Organocatalysis [review article]

1 Organocatalysis

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DOI: 10.1039/b927086h
Abstract
Reactions carried out with substoicheiometric quantities of organic molecules as catalysts have received much attention over the past decade. This review highlights progress in 2009 towards highly enantioselective organocatalytic systems and the natural product/biologically active compounds that can be prepared using these types of processes.

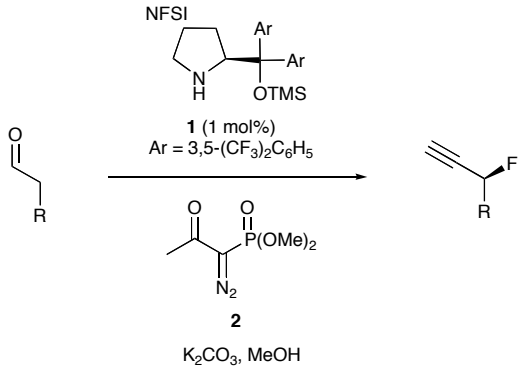
1.0 Introduction

The number of reports for organocatalysed reactions has again grown significantly with over 800 articles using the word organocatalysis in 2009 (compared to just over 700 in 2008).[1] Several excellent reviews have again been reported in this highly topical area.[2] The present review covers achievements from 2009, 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 sections on oxidation, domino reactions, theoretical considerations and a summary of some of the elegant natural product architectures prepared by organocatalysis in 2009 (section 8.0).

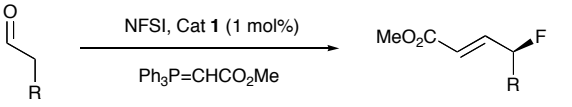
2.0 Iminium/Enamine Catalysis

Again this area has seen increased activity due 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 that can be captured by incoming nucleophiles or electrophiles with excellent levels of enantiomeric excess. Several related reports regarding the asymmetric α-hydroxylation, α-amination, α-sulfenylation and α-phosphorylation of aldehydes and ketones were reviewed in volumes 103,104 and 105.

Jørgensen and co-workers have reported the direct 'one pot' asymmetric synthesis of chiral propargylic and allylic fluorides.[3] This work is built from earlier reports from the group and others on the asymmetric α-fluorination of aldehydes using the proline-based catalyst **1**. Direct treatment of the resulting fluorinated aldehydes was carried out with either the Bestmann reagent **2** to install the alkyne moiety (Scheme 1) or a stabilized Wittig reagent to afford an *E*-alkene (Scheme 2). The proposed mechanism of these transformations is described in scheme 3.

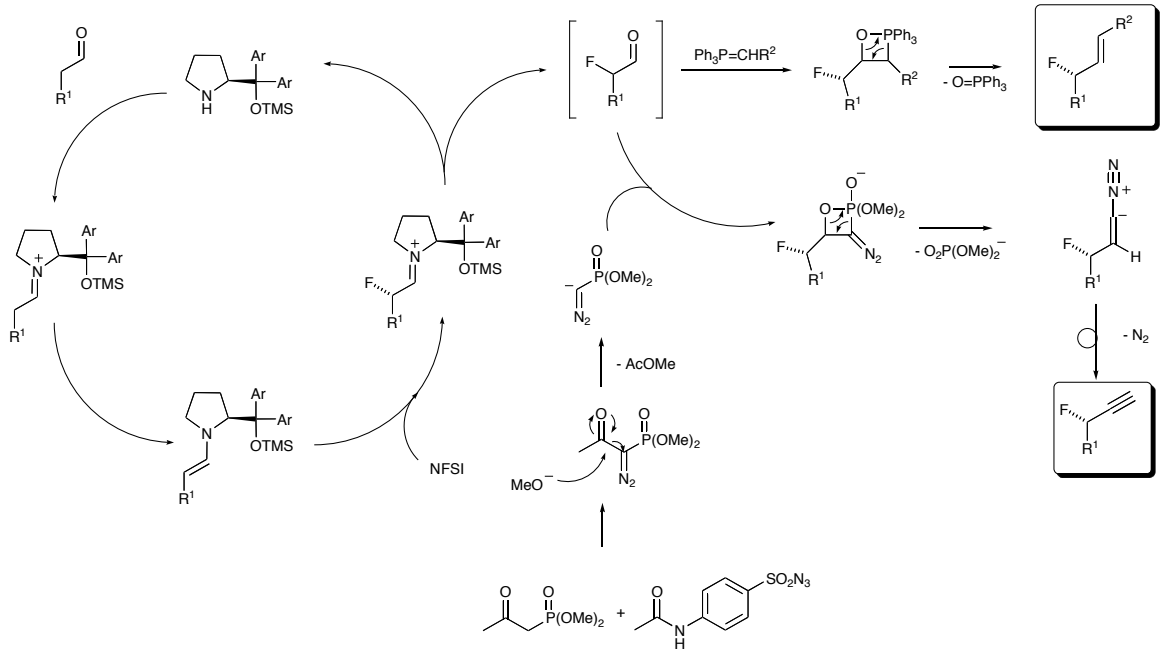


Scheme 1 Asymmetric synthesis of chiral propargylic fluorides



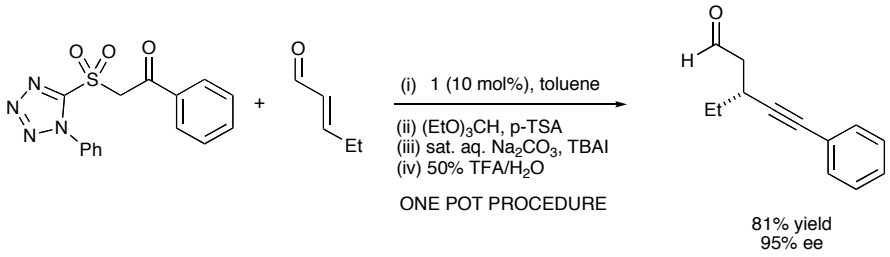
R = Bn = 47%, 93% ee
R = *p*-Br-Bn = 43%, 96% ee

Scheme 2 Asymmetric synthesis of chiral allylic fluorides

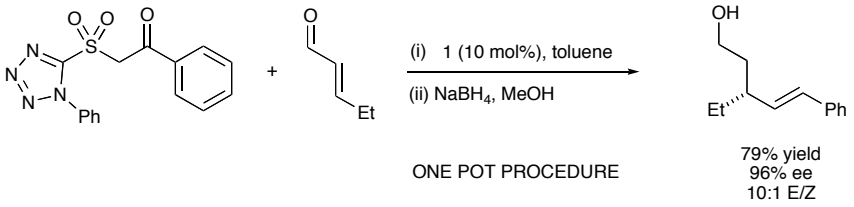


Scheme 3 Jørgensen's proposed mechanism for the formation of chiral propargylic and allylic fluorides

Using the same proline-based catalyst **1** Jørgensen and co-workers have also reported a related conjugate addition approach to alkynyl- and alkenyl- substituted products (Schemes 4 and 5).[4]

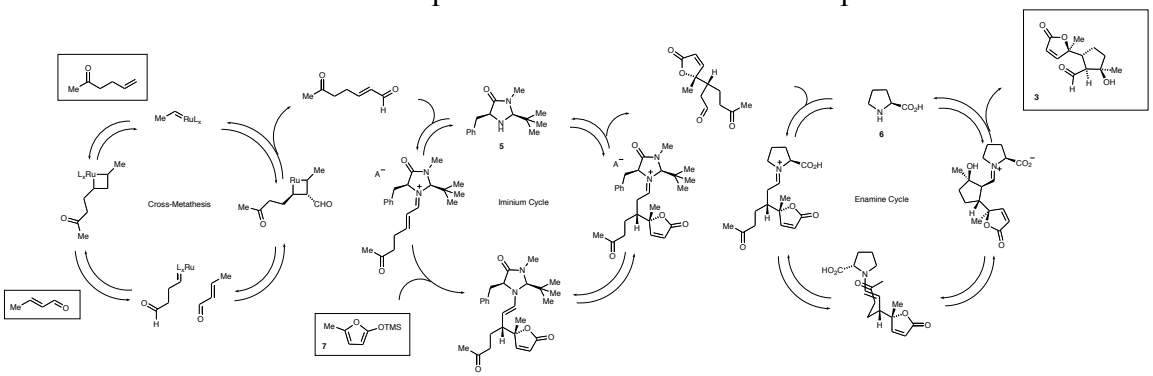


Scheme 4 Jørgensen's conjugate alkynylation of α,β-unsaturated aldehydes

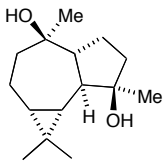


Scheme 5 Jørgensen's conjugate alkenylation of α,β-unsaturated aldehydes

MacMillan has reported a iminium, enamine and metathesis cascade reaction to form highly enantioenriched precursors for natural product syntheses.[5] For example, MacMillan and co-workers hypothesized that the bicyclic butenolide **3**, which contains four of the six stereocenters (all contiguous) and 12 of the 15 carbons found in aromadendranediol **4**, might be generated in a single operation. Sequential addition of Grubbs II catalyst, imidazolidinone **5**, and proline **6** along with the respective addition of crotonaldehyde, 5-hexene-2-one, and trimethylsilyloxyfuran **7** in wet dichloromethane/ ethyl acetate resulted in formation of the desired cascade adduct in 64% yield and 95% ee, and with a 5:1 preference for the desired diastereomer (Scheme 6). The synthesis of aromadendranediol was then completed with several further manipulations.

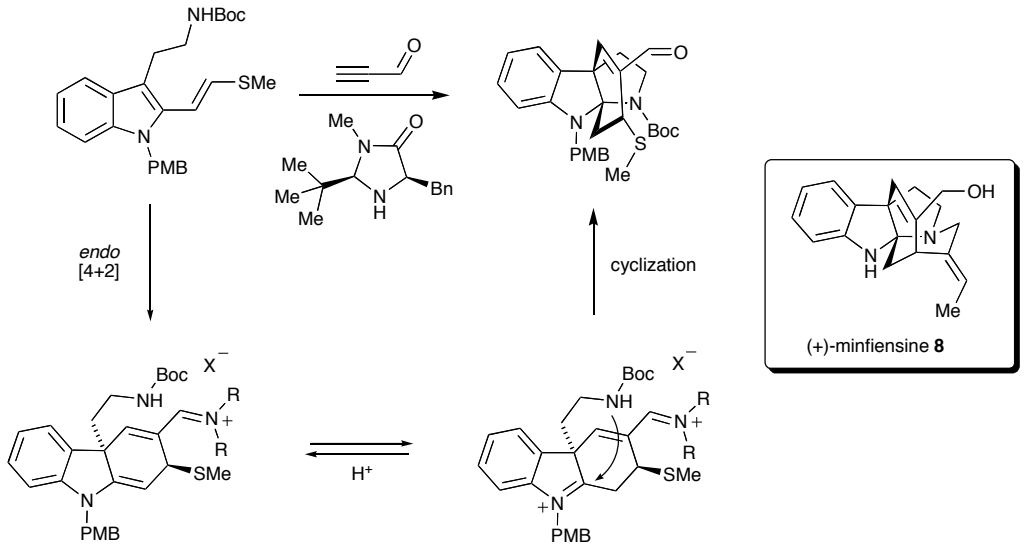


Scheme 6 MacMillan's proposed mechanism for an iminium, enamine and metathesis cascade reaction.



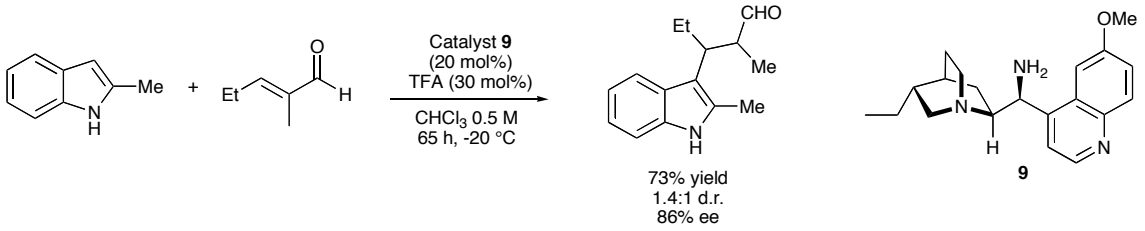
Aromadendranediol **4**

MacMillan and co-workers have also reported the total synthesis of (+)-minfiensine **8** using organocatalysis as a key step. The synthesis was completed in nine steps and 21% overall yield from commercial materials. Important features of this synthesis included (i) a new cascade organocatalysis sequence to build the central tetracyclic pyrroloindoline framework and (ii) a 6-*exo*-dig radical cyclization to form the final piperidinyl ring system.[6] The synthesis of the minfiensine core is shown in Scheme 7.

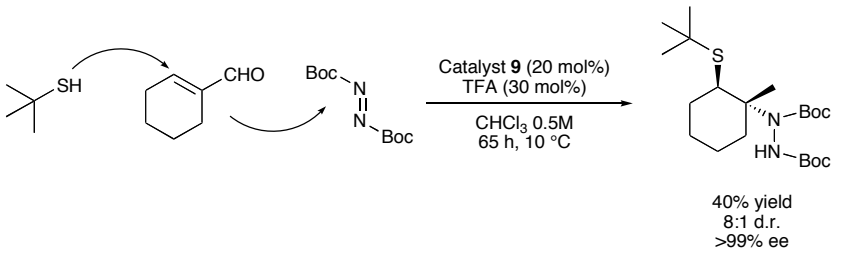


Scheme 7 Total synthesis of the core of (+)-minfiensine **8** using organocatalysis as a key step

Melchiorre and co-workers have reported an organocatalytic cascade reaction using the amine **9** with α-substituted α,β-unsaturated aldehydes (Scheme 8).[7] Preliminary investigations by the authors found that **9** was able to catalyse the transformation described in scheme 8. With this information in hand they then applied this system to a organocascade reaction (Scheme 9).

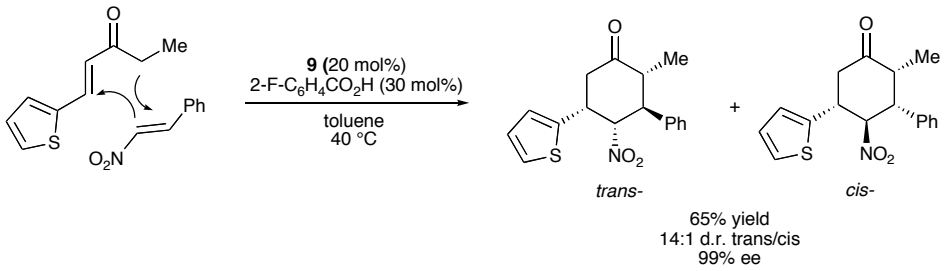


Scheme 8 Melchiorre and co-workers preliminary investigations



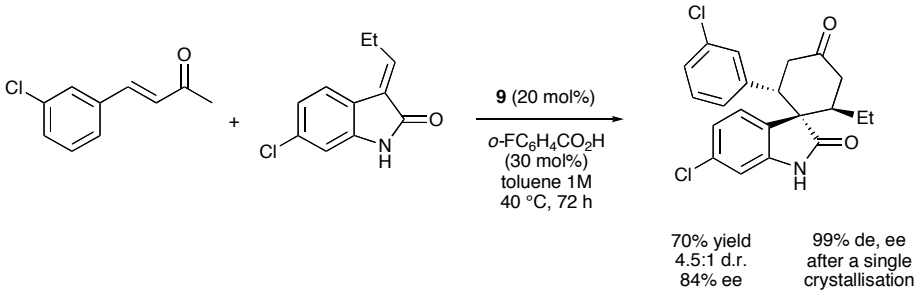
Scheme 9 Melchiorre and co-workers organocatalytic cascade reaction

Melchiorre has also reported the organocascade reaction of nitroalkenes and enones catalysed by the same amine-based organocatalyst. In this intriguing reaction four stereocentres are produced in one operation with high levels of diastereoselectivity and enantioselectivity (up to 99% ee, Scheme 10).[8]



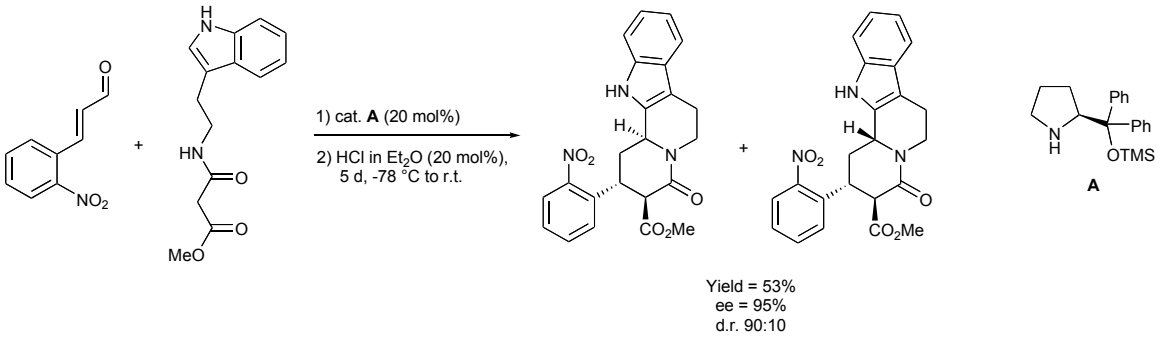
Scheme 10 Melchiorre and co-workers organocascade reaction of nitroalkenes

Further application of this organocatalyst by Melchiorre and co-workers has led to the construction of spirocyclic oxindoles.[9] The enantiomeric excess could be enhanced by a single recrystallization to afford essentially enantiomerically pure material.



Scheme 11 Melchiorre and co-workers organocascade reaction of enones and oxindoles

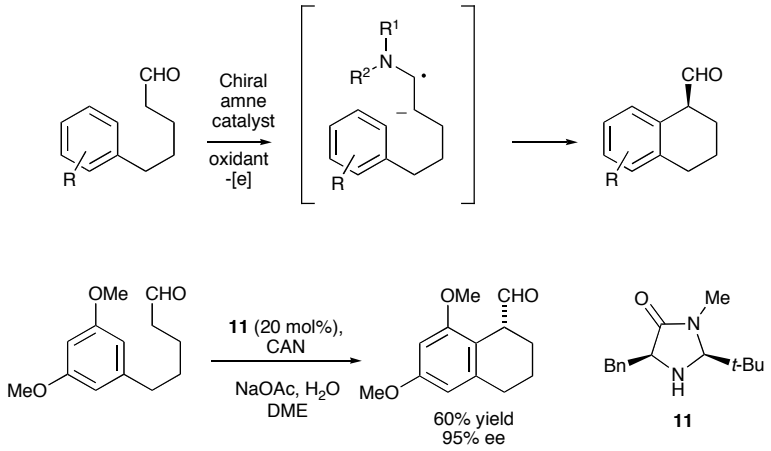
Franzén and Fisher have reported the use of the prolinol-based catalyst **10** for the one pot synthesis of quinolizidine derivatives (Scheme 12). Under the reaction conditions three new chiral centres are produced with good levels of diastereoselectivity and excellent levels of enantioselectivity.[10]



Scheme 12 Franzén and Fisher's synthesis of quinolizidine derivatives

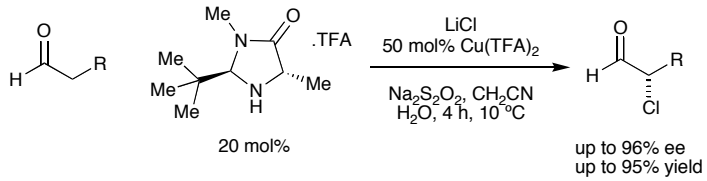
3.0 SOMO Catalysis

Nicolaou and co-workers have reported the enantioselective intramolecular Friedel-Crafts-type α-arylation of aldehydes using an imidazolidinone catalyst **11** and cerium(V) ammonium nitrate as oxidant (Scheme 13). Excellent ees were obtained and this methodology was applied to the synthesis of demethyl calamenene.[11]

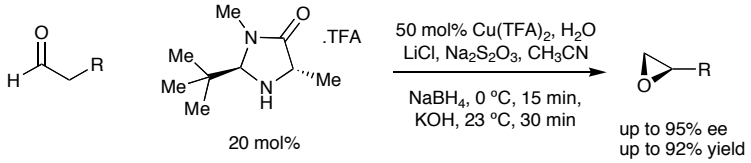


Scheme 13 Nicolaou's enantioselective intramolecular Friedel-Crafts-type α-arylation of aldehydes

MacMillan has again expanded the scope of amino/SOMO catalysis and has reported a new SOMO-activated aldehyde α-chlorination reaction which affords α-chloroaldehydes with high enantioselectivity (Scheme 14). This methodology can then be employed as part of a 'linchpin-catalysis' approach wherein the key induction step can lead to the enantioselective production of a broad range terminal epoxides by reduction of the aldehyde moiety and subsequent cyclization (Scheme 15). [12]

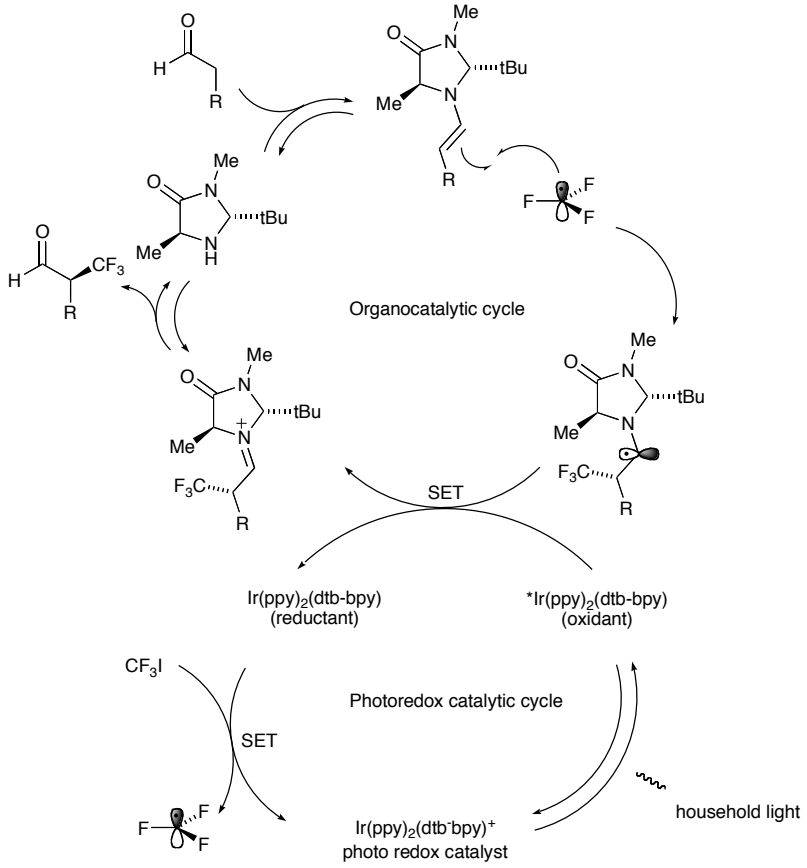


Scheme 14 The SOMO-activated aldehyde α-chlorination reaction



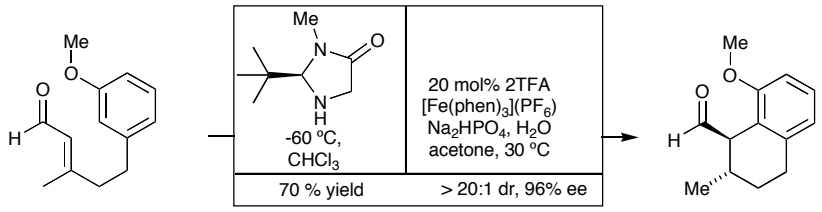
Scheme 15 MacMillan's enantioselective production of terminal epoxides

Trifluoromethyl groups are currently of great interest in the pharmaceutical industry and MacMillan and co-workers have reported the first enantioselective, organocatalytic α-trifluoromethylation and α-perfluoroalkylation of aldehydes (Scheme 16). This was accomplished by using a readily available iridium photocatalyst and a commercial imidazolidinone catalyst.[13]

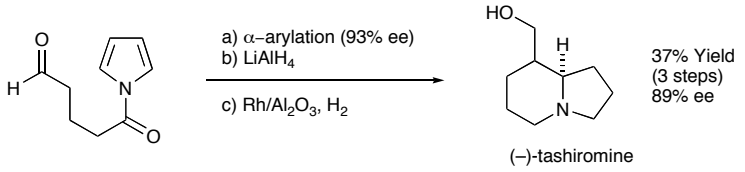


Scheme 16 The SOMO-activated aldehyde α-trifluoromethylation reaction

MacMillan and co-workers have been able to combine a SOMO α-arylation reaction into a two-step organocatalytic sequence that first involves a Hantzsch ester hydride (HEH) reduction of an anisole-tethered α,*β*-unsaturated aldehyde followed by treatment with catalyst **12** and $[Fe(phen)_3](PF_6)$. As shown in scheme 17, this sequence provides the resulting bicyclic ring system as a single (*anti*) diastereoisomer in 70% yield and 96% ee. MacMillan and co-workers have also been able to apply this carbonyl α-arylation methodology towards the total synthesis of (–)-tashiromine. Treatment of the pyrrole amide-tethered aldehyde **13** under the conditions described in scheme 18 provides the desired [6,5]-bicyclic ring system in 72% yield and in 93% ee. The resulting amide was then reduced in the presence of $AlCl_3$ with $LiAlH_4$ in 83% yield prior to pyrrole hydrogenation using catalytic Rh/Al_2O_3 to provide (–)-tashiromine in 62% yield.[14]

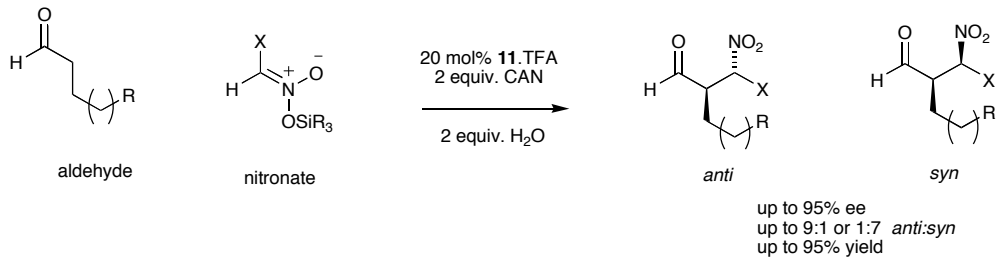


Scheme 17 Sequential Organocatalytic Conjugate Reduction-SOMO Arylation



Scheme 18 Enantioselective Synthesis of (–)-Tashiromine by Formyl α-Arylation

MacMillan and co-workers have also developed an enantioselective aldehyde α-nitroalkylation approach in which the major alkylated product, either *syn* or *anti*, can be prepared using the same catalyst (Scheme 19). The *anti* product is favoured when using acetone as the reaction solvent, the *syn* product is favoured in tetrahydrofuran.[15]

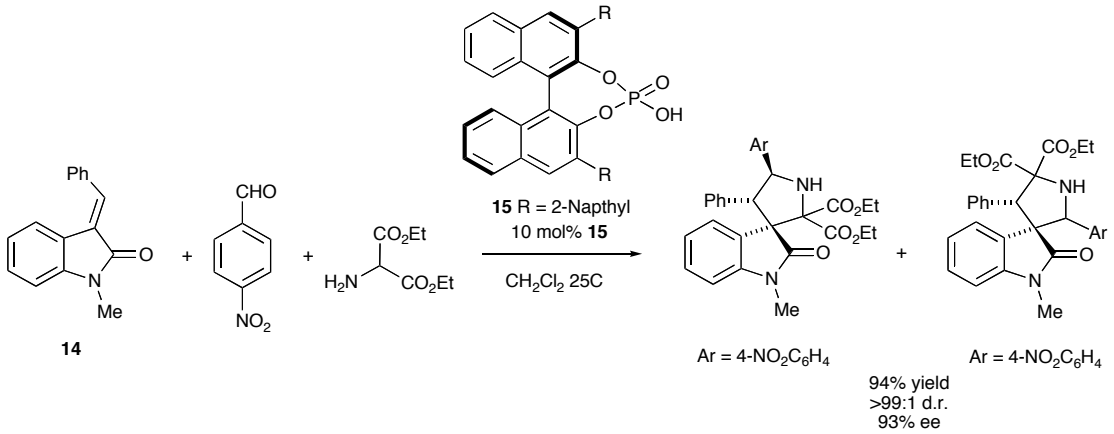


Scheme 19 MacMillan's enantioselective aldehyde α-nitroalkylation

4.0 Hydrogen Bonding Catalysis

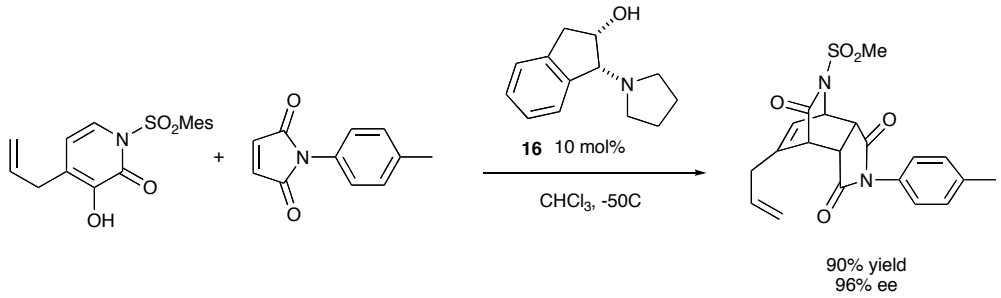
Hydrogen bonding catalysis was perhaps one of the most active areas of organocatalysis

during 2009.[16] For example, Gong and co-workers have developed a highly regio- and enantioselective three component approach to spiro[pyrrolidin-3,3'-oxidndoles] using binaphthyl phosphoric acid catalysis (Scheme 20).[17] Treatment of the oxindole **14** with an aldehyde, amine component and a phosphoric acid catalyst **15** affords the spiro oxindole in high yield. Theoretical calculations identified that both the azomethine ylide and the methyleneindolinone are hydrogen-bonded to the phosphoric acid catalyst in the transition state, thus affording high levels of regio- and enantio-control.



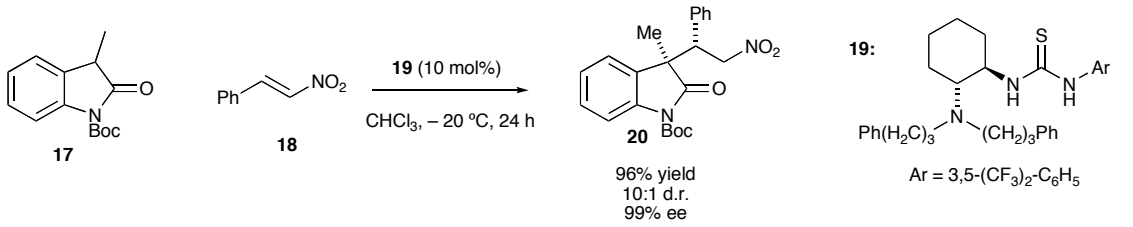
Scheme 20 Gong's highly regio- and enantioselective three component approach to spiro[pyrrolidin3,3'-oxidndoles]

Soh and Tan have developed an amino-indanol catalysed Diels-Alder reaction (Scheme 21).[18] They were interested in developing a new series of bifunctional catalysts based on small/simple molecules able to catalyse a range of organocatalytic reactions and have shown that simple amino-alcohols such as **16** are able to deliver high yields and enantioselectivities in the Diels-Alder reactions of 3-hydroxy-2-pyridines.



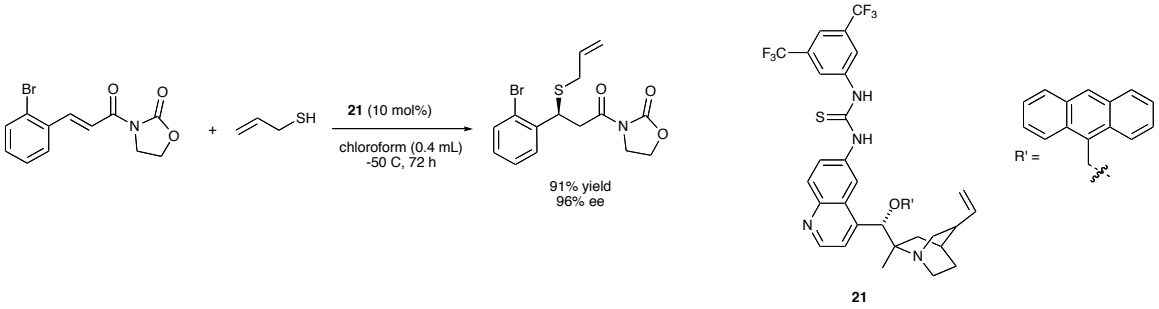
Scheme 21 Soh and Tan's amino-indanol catalysed Diels-Alder reaction

Barbas and co-workers have reported the thiourea-catalysed enantio- and diastereoselective addition of oxindoles to nitroolefins (Scheme 22). For example, treatment of the oxindole **17** with the nitro alkene **18** in the presence of the thiourea **19** affords the corresponding product **20** with 99% ee and a 10:1 dr. The authors then went on to apply this methodology in the synthesis of (+)-physostigmine and (–)-esermethole (See figure 1).[19]



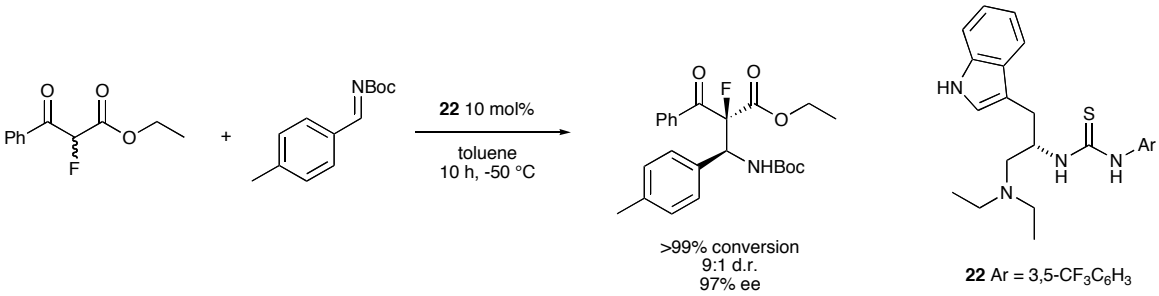
Scheme 22 Barbas' addition of nitroolefins to oxindoles

Deng has also employed thiourea catalyst **21** to effect an asymmetric conjugate addition of alkyl thiols to α,*β*-unsaturated *N*-acylated oxazolidin-2-ones (Scheme 23).[20] Excellent yields and ees are obtained over a wide variety of substrates and thiols.



Scheme 23 Deng's asymmetric conjugate addition of alkyl thiols to α,*β*-unsaturated *N*-acylated oxazolidin-2-ones

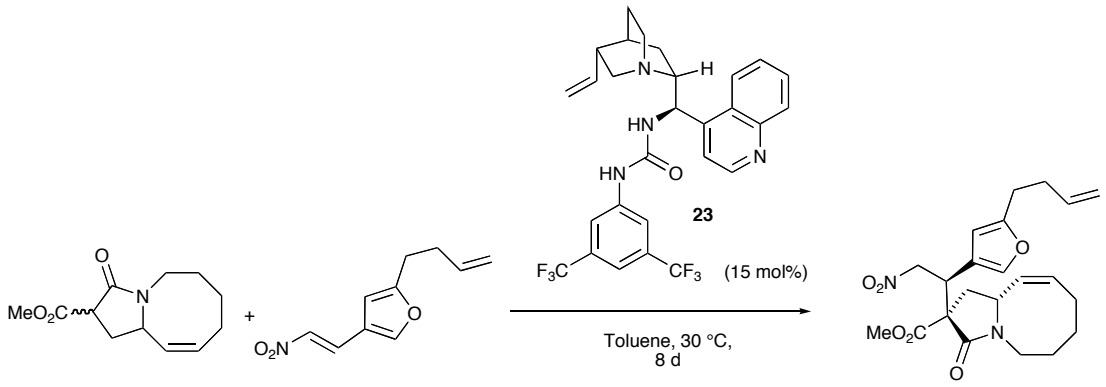
Huang and Lu have reported the asymmetric Mannich reaction of fluorinated ketoesters with a novel tryptophan-based bifunctional catalyst **22** which contains both a thiourea moiety and a tertiary amino functionality to act as base.[21] Excellent yields and ees are obtained. Interestingly, the resulting compounds with fluorinated quaternary and tertiary stereocentres can be converted into α-fluoro-*β*-amino acids and α-fluoro-*β*-lactams. The authors report that preliminary computational studies suggest the indole moiety of the catalyst plays a crucial role in substrate binding.



Scheme 24 Huang and Lu's asymmetric Mannich reaction of fluorinated ketoesters with a bifunctional thiourea catalyst

Dixon and co-workers have reported a highly diastereoselective and enantioselective nitro olefin Michael addition using the bifunctional organocatalyst **23** (Scheme 25). The

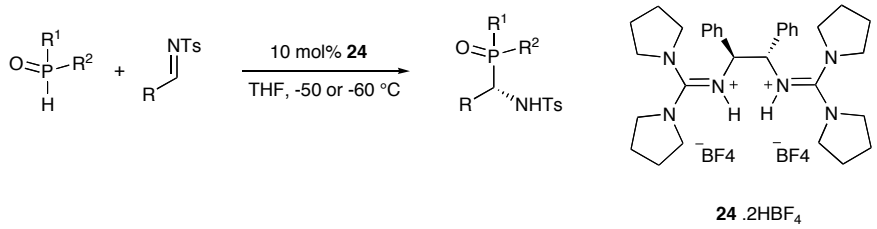
product of this reaction was then further manipulated to provide a total sysnthesis of (−)-nakadomarin A.[22]



Scheme 25 Dixon's highly diastereoselective and enantioselective nitro olefin Michael addition

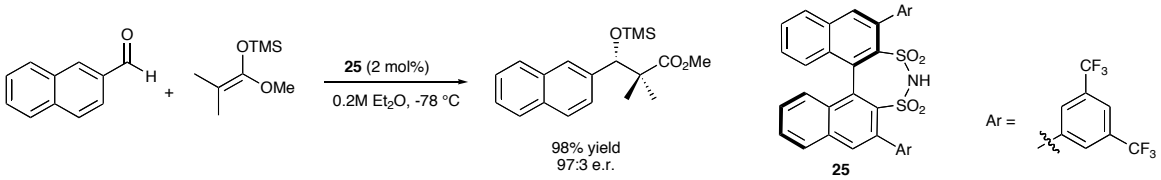
5.0 Counterion Catalysis

Tan and co-workers have described the use of the guanidinium salt **24** in the enantioselective phospha-Mannich reaction (Scheme 26).[23] Excellent yields and ees are obtained over a wide variety of substrates; for example when the 1-naphthyl substituted phosphine oxide is reacted with an imine in the presence of 1, the phospha-Mannich product can be isolated in 98% yield and 92% ee.



Scheme 26 The guanidinium salt-mediated phospha-Mannich reaction

List and co-workers have also reported the use of a chiral disulfonimide catalyst **25** for the Mukaiyama aldol reaction. Excellent ees are observed over a range of substrates and extremely high turnover numbers were observed for the catalyst (up to 8800).[24]

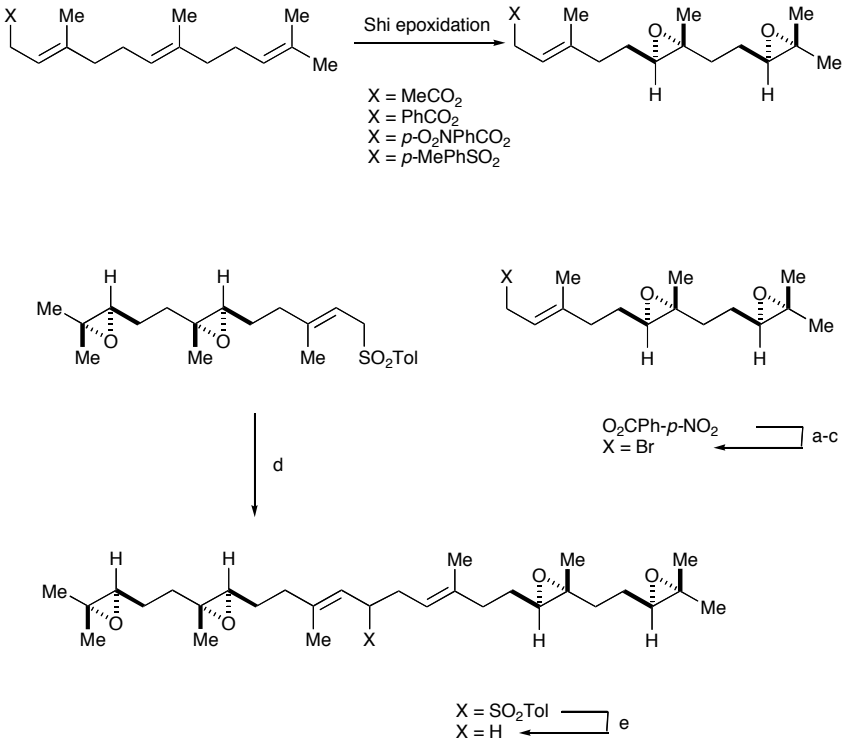


Scheme 27 List's chiral disulfonimide catalyst for the Mukaiyama aldol reaction

6.0 Epoxidation

Organocatalytic asymmetric epoxidation has again been an area of intense activity during

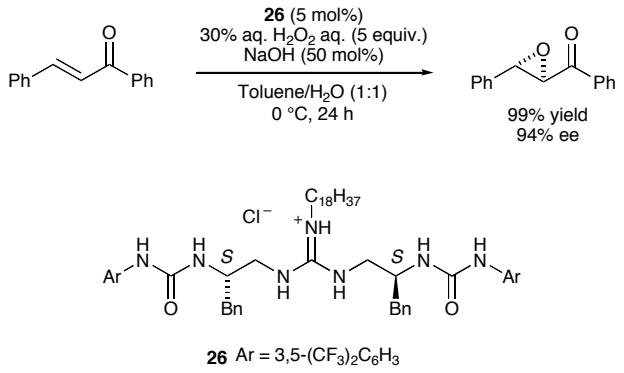
2009; the following are several representiative examples. The Shi epoxidation has been applied by McDonald and co-workers for the highly enantioselective synthesis of squalene tetraepoxide, a putative biosynthetic precursor to a variety of oxacyclic triterpenoid natural products (Scheme 28). It was efficiently synthesized by anionic coupling of two farnesol-derived diepoxides, which arose from electronic control of regioselectivity in organocatalytic enantioselective Shi epoxidations.[25]



(a) K_2CO_3, MeOH, 15 min (88% yield);
(b) MsCl, Et_3N, THF, -40 °C, 30 min; then LiBr, THF, 0 °C, 15 min (96% yield);
(c) KO-*t*-Bu, THF, -78 °C, 2 h (77% yield)
(d) $PdCl_2$(dppp) (20 mol%), $LiBEt_3H$, THF, 0 °C, 40 min (64% yield)

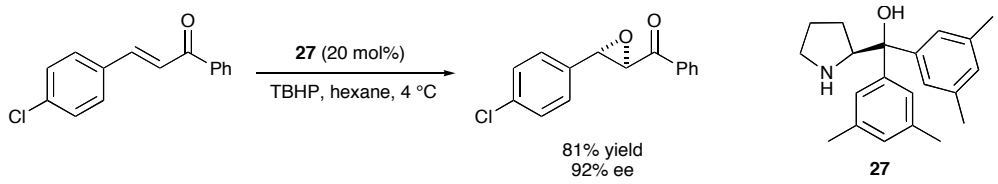
Scheme 28 McDonald's highly enantioselective synthesis of squalene tetraepoxide

Tanaka and Nagasawa have reported a guanidine-urea bifunctional organocatalyst **26** for the asymmetric epoxidation of chalcones using hydrogen peroxide as the stoicheometric oxidant (Scheme 29).[26] NMR studies suggest that the guanidine and urea moieties of the catalyst act cooperatively through urea-carbonyl and guanidine-hydrogen peroxide interactions to promote asymmetric epoxidation.



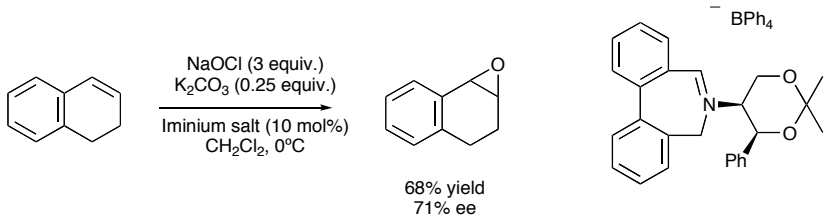
Scheme 29 Tanaka and Nagasawa's guanidine-urea bifunctional organocatalyst for asymmetric epoxidation

Russo and Lattanzi have reported the asymmetric oxidation of electron-poor alkenes promoted by a β-amino alcohol **27**/TBHP system (Scheme 30). Excellent yields and ees are observed for a range of chalcone-derived substrates.[27]

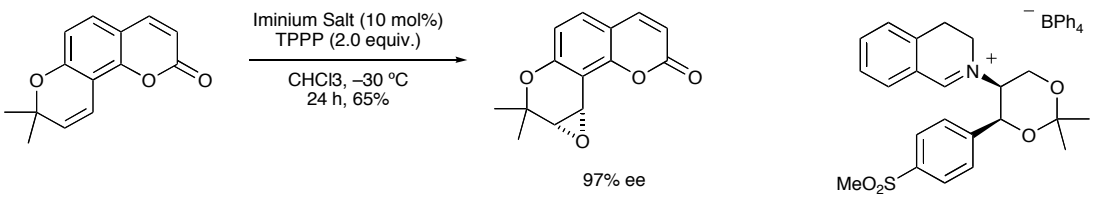


Scheme 30 Russo and Lattanzi's epoxidation of electron-poor alkenes

Page and co-workers have reported the use of bleach as a stoichiometric oxidant in oxaziridinium ion-mediated epoxidation with ees of up to 71% (Scheme 31);[28] a full report on the use of binaphthalene-based oxaziridinium ion catalysts in asymmetric epoxidation[29] and a paper on the application of dihydroisoquinolinium salts in the highly enantioselective total synthesis of (−)-(3'S)-lomatin and (+)-(3'S,4'R)-*trans*-khellactone (Scheme 32, Figure 1).[30]



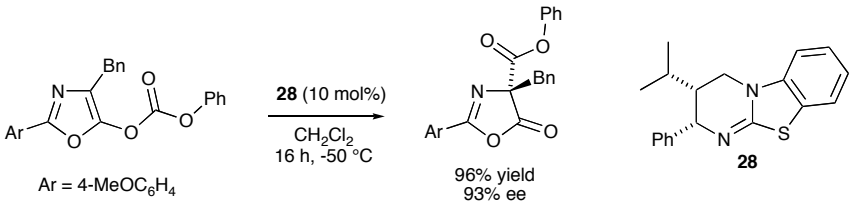
Scheme 31 Page's bleach-mediated oxaziridinium ion epoxidation



Scheme 32 Page's asymmetric epoxidation in the synthesis of (−)-(3'S)-lomatin and (+)-(3'S,4'R)-*trans*-khellactone

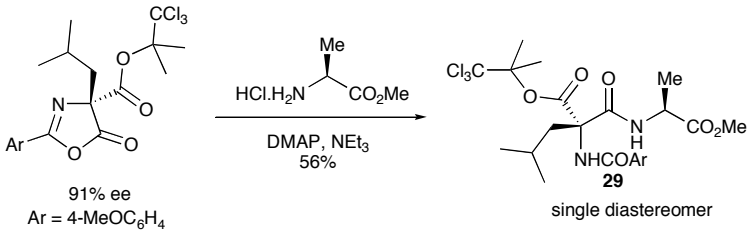
7.0 Nucleophilc Catalysis

The development of nucleophilc organocatalysts has been an area of interest for many years, for example the development of chiral DMAP derivatives.[31] Notable examples form 2009 include Smith and co-workers' report on the use of isothiourea catalyst **28** for the asymmetric carboxy group transfer reaction (Scheme 33). High yields and ees are obtained when oxazolyl carbonates are used as substrates.



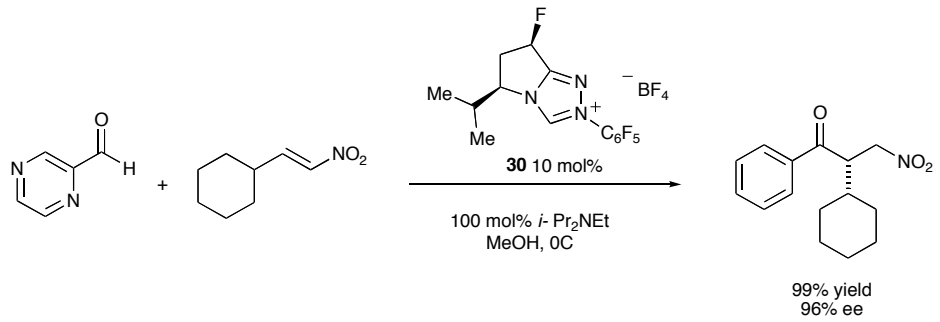
Scheme 33 Smith's highly enantioselective carboxy group transfer reaction

Smith has employed this methodology in the synthesis of the enantiomerically pure amide **29** (Scheme 34).[32]



Scheme 34 Application of Smith's methodology for the synthesis of amide **29**

Rovis and co-workers have reported an intermolecular Stetter reaction using fluorine-substituted *N*-heterocyclic carbene catalysts **30** (Scheme 35).[33] Addition of the fluorine atom in the backbone of the catalyst was found to increase the ee of the reaction (88% - 95%) and this was attributed to a conformational change in the bicyclic ring system.



Scheme 35 Rovis' intermolecular Stetter reaction using fluorine-substituted *N*-heterocyclic carbene catalysts

8.0 Natural Products Synthesized by Organocatalytic Reactions

Given the developments outlined in this review, it is again perhaps not surprising that organocatlysis is widely applied in the total synthesis of a range of natural products and biologically active compounds (Figure 1). Representative examples include: MacMillan's synthesis of aromadendranediol,[5] tashiromine[14] and minfiensine;[6] Franzen and Fisher's synthesis of quinolizidine derivatives (Scheme 12);[10] Gong's synthesis of spiro[pyrrolidin-3,3'-oxindoles] (Scheme 20);[17] Dixon's synthesis of nakadomarin;[22] MacDonald's synthesis of squalene tetraepoxide;[25] Page's synthesis of lomatin and *trans*-khellactone;[30] and Smith's synthesis of amino acid derivatives (Scheme 34).[32]

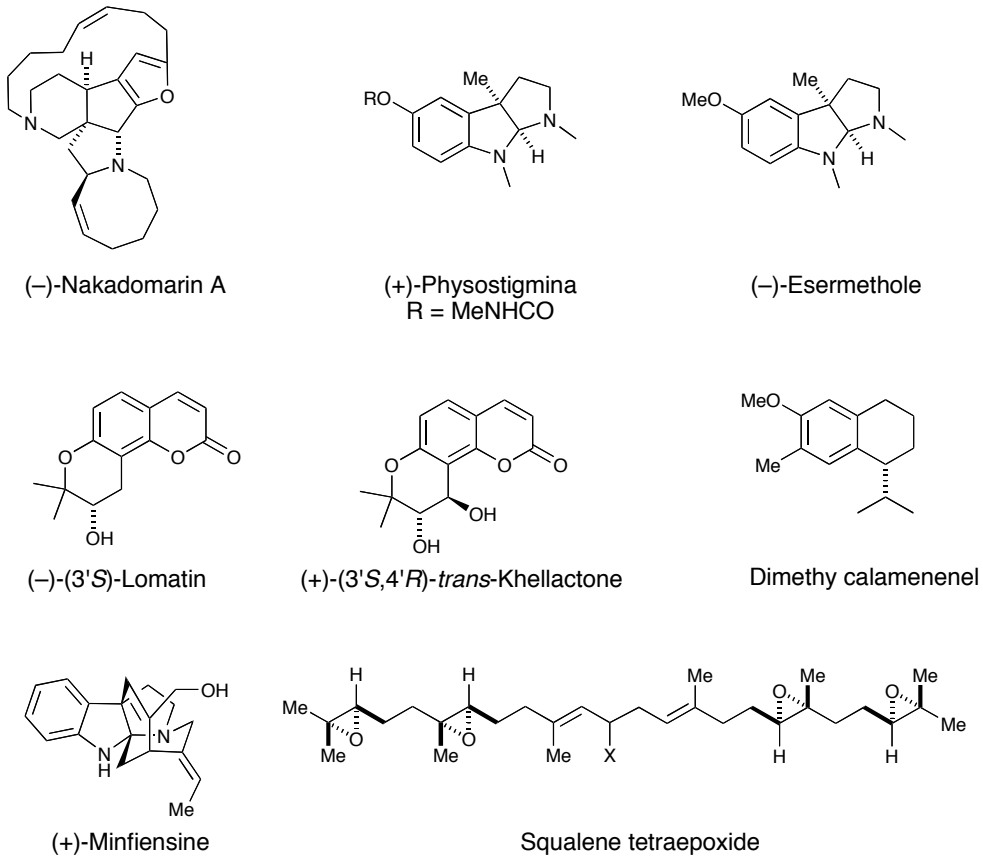


Figure 1 Some of the natural products produced using organocatalysis in 2009

9.0 Conclusion

Over the past year the development of non-metal catalysed reactions has again increased significantly. The level of enantiomeric excess and product yield obtained are now in many cases at excellent levels, with ees of over 95% commonplace. Catalyst loadings are still somewhat high when compared to transition metal catalysts, but as reported previously this can be offset, in some cases, by the relatively low cost of the catalyst. As we can see from the examples presented in this review, 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. Overall organocatalysis looks set to again move forward with significant vigour over the coming year.

10.0 References

1 Based on an ISI Web of Knowledge search on the word organocatalysis and its derivatives for the year 2009.

2 Review on organocatalytic reactions in water: M. Raj and V. K. Singh, *Chem. Commun.* 2009, 6687; Amide-based bifunctional organocatalysts: X. Liu, L. Lin and X. Feng, *Chem. Commun.* 2009, 6145; Bifunctional chiral organocatalysts: P. S. Bhadury, B. A. Song, S. Yang, *Curr. Org. Synth.,* 2009, **6**, 380; Organocatalytic domino reactions: A. N. Alba, X. Companyo, M. Viciano, *Curr. Org. Chem.,* 2009, **13**, 1432; A review on the intramolecular Stetter reaction: J. R. de Alaniz and T. Rovis, *Synlett* 2009, 1189; Organocatalysis-after the gold rush: S. Bertelson and K. A. Jørgensen *Chem. Soc. Rev.* 2009, **38**, 2178; Amino acids as catalysts in water: J. Paradowska, M. Stodulski and J. Mlynarski *Angew. Chem. Int. Ed.* 2009, **48**, 4288; Hypervalent iodine reagents in organocatalysis: T. Dohi and Y. Kita *Chem. Commun.* 2009, 2073; Bifunctional Binols: C. Nájera, J. M. Sansano and J. M. Saá *Eur. J. Org. Chem.* 2009, 2385; Primary amine based organocatalysts: L. W. Xu, J. Luo and X. Y. Lu *Chem. Commun.* 2009, 1807; (Thio)urea organocatalysis: Z. G. Zhang and P. R. Schreiner *Chem. Soc. Rev.* 2009, **38**, 1187 and S. J. Connon *Synlett* 2009, 354; Organocatalysis with chiral Brønsted bases: C. Palomo, M. Oiarbide and R. Lopez *Chem. Soc. Rev.* 2009, **38**, 632.

3 H. Jiang, A. Falcicchio, K. L. Jensen, M. W. Paixão, S. Bertelsen and K. A. Jørgensen *J. Am. Chem. Soc.* 2009, **131**, 7153.

4 M. Nielsen, C. B. Jacobsen, M. W. Paixão, N. Holub and K. A. Jørgensen *J. Am. Chem. Soc.* 2009, **131**, 10581.

5 B. Simmons, A. M. Walji, and D. W. C. MacMillan, *Angew. Chem. Int. Ed.* 2009, **48**, 4349.

6 S. B. Jones, B. Simmons, and D. W. C. MacMillan *J. Am. Chem. Soc.,* 2009, **131**, 13606.

7 P. Galzerano, F. Pesciaioli, A. Mazzanti, G. Bartoli and P. Melchiorre *Angew. Chem. Int. Ed.* 2009, **48**, 7892.

8 L.-Y.Wu, G. Bencivenni, M. mancinelli, A. Mazzanti, G. Bartoli and P. Melchiorre *Angew. Chem. Int. Ed.* 2009, **48**, 7196.

9 G. Bencivenni, L.-Y. Wu, A. Mazzanti, B. Giannichi, F. Pesciaioli, M.-P. Song, G. Bartoli and P. Melchiorre *Angew. Chem. Int. Ed.* 2009, **48**, 7200.

10 J. Franzén and A. Fisher *Angew. Chem. Int. Ed.* 2009, **48**, 787.

11 K. C. Nicolaou, R. Reingruber, D. Sarlah, and S Bräse *J. Am. Chem. Soc.* 2009, **131**, 2086.

12 M. Amatore, T. D. Beeson, S. P. Brown, and D. W. C. MacMillan, *Angew. Chem. Int. Ed.* 2009, **48**, 5121.

13 D. A. Nagib, M. E. Scott, and D. W. C. MacMillan *J. Am. Chem. Soc.,* 2009, **131**, 10875.

14 J. C. Conrad, J. Kong, B. N. Laforteza, and D. W. C. MacMillan *J. Am. Chem. Soc.,* 2009, **131**, 11640.

15 J. E. Wilson, A. D. Casarez, and D. W. C. MacMillan *J. Am. Chem. Soc.,* 2009, **131**, 11332.

16 See reference 1 for recent reviews in this area.

17 X.-H. Chen, Q. Wei, S.-W. Luo, H. Xiao and L.-Z. Gong, *J. Am. Chem. Soc.* 2009, **131**, 13819.

18 J. Y.-T. Soh and C.-H. Tan *J. Am. Chem. Soc.* 2009, **131**, 6904.

19 T. Bui, S. Syed and C. F. Barbas III *J. Am. Chem. Soc.* 2009, **131**, 8758.

20 Y. Liu, B. Sun, B. Wang, M. Wakem and L. Deng *J. Am. Chem. Soc.* 2009, **131**, 418.

21 X. Han, J. Kwiatkowski, F. Xue, K.-W. Huang and Y. Lu *Angew. Chem. Int. Ed.* 2009, **48**, 7604.

22 P. Jakubec, D. M. Cockfield and D. J. Dixon *J. Am. Chem. Soc.* 2009, **131**, 16632.

23 X. Fu, W.-T. Loh, Y. Zhang, T. Chen, T. Ma, H. Liu, J. Wang and C.-H. Tan *Angew. Chem. Int. Ed.* 2009, **48**, 7387.

24 P. García-García, F. Lay, P. García-García, C. Rabalakos and B. List *Angew. Chem. Int. Ed.* 2009, **48**, 4363.

25 R. Tong, M. A. Boone and F. E. McDonald *J. Org. Chem.* 2009, **74**, 8407.

26 S. Tanaka and K. Nagasawa *Synlett*, 2009, 667.

27 A. Russo and A. Lattanzi *Synthesis* 2009, 1551.

28 P. C. B. Page, P. Parker, B. R. Buckley, G. A. Rassias and D. Bethell *Tetrahedron* 2009, **65**, 2910

29 P. C. B. Page, B. R. Buckley, M. M. Farah and A. J Blacker *Eur. J. Org. Chem.,* 2009, 3413.

30 P. C. B. Page, L. F. Appleby, D. Day, Y. Chan, B. R. Buckley, S. M Allin, and M. J. McKenzie *Org. Lett.* 2009, **11**, 1991.

31 S. Yamada *J. Synth. Org. Chem. Jpn.* 2005, *63*, 339.

32 C. Joannesse, C. P. Johnston, C. Concellón, C. Simal, D. Philp and A. D. Smith *Angew. Chem. Int. Ed.,* 2009, **48**, 8914.

33 D. A. DiRocco, K. M. Oberg, D. M. Dalton and R. Rovis *J. Am. Chem. Soc.* 2009, **131**, 10872.