This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

Organocatalysis [review article]

PLEASE CITE THE PUBLISHED VERSION

<http://dx.doi.org/10.1039/c1oc90020j>

PUBLISHER

© The Royal Society of Chemistry

VERSION

AM (Accepted Manuscript)

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Buckley, Benjamin R., and Mohamud M. Farah. 2019. "Organocatalysis [review Article]". figshare.
<https://hdl.handle.net/2134/13926>.

This item was submitted to Loughborough's Institutional Repository (<https://dspace.lboro.ac.uk/>) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
<http://creativecommons.org/licenses/by-nc-nd/2.5/>

1 Organocatalysis

Benjamin R. Buckley*^a and Mohamud M. Farah^b

^a *Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, U.K.*

^b *Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.*

Abstract

Reactions carried out with substoichiometric quantities of organic molecules as catalysts have received much attention over the past decade. This review highlights progress in 2010 towards highly enantioselective organocatalytic systems and the natural product/biologically active compounds that can be prepared using these types of processes.

1.0 Introduction

Over 4000 publications in the area of organocatalysis have now been reported, with just over 1000 articles being published in 2010 (compared to just over 800 in 2009), a remarkable achievement considering it is only 10 years since the word “organocatalyst” first appeared (although organic molecule catalysed reactions were prevalent in the literature before the year 2000).^{1,2} Several excellent reviews have again been reported in this highly topical area.³ The present review covers achievements from 2010, but regrettably, with the considerable number of publications in this area, it is not possible to report every contribution to this field. This review is divided into sections according to the mode of action, followed by a summary of some of the elegant natural product architectures prepared by organocatalysis in 2010 (section 7.0).

2.0 Iminium/Enamine Catalysis

This is perhaps the area of most activity over the past few years owing to the ability of amine catalysts, such as proline, to condense with α,β -unsaturated aldehydes or ketones, so forming iminium ion or enamine intermediates which can be captured by incoming nucleophiles or electrophiles with excellent levels of enantiomeric excess. Although the first use of these generic modes of action was reported in 2000 there continues to be a large number of reports in this area. Below are a selected set of examples. In the majority of cases this mode is catalysed by proline or proline derivatives, however, some recent reports have now applied other catalysts in this area.

Arseniyadis and Cossy have applied enamine organocatalysis in their elegant total

syntheses of (–)-bitungolide F.⁴ Compound **1** is prepared using an enantioselective organocatalysed Michael addition using the proline derived catalyst **2**, originally reported by Chi and Gellman. A further eight steps afforded the natural product (–)-bitungolide F (Scheme 1).

Scheme 1 Arseniyadis and Cossy's enamine organocatalysis step in the total synthesis of (–)-bitungolide F.

Tius and co-workers have reported the first organocatalytic aza-Nazrov cyclization of an azirine using the diamine mono-triflate catalyst **3** (Scheme 2). In fact the process proceeds through asymmetric synthesis to afford **4** with overall kinetic resolution of the azirine **5**.⁵

Scheme 2 The first organocatalytic aza-Nazrov cyclization.

Hong and co-workers have applied cascade enamine/iminium ion catalysis in the synthesis of A, B, C-ring systems using catalyst **6**, for example, in the synthesis of both (+)-conicol and didehydroconicol (Scheme 3).⁶

Scheme 3 Cascade enamine/iminium ion catalysis in the synthesis of both (+)-conicol and didehydroconicol.

Organocatalytic autocatalysis has been reported by Wang and co-workers (Schemes 4 and 5). Application of the autocatalyst mimics **7** and **8** in the aldehyde Mannich reaction affords the corresponding products with respectable to excellent diastereo- and enantiocontrol.⁷

Scheme 4 Reaction of Wang's alkynyl based organocatalytic pseudo autocatalyst **7**.

Scheme 5 Wang's organocatalytic autocatalysis process.

Greck and co-workers have applied the findings of their own recent report dealing with organocatalytic α -amination of protected β -hydroxy aldehydes to the asymmetric synthesis of sphinganine and clavaminol H (Scheme 6).⁸ The esters **9** and **10** were reduced using diisobutylaluminium hydride to produce the corresponding O-protected β -hydroxy aldehydes, which were used directly in the organocatalytic transformation. The reaction was conducted in the presence of L-proline (20 mol%) and dibenzyl azodicarboxylate (1.5 equiv) as a source of electrophilic nitrogen in CH_3CN at room temperature. After completion of the reaction, NaBH_4 and EtOH were added to reduce

the aldehyde functionality. Monoprotected α -hydrazino 1,3-diols **11** and **12** were isolated in good yields of 75% and 76%, respectively, for the three steps.

Scheme 6 Greck's α -amination of protected β -hydroxy aldehydes to afford sphinganine and clavaminol H.

Choi and Kim have reported the asymmetric organocatalytic reaction of *o*-hydroxycinnamaldehydes with organoboronic acids in order to enantioselectively access chromanes and dihydrobenzopyranes (Scheme 7).⁹ The reactions were found to proceed with the highest ee when employing the tryptophan derived catalyst **13**, affording far superior ees to that of reactions carried out with the MacMillan type catalysts.

Scheme 7 Choi's and Kim's asymmetric organocatalytic reaction of *o*-hydroxycinnamaldehydes with organoboronic acids.

Jørgensen and co-workers have reported the first formal asymmetric *trans*-dihydroxylation (Scheme 8) and *trans*-aminohydroxylation (Scheme 9) of α,β -unsaturated aldehydes in an organocatalytic multibond-forming one-pot reaction cascade.¹⁰ This process, using catalyst **14**, converts α,β -unsaturated aldehydes into optically active *trans*-2,3-dihydroxyaldehydes and *trans*-3-amino-2-hydroxyaldehydes with the aldehyde moiety protected as an acetal. This one-pot protocol proceeds through the formation of 2,3-epoxy and 2,3-aziridine aldehyde intermediates, which subsequently rearrange to form acetal protected *trans*-2,3-dihydroxyaldehydes and *trans*-3-amino-2-hydroxyaldehydes. The authors also report a new enantioselective aziridination protocol using *N*-(tosyloxy)-4-toluenesulfonamide as the nitrogen source. The products obtained were applied in the synthesis of numerous important molecules for example compound **15**.

Scheme 8 Jørgensen's first formal asymmetric *trans*-dihydroxylation reaction.

Scheme 9 Jørgensen's *trans*-aminohydroxylation of α,β -unsaturated aldehydes.

Rios and co-workers have reported the synthesis of spiro compounds using a cascade Michael-Michael-aldol reaction (Scheme 10).¹¹ A range of heterocycles showed good to excellent levels of diastereo- and enantioselectivity when using the proline derived catalyst **16**.

Scheme 10 Rios and co-workers synthesis of spiro compounds.

Jørgensen and co-workers have also coupled anodic oxidation and organocatalysis (Scheme 11).¹² The direct α -arylation of aldehydes using electron-rich aromatic compounds affording *meta*-alkylated anilines is reported – a transformation not possible from a standard Friedel Crafts reaction. Good yields and excellent ees were observed over a range of substrate types.

Scheme 11 Jørgensen's coupled anodic oxidation and organocatalysis.

3.0 SOMO Catalysis

As reported in volume 104, MacMillan expanded the scope of aminocatalysis (iminium or enamine catalysis) by introducing a new mode of action.¹³ The intermediate enamine formed from the condensation of an aldehyde and a secondary amine can be intercepted by an oxidizing reagent to generate a singularly occupied molecular orbital (SOMO) at nitrogen. Subsequent reaction with, for example, allylsilane affords α -allylated aldehydes with good yields and excellent levels of enantioselectivity.

MacMillan and co-workers have reported the enantioselective α -benzylation of aldehydes using photoredox organocatalysis (Scheme 12).¹⁴ A short catalyst screen showed that **17** was the most effective affording products with up to 93% ee over a wide range of substrates. The authors proposed mechanism is highlighted in Scheme 13. Application of this work resulted in the synthesis of the angiogenesis inhibitor **18** (Figure 1).

Scheme 12 MacMillan's asymmetric aldehyde α -benzylation.

Scheme 13 MacMillan's proposed catalytic cycle for asymmetric aldehyde α -benzylation.

Figure 1 angiogenesis inhibitor **18**.

MacMillan and co-workers have also successfully merged the chemistry of iodonium salts with organocatalysis, leading to an effective solution to α -trifluoromethylation of aldehydes without the use of photolysis (Scheme 14).¹⁵ Treatment of a range of aldehydes with the trifluoromethyl iodonium salt **19** and the catalyst **20** affords enantiomerically enriched α -trifluoromethyl aldehydes. The group have also generated a successful polyene cyclization reaction using the amine **21** under SOMO catalysis (Scheme 15).¹⁶ They have also reported organo-SOMO cascade cycloadditions, with catalyst **22** and a variety of heterocycles (thiophene is shown in Scheme 16 but anisole, derivatives of indole and benzoxazole are also tolerated under the reaction conditions to afford products with high enantioselectivities).¹⁷ The group have introduced a method for direct and enantioselective α -allylation of ketones using SOMO catalysis (Schemes 17 and 18).¹⁸ In conjunction with MacMillan, Houk and co-workers have investigated the nature of the

intermediates involved in organo-SOMO catalysis of α -arylation of aldehydes.¹⁹ This was due to the fact that both the MacMillan group²⁰ and Nicolaou group²¹ have reported the intramolecular α -arylation of aldehydes, where cyclization of an enamine radical was shown to react *ortho* to the methoxy group (as in Scheme 19), but 1,3,4-substituted aldehydes were shown to have a different reaction profile, preferring to cyclize to afford *para* arylated products. The selectivity of the α -arylation reactions was attributed to the activation energies and relative stabilities of the isomeric transition states. In the case of the monomethoxyaryl system (Scheme 19), both *ortho* and *para* arylation barriers are possible under the reaction conditions. For the more highly substituted aldehydes, the energy of the *ortho*, *meta* transition states is increased with respect to the *para*, *meta* isomers. Thus, *ortho*, *meta* cyclization does not occur under the reaction conditions, resulting in the experimentally observed *para*, *meta* selectivity. Flowers and MacMillan have also investigated the mechanistic complexity of organo-SOMO catalysed reactions.²² In order to examine the process a series of studies were carried out using the reaction outlined in Scheme 20.²³ They found that the concentration of H₂O in the reaction is critical for the reaction to proceed, too little prevents solubilizing CAN and too much reverses the formation of the enamine intermediate required to initiate the reaction.

Scheme 14 MacMillan's α -trifluoromethylation of aldehydes without the use of photolysis.

Scheme 15 MacMillan's polyene cyclisation reaction.

Scheme 16 MacMillan's organo-SOMO cascade cycloaddition reaction.

Scheme 17 MacMillan's α -enolization reaction

Scheme 18 MacMillan's α -homobenzylation reaction

Scheme 19 Houk's theoretical investigation of the nature of the intermediates involved in organo-SOMO catalysis for the synthesis of α -arylated aldehydes.

Scheme 20 Flower's and MacMillan's investigation of the mechanistic complexity of organo-SOMO catalysed reactions.

4.0 Hydrogen Bonding Catalysis

Over the last few years, interest and applications of in hydrogen bonding catalysis have increased significantly; below are several interesting reports from 2010. Maruoka and co-workers have reported the use of a diamine-based organocatalyst **25** that is extremely useful for the highly enantioselective conjugate addition of heterosubstituted aldehydes to vinyl sulfones (Scheme 21).²⁴ The authors propose a transition state model (Figure 2) in which the generation of the *Z*-enamine derived from *N*-Boc *R*-aminophenylacetaldehyde and the catalyst **25** would be stabilized by hydrogen bonding between the ammonium hydrogen and the *N*-Boc group. The benzoic acid derivative is believed to shield the lower face of the *Z*-enamine, hence, 1,1-bis(benzenesulfonyl) ethylene will then approach from the upper face through additional hydrogen bonding of the sulfonyl group with the

triflamide hydrogen, leading to the desired product in high ee and S configuration.

Scheme 21 Maruoka's diamine-based H-bonding organocatalyst for conjugate additions.

Figure 2 Maruoka's proposed transition state model

Cao *et al.* have reported a range of pyrrolidine-ureas as bifunctional organocatalysts for asymmetric Michael additions of ketones to nitroalkenes (Scheme 22).²⁵ High ees are obtained for a variety of substrates, and they report an unexpected hydrogen bonding effect. Catalyst **26** with a single hydrogen bond was superior to related catalysts (see figure 3), that contained two hydrogen bonds in the asymmetric Michael addition of ketone with nitroolefins. The authors performed a theoretical study on the origin of this difference and found that the rigid structure formed between catalysts with two hydrogen bond donors and a nitroolefin through double hydrogen bonding retarded the approach of nucleophilic enamine intermediate.

Scheme 22 Cao *et al.*'s pyrrolidine-ureas as bifunctional organocatalysts

Figure 3 Cao *et. al.*'s proposed transition state model.

Barbas and co-workers have reported an impressive synthesis of iminosugar derivatives using the urea based catalyst **27**. This process selectively produces five new chiral centres in one operation (Scheme 23).²⁶ The diastereoselectivities and enantioselectivities between **28** and **29** are extremely high, and this is believed to stem from the highly organised six-membered transition state proposed by the authors in Figure 4. The process proceeds through an *anti*-Michael-*anti*-aza-Henry cascade.

Scheme 23 Barbas' synthesis of iminosugar derivatives.

Figure 4 Barbas' proposed transition state model.

Liang and Ye have reported the asymmetric vinylogous Michael reaction of α,β -unsaturated ketones with γ -butenolide utilizing the sulfonamide based multifunctional catalyst **30** (Scheme 24).²⁷ Excellent ees were obtained over a wide variety of substrate types (27 examples reported with ees all >95%). The process enables direct access towards synthetically versatile γ -substituted butenolides from simple 2(5*H*)-furanone with satisfactory yields (51-86%), and diastereo- and enantioselectivities (2 : 1 - 30 : 1 dr

and 95–99% ee).

Scheme 24 Liang's and Ye's asymmetric vinylogous Michael reaction of α,β -unsaturated ketones with γ -butenolide.

Jørgensen and co-workers have investigated the use of acyl phosphinates in hydrogen-bonding mediated catalysis (Scheme 25).²⁸ Good to excellent ees were observed for a variety of transformations using the phosphinate as a handle for H-bonding.

Scheme 25 Jørgensen's investigation of acyl phosphinates in hydrogen-bonding mediated catalysis.

5.0 Counterion Catalysis

The concept of counterion catalysis was first reported 2007, and this area continues to provide some interesting applications. For example, Borhan and co-workers have discovered a novel organocatalytic asymmetric chlorolactonization that affords chiral chlorolactones by action of (DHQD)₂PHAL and DCDPH (Scheme 26). This methodology represents the first example of a catalytic, enantioselective halolactonization that proceeds with synthetically useful enantioselectivities (80-90%).²⁹

Scheme 26 Borhan's novel organocatalytic asymmetric chlorolactonization.

Antilla and co-workers have used the chiral phosphoric acid catalyst **31** for the highly enantioselective addition of dihydropyrans to N-acyl imines (Scheme 27).³⁰ This approach has also been applied to the synthesis of spirocyclic oxazoletetrahydropyrans such as **32**.

Scheme 27 Antilla's highly enantioselective addition of dihydropyrans to N-acyl imines.

Zhong and co-workers have reported a enantioselective route to oxazolines such as **33**. Excellent enantioselectivities and yields were obtained at -40 °C for 24 h when using catalyst **34** (Scheme 28).³¹

Scheme 28 Zhong's enantioselective route to oxazolines.

Wakchaure and List have introduced the bifunctional Brønsted acid/base catalyst **35** for use in the desymmetrization of *meso*-anhydrides (Scheme 29).³² Excellent yields and ees

were observed over a wide range of substrate types. Application of this methodology resulted in the formal asymmetric synthesis of (+)-grandisol (Figure 5).

Scheme 29 Wakchaure's and List's bifunctional Brønsted acid/base catalysis for asymmetric desymmetrization

Figure 5 (+)-Grandisol

6.0 Miscellaneous

A range of novel types of organocatalysis that cannot be placed under a traditional mode of action or are a combination of activation types are described below.

Kwong and Lee have reported an organocatalytic cross-coupling reaction in which direct C–H arylation occurs with aryl halide coupling partners, catalysed by DMEDA (Scheme 30).³³ The reaction is believed to proceed through a radical anion, and several control reactions, for example addition of radical trapping agents such as TEMPO inhibited the reaction.

Scheme 30 Kwong's and Lee's organocatalytic C–H arylation reaction.

Melchiorre and co-workers have reported cooperative organocatalysis for the asymmetric γ -alkylation of α -branched enals.³⁴ Utilization of the amine **36** and the phosphoric acid **37** resulted in high levels of yield and enantioselectivity over a wide range of substrates (Scheme 31). The authors have proposed a mechanism for this dual catalytic system that relies on noncovalent interaction from the phosphoric acid partner (Figure 6).

Scheme 31 Melchiorre's cooperative organocatalysis.

Figure 6 Melchiorre's proposed mechanism for cooperative organocatalysis.

7.0 Natural Products/Biologically Active Compounds Synthesized by Organocatalytic Reactions

Given the developments outlined in this review, it is again perhaps not surprising that there is now the capacity for organocatalysts to be applied to the total synthesis of a wide variety of natural products (Figure 7). MacMillan has reported the three step synthesis of (+)-frondosin B, which is a micromolar inhibitor of interleukin-8 (IL-8) and protein kinase C (PKC) using a highly enantioselective organocatalytic alkylation of a benzoxazole trifluoroborate salt.³⁵ List has reported the formal asymmetric synthesis of (+)-grandisol through desymmetrization of a meso-anhydride.³² Arseniyadis and Cossy have applied enamine organocatalysis in their elegant total syntheses of (–)-bitungolide

F.⁴ Hong and co-workers have applied cascade enamine/iminium ion catalysis in the synthesis of (+)-conicol and didehydroconicol.⁶ MacMillan has also reported the asymmetric synthesis of the angiogenesis inhibitor **18**.

Figure 7 Several natural products produced using organocatalysis

8.0 Conclusion

The development of organocatalysed reactions has again been heavily reported in the literature for 2010. The level of enantiomeric excess and product yields obtained are now in many cases at excellent levels, with ees of over 95% commonplace. As can be seen from the examples presented in this review, enamine/iminium ion catalysis remains one of the most extensively studied areas within organocatalysis. However, with the use of hydrogen bonding catalysts, such as thioureas, and Brønsted acid/base catalysts, and now counterion catalysis, a wide range of new organocatalytic reactions has been discovered and these modes of organocatalysis are now firmly established protocols. The new addition of combining catalytic processes both metal (see for example MacMillan's SOMO catalysis for example) and non-metal (see for example Melchiorre's cooperative organocatalysis) mediated has emerged over the past two or so years, and this intriguing marriage looks set to move forward the organocatalysis arena with significant vigour over the coming year.

9.0 References

-
- 1 Based on a ISI Web of Knowledge search on the word organocatalysis and its derivatives.
 - 2 K. A. Ahrendt, C. J. Borths and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2000, **122**, 4243.
 - 3 See for example: Topics in Current Chemistry: Asymmetric Organocatalysis, Ed. B. List 2009; Enantioselective Organocatalytic Diels–Alder Reactions P. Merino, E. Marqués-López, T. Tejero, R. P. Herrera *Synthesis* 2010, 1; Cinchona Alkaloids in Asymmetric Organocatalysis T. Marcelli, H. Hiemstra *Synthesis* 2010, 1229; Enantioselective Phosphine Organocatalysis A. Marinetti, A. Voituriez, *Synlett* 2010 174; Chiral Phosphoric Acids as Versatile Catalysts for Enantioselective Transformations M. Terada, *Synthesis* 2010, 1929; Organocatalytic Asymmetric Synthesis of Organophosphorus Compounds Ł. Albrecht, A. Albrecht, H. Krawczyk, and K. A. Jørgensen *Chem. Eur. J.* 2010, **16**, 28; Asymmetric Organocatalytic Rearrangement Reactions A. Moyano, N. El-Hamdouni and A. Atlamsani *Chem. Eur. J.* 2010, **16**, 5260; Asymmetric Organocatalysis with Sulfones M. Nielsen, C. B. Jacobsen, N. Holub, M. W. Paixão and K. A. Jørgensen *Angew. Chem. Int. Ed.* 2010, **49**, 2668; When Organocatalysis Meets Transition-Metal Catalysis C. Zhong and X. Shi, *Eur. J. Org. Chem.* 2010, 2999; Organocatalytic cascade reactions as a new tool in total synthesis C. Grondal, M. Jeanty and D. Enders *Nat. Chem.* 2010, **2**, 167.
 - 4 A. ElMarrouni, S. R. Joolakanti, A. Colon, M. Heras, S. Arseniyadis, J. Cossy *Org. Lett.* 2010, **12**, 4074.
 - 5 N. Shimada, B. O. Ashburn, A. K. Basak, W. F. Bow, D. A. Vicica, M. A. Tius, *Chem. Commun.* 2010, **46**, 3774.
 - 6 B.-C. Hong, P. Kotame, C.-W. Tsai, J.-H. Liao *Org. Lett.*, 2010, **12**, 776.
 - 7 X. Wang, Y. Zhang, H. Tan, Y. Wang, P. Han, D. Z. Wang, *J. Org. Chem.* 2010, **75**, 2403.
 - 8 R. Ait-Youcef, X. Moreau, C. Greck *J. Org. Chem.* 2010, **75**, 5312.
 - 9 K.-S. Choi, S.-G. Kim *Tetrahedron Lett.* 2010, **51**, 5203.
 - 10 Ł. Albrecht, H. Jiang, G. Dickmeiss, B. Gschwend, S. G. Hansen and K. A. Jørgensen, *J. Am. Chem. Soc.* 2010, **132**, 9188.
 - 11 X. Companyó, A. Zea, A.-N. R. Alba, A. Mazzanti, A. Moyano and R. Rios, *Chem. Commun.* 2010, **46**, 6953.
 - 12 K. L. Jensen, P. T. Franke, L. T. Nielsen, K. Daasbjerg and K. A. Jørgensen, *Angew. Chem. Int. Ed.* 2010, **49**, 129.
 - 13 S. Mukherjee and B. List, *Nature* 2007, **447**, 152.
 - 14 H.-W. Shih, M. N. Vander Wal, R. L. Grange and D. W. C. MacMillan, *J. Am. Chem. Soc.* 2010, **132**, 13600.
 - 15 A. E. Allen and D. W. C. MacMillan, *J. Am. Chem. Soc.* 2010, **132**, 4986.
 - 16 S. Rendler and D. W. C. MacMillan, *J. Am. Chem. Soc.* 2010, **132**, 5027.
 - 17 N. T. Jui, E. C. Y. Lee and D. W. C. MacMillan, *J. Am. Chem. Soc.* 2010, **132**, 10015.
 - 18 A. Mastracchio, A. A. Warkentin, A. M. Walji and D. W. C. MacMillan, *PNAS*, 2010,

107, 20648.

- 19 J. M. Um, O. Gutierrez, F. Schoenebeck, K. N. Houk and D. W. C. MacMillan, *J. Am. Chem. Soc.* 2010, **132**, 6001.
- 20 J. C. Conrad, J. Kong, B. N. Laforteza, and D. W. C. MacMillan *J. Am. Chem. Soc.*, 2009, **131**, 11640.
- 21 K. C. Nicolaou, R. Reingruber, D. Sarlah, and S Bräse *J. Am. Chem. Soc.* 2009, **131**, 2086.
- 22 J. J. Devery III, J. C. Conrad, D. W. C. MacMillan, and R. A. Flowers, *Angew. Chem. Int. Ed.* 2010, **49**, 6106.
- 23 T. S. Beeson, A. Mastracchio, J.-B. Hong, K. Ashton and D. W. C. MacMillan, *Science* 2007, **316**, 582.
- 24 S. A. Moteki, S. Xu, S. Arimitsu, K. Maruoka, *J. Am. Chem. Soc.* 2010, **132**, 17074.
- 25 X.-Y. Cao, J.-C. Zhen, Y.-X. Li, Z.-C. Shu, X.-L. Sun, B.-Q. Wang, Y. Tang *Tetrahedron* 2010, **66**, 9703.
- 26 R. Imashiro, H. Uehara, C. F. Barbas III, *Org. Lett.*, 2010, **12**, 5250.
- 27 H. Huang, F. Yu, Z. Jin, W. Li, W. Wu, X. Liang, J. Ye, *Chem. Commun.* 2010, **46**, 5957.
- 28 H. Jiang, M. W. Paixão, D. Monge and K. A. Jørgensen, *J. Am. Chem. Soc.* 2010, **132**, 2775.
- 29 D. C. Whitehead, R. Yousefi, A. Jaganathan, B. Borhan, *J. Am. Chem. Soc.* 2010, **132**, 3298.
- 30 G. Li, M. J. Kaplan, L. Wojtas, J. C. Antilla, *Org. Lett.*, 2010, **12**, 776.
- 31 X. Zeng, K. Ye, M. Lu, P. J. Chua, B. Tan, G. Zhong, *Org. Lett.* 2010, **12**, 2414.
- 32 V. N. Wakchaure and B. List, *Angew. Chem. Int. Ed.* 2010, **49**, 4136.
- 33 W. Liu, H. Cao, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong and A. Lei, *J. Am. Chem. Soc.* 2010, **132**, 16737.
- 34 G. Bergonzini, S. Vera and P. Melchiorre, *Angew. Chem. Int. Ed.* 2010, **49**, 9685.
- 35 M. Reiter, S. Torsell, S. Lee and D. W. C. MacMillan, *Chem. Sci.* 2010, **1**, 37.