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A cascade synthesis of *S*-allyl benzoylcarbamothioates *via* Mumm-type rearrangement†

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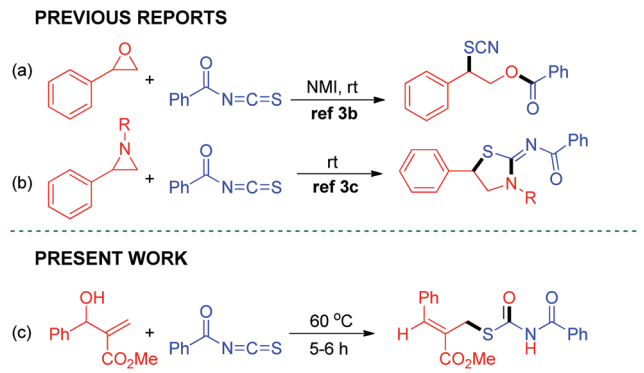
A catalyst and solvent free synthesis of *S*-allyl benzoylcarbamothioates has been achieved from the *in situ* generated benzoylcarbonimidothioates obtained by reacting MBH alcohols with aroyl isothiocyanates. An intramolecular thia-Michael addition of the *in situ* generated adduct triggers a Mumm-type rearrangement leading to a stereoselective synthesis of highly functionalised *S*-allyl benzoylcarbamothioates.

The progress of cascade synthetic methods, where structural divergence is selectively congregated at the molecular level from multifunctional small molecules in one pot, has been established as one of the key epitomes of modern organic chemistry. Toward this endeavor, cascade processes have found wide applications because they successfully implement the goal and principle of sustainability.[1] In many cascade approaches, aroyl isothiocyanates are important synthons and have found extensive use in the construction of biologically active acyclic and cyclic frameworks.[2a,b] Aroyl isothiocyanate, a hetero-cumulene, contains an acyl group and a thiocyanate group. Due to the presence of four reactive sites *viz.* the nucleophilic S and N-atoms, the electrophilic carbonyl and thiocarbonyl groups they serve either as an electrophile or an ambedient nucleophile. Especially, the carbonyl group in aroyl isothiocyanates divulges unique structural features and shows differential reactivity under various reaction conditions.[2c] In our previous report, we have established the efficacy of aroyl isothiocyanates as a nucleophile with α-bromoketones.[3a] While, both as an electrophile and a nucleophile during the ring opening of oxiranes[3b] and aziridines.[3c] In the former a concomitant transfer of a thiocyanate (as nucleophile) and an aroyl moiety (as electrophile) occurs (Scheme 1a) while in the latter a domino ring opening cyclisation of aziridine takes place (Scheme 1b).[3]

The synthetic utility and tendency of the Morita Baylis Hillman (MBH) adducts to afford multifunctional products have become increasingly evident in past decades. As understood by the numerous protocols that highlight its ability to undergo an array of chemical transformations for the construction of a diverse molecular targets.[4] Taking cues from the reactivity of aroyl isothiocyanate,[3] we articulated that this could be the precursor to afford *S*-allyl benzoylcarbamothioate upon reaction with MBH alcohol. Thus, a reaction was carried out between methyl 2-(hydroxy(phenyl)methyl)acrylate (**1**) and benzoyl isothiocyanate (**a**) in toluene (2 mL) at room temperature. A new allyl thioether (**1a**) containing two important moieties *viz.* imide and 2-methylthioacrylate, was isolated in 56% yield possibly *via* a Mumm type of rearrangement.

Among the sulphur based compounds allylic thioethers exhibits a broad range of biological activities. Despite the remarkable progress made to date, construction of allylic thioethers *via* metal-free C–S bond forming reactions is still lacking. Several strategies, including transition metal-catalysed substitution reaction, thiocarbonylation, insertion reaction, and transition metal-catalysed or organocatalysed Michael additions, have been well recognised over the years to construct C–S bonds.[5] Thus, the development of efficient and sus-



Scheme 1 Differential reactivity of aroyl isothiocyanate.

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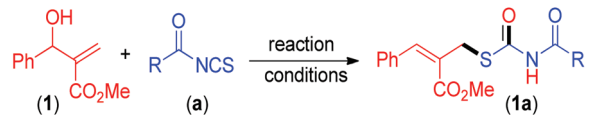
tainable methods for the construction of C–S bonds is deemed worthy of investigation.

Imides are significant structural motifs found in various natural products and pharmaceutical agents.[6a,b] As shown in Fig. S1 (see the ESI†), selected examples include diacetazotol (Dermagan),[6c] tetraacetylethylenediamine (TAED)[6d] and the anxiolytic drug aniracetam (Ampamet).[6c] Such an imide motif also appears in certain natural products such as fumaramidmycin,[6e,f] coniothyriomycin[6g] and unnatural compound SB-253514.[6h] They also appear as precursors in a variety of reactions, such as condensation, alkylation, acylation and cycloaddition.[7] The classical methodology for the synthesis of imides relies on the condensation of amides with carboxylic acids and its derivatives. *N*-Acylation of amides using aldehydes as the acyl source is one of the important synthetic tools in the construction of imides. There are limited precedents for the synthesis of imides based on metal-catalysed cross coupling strategies such as (i) Rh(II)-catalysed sulfamidation of aldehydes;[8a–c] (ii) Fe/Cu catalysed coupling of aldehydes and thioesters with carboxamides;[8d–g] (iii) oxidation of *N*-alkylbenzamides;[8h–j] and (iv) ceric ammonium nitrate (CAN)-promoted oxidation of 4,5-diphenyloxazoles.[8k] Though the above-mentioned protocols describe elegant methods for the construction of imide motifs but the limitation is, it is applicable for the derivatisation of sulfonamides or carboxamides only.[9] Despite several procedures available for their synthesis, the use of designer substrates, poor yields, cumbersome multistepped processes and inadequate product diversity are some of the limitations. Thus, the development of innovative methods for the synthesis of imides from readily available substrates under a mild condition is highly desirable.

In the pursuit to accomplish an appropriate reaction condition for this unparalleled transformation, other reaction parameters such as solvents and temperature were screened using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1**) and benzoyl isothiocyanate (**a**) as the reacting partners. Initially, different nonpolar solvents such as 1,4-dioxane, DCE, DCM and chlorobenzene were tested. When the reaction was carried out in 1,4-dioxane instead of toluene (Table 1, entry 2) the yield dropped to 35%, whereas the use of 1,2-dichloroethane (Table 1, entry 3) gave a comparable yield (59%). When the reaction was performed in DCM and chlorobenzene the product was isolated in 43% and 60% yields, respectively (Table 1, entries 4 and 5). Further, the use of polar solvents such as DMF (39%), DMSO (12%) and acetonitrile (9%) (Table 1, entries 6, 7 and 8) were found to be inferior to that of chlorobenzene (Table 1, entry 5). This reaction in water gave a 64% yield of the product (**1a**) (Table 1, entry 9) which however, was associated with number of other side products. In previous reports, maximum yield of products was obtained under a solvent free condition using aroyl isothiocyanates.[3] Thus, a reaction under a neat condition was attempted at room temperature. To our delight, an improved yield (70%) of the product (**1a**) was obtained (Table 1, entry 10). Interestingly, performing a neat reaction at elevated temperatures of 50 °C and 60 °C, not only improved the yield but also shortened the reaction time giving 83% and 96% of the product in 9 h and 5 h, respectively (Table 1, entries 11 and 12). However, no further improvement in the yield or reduction in reaction time was observed when the reaction was performed at 80 °C (Table 1, entry 13).

Table 1 Optimisation of reaction conditions[a,b]



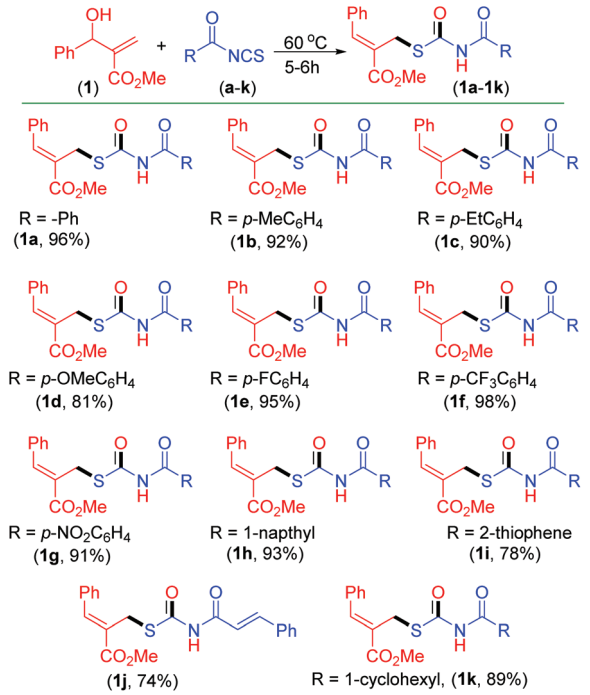
Entry	Solvent	Temp. (°C)	Time	Yield[b] (%)
1	Toluene	rt	24 h	56
2	1,4-Dioxane	rt	24 h	35
3	DCE	rt	24 h	59
4	DCM	rt	24 h	43
5	Chlorobenzene	rt	24 h	60
6	DMF	rt	24 h	39
7	DMSO	rt	24 h	12
8	CH_3CN	rt	24 h	9
9	H_2O	rt	24 h	64
10	—	rt	24 h	70
11	—	50	9 h	83
12	—	60	5 h	96
13	—	80	5 h	91

[a] Reaction conditions: (**1**) (0.2 mmol), (**a**) (0.2 mmol), solvent (2 mL), under air. [b] Isolated yield.

Encouraged by this catalyst and solvent free synthesis, various aroyl isothiocyanates (**a–k**) were reacted with MBH alcohol (**1**) to enhance the scope and generality of this rearrangement reaction (Scheme 2). As can be seen from Scheme 2, differently functionalised aroyl isothiocyanates bearing electron neutral –H (**a**), electron-donating (**b–d**) as well as electron-withdrawing groups reacted smoothly with (**1**) affording their desired products (**1a–1k**) in good to excellent yields. Benzoyl isothiocyanate (**a**) when reacted with (**1**) gave the product (**1a**) in 96% yield. The structure of the product (**1a**) has been unambiguously established by single crystal X-ray crystallography (Fig. 1).

Aroyl isothiocynates bearing electron-donating (EDG) substituents *viz*. *p*-Me (**b**), *p*-Et (**c**), and *p*-OMe (**d**) when reacted with (**1**) provided their corresponding products (**1b**, 92%), (**1c**, 90%) and (**1d**, 81%) in good yields. This protocol was also equally successful for aroyl isothiocyanates bearing moderately [*p*-F (**e**)] and strongly [*p*-CF_3 (**f**), and *p*-NO_2 (**g**)] electron-withdrawing groups (EWG) giving their respective products (**1e**, 95%), (**1f**, 98%), (**1g**, 91%) in excellent yields (Scheme 2). 2-Napthoyl isothiocyanate (**h**) reacted effectively with (**1**) giving its product (**1h**, 93%) in good yield. Heteroaromatic isothiocyanates such as thiophenoyl (**i**) also reacted competently with (**1**) affording its *S*-allyl benzoylcarbamothioate (**1i**) in 78% yield. In addition, aliphatic isothiocyanates such as cinnamoyl (**j**) and cyclohexoyl (**k**) furnished their rearranged products (**1j**, 74%) and (**1k**, 89%) in slightly lesser yields.

The substrate scope and generality of this protocol was further investigated by treating other Morita–Baylis–Hillman



Scheme 2 Substrate scope for the synthesis of *S*-allyl benzoylcarbamothioates. Reaction condition: (**1**) (0.5 mmol), (**a–k**) (0.5 mmol), under air at 60° C for 5–6 h. Isolated yield.

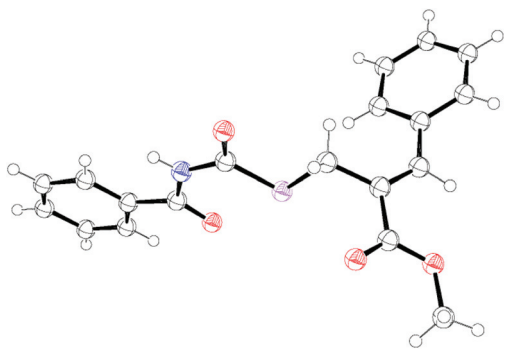
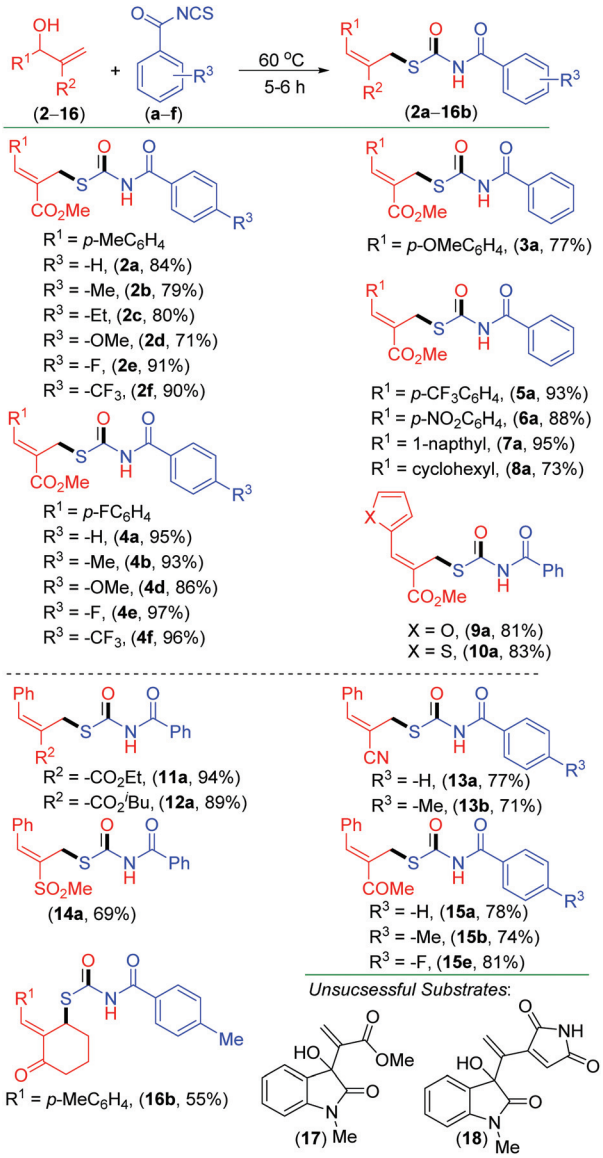


Fig. 1 ORTEP view of (**1a**) with 50% thermal ellipsoid probability.



Scheme 3 Scope of synthesis of *S*-allyl benzoylcarbamothioate with different MBH alcohols. Reaction conditions: (**2–16**) (0.50 mmol), **a–f** (0.50 mmol), under air at 60 °C for 5–6 h. Isolated pure product.

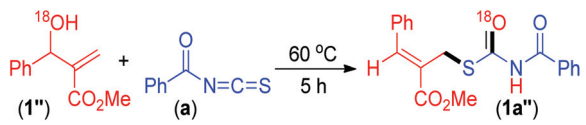
(MBH) alcohols (**2–16**) with various aroyl isothiocyanates (**a–f**) and the results are summarised in Scheme 3. The MBH alcohol (**2**) reacted with a variety of aroyl isothiocyanates (**a–f**) bearing electron-neutral (**a**), electron donating [*p*-Me (**b**), *p*-OMe (**c**), *p*-Et (**d**)] and electron withdrawing [*p*-F (**e**), *p*-CF_3 (**f**)] groups affording their anticipated *S*-allyl benzoylcarbamothioates (**2a**, 84%), (**2b**, 79%), (**2c**, 80%), (**2d**, 71%), (**2e**, 91%), (**2f**, 90%) in good to excellent yields (Scheme 3). A *p*-OMe substituted MBH alcohol (**3**) upon reaction with benzoyl isothiocyanate (**a**) gave the desired product (**3a**) in 77% yield. However, *p*-F (**4**) substituted MBH alcohol when reacted with different aroyl isothiocyanates (**a–f**) afforded their rearranged products (**4a**, 95%), (**4b**, 93%), (**4d**, 86%), (**4e**, 97%) and (**4f**, 96%) in excellent yields (Scheme 3). When the phenyl ring R^1 of MBH alcohol is substituted with strongly electron-withdrawing groups such as *p*-CF_3 (**5**) and *p*-NO_2 (**6**) their respective products (**5a**, 93%) and (**6a**, 88%) were obtained in good yields. A napthyl substituted MBH alcohol (**7**), when reacted with benzoyl isothiocyanate (**a**) afforded the product (**7a**) in 95% yield. Aliphatic MBH alcohol such as methyl 2-(cyclohexyl(hydroxy)methyl)acrylate (**8**) produced its rearranged product (**8a**) but in a relatively lower yield (73%). Moderate yields of products (**9a**, 81%) and (**10a**, 83%) were obtained when furan (**9**) and thiophene (**10**) containing MBH alcohols were reacted with benzoyl isothiocyanate (**a**) under the optimised reaction condition.

After successfully demonstrating the present strategy for R^2 as methyl ester (–CO_2Me), other esters such as –CO_2Et (**11**) and

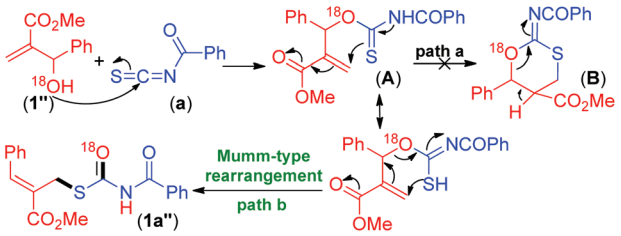
–$CO_2{}^i$Bu (**12**) were also screened and their corresponding products (**11a**, 94%), (**12a**, 89%) were obtained in good yields (Scheme 3). However, when R^2 as an ester was replaced by a –CN group (**13**) and reacted with aroyl isothiocyanates (**a**) and (**b**) their rearranged products (**13a**, 77%) and (**13b**, 71%) were obtained in moderate yields. The feasibility of the present strategy was further surveyed by replacing R^2 with –SO_2Me (**14**) and –COMe (**15**) and reacted with different aroyl isothiocyanates. To our delight their corresponding products (**14a**, 69%) and [(**15a**, 78%), (**15b**, 74%) and (**15e**, 81%)] were obtained in good to moderate yields. When cyclohex-2-en-1-one (**16**) derived MBH alcohol was reacted with 4-methylbenzoyl isothiocyanate (**b**) afforded its anticipated product (**16b**) in 55% yield. The reaction was not productive at all when isatin derived MBH alcohols (**17** and **18**) were reacted with benzoyl isothiocyanate (**a**) (Scheme 3). This might be due to the steric hindrance of MBH alcohols that prevents nucleophilic addition at the sp^2 carbon of the –N=C=S bond. Unlike aroyl isothiocyanates, both starting materials remain unconsumed even after 24 h. The configuration of the double bond of the *S*-allyl benzoylcarbamothioate was confirmed by 1D NOE experiment. It was appealing to note that the *Z*-isomer is obtained exclusively (see the ESI†). To demonstrate the scalability of the present methodology a reaction was carried out with methyl 2-(hydroxy(phenyl)methyl)acrylate (**1**) (5 mmol, 963 mg) and benzoyl isothiocynate (**a**) (5 mmol, 815 mg) under the standard optimised reaction condition giving 87% yield of the product (**1a**).

Further, systematic investigations were carried out to depict a plausible mechanism for this transformation. A reaction was carried out with a preformed ^{18}O-labeled MBH alcohol[10] and benzoyl isothiocyanate (**a**) under the optimised condition. A ^{18}O-labeled *S*-allyl benzoylcarbamothioate (**1a″**) was obtained as confirmed by HRMS analysis (see the ESI†). Further, ^{13}CNMR analysis of **1a″** shows two signals (δ 169.622 and 169.658 ppm) due to both labeled and unlabeled carbonyl groups of carbamothioate. This observation suggests that the carbonyl oxygen is originating from the –OH of MBH alcohol (Scheme 4).

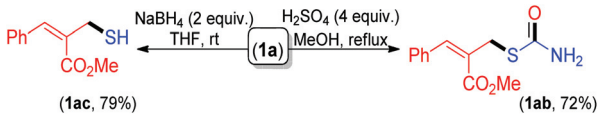
There are two possible paths that can account for this migration. The first possible route is the generation of a benzoylcarbonimidothioate intermediate (**A**) after nucleophilic addition of MBH alcohol (**1**) with benzoyl isothiocyanate (**a**) which undergo thia-Michael addition to form a cyclic intermediate 1,3-oxathiane (**B**). The intermediate (**B**) opens up to give an *S*-allyl benzoylcarbamothioate (**1a**) (Scheme 5, path a). However, a careful examination of ^{1}H NMR of the reaction mixture obtained by reacting (**1**) and (**a**) at different time intervals rules out the possible formation of any cyclic intermediate (**B**) (see ESI†). The other possibility is that the intermediate (**A**) undergoes a thia-Michael addition with concurrent Mumm-type of rearrangement (Scheme 5, path b). The Mumm rearrangement is a significant part of the Ugi reaction that involves the 1,3-acyl migration of an acyl imidate to an imide.[11] The above labeling experiment supports the occurrence of the Mumm-type rearrangement (Scheme 4).[10]



Scheme 4 ^{18}O labeling experiment.



Scheme 5 Plausible reaction mechanism.



Scheme 6 Synthetic transformations of **1a**.

To demonstrate the applicability of our protocol, the *S*-allyl benzoylcarbamothioate (**1a**) was subjected to a few useful organic transformations (Scheme 6). An acid hydrolysis of (**1a**) was carried out which was furnished (**1ab**) by cleavage of the imide bond. When (**1a**) was treated with $NaBH_4$, selective cleavage of the C–S bond takes place giving (**1ac**) in moderate yield. Other transformations are still under process.

In summary, we have developed an elegant approach for the synthesis of *S*-allyl benzoylcarbamothioate *via* a Mumm-type rearrangement. This methodology allows the useful synthesis of many valuable *S*-allyl benzoylcarbamothioate under mild condition and avoids the use of costly and harmful materials or cumbersome multi-stepped processes. The ^{18}O labeling experiments support the proposed mechanistic pathway. In this protocol, C–O and C–S bonds are assembled simultaneously and have the merits of wide range of substrate scope, neat condition and simple purification.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 (*a*) A. Padwa, *Chem. Soc. Rev.*, 2009, **38**, 3072; (*b*) R. Ardkhean, D. F. J. Caputo, S. M. Morrow, H. Shi, Y. Xiong and E. A. Anderson, *Chem. Soc. Rev.*, 2016, **45**, 1557; (*c*) S. Blouin, G. Blond, M. Donnard, M. Gulea and J. Suffert, *Synthesis*, 2017, **49**, 1767; (*d*) H. Pellissier, *Chem. Rev.*, 2013, **113**, 442; (*e*) M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.*, 2011, **111**, 1072.

2 (*a*) A. K. Mukerjee and R. Ashare, *Chem. Rev.*, 1991, **91**, 1; (*b*) T. Castanheiro, J. Suffert, M. Donnard and M. Gulea, *Chem. Soc. Rev.*, 2016, **45**, 494; (*c*) V. Ficeri, P. Kutschy, M. Dzurilla and J. Imrich, *Collect. Czech. Chem. Commun.*, 1994, **59**, 2650; (*d*) K. G. Bedane and G. S. Singh, *ARKIVOC*, 2015, **5**, 206 and references cited therein; (*e*) R. K. Saunthwal, M. Patel, R. K. Tiwari, K. Parang and A. K. Verma, *Green Chem.*, 2015, **17**, 1434; (*f*) R. K. Saunthwal, M. Patel, S. Kumar and A. K. Verma, *Tetrahedron Lett.*, 2015, **56**, 677; (*g*) R. K. Saunthwal, M. Patel, A. K. Danodia and A. K. Verma, *Org. Biomol. Chem.*, 2015, **13**, 1521.

3 (*a*) C. C. Palsuledesai, S. Murru, S. K. Sahoo and B. K. Patel, *Org. Lett.*, 2009, **11**, 3382; (*b*) A. Modi, W. Ali and B. K. Patel, *Org. Lett.*, 2017, **19**, 432; (*c*) A. Dahiya, W. Ali and B. K. Patel, *ACS Sustainable Chem. Eng.*, 2018, **6**, 4272.

4 (*a*) D. Basavaiah, A. J. Rao and T. Satyanarayana, *Chem. Rev.*, 2003, **103**, 811; (*b*) D. Basavaiah, B. S. Reddy and S. S. Badsara, *Chem. Rev.*, 2010, **110**, 5447; (*c*) W. Yang, D. Tan, R. Lee, L. Li, Y. Pan, K.-W. Huang, C.-H. Tan and Z. Jiang, *Chem. – Asian J.*, 2012, **7**, 771; (*d*) L. D. S. Yadav, R. Patel and V. P. Srivastava, *Tetrahedron Lett.*, 2009, **50**, 1335; (*e*) M. Ciclosi, C. Fava, R. Galeazzi, M. Orenaa and J. Sepulveda-Arquesb, *Tetrahedron Lett.*, 2002, **43**, 2199; (*f*) S. Bhowmik, A. Mishra and S. Batra, *RSC Adv.*, 2011, **1**, 1237; (*g*) J. Qi, J. Zheng and S. Cui, *Org. Lett.*, 2018, **20**, 1355; (*h*) Y. Wei and M. Shi, *Chem. Rev.*, 2013, **113**, 6659.

5 (*a*) P. Zhu, X. He, X. Chen, Y. You, Y. Yuan and Z. Weng, *Tetrahedron*, 2014, **70**, 672; (*b*) P. Singh, R. Bai, R. Choudhary, M. C. Sharma and S. S. Badsara, *RSC Adv.*, 2017, **7**, 30594; (*c*) L. Zhang, J. Zhu, J. Ma, L. Wu and W.-H. Zhang, *Org. Lett.*, 2017, **19**, 6308; (*d*) Q.-L. Xu, W.-B. Liu, L.-X. Dai and S.-L. You, *J. Org. Chem.*, 2010, **75**, 4615; (*e*) P. S. Reddy, M. A. Reddy, B. Sreedhar and M. V. B. Rao, *Synth. Commun.*, 2010, **40**, 2075.

6 (*a*) Y. Takeuchi, T. Shiragami, K. Kimura, E. Suzuki and N. Shibata, *Org. Lett.*, 1999, **1**, 1571; (*b*) S. M. Capitosti, T. P. Hansen and M. L. Brown, *Org. Lett.*, 2003, **5**, 2865; (*c*) *The Merck Index, version 12:3*, Merck&Co Inc., Whitehouse Station, NJ, USA, 1999; (*d*) E.-S. Kim, K. Y. Park, J.-M. Heo, B. J. Kim, K. D. Ahn and J.-G. Lee, *Ind. Eng. Chem. Res.*, 2010, **49**, 11250; (*e*) H. B. Maruyama, Y. Suhara, J. Suzuki-Watanabe, Y. Maeshima, N. Shimizu, M. Ogura-Hamada, H. Fujimoto and K. J. Takano, *Antibiot.*, 1975, **28**, 636; (*f*) Y. Suhara, H. B. Maruyama, Y. Kotoh, Y. Miyasaka, K. Yokose, H. Shirai, K. Takano, P. Quitt and P. J. Lanz, *Antibiot.*, 1975, **28**, 648; (*g*) K. Krohn, C. Franke, P. G. Jones, H.-J. Aust, D. Draeger and B. Schulz, *Liebigs Ann. Chem.*, 1992, 789; (*h*) I. L. Pinto, H. F. Boyd and D. M. B. Hickey, *Bioorg. Med. Chem. Lett.*, 2000, **10**, 2015.

7 (*a*) I. T. Raheem, S. N. Goodman and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2004, **126**, 706; (*b*) C. D. Vanderwal and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2004, **126**, 14724; (*c*) M. Gandelman and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2005, **44**, 2393; (*d*) E. P. Balskus and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2006, **128**, 6810; (*e*) S. Thompson, S. A. McMahon, J. H. Naismith and D. O'Hagen, *Bioorg. Chem.*, 2016, **64**, 37; (*f*) C. Feng, D. Feng and T.-P. Loh, *Chem. Commun.*, 2015, **51**, 342; (*g*) A. C. Wright, C. K. Haley, G. Lapointe and B. M. Stoltz, *Org. Lett.*, 2016, **18**, 2793.

8 (*a*) J. Chan, K. d. Baucom and J. A. Murry, *J. Am. Chem. Soc.*, 2007, **129**, 14106; (*b*) L. Wang, H. Fu, Y. Jiang and Y. Zhao, *Chem. – Eur. J.*, 2008, **14**, 10722; (*c*) J. Wang, C. Liu, J. Yuan and A. Lei, *Chem. Commun.*, 2014, **50**, 4736; (*d*) F. Wang, H. Liu, H. Fu, Y. Jiang and Y. F. Zhao, *Adv. Synth. Catal.*, 2009, **351**, 246; (*e*) H. Yu and Y. Zhang, *Eur. J. Org. Chem.*, 2015, 1824; (*f*) L. Wang, H. Fu, Y. Jiang and Y. Zhao, *Chem. – Eur. J.*, 2008, **14**, 10722; (*g*) H. Yu, Y. Chen and Y. Zhang, *Chin. J. Chem.*, 2015, **33**, 531; (*h*) K. C. Nicolaou and C. J. N. Mathison, *Angew. Chem., Int. Ed.*, 2005, **44**, 5992; (*i*) L. Xu, S. Zhang and M. L. Trudell, *Chem. Commun.*, 2004, 1668 and references therein; (*j*) D. A. Evans, P. Nagorny and R. Xu, *Org. Lett.*, 2006, **8**, 5669; (*k*) Y. Zhang, L. Pan, Y. Zou, X. Xu and Q. Liu, *Chem. Commun.*, 2014, **50**, 14334; (*l*) X. Yan, K. Fang, H. Liua and C. Xi, *Chem. Commun.*, 2013, **49**, 10650.

9 (*a*) H. Li, K. Dong, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2015, **54**, 10239; (*b*) Y. Lv, Y. Li, T. Xiong, Y. Lu, Q. Liu and Q. Zhang, *Chem. Commun.*, 2014, **50**, 2367; (*c*) Y. Li, F. Zhu, Z. Wang, J. Rabeah, A. Brückner and X.-F. Wu, *ChemCatChem*, 2017, **9**, 915; (*d*) A. O. Gálvez, C. P. Schaack, H. Noda and J. W. Bode, *J. Am. Chem. Soc.*, 2017, **139**, 1826.

10 (*a*) B. Zhu, L. Yan, Y. Pan, R. Lee, H. Liu, Z. Han, K.-W. Huang, C.-H. Tan and Z. Jiang, *J. Org. Chem.*, 2011, **76**, 6894.

11 (*a*) V. Mercalli, A. Nyadanu, M. Cordier, G. C. Tron, L. Grimaud and L. E. Kaim, *Chem. Commun.*, 2017, **53**, 2118; (*b*) J. Chen, Y. Shao, L. Ma, M. Ma and X. Wan, *Org. Biomol. Chem.*, 2016, **14**, 10723; (*c*) H.-W. Liang, Z. Yang, K. Jiang, Y. Ye and Y. Wei, *Angew. Chem., Int. Ed.*, 2018, **57**, 5720; (*d*) A. L. Chandgude and A. Dömling, *Org. Lett.*, 2017, **19**, 1228; (*e*) H. Harayama, T. Nagahama, T. Kozera, M. Kimura, K. Fugami, S. Tanaka and Y. Tamaru, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 445; (*f*) M. Sakamoto, M. Yoshiaki, M. Takahashi, T. Fujitaa and S. Watanabe, *J. Chem. Soc., Perkin Trans. 1*, 1995, 373.