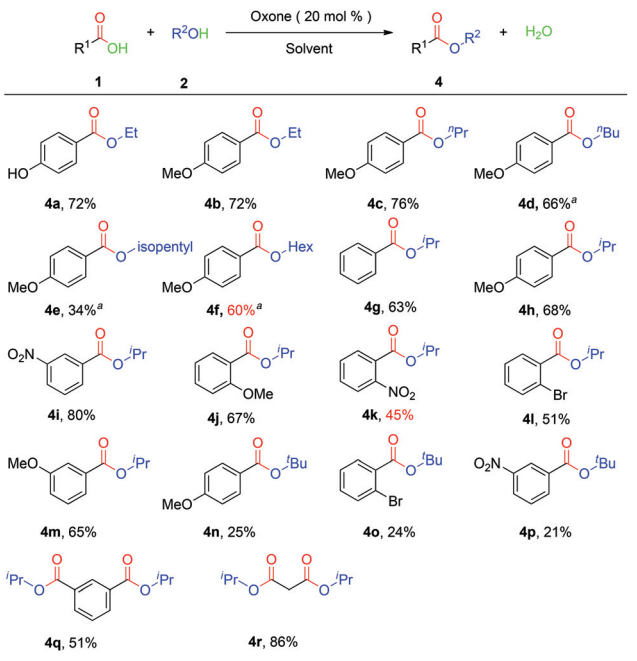
boxylic esters in high yields, and at the same time the reactions were tolerant to fluoro, chloro, bromo and iodine substituents on the aromatic ring (**3a–3q**). It is worth noting that with an electron-withdrawing group, such as $-NO_2$, the corresponding products (**3d** and **3j**) could be achieved in 82% yield. What's more, compound **3l** was obtained in 87% yield and did not require protection of the –OH group. When there were two strong electron-withdrawing groups on the aryl ring (**3r**), the yield was significantly increased to 98%. While when there were two different substituents on the aryl ring, the target product (**3s**) was obtained in a yield of 75%. In addition, cinnamic acid and 1-naphthoic acid gave their target products (**3t** and **3u**) in high yields of 86% and 89%. Fortunately, the double bond of cinnamic acid was successfully retained without being oxidized under the reaction system. For the heterocyclic carboxylic acids, the target products (**3v** and **3w**) can also be obtained in a certain yield. Interesting, for the large, sterically hindered 1-adamantanic acid and the long-chain carboxylic acid stearic acid, the target products (**3x** and **3ab**) can be obtained with 82% and 96% yields. As far as we know, no similar literature has been reported before. For dicarboxylic acids including aromatic and aliphatic substrates, the target products (**3y** and **3z**) can be obtained in good yields. 1,1-Cyclopropanedicarboxylic acid was also compatible and no ring-opening product was observed, with the target product (**3aa**) obtained in a moderate yield.

To develop a more general and useful method, we shifted to investigate alcohol partners (Scheme 3, all the yields are isolated yields). Under optimal conditions, a series of alcohols was tested. It was found that for the reaction of different primary alcohols and diverse carboxylic acids, the target products (**4a–4f**) can be obtained with moderate yields, and the yield range is 34%–76%. The experimental result shows that the length of the carbon chain and the presence of the branch have a certain impact on the yield of the target product. For the secondary alcohol, the target products (**4g–4m**) can be obtained with a yield of 45%–80%. When the large, sterically hindered *tert*-butanol was used as a substrate, the desired products (**4n–4p**) can also be obtained in a satisfactory yield. The steric hindrance surely has an influence on the experimental results. For dicarboxylic acid substrates, both aromatic and aliphatic, the target products (**4q** and **4r**) can be obtained with a yield of 51% and 86%.

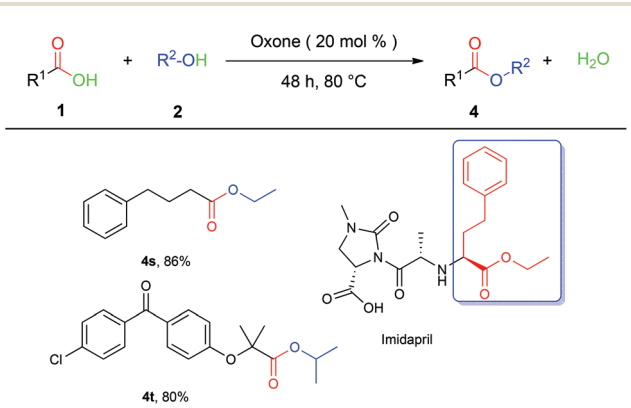
Imidapril is an angiotensin converting enzyme inhibitor prodrug and it can lower blood pressure.[26] Compound **4s** could be used as a precursor for the synthesis of imidapril and has great application value. It is most important that we successfully synthesized fenofibrate (**4t**) in one step to obtain the target product with a high yield of 80% (Scheme 4). Fenofibrate is mainly used to regulate blood fat and lower cholesterol, and is currently a popular non-prescription drug.[1d,27]

A gram-scale synthesis was examined using 5.0 g (32.8 mmol) of 4-methoxybenzoic acid and methanol as the solvent under the optimal reaction conditions (Scheme 5). As a result, the esterification reaction successfully worked to afford the target product (**3c**) in 83% yield (4.5 g of product).

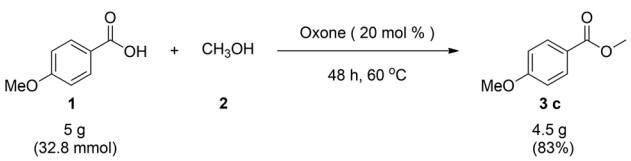
In order to verify the role of each component in oxone, control experiments were designed (Scheme 6). The experimental results show that under the same conditions within



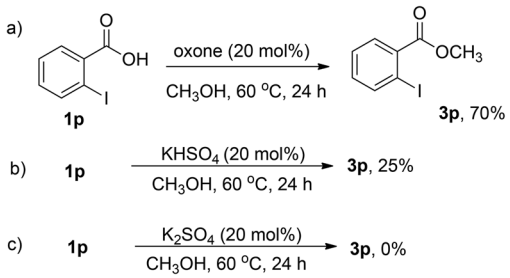
Scheme 3 Reactions of different alcohols and diverse carboxylic acids. Reaction conditions: **1** (0.5 mmol), **2** (3 mL), oxone (20 mol%), 80 °C, 48 h. [a] Reaction conditions: **1** (0.5 mmol), **2** (1.2 equiv.), toluene (3 mL), oxone (20 mol%), 80 °C, 48 h.



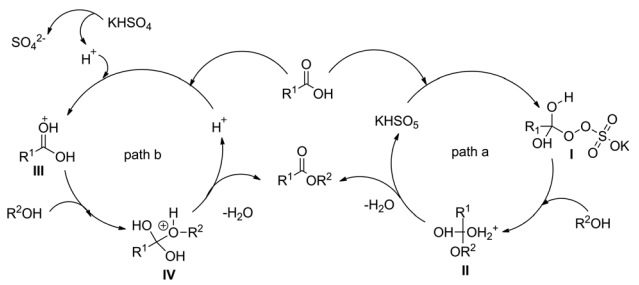
Scheme 4 Preparation of prodrugs and drugs.



Scheme 5 Gram-scale synthesis.



Scheme 6 Control experiment.



Scheme 7 Proposed mechanism.

24 h, oxone can obtain the target product **3p** in 70% yield (Scheme 6a). When $KHSO_4$ was tested without oxone, only 25% of **3p** was obtained (Scheme 6b), while K_2SO_4 did not produce the target product (Scheme 6c). So it may be that $KHSO_5$ and $KHSO_4$ work together in this esterification.

To further clarify the reaction mechanism, anhydrous methanol was used as the solvent, and anhydrous $CuSO_4$ was added to the system. The system was clear and transparent before starting the reaction. After the reaction was completed, the system turned blue, indicating that the system had generated water. Based on previous research,[28] HSO_5^- has been reported as a good nucleophile and oxone as slightly acidic.[24] Therefore, two possible mechanisms were proposed (Scheme 7). Possibility a: first, the carboxylic acid forms intermediate **I** under the action of $KHSO_5$. Then, it undergoes nucleophilic substitution under the action of an alcohol, and generate intermediate **II** under the action of protons while generating another molecule of $KHSO_5$ to continue the catalytic cycle. Finally, intermediate **II** was deprotonated and one molecule of water was removed to obtain the target product. Possibility b: First, $KHSO_4$ electrolysis releases hydrogen ions, which protonate the carboxylic acid to give intermediate **III**. Intermediate **III** was attacked by the alcohol affording **IV**, which was followed by electron transfer, dehydration and deprotonation to obtain the target product.[28f]

Conclusions

In summary, we have reported the use of oxone as an effective catalyst for the direct esterification of carboxylic acids with alcohols. The corresponding esters are obtained in moderate to excellent yields with a broad range of carboxylic acids, including aromatic, heteroaromatic and aliphatic substrates. At the same time, linear alcohols, branched alcohols and *tert*-butanol, which has greater steric hindrance, are compatible. The reaction system has a series of advantages, such as mild conditions, simple operation, green, high yields, and it can be smoothly enlarged to gram scale. Furthermore, it is easy to synthesize a series of pharmaceutical intermediates, providing a new strategy for the industrial production of esters.

Experimental

General procedure for the synthesis of compound 3a

The mixture of **1a** (0.50 mmol, 68 mg), methanol (3 mL) and oxone (20 mol%, 60 mg) was stirred at 60 °C for 48 h under air atmosphere. After the reaction completed as monitored by TLC analysis, 3.0 mL $NaHCO_3$ solution was added to the mixture to quench the reaction and it was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$. The residue was purified using column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 6) to give the corresponding product **3a** as a white solid (66 mg, 88% yield).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are thankful for financial support from the National Nature Science Foundation of China (No. 21562036) and the Scientific and Technological Innovation Engineering program of Northwest Normal University (NWNU-LKQN-15-1).

References

1 (*a*) J. Otera and J. Nishikido, *Esterification: Methods, Reactions, and Applications*, Wiley-VCH, Weinheim, 2nd edn, 2010; (*b*) J. D. Warren, J. S. Miller, S. J. Keding and S. J. Danishefsky, *J. Am. Chem. Soc.*, 2004, **126**, 6576–6578; (*c*) X. Li, H. Y. Lam, Y. Zhang and C. K. Chan, *Org. Lett.*, 2010, **12**, 1724–1727; (*d*) E. Vitaku, B. R. Smith, D. T. Smith and J. T. Njardarson, Top US pharmaceutical products of, 2013.

2 (*a*) J. S. Carey, D. Laffan, C. Thomson and M. T. Williams, *Org. Biomol. Chem.*, 2006, **4**, 2337–2347; (*b*) R. W. Dugger, J. A. Ragan and D. H. B. Ripin, *Org. Process Res. Dev.*, 2005, **9**, 253–258.

3 (*a*) T. Ogawa and M. Matsui, *J. Am. Chem. Soc.*, 1976, **98**, 1629–1630; (*b*) C. McDonald, H. Holcomb, K. Kennedy, E. Kirkpatrick, T. Leathers and P. Vanemon, *J. Org. Chem.*, 1989, **54**, 1213–1215; (*c*) J. M. Humphrey and A. R. Chamberlin, *Chem. Rev.*, 1997, **97**, 2243–2266;

(*d*) R. H. Dave and B. D. Hosangadi, *Tetrahedron Lett.*, 1996, **37**, 6375–6378; (*e*) K. Ishihara, *Tetrahedron*, 2009, **65**, 1085–1109; (*f*) S. Gaspa, A. Porcheddu and L. D. Luca, *Org. Lett.*, 2015, **17**, 3666–3669; (*g*) H. Kitano, H. Ito and K. Itami, *Org. Lett.*, 2018, **20**, 2428–2432.

4 (*a*) A. K. Twibanire and T. B. Grindley, *Org. Lett.*, 2011, **13**, 2988–2991; (*b*) W. Yin, S. Majumder and J. M. Cook, *Bioorg. Med. Chem.*, 2010, **18**, 7548–7564; (*c*) L. Crocetti and M. P. Giovannoni, *Bioorg. Med. Chem.*, 2011, **19**, 4460–4472; (*d*) Q. Sun, H. Li, C. Xian, Y. Yang, Y. Song and P. Cong, *Appl. Surf. Sci.*, 2015, **344**, 17–26.

5 (*a*) C. M. Scott and M. J. Madeleine, *Synth. Commun.*, 1994, **24**, 2367–2377; (*b*) E. E. Reid, *Ind. Eng. Chem.*, 1948, **40**, 1596–1601; (*c*) L. P. Marvin and W. W. John, *Ind. Eng. Chem.*, 1956, **48**, 1576–1584.

6 S. Palaniappan and M. S. Ram, *Green Chem.*, 2002, **4**, 53–55.

7 M. Minakawa, H. Baek, Y. M. A. Yamada, J. W. Han and Y. Uozumi, *Org. Lett.*, 2013, **15**, 5798–5801.

8 S. P. Morcillo, A. J. Mota and R. Robles, *J. Org. Chem.*, 2011, **76**, 2277–2281.

9 S. S. Chen, F. K. Chen and C. S. Ke, *Synth. Commun.*, 2013, **43**, 2615–2621.

10 (*a*) K. Steliou, A. Szczygielska-Nowosielska, A. Favre, M. A. Poupart and S. Hanessian, *J. Am. Chem. Soc.*, 1980, **102**, 7578–7579; (*b*) A. K. Kmar and T. K. Chattopadhyay, *Tetrahedron Lett.*, 1987, **28**, 3713–3714; (*c*) J. Otera, N. Danoh and H. Nozaki, *J. Org. Chem.*, 1991, **56**, 5307–5311; (*d*) K. Ishihara, S. Ohara and H. Yamamoto, *Science*, 2000, **290**, 1140–1142.

11 (*a*) M. Nakayama, A. Sato, K. Ishihara and H. Yamamoto, *Adv. Synth. Catal.*, 2004, **346**, 1275–1279; (*b*) C. T. Chen and Y. S. Munot, *J. Org. Chem.*, 2005, **70**, 8625–8627.

12 (*a*) K. Ishihara, S. Nakagawa and A. Sakakura, *J. Am. Chem. Soc.*, 2005, **127**, 4168–4169; (*b*) A. Sakakura, S. Nakagawa and K. Ishihara, *Tetrahedron*, 2006, **62**, 422–433; (*c*) T. Funatomi, K. Wakasugi, T. Misaki and Y. Tanabe, *Green Chem.*, 2006, **8**, 1022–1027; (*d*) K. Manabe, X. M. Sun and S. Kobayashi, *J. Am. Chem. Soc.*, 2001, **123**, 10101–10102.

13 (*a*) A. Voituriez and A. N. Saleh, *Tetrahedron Lett.*, 2016, **57**, 4443; (*b*) J. An, R. M. Denton, T. H. Lambert and E. D. Nacsa, *Org. Biomol. Chem.*, 2014, **12**, 2993; (*c*) M. März, J. Chudoba and R. Cibulka, *Org. Biomol. Chem.*, 2017, **15**, 1970–1975; (*d*) H. Huang and J. Y. Kang, *J. Org. Chem.*, 2017, **82**, 6604–6614; (*e*) D. Hirose, M. Gazvoda and J. Kosmrlj, *Org. Lett.*, 2016, **16**, 4036–4039.

14 J. A. Buonomo and C. C. Aldrich, *Angew. Chem., Int. Ed.*, 2015, **54**, 13041–13044.

15 (*a*) R. Y. Jagadeesh, A. Brückner and M. Beller, *J. Am. Chem. Soc.*, 2013, **135**, 10776–10782; (*b*) K. Ekoue-Kovi and C. Wolf, *Chem. – Eur. J.*, 2008, **14**, 6302–6315; (*c*) S. Tang, J. Yuan, C. Liu and A. Lei, *Dalton Trans.*, 2014, **43**, 13460–13470; (*d*) S. Gaspa, A. Porcheddu and L. De Luca, *Tetrahedron Lett.*, 2016, **57**, 3433–3440.

16 (*a*) S. Gaspa, A. Porcheddu and L. De Luca, *Org. Lett.*, 2015, **17**, 3666–3669; (*b*) S. Chun and Y. K. Chung, *Org. Lett.*, 2017, **19**, 3787–3790.

17 (*a*) C. Liu, S. Tang, L. W. Zheng, D. Liu, H. Zhang and A. Lei, *Angew. Chem., Int. Ed.*, 2012, **51**, 5662–5666; (*b*) M. Chen, Y. Li, H. Tang, H. Ding, M. Gao and A. Lei, *Asian J. Org. Chem.*, 2017, **6**, 1566–1568; (*c*) S. Gowrisankar, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **123**, 5245–5249; (*d*) J. Zhao and C. A. Muck-Lichtenfeld, *Adv. Synth. Catal.*, 2013, **355**, 1098–1106; (*e*) C. Marsden, E. Taarning, D. Hansen, L. Johansen, S. K. Klitgaard, K. Egeblad and C. H. Christensen, *Green Chem.*, 2008, **10**, 168–170; (*f*) B. A. Tschaen and G. A. Molander, *Org. Lett.*, 2013, **15**, 500–503; (*g*) H. Liu and M. S. Eisen, *Eur. J. Org. Chem.*, 2017, 4852–4858; (*h*) X. F. Wu and C. Darcel, *Eur. J. Org. Chem.*, 2009, 1144–1147.

18 R. Gopinath and B. K. Patel, *Org. Lett.*, 2000, **2**, 577–579.

19 B. R. Travis, M. Sivakumar, G. O. Hollist and B. Borhan, *Org. Lett.*, 2003, **5**, 1031–1034.

20 B. E. Maki and K. A. Scheidt, *Org. Lett.*, 2008, **10**, 4331–4334.

21 Y. F. Guo, S. J. Mahmood, B. H. Xu, X. H. Yao and S. J. Zhang, *J. Org. Chem.*, 2017, **82**, 1591–1599.

22 S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan and H. B. Ripin, *Chem. Rev.*, 2006, **106**, 2943–2989.

23 (*a*) G. W. Wang and J. Gao, *Green Chem.*, 2012, **14**, 1125–1131; (*b*) B. Yu, A. H. Liu, L. N. He, B. Li, Z. F. Diao and Y. N. Li, *Green Chem.*, 2012, **14**, 957–962.

24 (*a*) H. Hussain, I. R. Green and I. Ahmed, *Chem. Rev.*, 2013, **113**, 3329–3371; (*b*) M. Palomba, F. Trappetti, L. Bagnoli, C. Santi and F. Marini, *Eur. J. Org. Chem.*, 2018, 3914–3919; (*c*) C. Huo, X. He and T. H. Chan, *J. Org. Chem.*, 2008, **73**, 8583–8586; (*d*) W. G. Shuler, S. L. Johnson and M. K. Hilinski, *Org. Lett.*, 2017, **19**, 4790–4793; (*e*) M. D. Zhao and W. J. Lu, *Org. Lett.*, 2017, **19**, 4560–4563; (*f*) Y. Horiuchi, Y. Nishimura and A. Yamada, *Adv. Synth. Catal.*, 2016, **358**, 869–873; (*g*) B. V. Tamhankar, U. V. Desai, R. B. Mane, P. P. Wadgaonkar and A. V. Bedekar, *Synth. Commun.*, 2001, **31**, 2021–2027; (*h*) S. Hati, P. K. Dutta, S. Dutta, P. Munshi and S. Sen, *Org. Lett.*, 2016, **18**, 3090–3093; (*i*) R. Bikshapathi, S. P. Parvathaneni and V. J. Rao, *Green Chem.*, 2017, **19**, 4446–4450; (*j*) X. Y. Xing, N. R. O'Connor and B. M. Stoltz, *Angew. Chem., Int. Ed.*, 2015, **54**, 11186–11190.

25 (*a*) S. Shi, A. Kong, X. Zhao, Q. Zhang and Y. Shan, *Eur. J. Org. Chem.*, 2010, 2283–2289.

26 K. Hosoya and T. Ishimitsu, *Cardiovasc. Drug Rev.*, 2002, **20**, 93–110.

27 C. W. Cheung, M. L. Ploeger and X. L. Hu, *Nature*, 2017, **8**, 14878–14887.

28 (*a*) K. M. Kandepi and N. Narender, *Synthesis*, 2012, **44**, 15–26; (*b*) J. O. Edwards, R. H. Pater, R. Curci and F. DiFuria, *Photochem. Photobiol.*, 1979, **30**, 63–70; (*c*) R. Curci, L. Daccolti and C. A. Fusco, *Acc. Chem. Res.*, 2006, **39**, 1–9; (*d*) J. Yan, B. R. Travis and B. Borhan, *J. Org. Chem.*, 2004, **69**, 9301–9302; (*e*) M. Strudthoff and M. Eissen, *J. Chem. Educ.*, 2011, **88**, 284–291; (*f*) J. Otera, *Chem. Rev.*, 1993, **93**, 1449–1470.