ORGANIC LETTERS

2012
Vol. 14, No. 8
2062–2065

Lewis Acid Promoted Highly Diastereoselective Petasis Borono-Mannich Reaction: Efficient Synthesis of Optically Active β,γ-Unsaturated α-Amino Acids

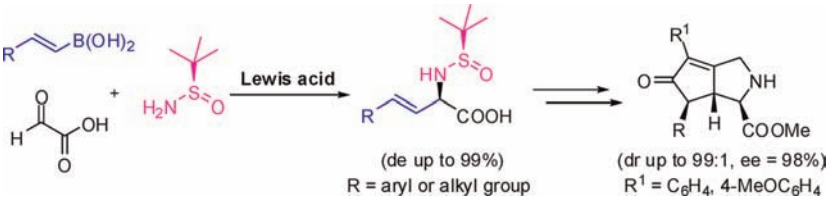
Yi Li and Ming-Hua Xu*

Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai 201203, China

xumh@mail.shcnc.ac.cn

Received March 7, 2012

ABSTRACT



An efficient and straightforward method for the preparation of highly enantiomerically enriched β,γ-unsaturated α-amino acid derivatives by a Lewis acid promoted diastereoselective Petasis reaction of vinylboronic acid, *N-tert*-butanesulfinamide, and glyoxylic acid has been developed. The synthetic utilities of the approach were demonstrated by the rapid and convenient construction of challenging cyclopenta[*c*]proline derivatives.

Optically pure nonproteinogenic amino acids are fascinating in the field of biological and medicinal chemistry and are also utilized as versatile building blocks in modern organic synthesis and new drug discovery.[1] An interesting class of these compounds is β,γ-unsaturated α-amino acids and their derivatives, which are important structural motifs present in many biologically active natural products and pharmaceutical compounds.[2] In the past decade, a great number of methods have been developed to access these valuable compounds.[2a,3,4] Among them, the asymmetric Petasis borono-Mannich reaction represents a

(1) For reviews, see: (a) *Amino Acids, Peptides, and Proteins in Organic Chemistry*; Hughes, A. B., Ed.; Wiley-VCH: Weinheim, 2009; Vols. 1 and 2. (b) Meierhenrich, U. *Amino Acids and the Asymmetry of Life*; Springer-Verlag: Heidelberg, 2008. (c) Barrett, G. C.; Elmore, D. T. *Amino Acids and Peptides*; Cambridge University Press: Cambridge, 1998. (d) Rutjes, F. P. J. T.; Wolf, L. B.; Schoemaker, H. E. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4197.

(2) For representative examples, see: (a) Berkowitz, D. B.; Charette, B. D.; Karukurichi, K. R.; McFadden, J. M. *Tetrahedron: Asymmetry* **2006**, *17*, 869. (b) Rando, R. R. *Acc. Chem. Res.* **1975**, *8*, 281. (c) Berkowitz., D. B.; Jahng, W.-J.; Pedersen, M. L. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2151. (d) Feng, L.; Kirsch, J. F. *Biochemistry* **2000**, *39*, 2436. (e) Soper, T. S.; Manning, J. M.; Marcotte, P. A.; Walsh, C. T. *J. Biol. Chem.* **1977**, *252*, 1571. (f) Sahm, U.; Knobloch, G.; Wagner, F. *J. Antibiot.* **1973**, *26*, 389. (g) Pruess, D. L.; Scannell, J. P.; Kellett, M.; Ax, H. A.; Janecek, J.; Williams, T. H.; Stempel, A.; Berger, J. *J. Antibiot.* **1974**, *27*, 229. (h) Kuroda, Y.; Okuhara, M.; Goto, T.; Kohsaka, M.; Aoki, H.; Imanaka, H. *J. Antibiot.* **1980**, *33*, 132.

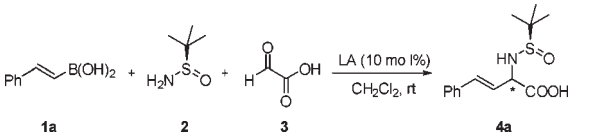
(3) For representative examples, see: (a) Ma, J.-A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4290. (b) Maruoka, K.; Ooi, T. *Chem. Rev.* **2003**, *103*, 3013. (c) Nájera, C.; Sansano, J. M. *Chem. Rev.* **2007**, *107*, 4584. (d) Porter, J. R.; Wirschun, W. G.; Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 2657. (e) Zhou, G.; Zheng, W.; Wang, D.; Zhang, P.; Pan, Y. *Helv. Chim. Acta* **2006**, *89*, 520. (f) Mehmandoust, M.; Petit, Y.; Larchevêque, M. *Tetrahedron Lett.* **1992**, *33*, 4313. (g) Berkowitz, D. B.; Pumphrey, J. A.; Shen, Q. *Tetrahedron Lett.* **1994**, *35*, 8743. (h) Rose, N. G. W.; Blaskovich, M. A.; Wong, A.; Lajoie, G. A. *Tetrahedron* **2001**, *57*, 1497. (i) Fadnavis, N. W.; Seo, S.-H.; Seo, J.-H.; Kim, B.-G. *Tetrahedron: Asymmetry* **2006**, *17*, 2199. (j) Hang, J. F.; Deng, L. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3856. (k) Armstrong, A.; Challinor, L.; Moir, J. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5369. (l) Kong, J.-R.; Cho, C.-W.; Krische, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 11269. (m) Armstrong, A.; Challinor, L.; Cooke, R. S.; Moir, J. H.; Treweeke, N. R. *J. Org. Chem.* **2006**, *71*, 4028. (n) Berkowitz, D. B.; McFadden, J. M.; Sloss, M. K. *J. Org. Chem.* **2000**, *65*, 2907. (o) Wipf, P.; Stephenson, C. R. J. *Org. Lett.* **2003**, *5*, 2449. (p) Berkowitz, D. B.; Maiti, G. *Org. Lett.* **2004**, *6*, 2661. (q) Jones, M. C.; Marsden, S. P.; Subtil, D. M. M. *Org. Lett.* **2006**, *8*, 5509. (r) Kang, Q.; Zhao, Z.-A.; You, S.-L. *Org. Lett.* **2008**, *10*, 2031. (s) Armstrong, A.; Emmerson, D. P. G. *Org. Lett.* **2011**, *13*, 1040.

10.1021/ol300581n
Published on Web 04/05/2012

powerful and most direct approach for the stereoselective preparation of β,γ-unsaturated α-amino acids.[4] To our knowledge, despite the fact that the strategies involving chiral amines,[4c,l] chiral boronate esters,[4l,m] and chiral organocatalysts[4n] have been employed, the results are far from satisfactory. Excellent stereoselectivities are only obtained in some cases of using chiral amines such as 2-phenylglycinol[4e] and α-methylbenzylamine;[4j] however, the hydrogenolytic conditions for removal of these *N*-benzylic groups also reduce the olefin functionalities leading to the corresponding saturated derivatives. From this point of view, a practical synthesis of β,γ-unsaturated α-amino acids via asymmetric Petasis reaction with great stereocontrol still remains a challenge.

N-*tert*-Butanesulfinamide has been proven to be a highly efficient chiral auxiliary in the asymmetric synthesis of various chiral amines by virtue of its excellent diastereocontrol and easy cleavage under mild conditions.[5,6] In 2003, Naskar and co-workers reported the first use of (*S*)-*N*-*tert*-butanesulfinamide in a Petasis reaction with arylboronic acids to generate arylglycines, but the results were disappointing, giving racemic diastereomers in low to moderate yields.[4k] In our earlier work,[6] we successfully demonstrated the use of chiral *N*-*tert*-butanesulfinylimino ester as a chiral glycine cation equivalent for the asymmetric synthesis of synthetically uesful diverse amino acids such as D-allylglycine,[6g] β-vinyl-α-arylalanines,[6j] α-(3-indolyl)-glycines,[6l] α-allenylglycines,[6m] and α-arylglycines.[6n] Taking into account these successes and the mechanistic proposal of the Petasis reaction,[4a,7] we envisaged that the possibility of an asymmetric Petasis reaction of vinylboronic acids with chiral *N*-*tert*-butanesulfinamide and glyoxylic acid might be expected if a proper Lewis acid is presented in the reaction system. The chelation of a Lewis acid with a *N*-sulfinyl imine intermediate should direct the intramolecular transfer of a vinyl group in a highly stereoselective manner, thus leading to the optically active β,γ-unsaturated α-amino acid products. Interestingly, during the course of our studies, a recent work disclosed that a Petasis reaction of styrenylboronic acids and glyoxylic acid with (*S*)-*tert*-butylsulfinamide can actually proceed with high stereoselectivities (10:1−20:1 dr) under similar Naskar[4k] conditions to further produce optically active β,γ-dehydrohomoarylalanine derivatives, but the reactions of alkenyl boronic acids all showed a low degree of diastereoselectivity (85:15 and 89:11 dr).[4g] Herein, we report our efforts to develop an efficient and convenient method for an asymmetric Petasis reaction of vinylboronic acid, *tert*-butylsulfinamide, and glyoxylic acid using a Lewis acid mediated coordination protocol. The method produces chiral β,γ-unsaturated α-amino acid derivatives with excellent disatereoselectivities (96−99% de) under practical conditions.

Table 1. Screening of Lewis Acids for Diastereoselective Petasis Reaction[a]



1a 2 3 4a

entry	catalyst	time (h)	yield (%)[b]	de (%)[c]
1	–	8	87	82
2	$In(OTf)_3$	12	64	92
3	$Yb(OTf)_3$	12	60	90
4	$Zn(OTf)_2$	8	71	90
5	$Cu(OTf)_2$	8	70	93
6	$Sc(OTf)_3$	12	61	93
7	$InCl_3$	8	84	90
8	$InBr_3$	12	51	98
9	$InBr_3$	24	53	98
10	$AgCOCF_3$	8	77	69
11	$FeCl_3$	24	43	97
12	$FeBr_3$	24	42	96
13	$FeCl_2$	8	71	92

[a] The reaction was performed with 10 mol % of catalyst, (*E*)-styrylboronic acid **1a** (0.30 mmol), (*R*)-*N*-*tert*-butanesulfinamide **2** (0.25 mmol), and glyoxylic acid **3** (0.25 mmol) in dry CH_2Cl_2 (1 mL) at room temperature. [b] Isolated yield. [c] The diastereoselectivity of the product was determined by LC-MS analysis.

Our initial investigation commenced with the reaction of (*E*)-styrylboronic acid **1a** with (*R*)-*N*-*tert*-butanesulfinamide **2** and glyoxylic acid **3** in CH_2Cl_2 at ambient temperature (Table 1). In the absence of any Lewis acid catalyst, the reaction can proceed well and afford the

(4) (a) Candeias, N. R.; Montalbano, F.; Cal, P. M. S. D.; Gois, P. M. P. *Chem. Rev.* **2010**, *110*, 6169. (b) Petasis, N. A. *Aust. J. Chem.* **2007**, *60*, 795. (c) Churches, Q. I.; Stewart, H. E.; Cohen, S. B.; Shröder, A.; Turner, P.; Hutton, C. A. *Pure Appl. Chem.* **2008**, *80*, 687. (d) Churches, Q. I.; Johnson, J. K.; Fifer, N. L.; Hutton, C. A. *Aust. J. Chem.* **2011**, *64*, 62. (e) Petasis, N. A.; Zavialov, I. A. *J. Am. Chem. Soc.* **1997**, *119*, 445. (f) Jiang, B.; Xu, M. *Org. Lett.* **2002**, *4*, 4077. (g) Churches, Q. I.; White, J. M.; Hutton, C. A. *Org. Lett.* **2011**, *13*, 2900. (h) Shevchuk, M. V.; Sorochinsky, A. E.; Khilya, V. P.; Romanenko, V. D.; Kukhar, V. P. *Synlett* **2010**, *1*, 73. (i) Petasis, N. A.; Patel, Z. D. *Tetrahedron Lett.* **2000**, *41*, 9607. (j) Jiang, B.; Yang, C.-G.; Gu, X.-H. *Tetrahedron Lett.* **2001**, *42*, 2545. (k) Naskar, D.; Roy, A.; Seibei, W. L.; Portlock, D. E. *Tetrahedron Lett.* **2003**, *44*, 8865. (l) Southwood, T. J.; Curry, M. C.; Hutton, C. A. *Tetrahedron* **2006**, *62*, 236. (m) Koolmeister, T.; Södergren, M.; Scobie, M. *Tetrahedron Lett.* **2002**, *43*, 5969. (n) Lou, S.; Schaus, S. E. *J. Am. Chem. Soc.* **2008**, *130*, 6922.

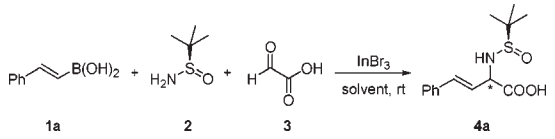
(5) (a) Robak, M. T.; Herbage, M. A.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 3600. (b) Ferreira, F.; Botuha, C.; Chemla, F.; Pérez-Luna, A. *Chem. Soc. Rev.* **2009**, *38*, 1162. (c) Senanayake, C. H.; Krishnamurthy, D.; Lu, Z.-H.; Han, Z.; Gallon, E. *Aldrichimica Acta* **2005**, *38*, 93.

(6) (a) Lin, G.-Q.; Xu, M.-H.; Zhong, Y.-W.; Sun, X.-W. *Acc. Chem. Res.* **2008**, *41*, 831. (b) Zhong, Y.-W.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2004**, *6*, 3953. (c) Zhong, Y.-W.; Isumi, K.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2004**, *6*, 4747. (d) Zhong, Y.-W.; Dong, Y.-Z.; Fang, K.; Isumi, K.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2005**, *127*, 11956. (e) Sun, X.-W.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2006**, *8*, 4979. (f) Liu, R.-H.; Fang, K.; Wang, B.; Xu, M.-H.; Lin, G.-Q. *J. Org. Chem.* **2008**, *73*, 3307. (g) Sun, X.-W.; Liu, M.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2008**, *10*, 1259. (h) Wang, R.; Fang, K.; Sun, B.-F.; Xu, M.-H.; Lin, G.-Q. *Synlett* **2009**, 2301. (i) Liu, M.; Sun, X.-W.; Xu, M.-H.; Lin, G.-Q. *Chem.—Eur. J.* **2009**, *15*, 10217. (j) Liu, M.; Shen, A.; Sun, X.-W.; Deng, F.; Xu, M.-H.; Lin, G.-Q. *Chem. Commun.* **2010**, *46*, 8460. (k) Shen, A.; Liu, M.; Jia, Z.-S.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2010**, *12*, 5154. (l) Ji, D.-M.; Xu, M.-H. *Chem. Commun.* **2010**, *46*, 1550. (m) Jin, S.-S.; Xu, M.-H. *Adv. Synth. Catal.* **2010**, *352*, 3136. (n) Li, Y.; Ji, D.-M.; Xu, M.-H. *Org. Biomol. Chem.* **2011**, *9*, 8452.

(7) (a) Schlienger, N.; Bryce, M. R.; Hansen, T. K. *Tetrahedron* **2000**, *56*, 10023. (b) Candeias, N. R.; Cal, P. M. S. D.; André, V.; Duarte, T.; Veiros, L.; Gois, P. M. P. *Tetrahedron* **2010**, *66*, 2736.

expected product in 87% yield and, surprisingly, with 82% de, unlike in reported cases of arylboronic acids[4k] (Table 1, entry 1). Encouraged by this result, we attempted to employ a Lewis acid as the catalyst to promote the reaction. As expected, when the reaction was performed in the presence of 10 mol % of $In(OTf)_3$, a considerable increase in product diastereomeric excess (92% de vs 82% de) was observed, but a slightly diminished yield was also obtained simultaneously (Table 1, entry 2). To achieve better results, a series of transition-metal-based Lewis acids were carefully screened. As sumarized in Table 1, the Lewis acid indeed plays an important role in reaction stereocontrol. In almost all cases, increased diastereoselectivities were attained, albeit with moderate yields which are due to incomplete conversion. With 10 mol % of $InBr_3$, the reaction gave the desired product **4a** in 51% yield with the best de of 98% after 12 h (entry 8). Prolonging the reaction time to 24 h did not lead to an increased yield (53%, entry 9). Notably, an equally high level of diastereocontrol (97% de) can be achieved when rather cheap $FeCl_3$ was used as a Lewis acid (entry 11).

Table 2. Optimization of the Reaction Conditions Using $InBr_3$ as Catalyst[a]

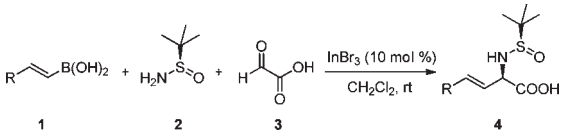


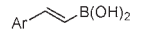
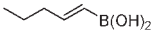
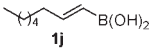
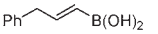
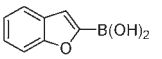
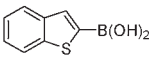
entry	mol %	solvent	time (h)	yield (%)[b]	de (%)[c]
1	10	CH_2Cl_2	12	51	98
2	10	toluene	24	43	97
3	10	THF	24	6	88
4	10	$Cl(CH_2)_2Cl$	12	53	96
5	10	HMPA	8	–[d]	–
6	5	CH_2Cl_2	8	71	95
7	20	CH_2Cl_2	12	50	98
8[e]	10	CH_2Cl_2	12	65	98
9[f]	10	CH_2Cl_2	12	56	98

[a] The reaction was performed with (*E*)-styrylboronic acid **1a** (0.30 mmol), (*R*)-*N*-*tert*-butanesulfinamide **2** (0.25 mmol), and glyoxylic acid **3** (0.25 mmol) in dry CH_2Cl_2 (1 mL) for 12 h at room temperature. [b] Isolated yield. [c] The diastereoselectivity was determined by LC-MS analysis. [d] No product. [e] The reaction was conducted at 0.3 M. [f] The reaction was conducted at 0.4 M.

Encouraged by these preliminary results, we decided to further explore the study to improve the reaction yield. As revealed in Table 2, the investigation of various solvents suggested that the use of CH_2Cl_2 was the best choice (entries 1 and 5). With lower catalyst loading (5 mol %), an increase in both the reaction rate and yield was observed, but the diastereoselectivity dropped to 95% de (entry 6). On the other hand, enhancing the loading amount of $InBr_3$ to 20 mol % had little effect on the reaction yield and diastereomeric excess (entry 7). Interestingly, the reaction yield was found to be sensitive to concentration (entries 8–9).[8] When the reaction was carried out at the concentration 0.3 M, **4a** could be isolated in an optimal yield of 65% without any loss in diastereoselectivity (entry 8).

Table 3. Diastereoselective Petasis Reaction of Boronic Acids with *N*-*tert*-Butanesulfinamide **2** and Glyoxylic Acid **3**[a]



entry	boronic acid **1**	**4**	yield (%)[b]	de (%)[c]
1	 **1a**, Ar = C_6H_4	**4a**	65	98
2	**1b**, Ar = 4-MeC_6H_4	**4b**	70	98
3	**1c**, Ar = 4-$MeOC_6H_4$	**4c**	71	99
4	**1d**, Ar = 4-FC_6H_4	**4d**	67	98
5	**1e**, Ar = 4-ClC_6H_4	**4e**	69	98
6	**1f**, Ar = 3-ClC_6H_4	**4f**	67	98
7	**1g**, Ar = 4-$CF_3C_6H_4$	**4g**	58	93
8	**1h**, Ar = 4-PhC_6H_4	**4h**	56	96
9	 **1i**	**4i**	62	97
10	 **1j**	**4j**	60	99
11	 **1k**	**4k**	57	98
12	 **1l**	**4l**	78	99
13	 **1m**	**4m**	60	96

[a] The reaction was performed with boronic acid **1** (0.36 mmol), (*R*)-*N*-*tert*-butanesulfinamide **2** (0.30 mmol), and glyoxylic acid **3** (0.30 mmol) in the presence of 10 mol % of $InBr_3$ in dry CH_2Cl_2 (1 mL) for 12 h at room temperature. [b] Isolated yield. [c] The diastereoselectivity was determined by LC-MS analysis; see Supporting Information for details.

Having identified the optimal reaction conditions, we sought to evaluate the scope and generality of the reaction. As presented in Table 3, a wide range of vinylboronic acids bearing different substituents were successfully reacted with glyoxylic acid and (*R*)-*tert*-butylsulfinamide (Table 3), giving the corresponding β,γ-unsaturated α-amino acid products **4** with excellent diastereoselectivities (93–99% de) in all cases. Generally, (*E*)-styrylboronic acids containing either electron-donating or -withdrawing groups underwent the Petasis reaction in moderate to good yields with high selectivities (entries 1–8). However, it is likely that the *para*-CF_3 substituent on the phenyl ring of the styrylboronic acid has little effect on the reaction stereoselectivity (entry 7). Gratifyingly, when differently

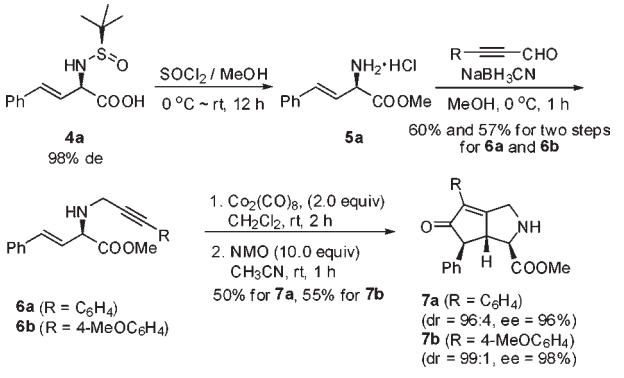
(8) See Supporting Information for details.

substituted linear substrate (*E*)-alkenyl boronic acids were employed, the reactions also proceeded smoothly and gave products **4i**−**k** in 57%−62% yields with up to 99% de (entries 9−11). Moreover, it is worth noting that benzofuran-2-boronic acid (**1l**) and benzothiophen-2-boronic acid (**1m**) are also found to be suitable substrates, as they exhibited high reactivity and led to the formation of highly optically active α-(2-benzofuranyl)-glycine **4l** and α-(2-benzothiophenyl)glycine **4m** (99% and 96% de, respectively, entries 12 and 13). These results are among the best in the asymmetric Petasis reaction of vinylboronic acid.

To understand the stereochemical outcome of the reaction, the chiral free α-styrylglycine was readily obtained by removal of the *N*-sulfinyl group under acidic conditions. Its absolute configuration was unambiguously determined to be (*R*) by comparison of the optical rotation with that of the known compound.[3i,8]

While the reactions are efficient to produce highly optically active *β*,*γ*-unsaturated α-amino acid products, we next turned our attention toward demonstrating the synthetic utility of these compounds. As illustrated in Scheme 1, treatment of the *N*-sulfinyl unsaturated amino acid **4a** with thionyl chloride in methanol followed by concomitant esterification led to removal of the sulfinyl group and gave methyl ester **5a**. Subsequently, reductive amination of **5a** with 3-phenyl-2-propynal or 3-(4-methoxyphenyl)-2-propynal provided the key intermediate **6a** or **6b**. Finally, under typical Pauson−Khand reaction conditions, the corresponding cyclopenta-[*c*]proline derivatives **7a** and **7b** were obtained in moderate yields with high diastereoselectivities (96:4 dr and >99:1 dr) and enantioselectivities. The stereochemistry of **7a** was determined by NOE experimentation. It has been well-known that the cyclopenta[*c*]proline and its derivatives, which contain a chiral bicyclic core structure of 3-azabicyclo[3,3,0]octane, have attracted a great deal of interest[9] and should be useful as a highly tunable chiral material.

Scheme 1. Synthetic Applicability of *β*,*γ*-Unsaturated α-Amino Acids



Based on the observed diastereofacial selectivity and our previous studies on metal chelation to *N*-sulfinyl imines, a possible working model was proposed (Figure 1). As shown in Figure 1, imine nitrogen and carbonyl oxygen of the quaternary boronate complex coordinated to a Lewis acidic metal to form a five-membered ring chelation. Since the uncoordinated *N*-sufinyl group adopts an approximately synperiplanar configuration,[10] the styryl group prefers to migrate from the *Re* face rather than the *Si* face of the imine C=N bond because the latter is strongly shielded by the bulky *tert*-butyl group, resulting in the *R*-configured product.

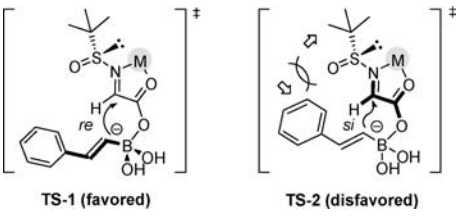


Figure 1. Mechanistic proposals for stereocontrol.

In summary, we have developed an extremely mild and practical approach for the asymmetric synthesis of *β*,*γ*-unsaturated α-amino acids through a Lewis acid promoted highly diastereoselective Petasis borono-Mannich three-component reaction of *N*-*tert*-butanesulfinamide with glyoxylic acid and vinylboronic acid. The reaction is general and efficient with respect to substrate scope and stereocontrol. It provides straightforward access to various enantiomerically enriched *β*,*γ*-unsaturated α-amino acids (up to 99% de) that are widely useful in medicinal chemistry and asymmetric synthesis. Further applications of the methodology are currently underway in our laboratory.

Acknowledgment. Financial support from the National Natural Science Foundation of China (21021063), the State Key Laboratory of Drug Research, SIMM, and National Science & Technology Major Project is greatly acknowledged.

Supporting Information Available. Experimental details including characterization data, copies of ^{1}H and ^{13}C NMR and HPLC/LC-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

(9) (a) Trabocchi, A.; Scarpi, D.; Guarna, A. *Amino Acids* **2008**, *34*, 1. (b) Jiang, B.; Xu, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2543. (c) Koep, S.; Gais, H.-J.; Raabe, G. *J. Am. Chem. Soc.* **2003**, *125*, 13243. (d) Tang, Y.; Deng, L.; Zhang, Y.; Dong, G.; Chen, J.; Yang, Z. *Org. Lett.* **2005**, *7*, 1657.

(10) For related crystal structures and theoretical calculations: (a) Owens, T. D.; Hollander, F. J.; Oliver, A. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 1539. (b) Owens, T. D.; Souers, A. J.; Ellman, J. A. *J. Org. Chem.* **2003**, *68*, 3. (c) Schenkel, L. B.; Ellman, J. A. *Org. Lett.* **2003**, *5*, 545. (d) Tietze, L. F.; Schuffenhauer, A. *Eur. J. Org. Chem.* **1998**, 1629. (e) Bharatam, P. V.; Uppal, P.; Kaur, A.; Kaur, D. *J. Chem. Soc., Perkin Trans. 2* **2000**, 43.

The authors declare no competing financial interest.