# Organic & Biomolecular Chemistry

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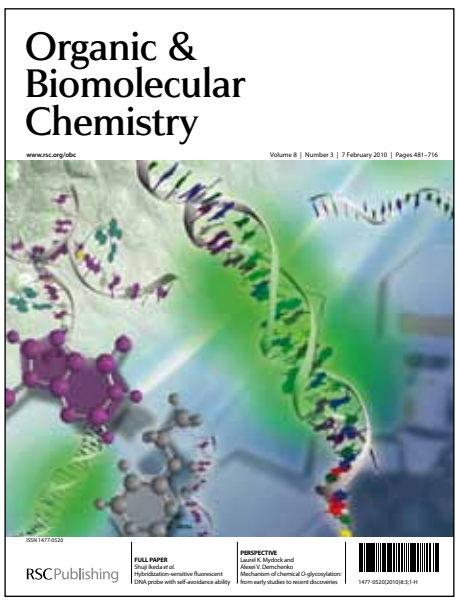


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# Highly Enantioselective Darzens Reaction between Diazo-Acetamides and Aldehydes Catalyzed by A (+)-Pinanediol-Ti($O^iPr$)$_4$ System

**Gang Liu,[a] Daming Zhang,[a] Jian Li,[a] Guangyang Xu[a] and Jiangtao Sun[a,*]**

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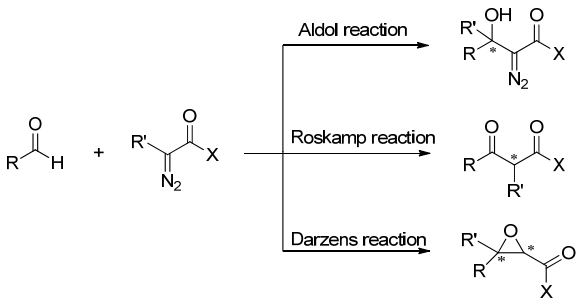
**A highly efficient enantioselective Darzens reaction of aldehydes with diazoacetamides catalyzed by a (+)-Pinanediol and Ti($O^iPr$)$_4$ has been developed. The *cis*-glycidic amides were obtained in high yields and with moderate to excellent enantioselectivity (up to 99%).**

Optically pure epoxides have been recognized as one of the most important chiral synthons in organic synthesis and substructures in natural products and pharmaceuticals.[1,2] Chiral glycidic esters and amides, as important types of epoxides, have broad applications because they can easily be converted to various target molecules just by simple transformation.[3] To access these compouds, many elegant approaches have been developed, including the asymmetric catalytic epoxidation of $\alpha$, $\beta$-unsaturated carbonyl compounds. However, asymmetric epoxidation of alkene catalyzed by organocatalysts or Lewis acids,[4] to some extent, have some limits because the alkene precursors have to be prepared in advance. So in order to broaden the substrate generality as well as to explore other efficient methods, many efforts have been made to achieve this goal.

Among the methods developed, the Darzens reaction offers an elegant way to achieve this goal by using readily available aldehydes as the substrates.[5] Using chiral phase transfer catalysts, Arai *et al*[6] and Bakó *et al*[7] realized the asymmetric Darzens reaction between phenacyl chloride and aldehydes with moderate enantioselectivity. In 2011, Deng and co-workers found 6'-OH cinchonium salts can catalyze the Darzens reaction more efficiently with high enantioselectivity.[8] For the Lewis acids catalyzed asymmetric Darzens reaction, North and co-workers utilized a chiral cobalt complex as catalyst to give the epoxy esters with moderate diastereo-selectivity and enantioselectivity.[9] By using stoichiometric amounts of camphor-derived sulfonium salts, Aggarwal and co-workers reported the synthesis of *trans*-glycidic amides with high enantioselectivity.[10] In 2009, a breakthrough was made by Gong and co-workers, which reported the highly enantioselective Darzens reaction between diazoacetamides and aldehydes with a simple and efficient catalytic system.[11a] Later, they also reported that a 3,3'-di-iodobinaphthol based zirconium complex could catalyze this reaction with excellent results.[11b]




**Scheme 1**. The reaction of diazo carbonyl compounds with aldehydes

Diazo compounds have been widely used in organic transformations for decades.[12] Generally, the reaction of diazo carbonyl compounds and aldehydes can proceed in three different ways, namely the Aldol reaction, Roskamp reaction and Darzens reaction, which generate the corresponding diazo alcohols, dicarbonyl compounds and epoxides respectively (Scheme 1). However, the competition of the three rearrangement pathways often leads to poor chemoselectivity. Moreover, the major product of the reaction depends on the types of substrates and Lewis acids used as well as other reaction conditions. Wang *et al*[13] and Trost *et al*[14] reported the asymmetric Aldol-type reaction between $\alpha$-H-diazoacetates and aldehydes using chiral Zr($O^tBu$)$_4$ and $Bu_2Mg$ based complexes. Feng *et al* disclosed an asymmetric Roskamp-type reaction between $\alpha$-alkyl-diazoesters with aromatic aldehydes using chiral *N*,*N*'-dioxide-scandium(III) complexes.[15] Just recently, Hwang and Ryu developed a highly enantioselective Roskamp reaction of $\alpha$-alkyl diazoesters with aldehydes using an oxazaborolidinium ion.[16] In addition, as reported by Wulff *et al*[17] and Maruoka *et al*[18], when *N*-Boc imines instead of aldehydes reacted with diazo compounds, the chiral Mannich-type products (chiral aziridines) were obtained. Inspired by the above outcomes, we considered whether it is possible to initiate the Darzens-type reaction using an appropriate chiral catalytic system. Herein, we wish to report a highly enantioselective Darzens reaction between aldehydes and diazoacetamides catalyzed by a readily accessible (*1S, 2S, 3R, 5S*)-(+)-Pinanediol /titanium (IV) complex, which yields the *cis*-glycidic amides in good yields and with moderate to excellent enantioselectivity.

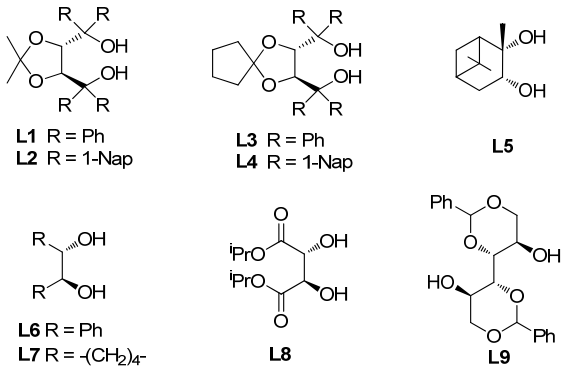
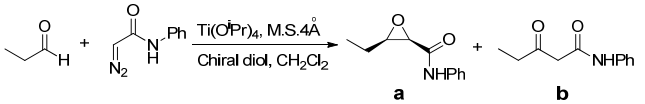



**Fig 1**. Chiral diols utilized in the asymmetric Darzens reaction

Initially, we examined the reaction of *N*-phenyl-diazoacetamide with propionaldehyde in the presence of molecular sieves 4Å at 0°C in dichloromethane using different chiral titanium complexes, which formed in situ from various chiral diols and $Ti(O^iPr)_4$ (Figure 1). Unexpectedly, chiral TADDOL ligands (**L1-L4**) showed lower reactivity and very low enantioselectivity (Table 1, entries 1 to 4). The chiral 1,2-vicinal diols (**L6-L8**) gave low enantioselectivity too (Table 1, entries 6 to 8). The mannitol derivative ligand **L9** gave moderate yield and very low enantioselectivity (Table 1, entry 9). To our delight, the reaction went smoothly and furnished the *cis*-glycidic amide in high yield (92%) with high enantioselectivity (93% ee) when chiral pinanediol (**L5**) was used (Table 1, entry 5). Significantly, these reactions exhibited excellent chemoselectivity and no formation of Aldol-type products and only small amounts of Roskamp-type products were detected in some cases.

**Table 1** Asymmetric Darzens reaction of propionaldehyde with diazoacetamide using various diol/Ti complexes[a]




| Entry | Ligand | Yield (%)[b] | Ee (%)[c] |
|---|---|---|---|
| 1 | **L1** | 69(5) | <5 |
| 2 | **L2** | 76(5) | <5 |
| 3 | **L3** | 72(2) | 29 |
| 4 | **L4** | 76(3) | 18 |
| 5 | **L5** | 92(-) | 93 |
| 6 | **L6** | 86(-) | 38 |
| 7 | **L7** | 84(-) | 52 |
| 8 | **L8** | 71(7) | 17 |
| 9 | **L9** | 52(14) | <5 |

[a] Unless otherwise noted, all reactions were carried out with $CH_3CH_2CHO$ (1.2 mmol), diazoacetamide (1 mmol), $Ti(O^iPr)_4$ (0.1 mmol), chiral ligand (0.12 mmol) and M.S. 4Å (150 mg) in $CH_2Cl_2$ (5 mL) at 0°C for 12 hours. [b]Isolated yield of **a** based on diazoacetamide. The number in the parenthesis is the percentage of **b** in crude products. [c]Determined by chiral HPLC analysis on a chiral stationary phase; The configuration was determined by comparison of the specific optical rotation with literature.[11]

Based upon the above results, we then used (+)-Pinanediol (**L5**)/$Ti(O^iPr)_4$ for further investigations. Firstly, we found that additives play an important role in the reaction. Both 4Å molecular sieves and $MgSO_4$ (Table 2, entries 2 and 3) gave positive effect on the yield and the enantioselectivity. Without any additive, moderate yield and moderate enantioselectivity was obtained (Table 2, entry 1). Next, a solvent screen showed dichloromethane was the best one according to the yield and enantioselectivity. Acetonitrile gave similar enantioselectivity but a little lower yield (Table 2, entry 8). Lowering the catalyst loading resulted in a slower reaction with diminished enantioselectivity (Table 2, entry 11). In addition, as a competitive reaction, the Darzens-type product and Roskamp-type product were measured by $^1$H-NMR analysis of the crude products. Obviously, different solvents gave different amounts of the Roskamp-type compound. Under the same reaction condition, higher temperature resulted in lower enantioselectivity and a small amount of Roskamp-type product 3-carbonyl-*N*-phenylpentanamide was detected (Table 2, entry 10). So lower temperature is essential for high chemoselectivity. Notably, when the reaction was carried out at -10°C in $CH_2Cl_2$, good yield and excellent enantioselectivity were observed, and no Roskamp-type product detected (98.2% ee, Table 2, entry 9), which means the reaction can be converted completely in 12 hours at -10°C with excellent chemoselectivity. Moreover, this reaction exhibited excellent diastereoselectivity and no *trans*-diastereomer was detected by $^1$H NMR analysis of the crude product. So we choose -10°C as the standard temperature for further investigations.

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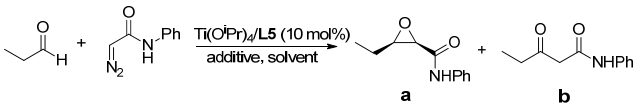
**Table 2** Asymmetric Darzens reaction of propionaldehyde with diazoacetamide using **L5**/Ti complexes[a]



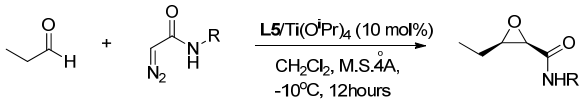

| Entry | Additive | Solvent | Yield (%)[b] | Ee (%)[c] |
|---|---|---|---|---|
| 1 | - | $CH_2Cl_2$ | 77(6) | 66.4 |
| 2 | M.S.4Å | $CH_2Cl_2$ | 92(-) | 93.2 |
| 3 | $MgSO_4$ | $CH_2Cl_2$ | 91(2) | 91.1 |
| 4 | M.S.4Å | $CHCl_3$ | 82(-) | 52.5 |
| 5[d] | M.S.4Å | Toluene | 56(8) | 61.2 |
| 6[d] | M.S.4Å | THF | 52(7) | 47.8 |
| 7 | M.S.4Å | DCE | 66(9) | 80.5 |
| 8 | M.S.4Å | $CH_3CN$ | 88(2) | 92.3 |
| 9[e] | M.S.4Å | $CH_2Cl_2$ | 92(-) | 98.2 |
| 10[f] | M.S.4Å | $CH_2Cl_2$ | 93(4) | 82.4 |
| 11[g] | M.S.4Å | $CH_2Cl_2$ | 80(-) | 93.1 |

[a] Unless otherwise noted, all reactions were carried out with $CH_3CH_2CHO$ (1.2 mmol), diazoacetamide (1 mmol), $Ti(O^iPr)_4$ (0.1 mmol), **L5** (0.12 mmol) in 5 mL solvent at 0°C for 12 hours. [b] Isolated yield. The number in the parenthesis is the percentage of **b** in crude products. [c] Determined by chiral HPLC analysis on a chiral stationary phase. The configuration was determined by comparison of the specific optical rotation with literature.[11] [d] Reaction time is 24 hours. [e] The reaction was carried out at -10°C. [f] The reaction was carried out at 25°C for 4 hours. [g] $Ti(O^iPr)_4$ (5 mmol%) and **L5** (6 mmol%) were used and the reaction time was 24 hours.

The influence of different substituted diazoacetamides was next investigated. The results were summarized in table 3. When *N*-(*p*-methoxylphenyl) and *N*-(*p*-chlorophenyl)-diazoacetamide were used as the diazo substrate, they all gave poor yields and low enantioselectivity (Table 3, entries 1 and 2). Moreover, the *N*-benzyl-diazoacetamide reacted sluggishly with aldehyde and only gave a trace amount of Darzens reaction product (Table 3,

entry 3). So we choose *N*-phenyl-diazoacetamide as the standard substrate for further investigations.

**Table 3** Asymmetric Darzens reaction of propionaldehyde with diazoacetamide using **L5**/Ti complexes[a]

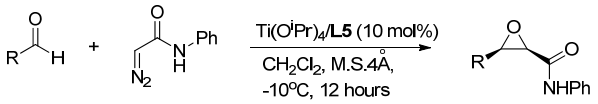


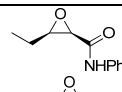
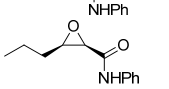
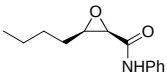
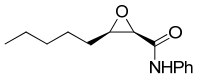
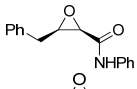
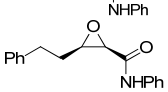
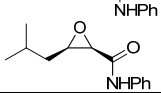
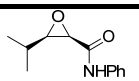
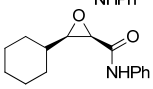

| Entry | R | Yield (%)[b] | Ee (%)[c] |
|---|---|---|---|
| 1 | *p*-ClPh | 49 | 58.6 |
| 2 | *p*-$CH_3OPh$ | 68 | 79.2 |
| 3 | Bn | trace | - |

[a] Unless otherwise noted, all reactions were carried out with $CH_3CH_2CHO$ (1.2 mmol), diazoacetamide (1.0 mmol), $Ti(O^iPr)_4$ (0.1 mmol), **L5** (0.12 mmol) and M.S. 4Å (150 mg) in $CH_2Cl_2$ (5 mL) at -10°C for 12 hours. [b] Isolated yield. [c] Determined by chiral HPLC analysis on a chiral stationary phase. The configuration was determined by comparison of the specific optical rotation with literature.[11]

Under the optimized reaction conditions, a series of aliphatic aldehydes were investigated. As shown in Table 4, with 10 mol% catalyst, all of the aldehydes reacted smoothly with *N*-phenyl-diazoacetamide, delivering the corresponding epoxy products in good yields and with excellent enantioselectivity. Moreover, we did not find any Roskamp-type products under these reaction conditions. The highest ee value was obtained when *n*-butyraldehyde used (99.1% ee; Table 4, entry 2). Besides the linear aliphatic aldehydes, even for the more sterically hindered branched aldehydes, excellent enantioselectivity was observed too (Table 4, entries 8 and 9).

**Table 4** Asymmetric Darzens reaction of *N*-phenyl-diazoacetamide with different aliphatic aldehydes[a]

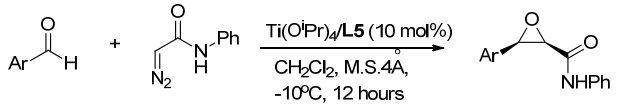


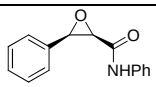
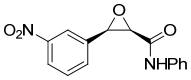
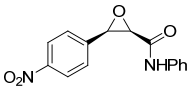
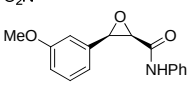
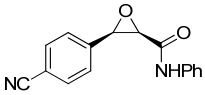
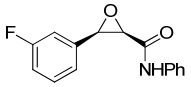
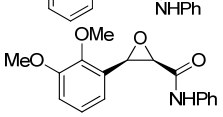
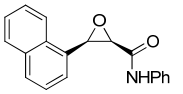
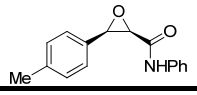

| Entry | Products | Yield (%)[b] | Ee (%)[c] |
|---|---|---|---|
| 1 |  | 92 | 98.2 |
| 2 |  | 90 | 99.1 |
| 3 |  | 91 | 97.1 |
| 4 |  | 88 | 96.7 |
| 5 |  | 83 | 95.4 |
| 6 |  | 84 | 97.7 |
| 7 |  | 81 | 97.7 |
| 8 |  | 83 | 98.1 |
| 9 |  | 85 | 96.2 |

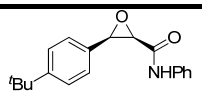
[a] All reactions were carried out with RCHO (1.2 mmol), *N*-phenyl-diazoacetamide (1 mmol), $Ti(O^iPr)_4$ (0.1 mmol), **L5** (0.12 mmol), M.S. 4Å (150 mg) in $CH_2Cl_2$ (5 mL) at -10°C for 12 hours. [b] Isolated yield based on diazoacetamide. [c] Determined by chiral HPLC analysis on a chiral stationary phase. The configurations were determined by comparison of the specific optical rotation with literature and the others were assigned by analogy.[11]

We next utilized different aromatic aldehydes as substrates under the optimized reaction conditions. As shown in Table 5, the Darzen-type products were obtained in good yields and with moderate to high ee values. Generally, benzaldehyde derivatives bearing electron-withdrawing substituents at the *para* or *meta* position in the phenyl ring or neutral aromatic aldehydes provided *cis*-epoxides in high yields and with high enantioselectivity (Table 5, entries 2 to 6), the highest ee value was obtained with *p*-Nitro-benzaldehyde (95.2% ee, entry 3). Electron-rich aromatic aldehydes also participated in clean Darzens reactions gave the *cis*-epoxides with moderate to high enantioselectivity and in moderate yields (Table 5, entries 8 to 10). Also, no Roskamp-type products formed.

**Table 5** Asymmetric Darzens reaction of *N*-phenyl-diazoacetamide with different aromatic aldehydes[a]




| Entry | Products | Yield (%)[b] | Ee (%)[c] |
|---|---|---|---|
| 1 |  | 81 | 85.1 |
| 2 |  | 90 | 88.5 |
| 3 |  | 88 | 95.2 |
| 4 |  | 83 | 92.6 |
| 5 |  | 84 | 92.5 |
| 6 |  | 78 | 89.2 |
| 7 |  | 81 | 73.6 |
| 8 |  | 67 | 70.4 |
| 9 |  | 76 | 84.3 |

| | | | |
|---|---|---|---|
| 10 |  | 73 | 82.1 |

[a] All reactions were carried out with ArCHO (1.2 mmol), *N*-phenyl-diazoacetamide (1 mmol), $Ti(O^iPr)_4$ (0.1 mmol), **L5** (0.12 mmol), M.S. 4Å (150 mg) in $CH_2Cl_2$ (5 mL) at -10°C for 12 hours. [b] Isolated yields based on diazoacetamide. [c] Determined by chiral HPLC analysis on a chiral stationary phase; The configurations were determined by comparison of the specific optical rotation with literature and the others were assigned by analogy.[11]

In conclusion, we have developed an excellent enantioselective and chemoselective Darzens reaction between aldehydes and diazoacetamides catalyzed by a chiral titanium complex formed in situ from commercially available (+)-Pinanediol and $Ti(O^iPr)_4$. When aliphatic aldehyes were used, the *cis*-glycidic amides were obtained in good yields (up to 92%) and with excellent enantioselectivity (up to 99% ee). For the aromatic aldehydes, the Darzens reaction products were obtained in good yields and with moderate to high enantiomeric purities. Compared with Gong's BINOL/Ti system,[11a] our system showed better yields and slightly better enantioselectivities for some aliphatic aldehydes, but lower enantioselectivities for most of the aromatic aldehydes. Under the optimized reaction condition, no Roskamp-type products formed for all of the cases. Also, no *trans*-diastereomer was detected by $^1H$ NMR analysis of the crude products. Currently, we are investigating other catalytic systems in the asymmetric Darzens reaction.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [details of experiment procedures, all of the spectra data of the compounds]. See DOI: 10.1039/b000000x/

1 For reviews, see: a) Q. Xia, H. Ge, C. Ye, Z. Liu, K. Su, *Chem. Rev*. 2005, **105**, 1603-1662; b) E. M. McGarrigle, E. L. Myers, O. Illa, M. A. Shaw, S. L. Riches, V. K. Aggarwal, *Chem. Rev*. 2007, **107**, 5841-5883; c) O. A. Wong, Y. Shi, *Chem. Rev*. 2008, **108**, 3958-3987.

2 P. H. Milner, N. J. Gilpin, S. R. Speat, D. S. Eggleston, *J. Nat. Prod*. 1996, **59**, 400-402.

3 For a review, see: D. Diez, M. G. Nunez, A. B. Anton, P. Garcia, R. F. Moro, N. M. Garrido, I. S. Marcos, P. Basabe, J. G. Urones, *Curr. Org. Synth*. 2008, **5,** 186-216.

4 a) T. Nemoto, H. Kakei, V. Gnanadesikan, S. Tosaki, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* 2002, **124**, 14544-14545; b) S. Tosaki, R. Tsuji, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* 2005, **127**, 2145-2155; c) H. Kakei, R. Tsuji, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* 2005, **127**, 8962-8963; d) L. Deng, E. N. Jacobsen, *J. Org. Chem*. 1992, **57**, 4320-4323.

5 For a review, see: T. Rosen, in *Comprehensive Organic Synthesis*, *Vol. 2* (Eds.; B. M. Trost, I. Fleming, H. Heathcock), Pegamon, Oxford, 1991, 409-439.

6 a) S. Arai, T. Shioiri, *Tetrahedron Lett*. 1998, **39**, 2145-2148; b) S. Arai, T. Ishida, T. Shioiri, *Tetrahedron Lett*. 1998, **39**, 8299-8302; c) S. Arai, Y. Shirai, T. Ishida, T. Shioiri, *Tetrahedron* 1999, **55**, 6375-6386; d) S. Arai, T. Shioiri, *Tetrahedron* 2002, **58**, 1407-1413; e) S. Arai, K. Tokumaru, T. Aoyama, *Tetrahedron Lett*. 2004, **45**, 1845-1848; f) S. Arai, Y. Shirai, T. Ishida, T. Shioiri, *Chem. Comm*. 1999, 49-50.

7 a) A. Bakó, P. Bombicz, L. Tõke, *Synlett* 1997, 291-292; b) A. Bakó, K. Vizárdi, L. Tõke, *Chem. Comm*. 1998, 1193-1195; c) A. Bakó, K. Vizárdi, S. Toppet, E. Van der Eycken, G. J. Hoornaert, L. Tõke, *Tetrahedron* 1998, **54**, 14975-14988; d) P. Bakó, A. Makó, G. Keglevich, M. Kubinyi, K. Pál, *Tetrahedron: Asymmetry* 2005, **16**, 1861-1871.

8 Y. Liu, B. A. Provencher, K. J. Bartelson, L. Deng, *Chem. Sci.* 2011, **2**, 1301-1304.

9 T. J. R. Achard, Y. N. Belokon, M. Ilyin, M. Moskalenko, M. North, F. Pizzato, *Tetrahedron Lett.* 2007, **48**, 2965-2969.

10 a) V. K. Aggarwal, G. Hynd, W. Picoul, J. -L. Vasse, *J. Am. Chem. Soc*. 2002, **124**, 9964-9965; b) V. K. Aggarwal, J. P. H. Charmant, D. Fuentes, J. N. Harvey, G. Hynd, D. Ohara, W.; Picoul, R. Robiette, C. Smith, J. L. Vasse, C. L. Winn, *J. Am. Chem. Soc*. 2006, **128**, 2105-2114.

11 a) W. J. Liu, B. D. Lv, L. Z. Gong, *Angew. Chem. Int. Ed*. 2009, **48**, 6503-6506; b) L. He, W. J. Liu, L. Ren, T. Lei, L. Z. Gong, *Adv. Synth. Catal*. 2010, **352**, 1123-1127.

12 For reviews see: a) A. Padwa, S. F. Hornbuckle, *Chem. Rev*. 1991, **91**, 263-309; b) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev*. 2003, **103**, 2861-2903; c) Y. Zhang, J. Wang, *Chem. Comm*. 2009, 5350-5361; d) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev*. 2010, **110**, 704-724.

13 W. Yao, J. Wang, *Org. Lett*. 2003, **5**, 1527-1530.

14 a) B. M. Trost, S. Malhotra, B. A. Fried. *J. Am. Chem. Soc*. 2009, **131**, 1674-1675; b) B. M. Trost, S. Malhotra, P. Koschker, P. Ellerbrock, *J. Am. Chem. Soc*. 2012, **134**, 2075-2084.

15 W. Li, J. Wang, X. Hu, K. Shen, W. Wang, Y. Chu, L. Lin, X. Liu, X. Feng, *J. Am. Chem. Soc.* 2010, **132**, 8532-8533.

16 L. Gao, B. C. Kang, G.-S. Hwang, D. H. Ryu, *Angew. Chem. Int. Ed*. 2012, **51**, 8322.

17 a) A. A. Desai, W. D. Wulff, *J. Am. Chem. Soc*. 2010, **132**, 13100-13103; b) M. J. Vetticatt, A. A. Desai, W. D. Wulff, *J. Am. Chem. Soc*. 2010, **132**, 13104-13107; c) G. Hu, A. K. Gupta, M. Mukherjee, W. D. Wulff, *J. Am. Chem. Soc*. 2010, **132**, 14669-14675; d) L. Huang, W. D. Wulff, *J. Am. Chem. Soc*. 2011, **133**, 8892-8895.

18 a) T. Hashimoto, N. Uchiyama, K. Maruoka, *J. Am. Chem. Soc*. 2008, **130**, 14380-14381; b) T. Hashimoto, H. Nakatsu, K. Yamamoto, K. Maruoka, *J. Am. Chem. Soc*. 2011, **133**, 9730-9733; c) T. Hashimoto, H. Miyamoto, Y. Naganawa, K. Maruoka, *J. Am. Chem. Soc*. 2009, **131**, 11280-11281.