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Enantioselective Michael addition of α,α-disubstituted aldehydes to nitroolefins catalyzed by a pyrrolidine-pyrazole

Togapur Pavan Kumar *, Kothapalli Haribabu

Division of Natural Products Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India

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ABSTRACT

An efficient protocol for the asymmetric catalytic Michael additions of α,α-disubstituted aldehydes to nitroolefins with a pyrrolidine-pyrazole is described. The desired products γ-nitrocarbonyl compounds possessing an all-carbon quaternary center, were obtained in good yields and with high levels of enantioselectivities under solvent-free reaction conditions, employing benzoic acid as an additive.

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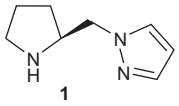
1. Introduction

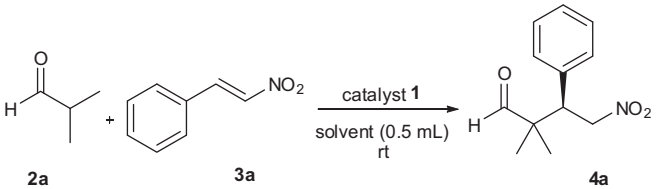
Over the past few years, remarkable advancements have been made in the development of organocatalytic asymmetric transformations. As a result, asymmetric organocatalysis[1] has gained significant attention from the scientific community and been realized as a powerful alternate and/or complementary protocol to the enzymatic and organometallic catalysis. In particular, asymmetric aminocatalysis has emerged as a useful tool for the construction of chiral building blocks by means of an enamine or iminium mechanism.[2] Among the wide range of organic transformations, the study of asymmetric Michael reactions has been the focus of many research groups, as it results in the formation of functionalized products with multiple stereogenic centers in a single step. A large number of designed organocatalysts bearing a pyrrolidine moiety have been developed and investigated in a wide variety of donor and acceptor substrates and found to be efficient.[3–5] Among the Michael products, γ-nitrocarbonyls are more prominent as they serve as versatile templates for the construction of various bioactive compounds.[5,6] The generation of all-carbon quaternary stereogenic centers is considered to be a challenging task in asymmetric synthesis.[7] Although a large number of organocatalysts are known to be highly efficient for the Michael addition of unmodified carbonyls to nitroolefins, only several of them have been found to be effective for Michael reactions between α,α-disubstituted aldehydes and nitroolefins.[8] Therefore, an investigation into new catalytic methods for this relatively underexplored transformation is highly desirable. In continuation of our research on organocatalysis,[9] we have recently developed the pyrrolidine-pyrazole **1** (Fig. 1) as an efficient catalyst for asymmetric Michael addition reaction of ketones to nitroolefins via an enamine mechanism under solvent-free conditions using TFA as an additive.[9e]

Having been encouraged by this study and considering the consistency of catalytic mechanisms, wherein the privileged chiral pyrrolidine backbone acts as the catalytically active site and the pyrazole appendage serves as the stereo-control unit,[10] we therefore started our investigations by testing whether catalyst **1** would also catalyze asymmetric Michael reactions of α,α-disubstituted aldehydes to nitroolefins. Herein we report on the use of pyrrolidine-pyrazole **1** as an effective organocatalyst for the asymmetric Michael reaction of α,α-disubstituted aldehydes to nitroolefins providing Michael adducts with an all-carbon quaternary center under solvent-free conditions.



1

Figure 1. Pyrrolidine-pyrazole.



2a 3a 4a

Scheme 1. Michael addition of isobutyraldehyde to nitrostyrene.

* Corresponding author. Tel.: +91 40 27191727; fax: +91 40 27160512.
E-mail address: pavantogapur@gmail.com (T.P. Kumar).

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Table 1
Screening of solvents and catalyst loading[a]

Entry	Solvent	**1** (mol%)	Time (d)	Yield[b] (%)	ee[c](%)
1	$CHCl_3$	10	5	47	61
2	$CHCl_3$	15	5	63	68
3	$CHCl_3$	20	4	70	72
4	Toluene	10	5	51	59
5	Toluene	15	4	59	66
6	Toluene	20	4	72	71
7	Neat	10	3	64	67
8	Neat	15	2	70	72
9	Neat	20	2	78	76
10	H_2O	10	7	45	49
11	H_2O	15	5	58	56
12	H_2O	20	5	67	65
13	MeOH	15	6	63	60
14	MeOH	20	4	69	64
15	THF	15	5	54	56
16	THF	20	4	60	62
17	CH_3CN	20	5	71	65
18	DMF	20	4	74	54
19	EtOH	20	5	66	61
20	Dioxan	20	5	70	58

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol).
[b] Isolated yields.
[c] Determined by chiral HPLC.

Table 2
Screening of additives[a]

Entry	additive	(mol%)	Time (h)	Yield[b] (%)	ee[c](%)
1	TFA	5	36	66	71
2	TFA	10	36	74	77
3	PhOH	5	48	57	65
4	PhOH	10	36	69	73
5	HCOOH	5	36	64	68
6	HCOOH	10	36	71	76
7	PhCOOH	5	36	78	81
8	PhCOOH	10	24	85	84
9	PhCOOH	15	24	87	85
10	PhCOOH	20	24	87	85

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol) catalyst **1** (20 mol %), neat, rt.
[b] Isolated yields.
[c] Determined by chiral HPLC.

Table 3
Effect of temperature[a]

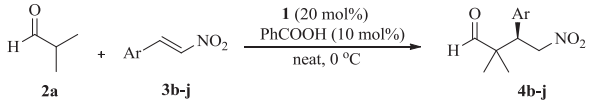
Entry	Temp.(°C)	Time (h)	Yield[b] (%)	ee[c](%)
1	10	36	89	86
2	0	36	93	92
3	-10	72	84	94
4	-20	72	81	94

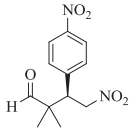
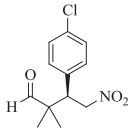
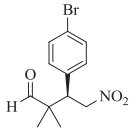
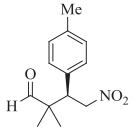
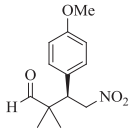
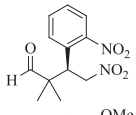
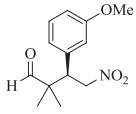
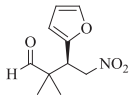
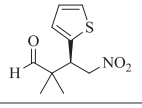
[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol) catalyst **1** (20 mol %), PhCOOH (10 mol %), neat.
[b] Isolated yields.
[c] Determined by chiral HPLC.

2. Results and discussion

In order to evaluate the efficacy of pyrrolidine-pyrazole catalyst **1** for asymmetric Michael additions of α,α-disubstituted aldehydes to nitroolefins, we started our investigations with a model reaction using isobutyraldehyde **2a** as a donor and nitrostyrene **3a** as an acceptor (Scheme 1); the reaction optimization involved variation of the solvent, additive, loading, and template. Initially, the reactions were simultaneously carried out in various solvents using 10–20 mol % of the catalyst at room temperature and the results are summarized in Table 1. As evident from the survey, the Michael reaction worked well in all of the solvents irrespective of their polar/non-polar nature to afford the product γ-nitrocarbonyl compound **4a** in good yield and enantioselectivity (Table 1, entries 1–20). However, the reaction performed under solvent-free conditions was found to be more effective in terms of yield (64–78%) and enantioselectivity (67–76% ee) among the conditions

Table 4
Enantioselective Michael addition of isobutyraldehyde to nitroolefins[a]



Entry	Product		Time (h)	Yield[b] (%)	ee[c](%)
1		**4b**	30	93	94
2		**4c**	30	88	90
3		**4d**	30	91	93
4		**4e**	48	79	81
5		**4f**	48	74	77
6		**4g**	30	94	92
7		**4h**	48	91	89
8		**4i**	36	85	90
9		**4j**	36	88	86

[a] Reaction conditions: isobutyraldehyde (4 mmol), nitrostyrene (1 mmol).
[b] Isolated yields.
[c] Determined by chiral HPLC.

tested and laid a platform for further screening studies (Table 1, entries 7–9).

Encouraged by these results, we next conducted experiments to test the effect of an acid additive in the above transformation. The presence of an acid additive could enhance the catalytic efficiency by accelerating enamine formation, thereby improving the overall productivity. In anticipation, we examined the effect of various acid additives under solvent-free conditions using 20 mol % of catalyst at room temperature and the results are summarized in Table 2. Benzoic acid turned out to be the most efficient additive in combination with catalyst **1** (Table 2, entries 7–10) and subsequent experiments were carried out by employing a 20:10 mol % catalyst-additive combination (Table 2, entry 8).

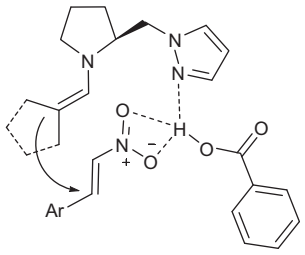
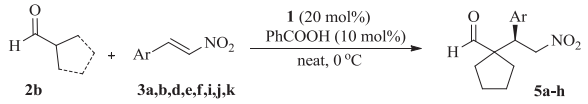
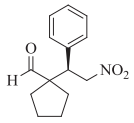
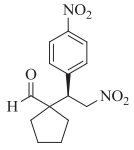
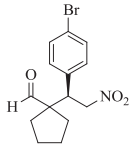
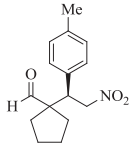
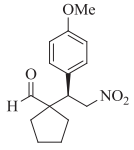
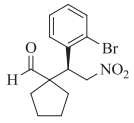
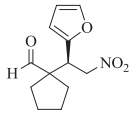
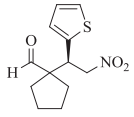


Figure 2. Proposed transition state.

Table 5
Enantioselective Michael addition of cyclopentanecarboxyaldehyde to nitroolefins[a]



2b **3a,b,d,e,f,i,j,k** **5a-h**

Entry	Product		Time (h)	Yield[b] (%)	ee[c](%)
1		**5a**	24	90	92
2		**5b**	24	95	96
3		**5c**	24	92	94
4		**5d**	48	81	83
5		**5e**	48	82	85
6		**5f**	24	94	93
7		**5g**	36	87	90
8		**5h**	36	85	89

[a] Reaction conditions: cyclopentanecarboxaldehyde (4 mmol), nitroolefin (1 mmol).
[b] Isolated yields.
[c] Determined by chiral HPLC.

With the aforementioned parameters, we then conducted experiments at different temperatures to determine the optimal temperature conditions required to maximize the catalytic ability of **1**. As shown in Table 3, the highest catalytic performance was observed at 0 °C (Table 3, entry 2), while the reactions conducted at other temperatures suffered either with long reaction times or a loss of yield with no substantial improvement in the enantioselectivity (Table 3, entries 1, 3, and 4).

Having determined the optimal reaction conditions for the Michael addition of isobutyraldehyde **2a** with nitrostyrene **3a**, we next explored the generality of this transformation for other substrate combinations under solvent-free reaction conditions using catalyst **1** (20 mol %) in combination with benzoic acid (10 mol %) at 0 °C. As shown in Tables 4 and 5, all substrate combinations involving variations in nitroolefins **3b**–**k** reacted smoothly with isobutyraldehyde **2a** (Table 4, entries 1–9) and cyclopentanecarboxaldehyde **2b** (Table 5, entries 1–8) under the optimized reaction conditions and the corresponding Michael products **4b**–**j** and **5a**–**h** were obtained in good yields and with high enantioselectivities, regardless of the nature of the substitution pattern in the nitroolefins. However, reactions of nitroolefins with electron donating substitutions were found to be slightly inferior in overall productivity compared to that of electron withdrawing substituents (Tables 4 and 5, entries 4 and 5, respectively). Overall, a good substrate scope was observed for the conjugate addition of α,α-disubstituted aldehydes to nitroolefins using a pyrrolidine-pyrazole catalyst, providing access to a variety of γ-nitrocarbonyl compounds with an all-carbon quaternary center with high enantioselectivities.

The absolute stereochemical outcome of this transformation could be realized by considering the possible transition state[10,11] model as shown in Figure 2. The pyrrolidine ring of the catalyst activates the aldehyde toward enamine formation and the neighboring pyrazole template serves as an efficient stereo-control element, which provides steric coverage and also participates in H-bonding interactions with the nitroolefin by the intermediacy of benzoic acid. The complete arrangement results in a tighter transition state, wherein the nucleophilic enamine attacks the nitroolefin from the *Si* face and leads to the formation of the desired products with high enantioselectivities.

3. Conclusion

In conclusion, we have demonstrated the application of pyrrolidine-pyrazole **1** as an effective organocatalyst for enantioselective Michael additions of α,α-disubstituted aldehydes to nitroolefins. The catalytic protocol was found to be effective in terms of yield and enantioselectivities when performed under solvent-free reaction conditions using 20 mol % of catalyst and 10 mol % of benzoic acid as an additive. Further investigations to extend the scope of this transformation are currently underway in our laboratory.

4. Experimental

4.1. General

All solvents and reagents were purified by standard techniques. Crude products were purified by column chromatography on silica gel of 60–120 mesh. IR spectra were recorded on a Perkin–Elmer 683 spectrometer. Optical rotations were obtained on a Jasco Dip 360 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian Gemini 200 and Bruker Avance 300. Chemical shifts were reported in parts per million with respect to internal TMS. Coupling constants (J) are quoted in Hz. Mass spectra were obtained on an Agilent Technologies LC/MSD Trap SL. Chiral HPLC analysis was carried out on chiral pak OD-H, IC, or IA columns using a mixture of isopropanol and hexanes as the eluent.

4.1.1. General procedure for the Michael addition of α,α-disubstituted aldehydes to nitroolefins

To a mixture of catalyst **1** (20 mol %) and α,α-disubstituted aldehyde (4 mmol) was added PhCOOH (10 mol %) and stirred for 20 min at 0 °C. Next, nitroolefin (1 mmol) was added to the resulting mixture and stirred for the appropriate time (Tables 4 and 5) at 0 °C. After completion of the reaction (monitored by TLC), the mixture was purified by silica-gel column chromatography to afford the desired product. Relative and absolute configurations of the products were determined by comparison of ^{1}H NMR, ^{13}C NMR, and specific rotation values with those reported in the literature.[8]

Acknowledgments

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References

1. (a) Berkessel, A.; Groger, H. *Asymmetric Organocatalysis*; Wiley-VCH: Weinheim, Germany, 2005; (b) Akiyama, T.; Itoh, J.; Fuchibe, K. *Adv. Synth. Catal.* **2006**, *348*, 999–1010; (c) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon: Oxford, 1992; (d) Sakthivel, K.; Notz, W.; Buli, T.; Barbas, C. F., III *J. Am. Chem. Soc.* **2001**, *123*, 5260–5267; (e) List, B.; Pojarliev, P.; Martin, H. J. *Org. Lett.* **2001**, *3*, 2423–2425; (f) Tokoroyama, T. *Eur. J. Org. Chem.* **2010**, 2009–2016; (g) Dondoni, A.; Massi, A. *Angew. Chem.* **2008**, *120*, 4716–4739. *Angew. Chem., Int. Ed.* **2008**, *47*, 4638–4660; (h) Trost, B. M.; Brindle, C. S. *Chem. Soc. Rev.* **2010**, *39*, 1600–1632; (i) Zhang, Y.; Wang, W. *Catal. Sci. Technol.* **2012**, *2*, 42–53; (j) Aleman, J.; Cabrera, S. *Chem. Soc. Rev.* **2013**, *42*, 774–793; (k) Scheffler, U.; Mahrwald, R. *Chem. Eur. J.* **2013**, *19*, 14346–14396.
2. (a) Melchiorre, P.; Marigo, M.; Carlone, A.; Bartoli, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 6138–6171; (b) Yu, X.; Wang, W. *Org. Biomol. Chem.* **2008**, *6*, 2037–2046; (c) Bertelsen, S.; Jorgensen, K. A. *Chem. Soc. Rev.* **2009**, *38*, 2178–2189; (d) Seayad, J.; List, B. *Org. Biomol. Chem.* **2005**, *3*, 719–724; (e) Vicario, J. L.; Badia, D.; Carrillo, L. *Synthesis* **2007**, 2065–2092.
3. For recent reviews on asymmetric Michael additions see: (a) Krause, N.; Hoffmann-Roder, A. *Synthesis* **2001**, 171–196; (b) Berner, O. M.; Tedeschi, L.; Enders, D. *Eur. J. Org. Chem.* **2002**, 1877–1894; (c) Christoffers, J.; Baro, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1688–1690; (d) Notz, W.; Tanaka, F.; Barbas, C. F. III *Acc. Chem. Res.* **2004**, *37*, 580–591; (e) Ballini, R.; Bosica, G.; Fiorini, D.; Palmieri, A.; Petrini, M. *Chem. Rev.* **2005**, *105*, 933–972; (f) Tsogoeva, S. B. *Eur. J. Org. Chem.* **2007**, 1701–1716; (g) Sulzer-Mosse, S.; Alexakis, A. *Chem. Commun.* **2007**, 3123–3135; (h) Krkkila, A.; Majander, I.; Pihko, P. M. *Chem. Rev.* **2007**, *107*, 5416–5470; (i) Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471–5569; (j) Davie, E. A. C.; Mennen, S. M.; Xu, Y.; Miller, S. J. *Chem. Rev.* **2007**, *107*, 5759–5812; (k) Almasi, D.; Alonso, D. A.; Gomez-Bengoa, E.; Negel, Y.; Najera, C. *Eur. J. Org. Chem.* **2007**, 2328–2343; (l) Enders, D.; Wang, C.; Liebich, J. X. *Chem. Eur. J.* **2009**, *15*, 11058–11076.
4. (a) Betancort, J. M.; Barbas, C. F., III *Org. Lett.* **2001**, *3*, 3737–3740; (b) Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2002**, *4*, 3611–3614; (c) Enders, D.; Seki, A. *Synlett* **2002**, 26–28; (d) Andrey, O.; Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2003**, *5*, 2559–2561; (e) Li, H. M.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906–9907; (f) Luo, S.; Xu, H.; Mi, X.; Li, J.; Zheng, X.; Cheng, J. P. *J. Org. Chem.* **2006**, *71*, 9244–9247; (g) Alza, E.; Cambeiro, X. C.; Jimeno, C.; Pericas, M. A. *Org. Lett.* **2007**, *9*, 3717–3720; (h) Cobb, A. J. A.; Longbottom, D. A.; Shaw, D. M.; Ley, S. V. *Chem. Commun.* **2004**, 1808–1809; (i) Cobb, A. J. A.; Longbottom, D. A.; Shaw, D. M.; Gold, J. B.; Ley, S. V. *Org. Biomol. Chem.* **2005**, *3*, 84–96; (j) Cao, C. L.; Ye, M. C.; Sun, X. L.; Tang, Y. *Org. Lett.* **2006**, *8*, 2901–2904; (k) Tsogoeva, S. B.; Wei, S. *Chem. Commun.* **2006**, 1451–1453; (l) Wei, S.; Yalaov, D. A.; Tsogoeva, S. B.; Schmatz, S. *Catal. Today* **2007**, *121*, 151–157; (m) Wang, J.; Li, H.; Lou, B.; Zu, L. S.; Guo, H.; Wang, W. *Chem. Eur. J.* **2006**, *12*, 4321–4332; (n) Zu, L.; Wang, J.; Li, H.; Wang, W. *Org. Lett.* **2006**, *8*, 3077–3079; (o) Wang, J.; Li, H.; Zu, L. S.; Wang, W. *Adv. Synth. Catal.* **2006**, *348*, 425–428; (p) Wang, W.; Wang, J.; Li, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1369–1371; (q) Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H. *J. Am. Chem. Soc.* **2004**, *126*, 9558–9559; (r) Ni, B.; Zhang, Q.; Headley, A. D. *Tetrahedron Lett.* **2008**, *49*, 1249–1252; (s) Xu, D. Z.; Shi, S.; Wang, Y. *Eur. J. Org. Chem.* **2009**, 4848–4853; (t) Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3093–3097; (u) Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. *Chem. Commun.* **2006**, 3687–3689; (v) Xu, D. Q.; Luo, S. P.; Wang, Y. F.; Xia, A. B.; Yue, H. D.; Wang, L. P.; Xu, Z. Y. *Chem. Commun.* **2007**, 4393–4395; (w) Li, H. M.; Wang, Y.; Tang, L.; Wu, F. H.; Liu, X. F.; Guo, C. Y.; Foxman, B. M.; Deng, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 105–108; (x) Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, N. X.; Takemoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 119–125; (y) Tsogoeva, S. B.; Yalalov, D. A.; Hateley, M. J.; Weckbecker, C.; Huthmacher, K. *Eur. J. Org. Chem.* **2005**, 4995–5000.
5. (a) McCooey, S. H.; Connon, S. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6367–6370; (b) Vakulya, B.; Varga, S.; Csampai, A.; Soos, T. *Org. Lett.* **2005**, *7*, 1967–1969; (c) Mosse, S.; Alexakis, A. *Org. Lett.* **2005**, *7*, 4361–4364; (d) Chi, Y. G.; Gellman, S. H. *Org. Lett.* **2005**, *7*, 4253–4256; (e) Hayashi, Y.; Gotho, H.; Hayashi, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4212–4215; (f) Luo, S. Z.; Mi, L. X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3093–3097; (g) Pansare, S. V.; Pandya, K. *J. Am. Chem. Soc.* **2006**, *128*, 9624–9625; (h) Mase, N.; Watanabe, K.; Yoda, H.; Takabe, K.; Tanaka, F.; Barbas, C. F., III *J. Am. Chem. Soc.* **2006**, *128*, 4966–4967; (i) Reyes, E.; Vicario, J. L.; Badia, D.; Carrillo, L. *Org. Lett.* **2006**, *8*, 6135–6138; (j) Vishnumaya; Singh, V. K. *Org. Lett.* **2007**, *9*, 1117–1119; (k) Clarke, M. L.; Fuentes, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 930–933; (l) Chen, H. B.; Wang, Y.; Wei, S. Y.; Sun, J. *Tetrahedron: Asymmetry* **2007**, *18*, 1308–1312; (m) Zhu, S. L.; Yu, S. Y.; Ma, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 545–548; (n) Ban, S. R.; Du, D. M.; Liu, H.; Yang, W. *Eur. J. Org. Chem.* **2010**, 5160–5164; (o) Lu, D. F.; Gong, Y. F.; Wang, W. Z. *Adv. Synth. Catal.* **2010**, *352*, 644–650; (p) Yang, W.; Du, D. M. *Adv. Synth. Catal.* **2011**, *353*, 1241–1246.
6. (a) Ikeda, S.; Shibuya, M.; Kanoh, N.; Iwabuchi, Y. *Org. Lett.* **2009**, *11*, 1833–1836; (b) Pansare, S. V.; Lingampally, R.; Kirby, R. L. *Org. Lett.* **2010**, *12*, 556–559; (c) Ma, H.; Liu, K.; Zhang, F. G.; Zhu, C. L.; Nie, J.; Ma, J. A. *J. Org. Chem.* **2010**, *75*, 1402–1409; (d) Nakamura, A.; Lectard, S.; Hashizume, D.; Hamashima, Y.; Sodeoka, M. *J. Am. Chem. Soc.* **2010**, *132*, 4036–4037; (e) Hong, B. C.; Kotame, P.; Tsai, C. W.; Liao, J. H. *Org. Lett.* **2010**, *12*, 776–779; (f) Krayer, M.; Ptaszek, M.; Kim, H. J.; Meneely, K. R.; Fan, D.; Secor, K.; Lindsey, J. S. *J. Org. Chem.* **2010**, *75*, 1016–1039.
7. (a) Bella, M.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 5672–5673; (b) Rigby, C. L.; Dixon, D. J. *Chem. Commun.* **2008**, 3798–3800; (c) Zhang, Z. H.; Dong, X. Q.; Chen, D.; Wang, C. J. *Chem. Eur. J.* **2008**, *14*, 8780–8783; (d) Li, H.; Song, J.; Liu, X.; Deng, L. *J. Am. Chem. Soc.* **2005**, *127*, 8948–8949.
8. (a) Zhang, X. J.; Liu, S. P.; Li, X. M.; Yan, M.; Chan, A. S. C. *Chem. Commun.* **2009**, 833–835; (b) Lalonde, M. P.; Chen, Y.; Jacobsen, E. N. *Angew. Chem.* **2006**, *118*, 6514–6518. *Angew. Chem., Int. Ed.* **2006**, *45*, 6366–6370; (c) Wang, J.; Li, H.; Lou, B.; Zu, L.; Guo, H.; Wang, W. *Chem. Eur. J.* **2006**, *12*, 4321–4332; (d) Wang, W.; Wang, J.; Li, H. *Angew. Chem.* **2005**, *117*, 1393–1395. *Angew. Chem., Int. Ed.* **2005**, *44*, 1369–1371; (e) Mase, N.; Thayumanavan, R.; Tanaka, F.; Barbas, C. F., III *Org. Lett.* **2004**, *6*, 2527–2530; (f) Sato, A.; Yoshida, M.; Hara, S. *Chem. Commun.* **2008**, 6242–6244; (g) McCooey, S. H.; Connon, S. J. *Org. Lett.* **2007**, *9*, 599–602; (h) Chang, C.; Li, S. H.; Reddy, R. J.; Chen, K. *Adv. Synth. Catal.* **2009**, *351*, 1273–1278; (i) Chen, J. R.; Cao, Y. J.; Zou, Y. Q.; Tan, F.; Fu, L.; Zhu, X. Y.; Xiao, W. J. *Org. Biomol. Chem.* **2010**, *8*, 1275–1279; (j) He, T.; Gu, Q.; Wu, X. Y. *Tetrahedron* **2010**, *66*, 3195–3198; (k) Chen, J. R.; Zou, Y. Q.; Fu, L.; Ren, F.; Tan, F.; Xiao, W. J. *Tetrahedron* **2010**, *66*, 5367–5372; (l) Nugent, T. C.; Bibi, A.; Sadiq, A.; Shoaib, M.; Umar, M. N.; Tehrani, F. N. *Org. Biomol. Chem.* **2012**, *10*, 9287–9294; (m) Avila, A.; Chinchilla, R.; Fiser, B.; Gomez-Bengoa, E.; Najera, C. *Tetrahedron: Asymmetry* **2014**, *25*, 462–467; (n) Junpeng, H.; Qiankun, C.; Bukuo, N. *Tetrahedron Lett.* **2014**, *55*, 3030–3032.
9. (a) Chandrasekhar, S.; Mallikarjun, K.; Reddy, G. P. K.; Rao, K. V.; Jagdeesh, B. *Chem. Commun.* **2009**, 4985–4987; (b) Chandrasekhar, S.; Tiwari, B.; Parida, B. B.; Rajireddy, C. *Tetrahedron: Asymmetry* **2008**, *19*, 495–499; (c) Chandrasekhar, S.; Johny, K.; Rajireddy, Ch. *Tetrahedron: Asymmetry* **2009**, *20*, 1742–1745; (d) Chandrasekhar, S.; Kumar, T. P.; Haribabu, K.; Rajireddy, Ch. *Tetrahedron: Asymmetry* **2010**, *21*, 2372–2375; (e) Chandrasekhar, S.; Kumar, T. P.; Haribabu, K.; Rajireddy, Ch.; Kumar, C. R. *Tetrahedron: Asymmetry* **2011**, *22*, 697–702; (f) Kumar, T. P.; Vavle, N. C.; Patro, V.; Haribabu, K. *Tetrahedron: Asymmetry* **2014**, *25*, 457–461; (g) Kumar, T. P.; Balaji, S. V. *Tetrahedron: Asymmetry* **2014**, *25*, 473–477.
10. (a) Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, *299*, 1691–1693; (b) Hayashi, Y.; Gotoh, H.; Hayashi, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4212–4215.
11. (a) Seebach, D.; Golinski, J. *Helv. Chem. Acta* **1981**, *64*, 1413–1423; (b) Betancort, J. M.; Sakthivel, K.; Thayumanavan, R.; Tanaka, F.; Barbas, C. F., III *Synthesis* **2004**, 1509–1521; (c) Ting, Y. F.; Chang, C.; Reddy, R. J.; Magar, D. R.; Chen, K. *Chem. Eur. J.* **2010**, *16*, 7030–7038.