

Synthesis of chiral *N*-phosphinyl α -imino esters and their application in asymmetric synthesis of α -amino esters by reduction

Yiwen Xiong¹, Haibo Mei^{1,2}, Lingmin Wu¹, Jianlin Han^{*1,2,3}, Yi Pan^{*1}
and Guigen Li^{2,4}

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Address:

¹School of Chemistry and Chemical Engineering, State of Key Laboratory of Coordination, Nanjing University, Nanjing, 210093, China, ²Institute for Chemistry & BioMedical Sciences, Nanjing University, Nanjing, 210093, China, ³High-Tech Research Institute of Nanjing University, Changzhou, 213164, China and ⁴Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, 79409-1061, USA

Email:

Jianlin Han* - hanjl@nju.edu.cn; Yi Pan* - yipan@nju.edu.cn

* Corresponding author

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Abstract

A variety of chiral *N*-phosphinyl α -imino esters have been synthesized for the first time from ketoesters and phosphinylamide, which were then reduced by L-selectride to give the corresponding *N*-phosphinyl-protected α -amino esters. The reduction proceeded very well with excellent chemical yields (88–98%) as well as high diastereoselectivities (96:4 to 99:1). Some of these products could be obtained without column chromatography and recrystallization. The chiral phosphinyl auxiliary could be easily cleaved under acidic conditions.

Introduction

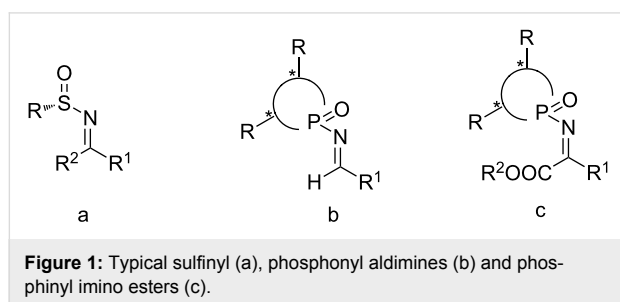
α -Imino esters play a very important role in the field of imine chemistry [1-3], because the ester group can serve as an activator to enhance the reactivity of the C=N double bond, thus making the following nucleophilic addition easier [4,5]. More attractively, the transformation of α -imino esters can provide an easy access to various natural and unnatural α -amino acid esters [6-10]. Up to now, a series of nucleophilic substrates have been

reported to react with α -imino esters, such as enamine [11-14], carbamate ammonium ylide [15], 1,3-dipolar cycle [16], boronic acid [17], acetylide [18], propargylic anion [19] and ketene silyl acetal [20]. These resulted α -amino acid derivatives are useful building blocks in modern organic synthetic and medicinal chemistry [21,22]. For example, we can easily find the active participation of α -imino esters in the total synthesis of

the bioactive molecule fumimycin [23]. Moreover, α -amino acids are the most general fragments constituting peptides and proteins, especially for human insulin [24–28].

One of the most straightforward methods to prepare α -amino esters is the direct reduction of α -imino esters [29,30]. Several heterocycle-based reduction reagents have been developed for this transformation in the past years [31–35]. They usually served as mild hydrogen donors, but the use of them also made the purification difficult at the same time. Hydrogen gas is a traditional reduction source [36] and silanes and boranes are also well documented as the choices of reduction reagents [37–39].

Recently, our groups have developed a new type of chiral phosphonyl auxiliaries for imines [40–44]. Compared with the reported sulfinyl auxiliaries (Figure 1a) [45–48], the phosphonyl ones exhibited advantages in the concise preparation method from readily available starting materials, an easy modification of the auxiliary and a highly diastereoselective control. Furthermore, the phosphonyl auxiliaries can do favor in the final purification, and it did not need any column chromatography or recrystallization, which was summarized as GAP (group assisted purification) [49–51]. So far, a number of *N*-phosphonyl aldimines (Figure 1b) have been synthesized and successfully used in many asymmetric additions [52–54]. In our continuous efforts on the chiral *N*-phosphonyl imine chemistry, we tried to develop novel *N*-phosphinyl protected α -imino esters and to use them for the asymmetric synthesis of α -amino esters. Herein, we report for the first time the synthesis of *N*-phosphinyl-protected α -imino esters (Figure 1c), followed by the reduction of these α -imino esters by L-selectride, to give the corresponding α -amino esters with excellent yields (88–98%) and virtually complete diastereoselectivities.

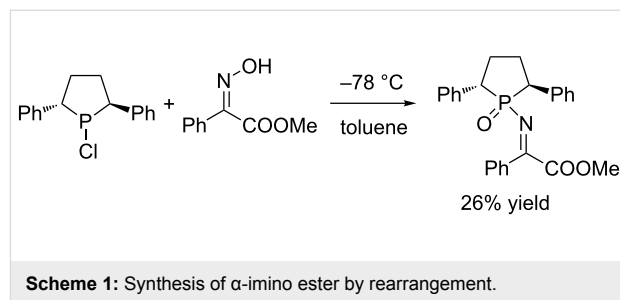


Results and Discussion

Preparation of the *N*-phosphinyl-protected α -imino esters

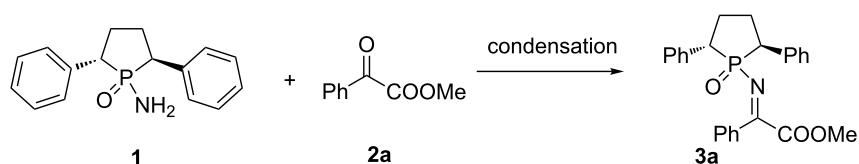
After screening the classical procedures for the synthesis of α -imino esters [3,55,56], we initially tried an approach with chlorophosphine and ester oxime as starting materials, which

proceeded through rearrangement at low temperature (Scheme 1). ^{31}P NMR and TLC of the crude product disclosed that several byproducts formed in this system. The isolation of the *N*-phosphinyl α -imino esters was very difficult and only 26% isolated yield of this product was obtained.



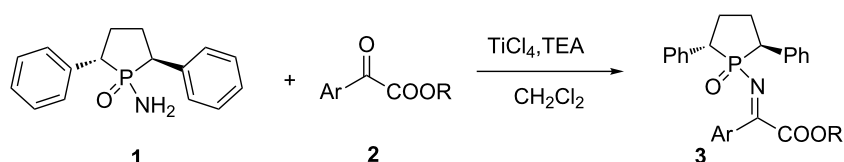
This unacceptable result shifted our attention to the previously reported methods for the preparation of *N*-phosphonyl aldimines, which was the condensation between aldehyde and phosphonyl amide [40,41]. Then, we carried out the optimization of the reaction conditions for the condensation of keto-ester **2a** and phosphinyl amide **1** (Table 1). Common dehydrating reagents, like 4 Å molecular sieves and magnesium sulfate, resulted in no desired product neither at room temperature nor under reflux (Table 1, entries 1–4). Very poor chemical yields of α -imino ester **3a** were detected when tetraethoxytitanium or tetraisopropoxytitanium was used as condensing reagent (Table 1, entries 5–8). Further treatment with titanium tetrachloride/triethyl amine gave a positive result and 46% chemical yield was obtained (Table 1, entry 9). Then, further investigation revealed that the best yield (47%) was observed when the reaction was conducted in the presence of $\text{TiCl}_4/\text{Et}_3\text{N}$ at room temperature for 12 h (Table 1, entries 9–16). ^{31}P NMR of the crude product predicted almost complete consumption of phosphinyl amide **1** but yields were very low. After careful study, we found that the obtained α -imino ester was not stable and decomposed slowly along with column chromatography purification and storage. For this reason, this α -imino ester was directly used in the following reaction after column chromatography to avoid decomposition.

With the optimized conditions in hand, we then used varieties of keto-esters **2** as starting materials for the preparation of chiral α -imino esters **3** (Table 2). As shown in Table 2, modest yields were obtained (29–59%) for all the cases. In general, electron-deficient substrates performed better and the best yield was found for the substrate with *para*-fluoro substituent (Table 2, entry 4). The substrate with *ortho*-substituent led to lower yield due to steric effects (Table 2, entry 7). Besides, the reaction with ethyl ester also worked well and resulted in a slightly lower yield (Table 2, entry 11).

Table 1: Optimization of the synthesis of α -imino ester **3a** by the condensation method.^a

entry	reagent	T (°C)	solvent	time (h)	yield (%) ^b
1	4 Å MS	rt	CH ₂ Cl ₂	24	NR
2	4 Å MS	reflux	CH ₂ Cl ₂	24	NR
3	MgSO ₄	rt	CH ₂ Cl ₂	24	NR
4	MgSO ₄	reflux	CH ₂ Cl ₂	24	NR
5	Ti(OEt) ₄ /Et ₃ N	rt	CH ₂ Cl ₂	24	trace
6	Ti(OEt) ₄ /Et ₃ N	reflux	CH ₂ Cl ₂	24	trace
7	Ti(OEt) ₄ /Et ₃ N	reflux	toluene	24	10
8	Ti(OiPr) ₄ /Et ₃ N	reflux	CH ₂ Cl ₂	24	trace
9	TiCl ₄ /Et ₃ N	rt	CH ₂ Cl ₂	24	46
10	TiCl ₄ /Et ₃ N	rt	CH ₂ Cl ₂	12	47
11	TiCl ₄ /Et ₃ N	rt	CH ₂ Cl ₂	6	33
12	TiCl ₄ /Et ₃ N	reflux	CH ₂ Cl ₂	12	21
13	TiCl ₄ /Et ₃ N	rt	Et ₂ O	12	20
14	TiCl ₄ /Et ₃ N	rt	THF	12	29
15	TiCl ₄ /Et ₃ N	rt	toluene	12	11
16	TiCl ₄ /DIPEA	rt	CH ₂ Cl ₂	12	31

^aRearrangement conditions: Phosphinyl amide **1** (0.5 mmol), ketoester **2a** (1.0 mmol), solvent (3.0 mL); ^bisolated yields.

Table 2: Synthesis of *N*-phosphinyl-protected α -imino esters^a.

entry	Ar	R	product	yield (%) ^b
1	C ₆ H ₅	Me	3a	47
2	4-BrC ₆ H ₄	Me	3b	50
3	4-ClC ₆ H ₄	Me	3c	49
4	4-FC ₆ H ₄	Me	3d	59
5	3-FC ₆ H ₄	Me	3e	53
6	3-CH ₃ C ₆ H ₄	Me	3f	40
7	2-CH ₃ C ₆ H ₄	Me	3g	38
8	3,5-Cl ₂ C ₆ H ₃	Me	3h	29
9	2-Naphthyl	Me	3i	26
10	4-Ph-C ₆ H ₄	Me	3j	35
11	C ₆ H ₅	Et	3k	43

^aReaction conditions: Phosphinyl amide **1** (0.5 mmol), ketoester **2** (1.0 mmol), titanium(IV) chloride (0.5 mmol), triethylamine (2.0 mmol), dichloromethane (4.0 mL), rt for 12 h; ^bisolated yields.

Optimization of the asymmetric reduction reaction conditions

Then, the obtained chiral *N*-phosphinyl α -imino esters were used for the asymmetric synthesis of α -amino esters through reduction. The reduction condition scan was firstly focused on the examination of reductants. A number of reductants, including Hantzsch ester, silanes, organoaluminum and boranes were tested in the system. Unfortunately, silanes failed to trigger the reduction (Table 3, entries 2 and 3). Hantzsch ester and DIBAL were also not suitable for this reduction, and almost no desired product was obtained (Table 3, entries 1 and 5). Lithium triethylborohydride (Table 3, entry 4) and sodium borohydride (Table 3, entry 6) were decent choices, giving modest yields and very poor diastereoselectivity. Further screening of reductants found that L-Selectride and N-Selectride were good candidates, especially for L-Selectride, 92% yield and virtually complete controlled diastereoselectivity (99:1) were found (Table 3, entry 7). It did not matter at all when the reaction time was shortened to 8 h. However, the yield decreased when the time was further shortened to 6 h (Table 3, entries 9 and 10). The examination of solvents showed that polar solvents (Table 3, entries 11 and 13) were superior to a non-polar one such as toluene (Table 3, entry 12). The temperature influenced the reaction obviously, and raising the tempera-

ture to $-40\text{ }^{\circ}\text{C}$ reduces the yield to 89% and the diastereoselectivity to 87:13 (Table 3, entry 14).

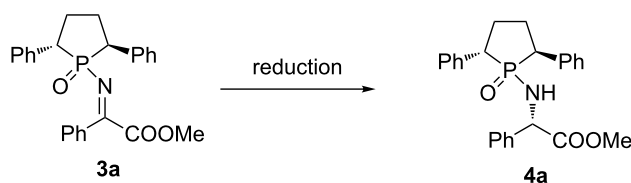
Scope of the asymmetric reduction reaction

After getting the optimized reduction conditions, several chiral *N*-phosphinyl α -imino esters prepared above were subjected to this system to examine the reaction scope. As shown in Table 4, reduction of these chiral α -imino esters provided excellent yields (up to 98%) and diastereoselectivities (up to 99:1). Almost all the reductions could achieve more than 90% yield, only for the case of *para*-phenyl-substituted substrate, a slightly lower yield was found (88%, Table 4, entry 10). The diastereoselectivities of the reactions were almost completely controlled, and most of them were 99:1. Except for the 4-bromo-substituted case, a dr of 96:4 was observed (Table 4, entry 2). It is interesting that GAP (group-assisted purification) was introduced into the reaction [49–51]. In five cases (Table 4, entries 1, 3–5 and 11), the final purified products were obtained by just washing with hexane, and no column chromatography or recrystallization was needed.

Determination of the absolute configuration

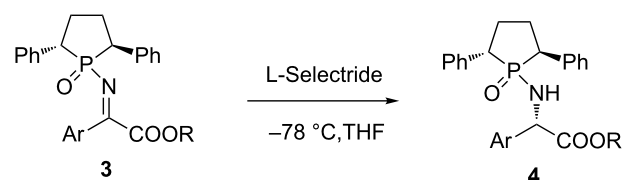
The phosphinyl auxiliary could be easily cleaved by treating with concentrated hydrochloric acid in methanol. After stirring

Table 3: Optimization of asymmetric reduction of α -imino esters^a.



entry	reagent	<i>T</i> ($^{\circ}\text{C}$)	solvent	time (h)	Yield (%) ^b	dr ^c
1	Hantzsch ester	-78	THF	12	Trace	—
2	HSiCl_3	-78	THF	12	NR	—
3	HSiEt_3	-78	THF	12	NR	—
4	LiBHEt_3	-78	THF	12	71	75:25
5	DIBAL	-78	THF	12	Trace	—
6	NaBH_4	-78	THF	12	48	66:34
7	L-Selectride	-78	THF	12	92	99:1
8	N-Selectride	-78	THF	12	90	90:10
9	L-Selectride	-78	THF	8	92	99:1
10	L-Selectride	-78	THF	6	85	99:1
11	L-Selectride	-78	4-MeTHF	8	90	99:1
12	L-Selectride	-78	toluene	8	47	96:4
13	L-Selectride	-78	diethyl ether	8	82	99:1
14	L-Selectride	-40	THF	8	89	87:13

^aReaction conditions: α -imino ester **3a** (0.15 mmol), reduction reagent (0.30 mmol), solvent (5.0 mL); ^bisolated yields; ^cdetermined by ^{31}P NMR of the crude reaction mixture.

Table 4: Scope of novel phophinyl substituted α -amino esters.^a


entry	Ar	R	α -amino ester	purification method	yield (%) ^b	dr ^c
1	C ₆ H ₅	Me	4a	GAP ^d	92	99:1
2	4-BrC ₆ H ₄	Me	4b	Column	90	96:4
3	4-ClC ₆ H ₄	Me	4c	GAP ^d	96	99:1
4	4-FC ₆ H ₄	Me	4d	GAP ^d	98	99:1
5	3-FC ₆ H ₄	Me	4e	GAP ^d	95	99:1
6	3-CH ₃ C ₆ H ₄	Me	4f	Column	95	99:1
7	2-CH ₃ C ₆ H ₄	Me	4g	Column	94	99:1
8	3,5-Cl ₂ C ₆ H ₃	Me	4h	Column	92	99:1
9	2-Naphthyl	Me	4i	Column	93	99:1
10	4-Ph-C ₆ H ₄	Me	4j	Column	88	99:1
11	C ₆ H ₅	Et	4k	GAP ^d	94	99:1

^aReaction conditions: α -imino esters **3** (0.15 mmol), L-Selectride (0.30 mmol), THF (5.0 mL); ^bisolated yields; ^cdetermined by ³¹P NMR; ^dgroup-assisted purification.

of **4a** with acid overnight, the conversion was complete and the corresponding amino ester hydrochloride was obtained. Then, the obtained free amino ester was directly converted into its *N*-Cbz-protected derivative **5a** by treating with CbzCl/Et₃N (Scheme 2). The absolute configuration of the newly formed chiral center was assigned as *S* by comparing the optical rotation with that of known sample [57]. The stereochemical assignments of other products were made by analogy correspondingly.

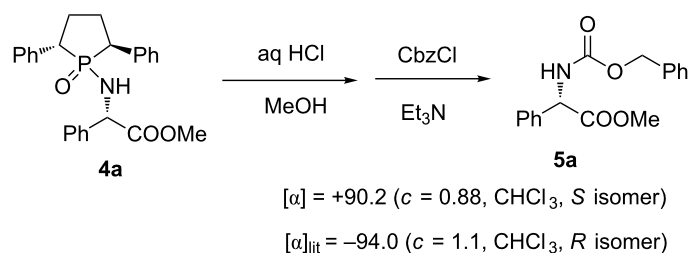
Conclusion

In conclusion, we have developed a method for the synthesis of chiral *N*-phophinyl α -imino esters for the first time, which have been used as precursors for asymmetric reductions with L-Selectride as reductant. Varieties of α -amino esters were obtained in excellent chemical yields and almost completely controlled diastereoselectivities. Furthermore, a part of the

products could be purified without use of any column chromatography or recrystallization, which provides an alternative way for the synthesis of α -amino esters. The auxiliary was easily removed by treatment with acid to result the free α -amino esters.

Experimental

General procedure for the asymmetric reduction of *N*-phophinyl α -imino esters: A reaction vial under argon was charged with L-Selectride (0.3 mmol) with THF (2.5 mL). The reaction mixture was then cooled to -78 °C for 10 min. Meanwhile, α -imino ester **3** (0.15 mmol, dissolved in 2.5 mL of THF) was cooled to -78 °C for 10 min. Then the α -imino ester **3** solution was transferred dropwise via a cannula at -78 °C and the reaction was kept at the same temperature for 8 h. The reaction mixture was quenched with saturated aqueous ammonium chlo-

**Scheme 2:** Cleavage of the chiral auxiliary.

ride (4.0 mL) and the organic layer was extracted with dichloromethane. The organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified using the GAP method or flash column chromatography on silica gel using EtOAc/hexanes (2:1, v/v) as the eluent to afford protected α -amino ester **4**.

Supporting Information

Supporting Information File 1

Experimental details and spectral data.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-10-57-S1.pdf>]

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References

- Skarpos, H.; Vorob'eva, D. V.; Osipov, S. N.; Odinets, I. L.; Breuer, E.; Röschenhaler, G. V. *Org. Biomol. Chem.* **2006**, *4*, 3669–3674. doi:10.1039/b607060d
- Gu, C.-L.; Liu, L.; Wang, D.; Chen, Y.-J. *J. Org. Chem.* **2009**, *74*, 5754–5757. doi:10.1021/jo900977y
- Collados, J. F.; Toledano, E.; Guijarro, D.; Yus, M. *J. Org. Chem.* **2012**, *77*, 5744–5750. doi:10.1021/jo300919x
- Dickstein, J. S.; Kozlowski, M. C. *Chem. Soc. Rev.* **2008**, *37*, 1166–1173. doi:10.1039/b709139g
- Taggi, A. E.; Hafez, A. M.; Lectka, T. *Acc. Chem. Res.* **2003**, *36*, 10–19. doi:10.1021/ar020137p
- Basra, S.; Fennie, M. W.; Kozlowski, M. C. *Org. Lett.* **2006**, *8*, 2659–2662. doi:10.1021/ol0602093
- Kang, Q.; Zhao, Z.-A.; You, S.-L. *Org. Lett.* **2008**, *10*, 2031–2034. doi:10.1021/ol800494r
- Yang, C.-F.; Shen, C.; Wang, J.-Y.; Tian, S.-K. *Org. Lett.* **2012**, *14*, 3092–3095. doi:10.1021/ol301180z
- Li, Y.; Ji, D.; Xu, M. *Org. Biomol. Chem.* **2011**, *9*, 8452–8458. doi:10.1039/c1ob06450a
- Dickstein, J. S.; Fennie, M. W.; Norman, A. L.; Paulose, B. J.; Kozlowski, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 15794–15795. doi:10.1021/ja8073006
- Zhang, H.; Mitsumori, S.; Utsumi, N.; Imai, M.; Garcia-Delgado, N.; Mifsud, M.; Albertshofer, K.; Cheong, P. H.; Houk, K. N.; Tanaka, F.; Barbas, C. F. *J. Am. Chem. Soc.* **2008**, *130*, 875–886. doi:10.1021/ja074907+
- Córdova, A.; Watanabe, S.; Tanaka, F.; Notz, W.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2002**, *124*, 1866–1867. doi:10.1021/ja017833p
- Córdova, A.; Barbas, C. F., III. *Tetrahedron Lett.* **2003**, *44*, 1923–1926. doi:10.1016/S0040-4039(03)00019-4
- Chowdari, N. S.; Suri, J. T.; Barbas, C. F., III. *Org. Lett.* **2004**, *6*, 2507–2510. doi:10.1021/ol049248+
- Jiang, J.; Ma, X.; Liu, S.; Qian, Y.; Lv, F.; Qiu, L.; Wu, X.; Hu, W. *Chem. Commun.* **2013**, *49*, 4238–4240. doi:10.1039/c3cc36972b
- Hernández-Toribio, J.; Padilla, S.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2012**, *51*, 8854–8858. doi:10.1002/anie.201203828
- Chen, J.; Lu, X.; Lou, W.; Ye, Y.; Jiang, H.; Zeng, W. *J. Org. Chem.* **2012**, *77*, 8541–8548. doi:10.1021/jo301423e
- Rueping, M.; Antonchick, A. P.; Brinkmann, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6903–6906. doi:10.1002/anie.200702439
- Jin, S.-S.; Xu, M.-H. *Adv. Synth. Catal.* **2010**, *352*, 3136–3140. doi:10.1002/adsc.201000688
- Saaby, S.; Nakama, K.; Lie, M. A.; Hazell, R. G.; Jørgensen, K. A. *Chem.–Eur. J.* **2003**, *9*, 6145–6154. doi:10.1002/chem.200305302
- Williams, R. M.; Hendrix, J. A. *Chem. Rev.* **1992**, *92*, 889–917. doi:10.1021/cr00013a007
- Mortensen, M.; Husmann, R.; Veri, E.; Bolm, C. *Chem. Soc. Rev.* **2009**, *38*, 1002–1010. doi:10.1039/b816769a
- Gross, P. J.; Bräse, S. *Chem.–Eur. J.* **2010**, *16*, 12660–12667. doi:10.1002/chem.201001036
- Kricheldorf, H. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5752–5784. doi:10.1002/anie.200600693
- Darbre, T.; Reymond, J.-L. *Acc. Chem. Res.* **2006**, *39*, 925–934. doi:10.1021/ar050203y
- Bell, D. S. H. *Drugs* **2007**, *67*, 1813–1827. doi:10.2165/00003495-200767130-00002
- Chapman, T. M.; Perry, C. M. *Drugs* **2004**, *64*, 2577–2595. doi:10.2165/00003495-200464220-00008
- Simpson, D.; McCormack, P. L.; Keating, G. M.; Lyseng-Williamson, K. A. *Drugs* **2007**, *67*, 407–434. doi:10.2165/00003495-200767030-00006
- Li, G.; Liang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 5830–5831. doi:10.1021/ja070519w
- Xue, Z.-Y.; Jiang, Y.; Yuan, W.-C.; Zhang, X.-M. *Eur. J. Org. Chem.* **2010**, 616–619. doi:10.1002/ejoc.200901312
- Bachu, P.; Zhu, C.; Akiyama, T. *Tetrahedron Lett.* **2013**, *54*, 3977–3981. doi:10.1016/j.tetlet.2013.05.071
- Kang, Q.; Zhao, Z.-A.; You, S.-L. *Adv. Synth. Catal.* **2007**, *349*, 1657–1660. doi:10.1002/adsc.200700235
- Zhu, C.; Akiyama, T. *Adv. Synth. Catal.* **2010**, *352*, 1846–1850. doi:10.1002/adsc.201000328
- Zheng, C.; You, S. L. *Chem. Soc. Rev.* **2012**, *41*, 2498–2518. doi:10.1039/c1cs15268h
- Reeping, M.; Dufour, J.; Schoepke, F. R. *Green Chem.* **2011**, *13*, 1084–1105. doi:10.1039/c1gc15027h
- Shang, G.; Yang, Q.; Zhang, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 6360–6362. doi:10.1002/anie.200601540
- Colyer, J. T.; Andersen, N. G.; Tedrow, J. S.; Soukup, T. S.; Faul, M. M. *J. Org. Chem.* **2006**, *71*, 6859–6862. doi:10.1021/jo0609834
- Reddy, L. R.; Gupta, A. P.; Liu, Y. *J. Org. Chem.* **2011**, *76*, 3409–3415. doi:10.1021/jo200401a
- Guizzetti, S.; Benaglia, M.; Rossi, S. *Org. Lett.* **2009**, *11*, 2928–2931. doi:10.1021/ol900945h
- Han, J.; Ai, T.; Li, G. *Synthesis* **2008**, 2519–2526. doi:10.1055/s-2008-1067189
- Han, J.; Ai, T.; Nguyen, T.; Li, G. *Chem. Biol. Drug Des.* **2008**, *72*, 120–126. doi:10.1111/j.1747-0285.2008.00682.x
- Kattamuri, P. V.; Xiong, Y.; Pan, Y.; Li, G. *Org. Biomol. Chem.* **2013**, *11*, 3400–3408. doi:10.1039/c3ob40251g

43. Pindi, S.; Kaur, P.; Shakya, G.; Li, G. *Chem. Biol. Drug Des.* **2011**, *77*, 20–29. doi:10.1111/j.1747-0285.2010.01047.x
44. Sun, H.; Rajele, T.; Pan, Y.; Li, G. *Tetrahedron Lett.* **2010**, *51*, 4403–4407. doi:10.1016/j.tetlet.2010.06.072
45. Robak, M. T.; Herbage, M. A.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 3600–3740. doi:10.1021/cr900382t
46. Xie, C.; Mei, H.; Wu, L.; Soloshonok, V. A.; Han, J. L.; Pan, Y. *RSC Adv.* **2014**, *4*, 4763–4768. doi:10.1039/c3ra45773g
47. Mei, H.; Xie, C.; Wu, L.; Soloshonok, V. A.; Han, J.; Pan, Y. *Org. Biomol. Chem.* **2013**, *11*, 8018–8021. doi:10.1039/c3ob41785a
48. Mei, H.; Xiong, Y.; Han, J.; Pan, Y. *Org. Biomol. Chem.* **2011**, *9*, 1402–1406. doi:10.1039/c0ob00586j
49. Pindi, S.; Wu, J.; Li, G. *J. Org. Chem.* **2013**, *78*, 4006–4012. doi:10.1021/jo400354r
50. Kattamuri, P. V.; Ai, T.; Pindi, S.; Sun, Y.; Gu, P.; Shi, M.; Li, G. *J. Org. Chem.* **2011**, *76*, 2792–2797. doi:10.1021/jo200070d
51. Kaur, P.; Wever, W.; Pindi, S.; Milles, R.; Gu, P.; Shi, M.; Li, G. G. *Green Chem.* **2011**, *13*, 1288–1292. doi:10.1039/c1gc15029d
52. Xiong, Y.; Mei, H.; Xie, C.; Han, J.; Li, G.; Pan, Y. *RSC Adv.* **2013**, *3*, 15820–15826. doi:10.1039/c3ra42927j
53. Kaur, P.; Nguyen, T.; Li, G. *Eur. J. Org. Chem.* **2009**, 912–916. doi:10.1002/ejoc.200801061
54. Chen, Z. X.; Ai, T.; Kaur, P.; Li, G. G. *Tetrahedron Lett.* **2009**, *50*, 1079–1081. doi:10.1016/j.tetlet.2008.12.093
55. Qian, Y.; Jing, C.; Zhai, C.; Hu, W.-h. *Adv. Synth. Catal.* **2012**, *354*, 301–307. doi:10.1002/adsc.201100615
56. Masumoto, S.; Usuda, H.; Suzuki, M.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 5634–5635. doi:10.1021/ja034980+
57. Xu, B.; Zhu, S.-F.; Xie, X.-L.; Shen, J.-J.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2011**, *50*, 11483–11486. doi:10.1002/anie.201105485

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