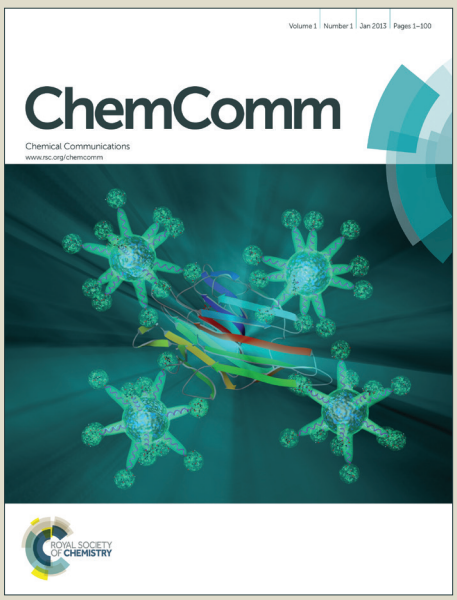
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Chemical Communications

RSCPublishing

COMMUNICATION

Enantioselective sp^3 C-H alkylation of γ-butyrolactam by a chiral Ir(I) catalyst for the synthesis of 4-substituted γ-amino acids

Cite this: DOI: 10.1039/x0xx00000x

Received
Accepted

DOI: 10.1039/x0xx00000x

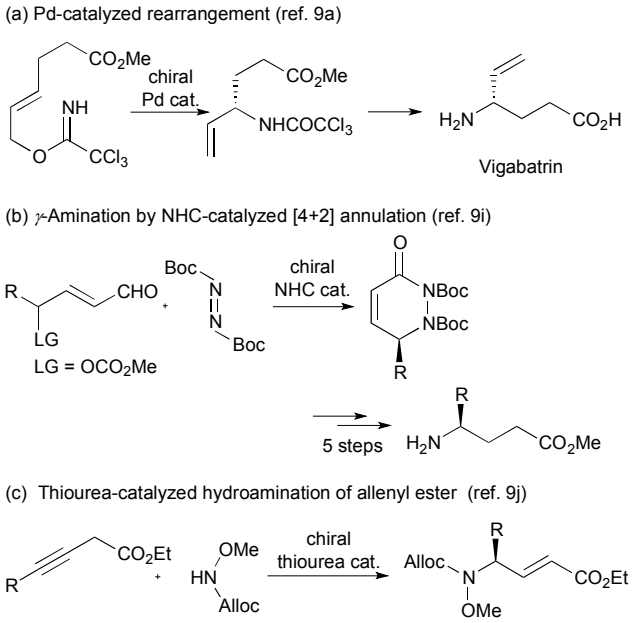
www.rsc.org/

Yu-ki Tahara,[a] Masamichi Michino,[a] Mamoru Ito,[a] Kyalo Stephen Kanyiva,[b] and Takanori Shibata*[a,c]

Ir-catalyzed sp^3 C-H alkylation of γ-butyrolactam with alkenes was used for the highly enantioselective synthesis of 5-substituted γ-lactams, which were readily converted into chiral 4-substituted γ-amino acids. A broad scope of alkenes was amenable as coupling partners, and the alkylated product using acrylate could be transformed into the key intermediate of pyrrolam A synthesis.

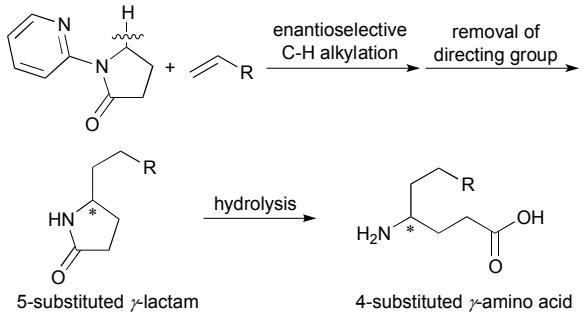
γ-Amino acid derivatives have attracted much attention as biologically active compounds in relation to γ-aminobutyric acid (GABA), a major inhibitory neurotransmitter in the central nervous system (CNS) of mammals.[1] Several γ-aminobutyric acid derivatives with substituent(s) on the carbon chain, such as anticonvulsant drug, anti-seizure drug, and anti-epilepsy drug, have been developed as pharmaceutical agents. For example, Baclofen,[2] Gabapentin,[3] Pregabalin,[4] and Vigabatrin[5] were commercialized pharmaceutical agents. On the other hand, structural functions of γ-amino acid derivatives have also been reported over the past few years: peptidic foldamers including γ-amino acids form novel helical structure[6] and self-assembling peptide nanotubes[7].

Against these backgrounds, various asymmetric syntheses of γ-amino acid derivatives have been developed.[8] In particular, a great deal of effort has been devoted to the enantioselective synthesis, and there are several examples reported for the synthesis of 4-substituted γ-aminobutyric acid derivatives.[9] However, most of them are the synthesis of γ-aminobutyric acids having more than one substituent on the carbon chain, and the enantioselective synthesis of γ-aminobutyric acids having a substituent only at the 4 position is limited (Scheme 1). Pd-catalyzed rearrangement of allylic trichloroacetamidate gave 4-vinyl γ-aminobutyric acid (Scheme 1a).[9a] Chiral NHC-catalyzed [4+2] annulation of enals possessing a leaving group at the γ-position with azodicarboxylates gave γ-aminated products, which were derived into γ-aminobutyric acids in 5 steps (Scheme 1b).[9i] Chiral thiourea-catalyzed hydroamination of in situ-generated allenyl esters with *N*-methoxy carbamate is a potentially efficient protocol (Scheme 1c)[9j]. However, these methods have limited scope of substituents and/or require multiple steps for the transformation into the γ-amino acids. Therefore, more broadly-applicable protocols of the enantioselective synthesis of chiral 4-substituted γ-aminobutyric acids are strongly desired.



Scheme 1 Selected examples of enantioselective synthesis of 4-substituted γ-amino acid derivatives.

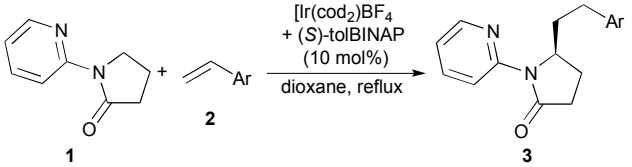
We chose C-H bond activation as a key strategy for the creation of the stereogenic center of the amino acids, because pre-activation of the substrate is unnecessary, therefore it leads to a shorter and more atom-economical process.[10] Enantioselective activation of sp^3 C-H bond is an ideal transformation, but is still a challenging topic.[11] We have comprehensively studied Ir-catalyzed C-H bond activation for the carbon-carbon bond forming reaction.[12] Furthermore, we reported enantioselective sp^3 C-H alkylation of alkyl amines possessing 2-pyridyl group as a directing group on the nitrogen atom with alkenes.[11e,11f] We considered that the enantioselective C-H alkylation of γ-butyrolactam possessing a directing group could give chiral 5-substituted γ-butyrolactams after removal of the directing group (Scheme 2). Chiral γ-lactam skeleton is also found in a lot of biologically active compounds[13] and natural products[14], and asymmetric synthesis of γ-lactam derivatives is quite important.[15] Herein, we describe a new approach to the efficient asymmetric synthesis of 5-alkylated γ-lactams and 4-substituted γ-amino acid derivatives initiated by Ir-catalyzed enantioselective sp^3 C-H bond activation.



Scheme 2 Approach to the enantioselective synthesis of γ-amino acids

We determined *N*-(2-pyridyl)-γ-butyrolactam (**1**) as a model substrate and investigated the alkylation in the presence of various chiral cationic iridium catalysts.[16] As a result, Ir-tolBINAP catalyst gave the best result. We further examined the reaction of styrene (**2a**) and various substituted styrenes **2b**-**2f** under the optimal reaction conditions (Table 1). The reaction of **1** with styrene (**2a**) proceeded, and the desired chiral lactam **3a** was obtained in high yield and ee (Entry 1). When styrenes with methyl or trifluoromethyl group on its *para*-position were used, the corresponding alkylated lactams **3b** and **3c** were obtained with the almost same ee as that of **3a** (Entries 2 and 3). Halogenated styrenes were also good coupling partners, and chiral γ-lactams **3d** and **3e** were obtained in moderate yield with high ee (Entries 4 and 5). In the reaction with pentafluorostyrene (**2f**), the enantioselectivity was well above 90% (Entry 6).[17]

Table 1 Enantioselective alkylation of γ-lactam **1** with styrenes

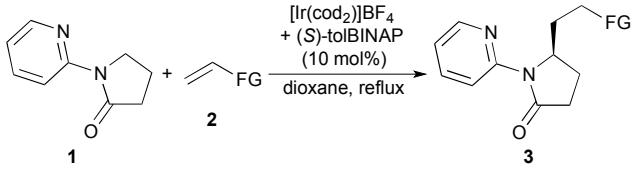


Entry[a]	Ar	Yield (%)	Ee (%)[c]
1	Ph (**2a**)	85 (**3a**)	82
2	4-MeC_6H_4 (**2b**)	56 (**3b**)	84
3	4-$CF_3C_6H_4$ (**2c**)	87 (**3c**)	85
4	4-FC_6H_4 (**2d**)	60 (**3d**)	83
5	4-BrC_6H_4 (**2e**)	50 (**3e**)	84
6	C_6F_5 (**2f**)	69 (**3f**)	94

[a] The ratio of γ-lactam **1**/styrene **2** was 1/8. The initial concentration of **1** was 2.0 M, and the reaction was run for a week.

We further examined functionalized alkenes under the same reaction conditions (Table 2). Acrylates were the best coupling partners: less amount of ethyl acrylate **2h** gave the desired product in high yield and ee in less reaction time (Entries 1 and 2).[18] It is noteworthy that this reaction could be carried out in one-gram scale (Entry 3). Vinyl sulfonate **2i** and vinyl phosphonate group **2j** were also accepted in this reaction, and the desired chiral γ-lactams **3i** and **3j** were obtained (Entries 4 and 5).

Table 2 Enantioselective alkylation of γ-lactam **1** with functionalized alkenes



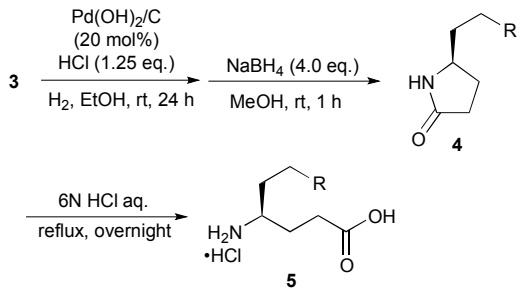
Entry[a]	FG	Yield (%)	Ee (%)
1	CO_2Me (**2g**)	82 (**3g**)	91
2[b]	CO_2Et (**2h**)	87 (**3h**)	91
3[b,c]	CO_2Et (**2h**)	85 (**3h**)	94
4	SO_2Ph (**2i**)	70 (**3i**)	82
5	$P(O)(OEt)_2$ (**2j**)	82 (**3j**)	76

[a] The ratio of γ-lactam **1**/alkene **2** was 1/8. The initial concentration of **1** was 0.5 M, and the reaction was run for a week. [b] The ratio of γ-lactam **1**/ethyl acrylate **2h** was 1/4. The initial concentration of **1** was 0.5 M, and the reaction was run for 3 days. [c] The reaction was performed in one-gram scale.

We next examined the transformation of the obtained alkylated products into *N*-unprotected γ-lactams **4** and γ-amino acids **5** (Table 3). The first step is removal of the pyridyl group. The γ-lactam **3a** (82% ee) was submitted to hydrogenation with a catalytic amount of $Pd(OH)_2/C$ under acidic conditions. Subsequent reduction using sodium borohydride gave deprotected γ-lactam **4a** in 78% yield (Entry 1). Aabsolute configuration of **4a** was determined by the comparison of the sign of optical rotation in the literature.[19] Retention of enantiomeric excess was ascertained in this transformation (**4a**: 82% ee). Other alkylated products **3b**-**3j** were also converted to non-protected lactams **4b**-**4j** in moderate to high yields under the same conditions (Entries 2-7).

The second step is hydrolysis of γ-lactams **4**. Acidic hydrolysis of γ-lactam **4a** gave phenethyl substituted γ-amino acid **5a** in 86% yield, and no decrease of ee was observed (**5a**: 82% ee) (Entry 1). Other aryl- and sulfonylethyl-substituted γ-lactams **4b**-**4i** were also transformed into the corresponding amino acid hydrochloride salts **5b**-**5i** in good to high yield (Entries 2-6). In the case of γ-lactam **4j**, the phosphate moiety also underwent hydrolysis, and phosphono amino acid **5j** was obtained in moderate yield (Entry 7).

Table 3 Removal of pyridyl group and hydrolysis of lactams



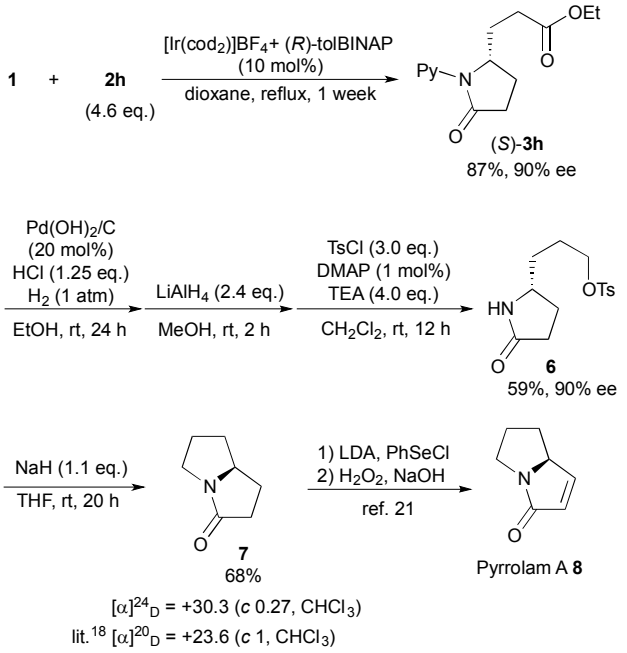
Entry	R	Yield of **4** (%)	Yield of **5** (%)
1	Ph (**3a**)	78 (**4a**)	86 (**5a**)
2	4-MeC_6H_4 (**2b**)	85 (**4b**)	71 (**5b**)
3	4-$CF_3C_6H_4$ (**2c**)	73 (**4c**)	79 (**5c**)
4	4-FC_6H_4 (**2d**)	62 (**4d**)	93 (**5d**)
5	C_6F_5 (**3f**)	81 (**4f**)	71 (**5f**)
6	SO_2Ph (**3i**)	52 (**4i**)	64 (**5i**)
7	$P(O)(OEt)_2$ (**3j**)	85 (**4j**)	56 (**5j**)[a]

[a] R in **5j** is $P(O)(OH)_2$.

Finally, we synthesized bicyclic lactam **7**, which is a known synthetic precursor of pyrrolam A (Scheme 3). Pyrrolam A **8** has been isolated from the bacterial strain *Streptomyces olivaceus* along with the related bicyclic lactams pyrrolam B-D.[20] The unique chiral bicyclic lactam with a double bond in conjugate system has attracted considerable attention of synthetic chemists, and various synthetic strategies have been developed for its total syntheses.[21] We here tried to use our originally developed C-H alkylation of γ-lactam for the synthesis of dihydro-pyrrolam A **7**. We examined Ir-catalyzed C-H alkylation with ethyl acrylate (**2h**) using (*R*)-tolBINAP for the synthesis of natural type of pyrrolam A and obtained (*S*)-**3h** in good yield with high ee. The next three steps, which include removal of the pyridyl group, reduction of ester moiety, and tosylation of the primary alcohol, were executed without purification of the intermediates. As a result, he tosylate **6** was afforded in 59% yield along with the retention of enantiomeric excess (90% ee) after the 3 steps.[22] Then, the cyclization of **6** using sodium hydride gave desired bicyclic lactam **7** in 68% yield,[22] whose sign of optical rotation accorded with that in the literature.[20] The final step to pyrrolam A **8** is a known procedure.[23]

Conclusions

We have developed enantioselective Ir-catalyzed sp^3 C-H bond activation of the γ-butyrolactam with various alkenes, such as styrene derivatives and electron-deficient olefins. The present reaction provides a new simple protocol for the synthesis of chiral 5-alkylated γ-lactams and 4-alkylated γ-amino acids. This protocol could be used for the efficient enantioselective synthesis of bicyclic lactam **7**, precursor of pyrrolam A **8**. Further studies for the use of our originally developed C-H bond activation in the syntheses of other natural products and unnatural amino acid derivatives are underway in our laboratory.



$[\alpha]^{24}_D$ = +30.3 (*c* 0.27, $CHCl_3$)
lit.[18] $[\alpha]^{20}_D$ = +23.6 (*c* 1, $CHCl_3$)

Scheme 3 Formal asymmetric synthesis of pyrrolam A

Acknowledgments

This work was supported by Grand-in-Aid for Scientific Research on Innovative Areas, "Molecular Activation Directed toward Straightforward Synthesis," MEXT, JST, ACT-C, and Grants for Excellent Graduate School (Practical Chemical Wisdom), Waseda University, MEXT, Japan.We also thank Mr. Shun Yuzawa (Waseda Univ.) for his assistance in the preliminary work.

Notes and references

[a] Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.
[b] International Center for Science and Engineering Programs (ICSEP), Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.
[c] JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.
* E-mail: tshibata@waseda.jp

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1 a) E. Roberts, *Biochem. Pharmacol.,* 1974, **23**, 2637-2649; b) I. A. Sytinsky, A. T. Soldatenkov, *Prog. Neurobiol.,* 1978, **10**, 89-133; c) G. A. R. Johnston, *Pharmacol. Ther.,* 1996, **69**, 173-198.
2 a) B. A. Sachais, J. N. Logue, M. S. Carey, *Arch Neurol.,* 1977, **34**, 422-428; b) G. H. Fromm, C. F. Terrence, A. S. Chattha, J. D. Glass, *Arch Neurol.,* 1980, **37**, 768-771; c) G. Costantino, A. Macchiarulo, A. E. Guadix, R. Pellicciari, *J. Med. Chem.,* 2001, **44**, 1827-1832.
3 a) L. Singh, M. J. Field, P. Ferris, J. C. Hunter, R. J. Oles, R. G. Williams, G. N. Woodruff, *Psychopharmacology,* 1996, **127**, 1-9; b) J. S. Bryans, N. Davies, N. S. Gee, V. U. K. Dissanayake, G. S. Ratcliffe, D. C. Horwell, C. O. Kneen, A. I. Morrell, R. J. Oles, J. C. O'Toole, G. M. Perkins, L. Singh, N. Suman-Chauhan, J. A. O'Neill, *J. Med. Chem.,* 1998, **41**, 1838-1845.
4 a) P. Yuen, G. D. Kanter, C. P. Taylor, M. G. Vartanian, *Bioorg. Med. Chem. Lett.,* 1994, **4**, 823-826; b) M. S. Hoekstra, D. M. Sobieray, M. A. Schwindt, T. A. Mulhern, T. M. Grote, B. K. Huckabee, V. S. Hendrickson, L. C. Franklin, E. J. Granger, G. L. Karrick, *Org, Proc. Res. Dev.,* 1977, **1**, 26-38; c) G. J. Sills, *Curr. Opin. Pharmacol.,* 2006, **6**, 108-113.

5 B. Lippert, B. W. Metcalf, M. J. Jung, P. Casara, *Eur. J. Biochem.,* 1977, **74**, 441-445.
6 a) T. A. Martinek, F. Fülöp, *Chem. Soc. Rev.,* 2012, **41**, 687-702; b) M. W. Giuliano, S. J. Maynard, A. M. Almeida, L. Guo, I. A. Guzei, L. C. Spencer, S. H. Gellman, *J. Am. Chem. Soc.,* 2014, **136**, 15046-15053.
7 a) M. Amorín, R. J. Brea, L. Castedo, J. R. Granja, *Org. Lett.,* 2005, **7**, 4681-4684; b) C. Baldauf, R. Günther, H.-J. Hofmann, *J. Org. Chem*., 2005, **70**, 5351-5361; c) R. J. Brea, L. Castedo, J. R. Granja, *Chem. Commun*., 2007, 3267-3269; d) C. Reiriz, L. Castedo, J. R. Granja, *J. Pept. Sci.,* 2008, 14, 241-249; e) R. G.-Fandiño, L. Castedo, J. R. Granja, S. A. Vázquez, *J. Phys. Chem. B,* 2010, **114**, 4973-4983; f) R. G.-Fandiño, M. Amorín, L. Castedo, J. R. Granja, *Chem. Sci.,* 2012, **3**, 3280-3285; g) A. Guerra, R. J. Brea, M. Amorín, L. Castedo, J. R. Granja, *Org. Biomol. Chem.*, 2012, **10**, 8762-8766; h) N. R.-Vázquez, S. Salzinger, L. F. Silva, M. Amorín, J. R. Granja, *Eur. J. Org. Chem.,* 2013, 3477-3493; i) S. V. Jadhav, R. Misra, H. N. Gopi, *Chem. Eur. J.,* 2014, **20**, 16523-16528.
8 M. Ordóñez, C. Cativiela, *Tetrahedron: Asymmetry*, 2007, **18**, 3-99.
9 Enantioselective synthesis of 4-substituted γ-amino acid derivatives, see: a) C. E. Anderson, L. E. Overman, *J. Am. Chem. Soc.,* 2003, **125**, 12412-12413; b) T. Ooi, S. Fujioka, K. Maruoka, *J. Am. Chem. Soc.,* 2004, **126**, 11790-11791; c) W. J. Nodes, D. R. Nutt, A. M. Chippindate, A. J. A. Cobb, *J. Am. Chem. Soc*., 2009, **131**, 16016-16017; d) L.-T. Shen, L.-H. Sun, S. Ye, *J. Am. Chem. Soc*., 2011, **133**, 15894-15897; e) K. L. Kimmel, J. D. Weaver, J. A. Ellman, *Chem. Sci.,* 2012, **3**, 121-125; f) C. Appayee, A. J. Fraboni, S. E. Brenner-Moyer, *J. Org. Chem.,* 2012, **77**, 8828-8834; g) Y.-Y. Zhou, L.-J. Wang, J. Li, X.-L. Sun, Y. Tang, *J. Am. Chem. Soc.,* 2012, **134**, 9066-9069; h) H. Bao, U. K. Tambar, *J. Am. Chem. Soc.,* 2012, **134**, 18495-18498; i) X.-Y. Chen, F. Xia, J.-T. Cheng, S. Ye, *Angew. Chem. Int. Ed*., 2013, **52**, 10644-10647; j) Y.-Q. Fang, P. M. Tadross, E. N. Jacobsen, *J. Am. Chem. Soc.,* 2014, **136**, 17966-17968.
10 For selected reviews, see: a) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.,* 2002, **102**, 1731–1769; b) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.,* 2003, **345**, 1077–1101; c) K. Godula, D. Sames, *Science,* 2006, **312**, 67–72; d) H. M. L. Davies, J. R. Manning, *Nature,* 2008, **451**, 417–424; e) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.,* 2009, **48**, 5094–5115; f) T. W. Lyons, M. S. Sanford, *Chem. Rev.,* 2010, **110**, 1147–1169; g) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.,* 2010, **46**, 677–685; h) C. S. Yeung, V. M. Dong, *Chem. Rev.,* 2011, **111**, 1215–1292; i) S. M. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev*., 2011, **40**, 5068–5083.
11 a) Z. Li, C.-J. Li, *Org. Lett*. 2004, **6**, 4997; b) B.-F. Shi, N. Maugel, Y.-H. Zhang, J.-Q. Yu, *Angew. Chem. Int. Ed*., 2008, **47**, 4882-4886; c) M. Wasa, K. M. Engle, J.-Q. Yu, *Isr. J. Chem*., 2010, **50**, 605-616; d) M. Wasa, K. M. Engle, D. W. Lin, E. J. Yoo, J.-Q. Yu, *J. Am. Chem. Soc*. 2011, **133**, 19598.; e) S. Pan, K. Endo, T. Shibata, *Org. Lett*., 2011, **13**, 4692-4695; f) S. Pan, Y. Matsuo, K. Endo, T. Shibata, *Tetrahedron,* 2012, **68**, 9009–9015; g) K.-J. Xiao, D. W. Lin, M. Miura, R.-Y. Zhu, W. Gong, M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc*., 2014, **136**, 8138–8142.
12 a) K. Tsuchikama, M. Kasagawa, Y. Hashimoto, K. Endo, T. Shibata, *J. Organomet. Chem.,* 2008, **693**, 3939–3942; b) K. Tsuchikama, M. Kasagawa, K. Endo, T. Shibata, *Org. Lett.,* 2009, **11**, 1821–1823; c) K. Tsuchikama, M. Kasagawa, K. Endo, T. Shibata, *Synlett,* 2010, 97–100; d) T. Shibata, H. Hirashima, M. Kasagawa, K. Tsuchikama, K. Endo, *Synlett,* 2011, 2171-2176; e) S. Takebayashi, T. Shibata, *Organometallics,* 2012, **31**, 4114-4117; f) S. Pan, N. Ryu, T. Shibata, *J. Am. Chem. Soc*., 2012, **134**, 17474–17477; g) S. Pan, N. Ryu, T. Shibata, *Adv. Synth. Catal*., 2014, **356**, 929-933; h) S. Pan, T. Wakaki, N. Ryu, T. Shibata, *Chem. Asian J.,* 2014, **9**, 1257-1260; i) T. Shibata, T. Shizuno, *Angew. Chem. Int. Ed*., 2014, **53**, 5410-5413; j) T. Shibata, Y. Matsuo, *Adv. Synth. Catal*., 2014, **356**, 1516-1520; k) T. Shibata, N. Ryu, H. Takano, *Adv. Synth. Catal*., 2015, **357**, 1131-1135; l) T. Shibata, T. Shizuno, T. Sasaki, *Chem. Commun*., 2015, **51**, 7802-7804, m) T. Shibata, H. Takano, *Org. Chem. Front*., 2015, **2**, 383-387; n) Y. Tahara, M. Ito, K. S. Kanyiva, T. Shibata, *Chem. Eur. J.*, 2015, **21**, 11340-11343.
13 For recent selected examples, see: a) E. Choi, C. Lee, M. Cho, J. J. Seo, J. S. Yang, S. J. Oh, K. Lee, S.-K. Park, H. M. Kim, H. J. Kwon, G. Han, *J. Med. Chem.,* 2012, **55**, 10766-10770; b) J. Park, C. Song, K. Choi, T. Sim, B. Moon, E. J. Roh, *Bioorg. Med. Chem. Lett.,* 2013, **23**, 5515-5518; c) G. Giannini, L. Vesci, G. Battistuzzi, D. Vignola, F. M. Milazzo, M. B. Guglielmi, M. Barbarino, M. Santaniello, N. Fantò, M. Mor, S. Rivara, D. Pala, M. Taddei, C. Pisano, W. Cabri, *J. Med. Chem.,* 2014, **57**, 8358-8377.
14 For recent selected examples, see: a) A. Younai, G. F. Chin, J. T. Shaw, *J. Org. Chem.,* 2010, **75**, 8333-8336; b) T. A. M. Gulder, B. S. Moore, *Angew. Chem. Int. Ed*., 2010, **49**, 9346-9367; c) M. C. Wilson, S.-J. Nam, T. A. M. Gulder, C. A. Kauffman, P. R. Jensen, W. Fenical, B. S. Moore, *J. Am. Chem. Soc.,* 2011, **133**, 1971-1977; d) M. Masi, S. Meyer, S. Clement, A. Andolfi, A. Cimmino, A. Evidente, *Tetrahedron,* 2014, **70**, 1497-1501; e) T. Matsumoto, S. Nakamura, T. Ohta, K. Fujimoto, M. Yoshikawa, K. Ogawa, H. Matsuda, *Org. Lett*., 2014, **16**, 3076-3078.
15 For a recent review of transition metal-catalyzed synthesis of γ-lactams, see: L.-W. Ye, C. Shu, F. Gagosz, *Org. Biomol. Chem*., 2014, **12**, 1833-1845.
16 Optimization of the catalysts was listed in supplementary information.
17 The reaction of **1** with 1-nonene gave a poor result (5%, 23% ee).
18 The reaction of **1** with methyl metacrylate, (*E*)-methyl crotonate or cinnamate did not proceed at all.
19 Determination of absolute configuration of **4a**, see: C. Dong, F. Mo, J. Wang, *J. Org. Chem.,* 2008, **73**, 1971-1974.
20 R. Grote, A. Zeeck, J. Stümpfel, H. Zähner, *Liebigs Ann. Chem.,* 1990, 525-530.
21 A review on total synthesis of pyrrolam A, see: a) M. S. Majik, S. G. Tilve, *Synthesis,* 2012, **44**, 2673-2681; a recent example, see: b) B. J. Marsh, H. Adams, M. D. Barker, I. U. Kutama, S. Jones, *Org. Lett*., 2014, **16**, 3780-3783.
22 S. Lemaire, G. Giambastiani, G. Prestat, G. Poli, *Eur. J. Org. Chem.,* 2004, 2840-2847.
23 M. S. Majik, J. Shet, S. G. Tilve and P. S. Parameswaran, *Synthesis*, 2007, 663-665.

