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ARTICLE TYPE

Regiospecific and Highly Stereoselective Synthesis of β-Amino (*Z*)-Enylphosphonates *via* β-Hydrogen Migration Reaction of Dialkyl α-Diazophosphonates Catalyzed by AgOTf

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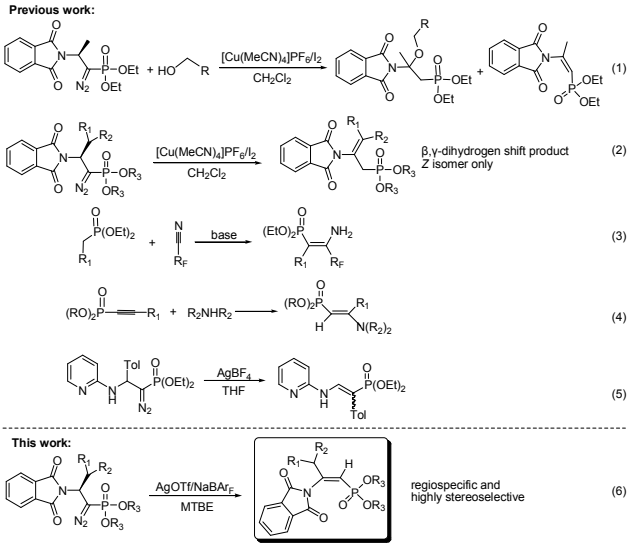
A series of dialkyl α-diazophosphonates bearing different substituents have been prepared from natural amino acids in order to investigate the steric effect in 1,2-migration reaction of metal carbene. The diazo decomposition of the diazophosphonates with AgOTf/NaBAr$_F$ complex resulted in β-hydrogen migration to give β-amino (*Z*)-enylphosphonates in good yields with high regio- and stereoselectivity. A possible reaction mechanism shows that the steric effect could dramatically influence the geometric isomerism aptitude. This new method for constructing (*Z*)-β-amino vinylphosphonates should be of general utility in organic synthesis.

Diazo compounds are commonly used important precursors of metal carbene, which can subsequently undergo diverse chemical transformation.[1] Numerous efficient transformation such as cyclopropanations,[2] X-H (X = C, Si, O, N, S, etc) insertions,[3] cycloadditions[4] and ylide transformations[5] have been developed, as well as studies on reactivities and mechanisms of the involved transition-metal carbenoids.[6] In the catalytic reaction of α-diazo carbonyl compounds with both metal carbene and free carbene as reactive intermediates, 1,2-hydrogen migration is a frequently encountered reaction, which referred to as β-hydride shift.[7] In some cases, 1,2-hydrogen migration can find useful application in organic synthesis. For example, Taber and co-workers have shown that α-diazo esters undergo β-hydride elimination with rhodium (II) trifluoroacetate dimer produce (*Z*)-α,β-unsaturated esters in good yields.[8] Wang has found that the diazo decomposition of β-(*N*-tosyl)amino diazo carbonyl compounds gives either 1,2-aryl migration or 1,2-hydride migration products as the major products, depending on the reaction conditions.[9]

In contrast to that found in α-diazo carbonyl compounds, α-diazophosphonyl compounds have not been studied systematically in metal carbene reactions.[10] Recently, we reported a kind of novel α-diazophosphonyl compounds prepared from natural amino acid, which could afford β-alkoxy substituted β-amino phosphonates derivatives through a combined C-H functionalization/O-H insertion process (Scheme 1, eq. 1).[11] As a natural extension of the diazo compounds 1,2-hydride migration reaction, we developed a stereoselective [Cu(MeCN)$_4$]PF$_6$/I$_2$ catalyzed β,γ-dihydrogen shift reaction for the synthesis of (Z)-β-alkenyl substituted β-aminophosphonates (Scheme 1, eq. 2).[12]

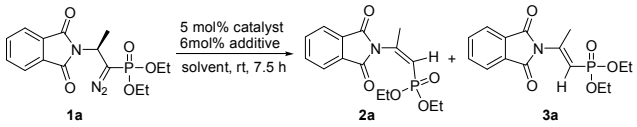


Scheme 1. Previous and proposed work.

β-Aminophosphonates are the phosphorus analogues of β-amino acids, and therefore have widely used for biological and pharmaceutical applications, such as enzyme inhibitors, agrochemicals, or antivirus activities.[13] β-Amino vinylphosphonates can be regarded as isosters of β-aminophosphonates. These compounds can be prepared *via* formation of C-C-, C-N-, and C-P-bonds.[14] For example, Palacios reported the preparation of fluoroalkyl β-enaminophosphonates from alkylphosphonates and perfluoroalkyl nitriles (Scheme 1, eq. 3).[14a] Ionin also reported the addition reaction of secondary amines to alkynylphosphonates catalyzed by Cu(I) salts to form (*E*)-β-enaminophosphonates (Scheme 1, eq. 4).[14b] In spite of these results up to now there is only one example of the synthesis of β-enaminophosphonates from the corresponding α-diazoethylphosphonates underwent an exclusive 1,2-aryl shift to form the enamine products (Scheme 1, eq. 5).[14c] Continuing with our interest in the chemistry of aminophosphorus derivatives,[15] here we report the first example for converting dialkyl α-diazophosphonates into β-amino (*Z*)-enylphosphonates in a regiospecific and highly stereoselective manner (Scheme 1, eq.

6).

Table 1. Optimization of the reaction conditions.[a]



1a 2a 3a

Entry	Catalysts	Solvent	Additive	*Z*/*E* ratio (**2a**:**3a**)[b]	Overall yield (%)[c]
1	$Cu(MeCN)_4PF_4$	CH_2Cl_2	—	7:93	38
2	CuOTf	CH_2Cl_2	—	63:37	11
3	$Rh_2(OAc)_4$	CH_2Cl_2	—	23:77	15
4	$Hg(OTf)_2$	CH_2Cl_2	—	—	N.R.
5	AgOTf	CH_2Cl_2	—	73:27	64
6	AgOTf	MTBE[d]	—	76:24	65
7	AgOTf	CH_2Cl_2	$NaBAr_F$[e]	63:37	77
8	AgOTf	CH_2Cl_2	$PhCONH_2$[f]	64:36	63
9	AgOTf	CH_2Cl_2	CH_3CONH_2[g]	61:39	71
10	AgOTf	CH_2Cl_2	*t*-BuOH[h]	60:40	75
11	AgOTf	CH_2Cl_2	DMF[i]	69:31	65
12	AgOTf	CH_2Cl_2	PhOH[j]	62:38	70
13	AgOTf	MTBE	$NaBAr_F$	78:22	73
14	AgOTf	Et_2O	$NaBAr_F$	86:14	51
15	AgOTf	$PhCH_3$	$NaBAr_F$	78:22	61
16	AgOTf	*i*-Pr_2O	$NaBAr_F$	80:20	60
17	AgOTf	PhOMe	$NaBAr_F$	80:20	51
18	AgOTf	acetone	$NaBAr_F$	73:27	45
19[k]	AgOTf	MTBE	$NaBAr_F$	80:20	75
20[l]	AgOTf	MTBE	$NaBAr_F$	75:25	73
21[m]	AgOTf	MTBE	$NaBAr_F$	80:20	77

[a] Unless otherwise noted, all reactions were carried out using α-diazophosphonate **1a** (0.28 mmol, 1 equiv) in 2 mL solvent with 5 mol% of catalyst and 6 mol% additive in 2 mL solvent at 25 °C for 7.5 h (before addition 1.5 h, after addition 6 h). [b] The product ratio was determined by ^{31}P NMR of the crude product. [c] Overall yield of the mixture of **2a** and **3a** after silica gel chromatograph. [d] MTBE = methyl *tert*-butyl ether. [e] $NaBAr_F$ = sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate. [f] 50 mol% $PhCONH_2$ was used. [g] 50 mol% CH_3CONH_2 was used. [h] 5eq. *t*-BuOH was used. [i] 5 eq. DMF was used. [j] 5 eq. PhOH was used. [k] 4 mL MTBE was used to dissolve α-diazophosphonate **1a**. [l] 2mol% AgOTf and 3mol% $NaBAr_F$ was used. [m] 10mol% AgOTf and 11mol% $NaBAr_F$ was used.

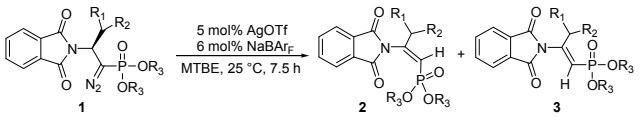
Initially, the amino acid derived α-diazophosphonyl compound **1a**[11] was the first substrate studied to examine the effect of the catalysts on the reaction, and the results were summarized in Table 1. The results revealed that $Cu(MeCN)_4PF_6$ decomposed **1a** mainly afforded (*E*)-α,β-unsaturated phosphonate **3a** in low yield (Table 1, entry 1). CuOTf and $Rh_2(OAc)_4$ could only decompose **1a** with low yields and obtain **2a** and **3a** with poor stereoselectivities (Table 1, entries 2-3). $Hg(OTf)_2$ could not decompose **1a** at all and the starting material recovered (Table 1, entry 4). To our delight AgOTf could promote the reaction smoothly with higher yield and good stereoselectivity (*Z*/*E* = 73:27) (Table 1, entry 5). When the reaction proceeded in MTBE, the *Z*/*E* ratio will increase to 76:24 (Table 1, entry 6). To further improve the reactivity and stereoselectivity, the effects of additive and solvent were investigated. In recent years the use of weakly or noncoordinating anions as counter anions is of significant interest in both synthesis and catalysis.[16] The lack of reactivity and non-nucleophilic character of $[BAr_F]^-$ have led to the widespread use as noncoordinating.[17] In our investigation, after screening $NaBAr_F$, it was found that $PhCONH_2$, CH_3CONH_2, *t*-BuOH, DMF and PhOH could not give superior results in terms of reactivity and stereoselectivity (Table 1, entries 7-12).

With the best AgOTf catalyst combined with $NaBAr_F$ as additive (Table 1, entry 7), we next carried out the reaction in different solvents to determine the best solvent for this reaction. Among the various solvents tested, diethyl ether, toluene, isopropyl ether, anisole and acetone afforded lower yields of the expected products **2a** and **3a** with moderate stereoselectivities (Table 1, entries 14-18). The most suitable solvent was found to be methyl *tert*-butyl ether (MTBE), (*Z*)-diethyl 2-(1,3-dioxoisoindolin-2-yl)prop-1-enylphosphonate **2a** was obtained in good yield and stereoselectivity (Table 1, entry 13). With further optimization of the reaction conditions, we found that increasing the solvent amount to 6 mL, the *Z*/*E* ratio could increase to 80:20 with good yield (Table 1, entry 19). Furthermore, a decrease in the catalyst loading to 2 mol% of AgOTf and 3 mol% of $NaBAr_F$ led to a decrease in yield and stereoselectivity (Table 1, entry 20). Similar result was obtained when the reaction was performed in MTBE with increasing the catalyst loading to 10 mol% of AgOTf and 11 mol% of $NaBAr_F$ (Table 1, entry 21). Thus, the optimal reaction conditions for this transformation were determined to be 0.28 mmol α-diazophosphonate **1a**, 5 mol% of AgOTf as catalyst and 6 mol% of $NaBAr_F$ as additive in 6 mL MTBE as solvent at room temperature. The two stereoisomers **2a** and **3a** could be separated after purification.

Based on the above optimization efforts, the substrate scope of this reaction was investigated (Table 2). The impact of substituent groups on β-position of dialkyl α-diazophosphonates **1** which derived from different natural amino acids was evaluated. The tested α-diazophosphonates **1a-b** with different substituents on β-position, such as methyl and isobutyl groups afforded good level yields of β-amino-α,β-unsaturated phosphonates **2a-b** in favor of the *Z* isomer (Table 2, entries 1-2). In cases where the substituent groups on β-position of dialkyl α-diazophosphonates **1** change to benzyl, 2-propylisoindoline-1,3-dione, and *p*-tolyl acetate groups, a significant amount of *Z*-isomers **2c-e** was formed (Table 2, entries 3-5).

It was found that the *Z*/*E* isomer selectivity of **2** and **3** impacted by the size of the R_1 and R_2 groups of α-diazophosphonates **1**. With the increasing bulk of R_1 group, the *Z*/*E* ratio of **2** and **3** ranged from 80:20 to 98:2 with moderate to good yields (Table 2, entries 1-5). In cases where the substituent groups on β-position of dialkyl α-diazophosphonates change to isopropyl and isobutyl groups, no desired products **2f-g** and **3f-g** obtained due to the poor solubility of substrate **1f-g** in MTBE. When use CH_2Cl_2 as solvent without the add of $NaBAr_F$, a significant amount of *Z* isomers **2f-g** were formed with good yields (Table 2, entries 6-7). It is worthwhile to note that diethyl α-diazophosphonate **1h** which derived from methionine can not proceed this reaction and get the desired product (Table 2, entry 8).

Table 2. Scope of the reaction.[a]



Entry	Substrate	R^1	R^2	R^3	*Z*/*E* ratio (**2**:**3**)[b]	Overall yield (%)[c]
1	**1a**	H	H	Et	80:20	75
2	**1b**	$CH(CH_3)_2$	H	Et	80:20	87
3	**1c**	Ph	H	Et	93:7	87
4	**1d**	$(CH_2)_3$NPhth	H	Et	91:9	62
5	**1e**	*p*-AcOPh	H	Et	98:2	63
6[d]	**1f**	CH_3	CH_3	Et	100:0	76
7[d]	**1g**	CH_3	Et	Et	100:0	73
8	**1h**	CH_2SCH_3	H	Et	—	N.R.
9	**1i**	H	H	Me	90:10	62
					(69:31)[d]	(71)[d]
10	**1j**	H	H	*i*-Pr	78:22	71
					(72:28)[d]	(72)[d]
11	**1k**	H	H	*n*-Bu	72:28	61
					(69:31)[d]	(89)[d]
12	**1l**	Ph	H	Me	90:10	79
13	**1m**	Ph	H	*i*-Pr	96:4	51
					(88:12)[d]	(79)[d]
14	**1n**	Ph	H	*n*-Bu	92:8	28
					(89:11)[d]	(94)[d]

[a] Reaction conditions: α-diazophosphonate **1** (0.28 mmol) in 6 mL of MTBE at 25°C in the presence of 5 mol% of AgOTf and 6 mol% of $NaBAr_F$ for 7.5 h (before addition 1.5 h, after addition 6 h). [b] The product ratio was determined by ^{31}P NMR of the crude product and the configuration of **2** was assigned as *Z* by the ^1H-^1H NOESY spectrum. [c] Overall yield of the mixture of **2** and **3** after silica gel chromatograph. [d] CH_2Cl_2 was used as the solvent without the addition of $NaBAr_F$.

To access the effect of substrates on product selectivity, we set out to study reactions of a series of dialkyl α-diazophosphonates **1i-n** under AgOTf/$NaBAr_F$ catalytic condition. The migratory product aptitude was dependent upon the size of the R^3 group. When the bulk of R^3 group was increased from methyl to butyl, the *Z*/*E* isomer products **2** and **3** were obtained with lower yields. Interestingly, when the reaction proceeding in CH_2Cl_2 without the add of $NaBAr_F$, the low yields could be improved with some changes for the *Z*/*E* isomer selectivities (Table 2, entries 9-14). The structure of **2a** was confirmed by single crystal X-ray diffraction (see the ESI† for details).[18]

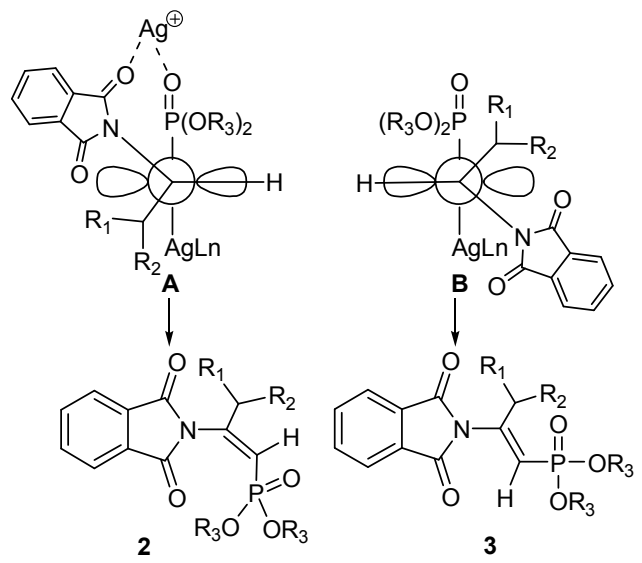


Figure 2. Conformations leading to β-hydrogen migration.

The *Z*/*E* stereoselectivity of β-amino-α,β-unsaturated phosphonates implies that conformational factors may play a role in the migration process. For the migration to occur, it is necessary that the migrating bond needs to be parallel to the *p* orbital of the carbene carbon in the transition states.[19] Of the two conformations **A** and **B**, **B** is likely to be disfavored because of steric hindrance between the phosphonate group and the R_1 group. Thus, the β-hydrogen migration is proposed to occur *via* transition state **A** which leads to the observed *Z*-isomer. The effect is most likely due to the increased steric hindrance between R_1 and the phosphonate group, which affects the populations and barriers to their interconversion, of the stereoelectronically required conformations for migration. Besides the steric hindrance affluence, Ag^+ participates chelation effect should not be ruled out. As shown in Figure 2, Ag^+ may coordinate with phosphonate group and phthalimide group in transition state **A** which lead to the formation of *Z*-isomer. In transition state **B**, the chelation effect is lacked, therefore conformation **A** is more favored than **B**.

In conclusion, we have developed a new and convenient

synthesis of β-amino (*Z*)-enylphosphonates from amino acid-derived dialkylphosphonates with complete control over regio- and stereochemistry. The influence factors on the *Z*/*E* isomer selectivity have been discussed. The investigation demonstrated that, steric factors play the important role in affecting the geometric isomerism aptitude in this carbene reaction. Further researches for extension of this reaction are currently underway in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, characterization of all compounds, and copies of ^{1}H and ^{13}C NMR spectra for selected compounds. CCDC 893994. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

1 For recent reviews, see: (a) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou and T. Ye, *Chem. Rev.,* **2010**, *110*, 704; (b) A. Padwa, *Chem. Soc. Rev*., **2009**, *38*, 3072; (c) H. M. L. Davies and J. R. Denton, *Chem. Soc. Rev*., **2009**, *38*, 3061; (d) Z. H. Zhang and J. B. Wang, *Tetrahedron* **2008**, *64*, 6577; (e) H. M. L. Davies and S. J. Hedley, *Chem. Soc. Rev*., **2007**, *36*, 1109; (f) H. M. L. Davies and R. E. J. Bechwith, *Chem. Rev.,* **2003**, *103*, 2861; (g) M. P. Doyle, M. A. McKervey and T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*: *From Cyclopropanes to Ylide*; Wiley: New York, **1998**; pp 433-436; (h) D. J. Miller and D. J. Moody, *Tetrahedron,* **1995**, *51*, 10811.

2 For selected recent examples, see: (a) C. Schnaars and T. Hansen, *Org. Lett*., **2012**, *14*, 2794; (b) S. R. Ovalles, J. H. Hansen and H. M. L. Davies, *Org. Lett*. **2011**, *13*, 4284; (c) J. F. Briones and H. M. L. Davies, *Tetrahedron,* **2011**, *67*, 4313; (d) V. N. G. Lindsay, C. Nicolas and A. B. Charette, *J. Am. Chem. Soc.,* **2011**, *133*, 8972; (e) M. P. Doyle, *Angew. Chem. Int. Ed*., **2009**, *48*, 850.

3 For selected examples on carbenoid C-H insertion, see: (a) M. P. Doyle, M. Ratnikov and Y. Liu, *Org. Biomol. Chem*., **2011**, *9*, 4007; (b) A. DeAnglis, V. W. Shurtleff, O. Dmitrenko and J. M. Fox, *J. Am. Chem. Soc.,* **2011**, *133*, 1650; (c) S. A. Wolckenhauser, A. S. Devlin and J. Du Bois, *Org. Lett*., **2007**, *9*, 4363; (d) H. M. L. Davies, *Angew. Chem. Int. Ed*., **2006**, *45*, 6422; (e) H. M. L. Davies and R. J. Townsend, *J. Org. Chem*., **2001**, *66*, 6595. For selected examples on carbenoid O-H insertion, see: (f) S. F. Zhu, X. G. Song, Y. Li, Y. Cai and Q. L. Zhou, *J. Am. Chem. Soc.,* **2010**, *132*, 16374; (g) S. F. Zhu, Y. Cha, H. X. Mao, J. H. Xie and Q. L. Zhou, *Nature Chemistry,* **2010**, *2*, 546; (h) S. F. Zhu, C. Chen, Y. Cai and Q. L. Zhou, *Angew. Chem. Int. Ed.,* **2008**, *47*, 932; (i) C. Chen, S. F. Zhu, B. Liu, L. X. Wang and Q. L. Zhou, *J. Am. Chem. Soc.,* **2007**, *129*, 12616; (j) T. C. Maier and G. C. Fu, *J. Am. Chem. Soc.,* **2006**, *128*, 4594. For selected examples on carbenoid N-H insertion, see: (k) S. F. Zhu, B. Xu, G. P. Wang and Q. L. Zhou, *J. Am. Chem. Soc*., **2012**, *134*, 436; (l) Z. R. Hou, J. Wang, P. He, J. Wang, B. Qin, X. H. Liu, L. L. Lin and X. M. Feng, *Angew. Chem. Int. Ed*., **2010**, *49*, 4763; (m) B. Liu, S. F. Zhu, W. Zhang, C. Chen and Q. L. Zhou, *J. Am. Chem. Soc*., **2007**, *129*, 5834; (n) C. J. Moody, *Angew. Chem. Int. Ed*., **2007**, *49*, 9148. For selected examples on carbenoid Si-H insertion, see: (o) Y. Z. Zhang, S. F. Zhu, L. X. Wang and Q. L. Zhou, *Angew. Chem. Int. Ed*., **2008**, *47*, 8496. For selected examples on carbenoid S-H insertion, see: (p) Y. Z. Zhang, S. F. Zhu, Y. Cai, H. X. Mao and Q. L. Zhou, *Chem. Commun*., **2009**, 5362.

4 For selected recent examples, see: (a) X. Wang, X. Xu, P. Y. Zavalij and M. P. Doyle, *J. Am. Chem. Soc*., **2011**, *133*, 16402; (b) Y. Lian and H. M. L. Davies, *J. Am. Chem. Soc*., **2010**, *132*, 440; (c) Y. Lian, L. C. Miller, S. Born, R. Sarpong and H. M. L. Davies, *J. Am. Chem. Soc*., **2010**, *132*, 12422; (d) T. Kano, T. Hashimoto and K. Maruoka, *J. Am. Chem. Soc*., **2006**, *128*, 2174.

5 For selected recent examples, see: (a) Z. J. Li, B. T. Parr and H. M. L. Davies, *J. Am. Chem. Soc*., **2012**, *134*, 10942; (b) X. F. Xu, W. H. Hu, P. Y. Zavalij and M. P. Doyle, *Angew. Chem. Int. Ed.,* **2011**, *50*, 11152; (c) Z. J. Li and H. M. L. Davies, *J. Am. Chem. Soc*., **2010**, *132*, 396; (d) A. DeAngelis, M. T. Taylor and J. M. Fox, *J. Am. Chem. Soc*., **2009**, *131*, 1101; (e) H. X. Huang, X. Guo and W. H. Hu, *Angew. Chem. Int. Ed.,* **2007**, *46*, 1337.

6 (a) J. D. Xue, H. L. Luk and M. S. Platz, *J. Am. Chem. Soc*., **2011**, *133*, 1763; (b) Y. Liang, H. L. Zhou and Z. X. Yu, *J. Am. Chem. Soc*., **2009**, *131*, 17783; (c) J. Hansen, J. Autschbach and H. M. L. Davies, *J. Org. Chem*., **2009**, *74*, 6555; (d) M. C. Pirrung, H. Liu and A. T. Morehead, *J. Am. Chem. Soc*., **2002**, *124*, 1014; (e) E. Nakamura, N. Yoshikai and M. Yamanaka, *J. Am. Chem. Soc*., **2002**, *124*, 7181.

7 (a) L. Zhou, Y. Z. Liu, Y. Zhang and J. B. Wang, *Chem. Comm*., **2011**, *47*, 3622; (b) F. Xu, S. W. Zhang, X. N. Wu, Y. Liu, W. F. Shi and J. B. Wang, *Org. Lett*., **2006**, *8*, 3207; (c) F. P. Xiao and J. B. Wang, *J. Org. Chem*., **2006**, *71*, 5789; (d) F. Xu, W. F. Shi and J. B. Wang, *J. Org. Chem.,* **2005**, 70, 4191; (e) N. Jiang, Z. H. Qu and J. B. Wang, *Org. Lett*., **2001**, *3*, 2989; (f) A. DeAngelis, O. Dmitrenko and J. M. Fox, *J. Am. Chem. Soc*. **2011**, *134*, 11035; (g) C. M. Qin and H. M. L. Davies, *J. Am. Chem. Soc*., **2013**, *135*, 14516; (h) J. D. Dudones and P. Sampson, *Tetrahedron,* **2000**, *56*, 9555; (i) M. Otte, P. F. Kuijpers, O. Troeppner, I. Ivanović-Burmazović, J. N. H. Reek and B. De Bruin, *Chem.-Eur. J.* **2013**, *19*, 10170.

8 (a) D. F. Taber, M. J. Hennessy and J. P. Louey, *J. Org. Chem.,* **1992**, *57*, 436; (b) D. F. Taber, R. J. Herr, S. K. Pack and J. M. Geremia, *J. Org. Chem.,* **1996**, *61*, 2908.

9 N. Jiang, Z. H. Ma, Z. H. Qu, X. Y. Xing, L. F. Xie and J. B. Wang, *J. Org. Chem*., **2003**, *68*, 893.

10 (a) S. F. Zhu, W. Q. Chen, Q. Q. Zhang, H. X. Mao and Q. L. Zhou, *Synlett* **2011**, 919; (b) C. Y. Zhou, J. C. Wang, J. H. Wei, Z. J. Xu, Z. Guo, K. H. Low and C. M. Che, *Angew. Chem. Int. Ed*., **2012**, *51*, 11376; (c) J. F. Briones and H. M. L. Davies, *Org. Lett.,* **2011**, *13*, 3984; (d) V. N. G. Lindsay, D. Fiset, P. J. Gritsch, S. Azzi and A. B. Charette, *J. Am. Chem. Soc*., **2013**, *135*, 1463; (e) J. Wang, V. Boyarshikh and J. D. Rainier, *Org. Lett.,* **2011**, *13*, 700; (f) H. M. L. Davies and G. H. Lee, *Org. Lett.,* **2004**, *6*, 2117; (g) H. Zhang, X. J. Wen, L. H. Gan and Y. G. Peng, *Org. Lett.,* **2012**, *14*, 2126; (h) T. Hashimoto and K. Maruoka, *J. Am. Chem. Soc*. **2007**, *129*, 10054.

11 Y. Cai, Y. C. Lu, C. B. Yu, H. R. Lyu and Z. W. Miao, *Org. Biomol. Chem.,* **2013**, *11*, 5491.

12 Y. Cai, H. R. Lyu, C. B. Yu and Z. W. Miao, *Adv. Synth. Catal.* **2014**, *356*, 596.

13 For recent review see the following: (a) F. Palacios, C. Alonso and J. M. de los Santos, *Chem. Rev.,* **2005**, *105*, 899; (b) F. Palacios, C. Alonso and J. M. de los Santos, In *Enantioselective Synthesis of β-Amino Acids*, 2nd ed.; (Eds: E. Juaristi, V. A. Soloshonok), Wiley: New York, **2005**; pp 277-317.

14 (a) F. Palacios, A. M. Ochoa de Retana, S. Pascual and J. Oyarzabal, *J. Org. Chem*., **2004**, *69*, 8767; (b) A. E. Panarina, A. V. Dogadina, V. I. Zakharov and B. I. Ionin, *Tetrahedron Lett.,* **2001**, *42*, 4365; (c) A. V. Gulevich, V. Helan, D. J. Wink and V. Gevorgyan, *Org. Lett.,* **2013**, *15*, 956.

15 (a) S. S. Kong, W. D. Fan, G. P. Wu and Z. W. Miao, *Angew. Chem. Int. Ed.,* **2012**, *51*, 8864; (b) Z. J. Fang, H. H. Yang, Z. W. Miao and R. Y. Chen, *Helv. Chim. Acta* **2011**, *94*, 1586; (c) Y. D. Wang, Y. Y. Wang, J. P. Yu, Z. W. Miao and R. Y. Chen, *Chem.-Eur. J.* **2009**, *15*, 9290; (d) Y. D. Wang, F. Wang, Y. Y. Wang, Z. W. Miao and R. Y. Chen, *Adv. Synth. Catal.,* **2008**, *350*, 2339.

16 (a) S. F. Rach and F. E. Kühn, *Chem. Rev.* **2009**, *109*, 2061; (b) M. Vierle, Y. Zhang, E. Herdtweck, M. Bohnenpoll, O. Nuyken and F. E. Kühn, *Angew. Chem. Int. Ed.,* **2003**, *42*, 1307; (c) I. Krossing and I. Raabe, *Angew. Chem. Int. Ed.,* **2004**, *43*, 2066.
17 M. Brookhart, B. Grant and A. F. Volpe, *Organometallics,* **1992**, *11*, 3920.
18 The CCDC number of compound **2a** is 893994.
19 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper Collins Publishers: New York, **1987**.