Tetrahedron 65 (2009) 8277–8282

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Rhodium(II) catalyzed multi-component reactions of aryldiazoacetates with titanium(IV) isopropoxide and imines

Xu Zhang [a,b,c], Na Zhang [a], Xin Guo [a], Liping Yang [a], Wenhao Hu [a,*]

[a] Department of Chemistry, East China Normal University, Shanghai 20062, China
[b] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China
[c] Graduate School of the Chinese Academy of Sciences, Beijing, China

ARTICLE INFO

Article history:
Received 9 April 2009
Received in revised form 17 July 2009
Accepted 22 July 2009
Available online 25 July 2009

Keywords:
Oxonium ylide
Multi-component reaction
Aryldiazoacetate
Titanium(IV) isopropoxide

ABSTRACT

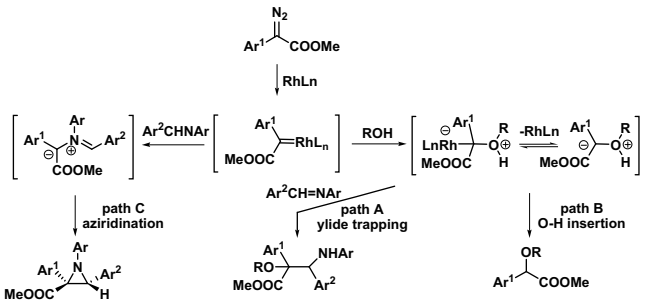
$Rh_2(OAc)_4$ catalyzed diazo decomposition of aryldiazoacetates in the presence of titanium(IV) isopropoxide generated oxonium ylide intermediates. Trapping of the oxonium ylide intermediates with imines occurred subsequently via a nucleophilic addition. The three-component reaction of aryldiazoacetates, titanium(IV) isopropoxide, and imines gave α-alkoxyl-β-amino acid derivatives with C–N/C–C bond formation in a single step. Extension of the study to a four-component reaction with in situ generated imine was also investigated.

1. Introduction

Among the wide variety of organometallic compounds, titanium reagent is one of those inexpensive and safely handled organometallic derivatives.[1] Titanium chlorides, titanium alkoxides, and titanocene derivatives are the commonly commercially available. The major advantages of titanium reagents are the abundance of this element and low biological activity.[2] Titanium alkoxides are widely used in the form of the Sharpless epoxidation[3] and as the McMurry coupling reagents[4] in the chemical industry. Due to their mild Lewis-acidity character, these compounds are able to coordinate with carbonyl oxygen or be involved in the reaction by transmetallation or ligand exchange processes. Chiral titanium catalysts were used in a number of chemo- and stereoselective C–C bond formation reactions.[5]

The metal-catalyzed decomposition of α-diazocarbonyl compounds is an important transformation in organic synthesis.[6] Particularly, corresponding ylide chemistry has been widely investigated.[7] For example, 1,3-dipolar cycloaddition[8] or epoxidation[9]/aziridination[6,9] reactions occurred from corresponding carbonyl/ammonium ylides. 1,2-Stevens rearrangement may occur with oxonium ylide generated from an ether.[10] In contrast, an O–H insertion product can be obtained in the reaction of carbenes/carbenoids and an alcohol, and one possible reaction pathway was proposed involving an alcoholic oxonium ylide intermediate.[11] Most recently, highly enantioselective O–H insertions using chiral copper catalysts were reported.[11b–d]

Recently, we found that the aforementioned alcoholic oxonium ylide can be trapped by a number of electrophiles including aldehydes and imines.[12] In the rhodium catalyzed three-component reaction of a methyl aryldiazoacetate, an imine and an alcohol, the trapping process (Path A) competed with the O–H insertion (Path B) and aziridination (Path C) (Scheme 1). The three-component reaction was limited to electron-deficient imines.[12d] To drive the reaction kinetics to the desired trapping products, several approaches were used to enhance the electrophilicity of the imines. Imines derived from 2-aminophenol and aldehydes were successfully



Scheme 1. The possible pathways of trapping alcoholic oxonium ylide with imines.

* Corresponding author. Tel.: +86 136 36307166; fax: +86 021 62233176.
E-mail address: whu@chem.ecnu.edu.cn (W. Hu).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.07.049

employed. Due to an intramolecular hydrogen bond activation of the imine by the adjacent phenol, excellent diastereoselectivity and high chemoselectivity were observed together with a broad substrate scope.[12f] On the other hand, the imine could be activated by a Lewis acid, as this approach has been demonstrated in the Lewis acid co-catalyzed reaction with aldehydes[12d,h] and α-ketoesters.[12i] For example, we have demonstrated that $Ti(O^tBu)_4$ served as a Lewis acid to activate aldehydes, and the reaction scope was extended to electron-rich aldehydes, affording the desired trapping products in good yield.[12d] Interestingly, when $Ti(O^iPr)_4$ was introduced, it served not only as an activating agent but also as an alternative of the alcohol precursor to form an oxonium ylide. Subsequent transfer of the isopropoxy group of titanium(IV) tetraisopropoxide to the final products occurred. The use of $Ti(O^iPr)_4$ as a reagent further expanded substrate scope of the three-component reaction to aliphatic aldehydes.[12e] This unique oxonium ylide generated from diazo compounds and $Ti(O^iPr)_4$ trapped by *p*-benzoquinones has also been reported by another research group.[13] The most advantage of using $Ti(O^iPr)_4$ is total avoidance of O–H insertion side product in the previous three-component reaction that used an alcohol as a reagent. Herein, we report our full investigation of this oxonium ylide generated from the diazo compounds and titanium(IV) alkoxide, which is trapped by imines derived from 2-aminophenol and aldehydes. The reaction provides an efficient method for the synthesis of α-alkoxyl-β-amino acid derivative.[14]

2. Results and discussion

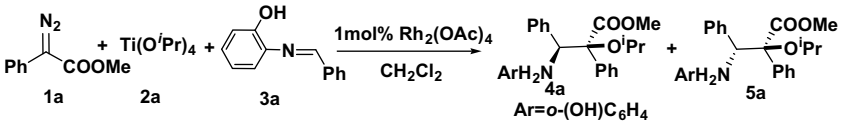
2.1. Titanium(IV) alkoxide and diazoacetate involved three-component Mannich-type reaction

Initially, the reaction was conducted with 1.0 equiv of methyl phenyldiazoacetate (**1a**), 1.1 equiv of titanium(IV) tetraisopropoxide (**2a**), 1.0 equiv of imine (**3a**) in the presence of 1 mol% dirhodium(II) acetate in refluxing dichloromethane. The desired α-alkoxyl-β-amino acid derivative **4a** was obtained in 65% isolated yield with 71:29 diastereomeric ratio (dr) (Table 1, entry 1). No aziridination products but a mixture of 2,3-diphenyl fumarate and maleate was observed as main side products. It was found that temperature had a significant effect on the reaction, 61% yield and good dr value (**4a**:**5a**=86:14) were obtained at room temperature (Table 1, entry 2). However, the yield was decreased to 20% when the reaction was conducted at 0 °C (Table 1, entry 3). As more than one alkoxyl group of the titanium(IV) reagent could be transferred to the three-component product in the reaction,[12e] tests were carried out with decreased amounts of the titanium reagent (Table 1, entries 4 and 5). Isolated yield of 55% was obtained with the use of 0.5 equiv of the titanium tetraisopropoxide indicating that more than one isopropoxy group in the titanium reagent could be involved in the reaction (Table 1, entry 4). Solvents including toluene, $CHCl_3$, and $(CH_2Cl)_2$ have been tested, and it turned out that polar solvent gave slightly higher product yield than non-polar solvent (Table 1, entries 6–8). Starting material methyl phenyldiazoacetate (**1a**) was recovered when $Cu(OTf)_2$ and copper(II) 1,1,1,5,5,5-hexafluoro-acetylacetonate hydrate ($Cu(pfacac)_2$) were used as catalysts (Table 1, entries 9 and 10), probably due to catalyst poisoning resulted from chelation of the metal with the bidentate imine **3**.[8q,15] To further examine if the bidentate chelation is necessary for the titanium reagent to activate the imine, a control experiment was conducted with an imine derived benzaldehyde and aniline. No desired three-component product was observed under the same conditions as used for imine **3**, indicating the importance of the chelating control.

Under the optimal reaction conditions (Table 1, entry 2), different aryldiazoacetates **1**, titanium(IV) reagents **2**, and imines **3** were employed (Table 2). Good dr values were observed from imines bearing both electron-donating groups and weak electron-withdrawing groups (Table 2, entries 1–5). Imines bearing electron-donating groups (Table 2, entries 2 and 3) gave higher yields than those bearing weak electron-withdrawing groups (Table 2, entries 4 and 5). Both decreased yield and dr were observed when the imine bearing an electron-withdrawing group was used (Table 2, entry 7). The imine derived from furyl aldehyde also afforded corresponding three-component product in moderate yield and good dr value (Table 2, entry 8). The imines derived from *o*-chlorobenzaldehyde and 1-naphthaldehyde gave only 26% (Table 2, entry 9) and 41% (Table 2, entry 10) yield, respectively. The low yield is probably due to the steric effect of the imines. The dr value was decreased to 64:36 from 86:14 when $Ti(OEt)_4$ was used instead of $Ti(O^iPr)_4$ (Table 2, entry 11 vs 1).

The reaction was further extended to a number of other diazoacetates. Aryldiazoacetates bearing electron-withdrawing groups gave higher yields and dr values than those bearing electron-donating groups (Table 2, entries 12–15 vs 16 and 17). The reaction did not work well with ethyl diazoacetate. The stereochemistry of the

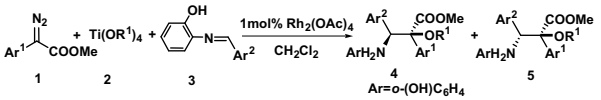
Table 1
Reaction condition optimization for the three-component reaction of **1a**, **2a**, and **3a**[a]



Entry	Ti(IV) (equiv)	*T* (°C)	Solvent	Cat. (mol%)	Yield[b] (**4a**) (%)	dr[c] (**4a**:**5a**)
1	1.1	Reflux	CH_2Cl_2	$Rh_2(OAc)_4$ (1)	65	71:29
2	1.1	25	CH_2Cl_2	$Rh_2(OAc)_4$ (1)	61	86:14
3	1.1	0	CH_2Cl_2	$Rh_2(OAc)_4$ (1)	20	88:12
4	0.5	25	CH_2Cl_2	$Rh_2(OAc)_4$ (1)	55	84:16
5	0.25	25	CH_2Cl_2	$Rh_2(OAc)_4$ (1)	22	85:15
6	1.1	25	$CHCl_3$	$Rh_2(OAc)_4$ (1)	47	77:23
7	1.1	25	Toluene	$Rh_2(OAc)_4$ (1)	40	82:18
8	1.1	25	$(CH_2Cl)_2$	$Rh_2(OAc)_4$ (1)	53	78:22
9	1.1	25	CH_2Cl_2	$Cu(OTf)_2$ (5)	n.d.[d]	n.d.[d]
10	1.1	25	CH_2Cl_2	$Cu(pfacac)_2$ (5)	n.d.[d]	n.d.[d]

[a] Reactions were carried out at 0.2 mmol scale.
[b] Isolated yields after chromatography.
[c] Determined by ^1H NMR of crude reaction mixtures.
[d] Not determined due to very low yield.

Table 2
The three-component reactions of methyl aryldiazoacetates (**1**) with titanium(IV) reagents (**2**) and imines (**3**)[a]



Entry	Ar^1	Ar^2	Yield[b] (%)	dr[c] (**4**:**5**)
1	Ph	Ph	61 (**4a**)	86:14
2	Ph	*p*-MeOPh	60 (**4b**)	83:17
3	Ph	3,4-(OCH_2O)Ph	64 (**4c**)	94:6
4	Ph	*p*-ClPh	50 (**4d**)	82:18
5	Ph	*m*-ClPh	42 (**4e**)	90:10
6	Ph	*p*-CNPh	50 (**4f**)	84:16
7	Ph	*p*-NO_2Ph	45 (**4g**)	60:40
8	Ph	Furyl	56 (**4h**)	82:18
9	Ph	*o*-ClPh	26 (**4i**)	88:22
10	Ph	1-Naph	41 (**4j**)	92:8
11[d]	Ph	Ph	58 (**4k**)	64:36
12	*p*-BrPh	Ph	52 (**4l**)	90:10
13	*p*-BrPh	*p*-MeOPh	52 (**4m**)	87:13
14	*p*-BrPh	*p*-ClPh	50 (**4n**)	88:12
15	*m*-BrPh	Ph	48 (**4o**)	86:14
16	*p*-MeOPh	*p*-NO_2Ph	35 (**4p**)	68:32
17	*p*-MeOPh	Ph	<5%	—

[a] Reactions were carried out in CH_2Cl_2 in the presence of $Rh_2(OAc)_4$ (1 mol %) with **1**:**2**:**3**=1.0:1.1:1.0 equiv.
[b] Isolated yields after chromatography.
[c] Determined by ^1H NMR of crude reaction mixtures.
[d] $Ti(OEt)_4$ has been used.

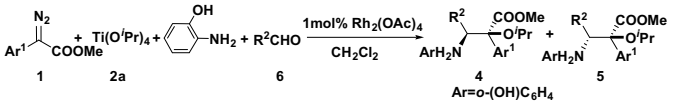
major stereoisomer **4a** was established to be *erythro*- by comparison with published data of the corresponding product.[12d,f]

2.2. Titanium(IV) alkoxide and diazoacetate involved four-component Mannich-type reaction

Since the imines could be generated in situ from 2-aminophenol and corresponding aldehydes, we next studied four-component reactions of 2-aminophenol, aldehydes, diazocarbonyl compounds, and titanium (IV) isopropoxide. An advantage of this approach is that the reactions could be carried out without a separate step for the imine preparation prior to the trapping process.[12j] However, an initial reaction of 1.0 equiv of methyl phenyldiazoacetate (**1a**), 1.1 equiv of titanium(IV) tetraisopropoxide (**2a**), 1.0 equiv of benzaldehyde (**6a**), and 1.0 equiv of 2-aminophenol resulted in lower yield (25%) and moderate dr value (78:22) (Table 3, entry 1). The reaction conditions were modified. The yield was increased from 25% to 38% by adding 4 Å MS, because that the addition of 4 Å MS could promote the imine formation (Table 3, entry 2). 51% yield was obtained when 2.0 equiv of diazo compound **1a** was used (Table 3, entry 3). Similar yield was obtained when the reaction was conducted in refluxing CH_2Cl_2 (Table 3, entry 4). Side products (**7a**+**8a**) resulted from trapping of the oxonium ylide with the aldehydes and a mixture of 2,3-diphenyl fumarate and maleate have been observed in the reaction.

Under the reaction conditions shown in Table 3, entry 3, the four-component reaction was extended to a number of diazo compounds and aldehydes. The desired four-component products were isolated in moderate yield and dr Similar to the three-component reaction, aldehydes bearing electron-donating groups (Table 4, entries 2 and 3) gave slightly higher yields than those bearing electron-withdrawing groups (Table 4, entries 4 and 5). Decreased dr (**4**:**5**=60:40) was observed with the imine derived from *para*-nitro benzaldehyde (Table 4, entry 5). The imine derived from heterocyclic furyl aldehyde also gave corresponding four-component product in moderate yield and dr value (Table 4, entry 6). Extension of substrates to substituted aryldiazoacetates gave similar results (Table 4, entries 7–10). Attempts to achieve the four-component reaction with aliphatic aldehydes were also made, but only less than 10% yield was obtained with the use of 3-butenal (Table 4, entry 11).

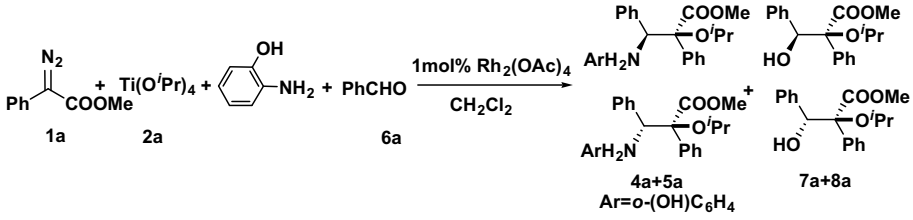
Table 4
The four-component reactions of methyl aryldiazoacetates (**1**) with titanium(IV) isopropoxide (**2a**), 2-aminophenol, and aldehydes (**6**)[a]



Entry	Ar^1	R^2	Yield[b] (%)	dr[c] (**4**:**5**)
1	Ph	Ph	51 (**4a**)	79:21
2	Ph	*p*-MeOPh	52 (**4b**)	70:30
3	Ph	3,4-(OCH_2O)Ph	58 (**4c**)	85:15
4	Ph	*p*-ClPh	37 (**4d**)	74:26
5	Ph	*p*-NO_2Ph	37 (**4g**)	60:40
6	Ph	Furyl	46 (**4h**)	76:24
7	*p*-BrPh	Ph	46 (**4l**)	77:23
8	*p*-BrPh	*p*-MeOPh	48 (**4m**)	75:25
9	*p*-BrPh	*p*-ClPh	43 (**4n**)	74:26
10	*p*-MeOPh	*p*-NO_2Ph	32 (**4p**)	53:47
11	Ph	Allyl	<10	n.d.

[a] Reactions were carried out in CH_2Cl_2 in the presence of $Rh_2(OAc)_4$ (1 mol %) with **1**:**2**:**6**:2-aminophenol=2.0:1.1:1.0:1.0 equiv.
[b] Isolated yields after chromatography.
[c] Determined by ^1H NMR of crude reaction mixtures.

Table 3
Titanium(IV) isopropoxide (**2a**) involved four-component Mannich-type reaction with different ratios of reactants[a]

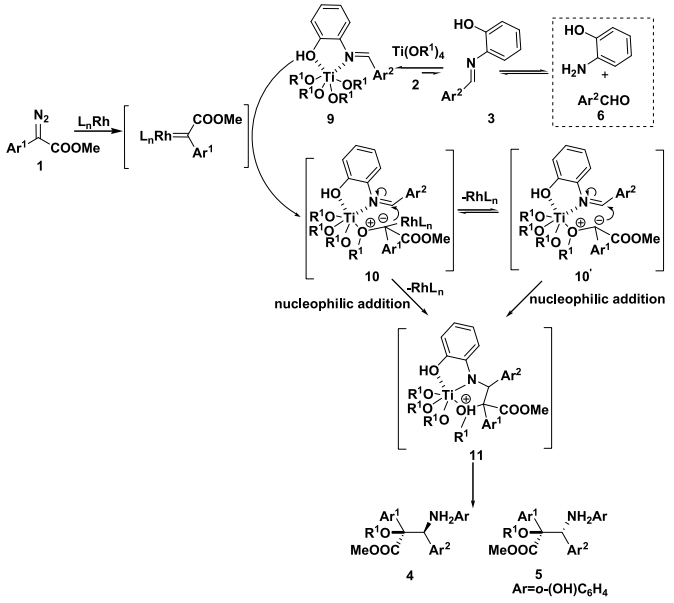


Entry	Diazo (equiv)	4 Å MS (mg)	*T* (°C)	dr[c] (**4a**:**5a**)	(**4a**+**5a**):(**7a**+**8a**)[c]	Yield[b] of (**4a**) (%)
1	1.0	—	25	78:22	n.d.[d]	25
2	1.0	100	25	77:23	52:48	38
3	2.0	100	25	79:21	60:40	51
4	2.0	100	Reflux	55:45	55:45	48

[a] Reactions were carried out at 0.2 mmol scale with **2a**:**6a**:2-aminophenol=1.1:1.0:1.0 equiv.
[b] Isolated yields after chromatography.
[c] Determined by ^1H NMR of crude reaction mixtures.
[d] The data were not detected.

3. Conclusion

A proposed reaction pathway was given below (Scheme 2). The three/four-component reaction was likely to proceed through a Lewis acid promoted nucleophilic addition of an oxonium ylide to C=N. The titanium reagent played a dual role in this multi-component reaction. It functioned as a Lewis acid to activate the imine in proposed intermediate **9**. In the mean time, it served as a reagent to generate the oxonium ylide by providing an alkoxyl group to form intermediates **10** and **10′**. An intramolecular addition of the oxonium ylide to the imine resulted in intermediate **11**. The products **4** and **5** were obtained after aqueous work-up.



Scheme 2. Proposed mechanism of titanium(IV) alkoxide involved three/four-component reactions.

In conclusion, we have developed multi-component reactions of aryldiazoacetates, titanium(IV) alkoxide, and imines in the presence of rhodium(II) acetate. Trapping of the oxonium ylide intermediates generated from aryldiazoacetates and titanium(IV) alkoxide with imines occurred to give α-alkoxyl-β-amino acid derivatives in moderate to good yield.

4. Experimental section

4.1. General

NMR spectroscopy was performed on a Bruker model AMX-300 or 500 spectrometer, operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) or 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad). TMS (tetramethylsilane) was used as an internal standard. High-resolution mass spectra (HRMS) were obtained on a Varian QFT-ESI mass spectrometer. Solvents were distilled and dried over MS 4 Å. All reagents were obtained from commercial suppliers and were used without further purification.

4.2. General procedure for the preparation of α-alkoxyl-β-amino acid derivatives

4.2.1. General procedure for the three-component reactions. A solution of **1** (0.20 mmol) in CH_2Cl_2 (2 mL) was added over 1 h by a syringe pump to a solution of $Rh_2(OAc)_4$ (1 mol %), **2** (0.22 mmol), and **3** (0.20 mmol) in CH_2Cl_2 (2 mL) at room temperature under an argon atmosphere. When the α-diazocarbonyl compound was decomposed completely (detected by TLC), the solvent was removed. Then 10 mL of ethyl acetate was added, the reaction mixture was washed with 10 mL of saturated aqueous NH_4Cl and the aqueous phase was extracted with 10 mL of EtOAc (×2). The combined organic phase was washed with 10 mL of water, then washed with saturated brine, and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed, and a portion of crude product was subjected to ^{1}H NMR analysis for the determination of the product ratio. The crude product was purified by flash chromatography on silica gel eluting with a mixture of petroleum ester and ethyl acetate to afford the corresponding products **4**.

4.2.2. General procedure for the four-component reactions. Compound **6** (0.20 mmol), 2-aminophenol (0.2 mmol), and 100 mg 4 Å MS was charged with 2 mL of CH_2Cl_2 and the reaction mixture was stirred at room temperature under an argon atmosphere for 1 h. Then a solution of $Rh_2(OAc)_4$ (1 mol %), **2** (0.22 mmol) in CH_2Cl_2 (0.5 mL) was added successfully. A solution of **1** (0.40 mmol) in CH_2Cl_2 (2 mL) was added over 1 h by a syringe pump to the reaction mixture. When the α-diazocarbonyl compound was decomposed completely (detected by TLC), the solvent was removed. Then 10 mL of ethyl acetate was added, the reaction mixture was washed with 10 mL of saturated aqueous NH_4Cl and the aqueous phase was extracted with 10 mL of EtOAc (×2). The combined organic phase was washed with 10 mL of water, then washed with saturated brine, and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed, and a portion of crude product was subjected to ^{1}H NMR analysis for the determination of the product ratio. The crude product was purified by flash chromatography on silica gel eluting with a mixture of petroleum ester and ethyl acetate to afford the corresponding products **4**.

*4.2.3. Methyl 3-(2-hydroxyphenylamino)-2-isopropoxy-2,3-diphenylpropanoate. Compound **4a**.* Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.25–7.35 (m, 5H), 7.10–7.13 (m, 3H), 6.97–6.99 (m, 2H), 6.51–6.71 (m, 4H), 5.80 (br, 1H), 5.10 (s, 1H), 4.67 (br, 1H), 3.91 (m, 1H), 3.70 (s, 3H), 1.18 (d, 3H, J=6.1 Hz), 0.97 (d, 3H, J=6.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 172.6, 145.8, 138.1, 136.5, 134.5, 129.2, 129.0, 128.2, 127.4, 127.3, 127.1, 120.9, 119.5, 116.6, 114.7, 86.9, 68.8, 64.5, 51.9, 23.8, 23.2.[12f]

*4.2.4. Methyl 3-(2-hydroxyphenylamino)-2-isopropoxy-3-(4-methoxyphenyl)-2-phenylpropanoate. Compound **4b**.* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.26–7.38 (m, 5H), 6.89–6.92 (d, 2H), 6.51–6.69 (m, 6H), 5.95 (br, 1H), 5.06 (s, 1H), 4.45 (br, 1H), 3.92 (m, 1H), 3.72 (s, 6H), 1.18 (d, 3H, J=6.1 Hz), 0.97 (d, 3H, J=6.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.7, 158.6, 145.7 136.5, 134.5, 130.2, 130.1, 129.0, 128.2, 127.4, 120.8, 119.4, 116.5, 114.6, 112.5, 86.9, 68.7, 63.8, 55.0, 52.0, 23.8, 23.1; HRMS: calcd for: $C_{26}H_{29}NO_5$; 436.2119; found: 436.2117 $[M+H]^+$.

*4.2.5. Methyl 3-(benzo[d][1,3]dioxol-5-yl)-3-(2-hydroxyphenylamino)-2-isopropoxy-2-phenylpropanoate. Compound **4c**.* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39–7.42 (m, 2H), 7.28–7.33 (m, 2H), 6.44–6.69 (m, 6H), 5.87 (br, 1H), 5.84 (br, 1H), 5.02 (s, 1H), 4.85 (br, 1H), 3.94 (m, 1H), 3.70 (s, 3H), 1.19 (d, 3H, J=6.1 Hz), 0.95 (d, 3H, J=6.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.5, 146.8, 146.6, 145.4, 136.6, 134.4, 132.1, 129.0, 128.3, 127.5, 122.8, 121.0, 119.2, 116.0, 114.6, 109.4, 106.9, 100.7, 86.9, 68.8, 64.1, 51.972, 23.8, 23.2; HRMS: calcd for: $C_{26}H_{27}NO_6$: 450.1911; found: 450.1915 $[M+H]^+$.

*4.2.6. Methyl 3-(4-chlorophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-2-phenylpropanoate. Compound **4d**.* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.25–7.34 (m, 4H), 7.08 (d, 2H, J=8.5 Hz), 6.91 (d, 2H, J=8.5 Hz), 6.48–6.71 (m, 4H), 5.65 (br, 1H), 5.11 (br, 1H),

4.59 (br, 1H), 3.92 (m, 1H), 3.73 (s, 3H), 1.17 (d, 3H, J=5.9 Hz), 0.97 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.4, 145.5, 136.6, 136.0, 134.2, 133.1, 130.5, 129.0, 128.4, 127.5, 127.3, 121.0, 119.5, 116.3, 114.7, 86.7, 68.9, 63.8, 52.1, 23.9, 23.1; HRMS: calcd for: $C_{25}H_{26}ClNO_4$: 440.1623; found: 440.1615 $[M+H]^+$.

4.2.7. Methyl 3-(3-chlorophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-2-phenylpropanoate. Compound ***4e***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39–7.41 (d, 2H), 7.13–7.22 (m, 4H), 6.96–6.99 (m, 2H), 6.54–6.67 (m, 4H), 5.66 (br, 1H), 5.14 (br, 1H), 4.57 (br, 1H), 3.84 (m, 1H), 3.72 (s, 3H), 1.18 (d, 3H, J=5.9 Hz), 0.98 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.1, 145.3, 137.6, 135.4, 134.4, 130.9, 130.43, 129.1, 127.4, 127.2, 122.5, 121.1, 119.4, 116.1, 114.6, 86.5, 69.0, 64.2, 52.1, 23.9, 23.0; HRMS: calcd for: $C_{25}H_{26}ClNO_4$: 440.1623; found: 412.1625 $[M+H]^+$.

4.2.8. Methyl 3-(3-cyanophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-2-phenylpropanoate. Compound ***4f***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39–7.41 (d, 2H, J=8.2 Hz), 7.24–7.35 (m, 2H), 7.08–7.11 (d, 1H, J=8.2 Hz), 6.47–6.71 (m, 4H), 5.57 (br, 1H), 5.25 (br, 1H), 4.69 (br, 1H), 3.89 (m, 1H), 3.74 (s, 3H), 1.15 (d, 3H, J=5.9 Hz), 0.98 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.93, 144.9, 143.9, 135.4, 130.9, 129.9, 128.8, 128.6, 127.6, 121.2, 119.4, 118.9, 115.4, 114.7, 111.0, 86.6, 69.1, 63.8, 52.2, 23.9, 23.0; HRMS: calcd for: $C_{26}H_{26}N_2O_4$: 431.1965; found: 431.1959 $[M+H]^+$.

4.2.9. Methyl 3-(2-hydroxyphenylamino)-2-isopropoxy-3-(4-nitrophenyl)-2-phenylpropanoate. Compound ***4g***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.96 (d, 2H, J=8.8 Hz), 7.26–7.34 (m, 7H), 7.15 (d, 2H, J=8.8 Hz), 6.60–6.69 (m, 3H), 6.47–6.50 (m, 2H), 5.43 (br, 1H), 5.32 (d, 1H, J=10.7 Hz), 4.78 (d, 1H, J=10.7 Hz), 3.90 (m, 1H), 3.75 (s, 3H), 1.66 (br, 1H), 1.22 (d, 3H, J=5.9 Hz), 0.99 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.9, 147.2, 146.0, 144.9, 135.3, 133.845, 130.1, 128.8, 128.7, 127.7, 127.0, 122.2, 121.2, 119.5, 115.3, 114.7, 86.49, 69.112, 63.6, 52.3, 23.9, 23.0; HRMS: calcd for: $C_{25}H_{26}N_2O_6$: 451.1864; found: 451.1858 $[M+H]^+$.

4.2.10. Methyl 3-(furan-2-yl)-3-(2-hydroxyphenylamino)-2-isopropoxy-2-phenylpropanoate. Compound ***4h***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.17–7.32 (m, 6H), 6.83–6.84 (m, 2H), 6.57–6.63 (m, 2H), 6.19 (br, 1H), 5.58 (br, 1H), 4.93 (br, 1H), 4.04 (m, 1H), 3.85 (s, 3H), 1.17 (d, 3H, J=5.9 Hz), 1.10 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.7, 151.5, 149.2, 141.1, 136.6, 133.5, 128.3, 128.2, 127.5, 123.3, 121.2, 120.0, 115.3, 110.1, 109.2, 86.3, 69.1, 61.5, 52.4, 23.7, 23.4; HRMS: calcd for: $C_{23}H_{25}NO_5$: 396.1806; found: 396.1811 $[M+H]^+$.

4.2.11. Methyl 3-(2-chlorophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-2-phenylpropanoate. Compound ***4i***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50–7.53 (m, 1H), 7.32–7.37 (m, 4H), 7.06–7.25 (m, 3H), 6.66–6.68 (m, 3H), 5.83 (br, 1H), 5.44 (br, 1H), 5.00 (br, 1H), 3.97 (m, 1H), 3.62 (s, 3H), 1.26 (d, 3H, J=5.9 Hz), 0.87 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.5, 144.6, 137.2, 137.1, 135.3, 129.9, 129.0, 128.9, 128.7, 128.5, 128.4, 127.7, 127.6, 126.2, 121.3, 118.5, 114.8, 114.4, 86.9, 78.8, 68.8, 58.3, 23.7, 23.4; HRMS: calcd for: $C_{25}H_{26}ClNO_4$: 440.1623; found: 440.1617 $[M+H]^+$.

4.2.12. Methyl 3-(2-hydroxyphenylamino)-2-isopropoxy-3-(naphthalen-1-yl)-2-phenylpropanoate. Compound ***4j***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.49 (d, 1H J=8.5 Hz), 7.77 (m, 1H), 7.67 (d, 1H, J=8.1 Hz), 7.50–7.66 (m, 1H), 7.43–7.44 (m, 2H), 7.17–7.36 (m, 12H), 6.76–6.78 (d, 1H, J=7.2 Hz), 6.62 (br, 1H), 5.55 (br, 1H), 4.80 (br, 1H), 3.83 (m, 1H), 3.59 (s, 3H), 1.15 (d, 3H, J=5.9 Hz), 0.74 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.6, 145.0, 136.0, 134.9, 134.5, 133.4, 133.2, 129.4, 128.3, 128.2, 127.9, 127.3, 126.0, 125.1, 124.9, 124.9, 124.5, 121.2, 118.8, 115.5, 114.5, 88.2, 68.8, 57.7, 52.0, 23.8, 23.0; HRMS: calcd for: $C_{29}H_{29}NO_4$: 456.2169; found: 456.2162 $[M+H]^+$.

4.2.13. Methyl 2-ethoxy-3-(2-hydroxyphenylamino)-2,3-diphenylpropanoate. Compound ***4k***. Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.28–7.49 (m, 5H), 7.10–7.14 (m, 4H), 6.94–6.95 (m, 2H), 4.94 (s, 1H), 3.75 (s, 3H), 3.54 (m, 1H), 3.42 (q, 2H), 1.25 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 171.8, 146.6, 137.9, 135.5, 134.3, 129.5, 129.0, 128.4, 128.2, 127.6, 127.4, 127.3, 127.2, 127.1, 120.7, 120.4, 117.8, 114.7, 87.5, 65.6, 61.6, 52.2, 29.7, 15.3; HRMS: calcd for: $C_{24}H_{25}NO_4$: 392.1856; found: 392.1858 $[M+H]^+$.

4.2.14. Methyl 2-(4-bromophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-3-phenylpropanoate. Compound ***4l***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.27–7.30 (m, 2H), 7.03–7.13 (m, 5H), 6.90–6.91 (m, 2H), 6.48–6.57 (m, 4H), 5.08 (s, 1H), 3.72 (m, 1H), 3.61 (s, 3H), 1.07 (d, 3H, J=6.0 Hz), 0.90 (d, 3H, J=6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.5, 145.3, 137.8, 135.6, 134.7, 131.1, 130.7, 129.3, 127.5, 123.0, 122.8, 121.3, 119.3, 115.8, 114.8, 86.7, 69.2, 64.1, 52.5, 24.2, 23.3; HRMS: calcd for: $C_{25}H_{26}BrNO_4$: 484.1118; found: 484.1120 $[M+H]^+$.

4.2.15. Methyl 2-(4-bromophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-3-(4-methoxyphenyl) propanoate. Compound ***4m***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39 (d, 2H, J=7.9 Hz), 7.20–7.26 (m, 2H), 7.21 (d, 2H, J=8.0 Hz), 6.53–6.70 (m, 6H), 5.85 (br, 1H), 5.09 (br, 1H), 4.50 (br, 1H), 3.83 (m, 1H), 3.73 (s, 3H), 1.16 (d, 3H, J=6.1 Hz), 0.97 (d, 3H, J=6.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.2, 158.8, 145.3, 135.4, 134.4, 130.9, 130.4, 130.1, 129.6, 122.5, 121.0, 119.3, 116.1, 114.5, 112.6, 86.5, 68.9, 63.6, 55.0, 52.1, 23.8, 23.0; HRMS: calcd for: $C_{26}H_{28}BrNO_5$: 514.1224; found: 514.1216 $[M+H]^+$.

4.2.16. Methyl 2-(4-bromophenyl)-3-(4-chlorophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy propanoate. Compound ***4n***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, 2H, J=8.4 Hz), 7.18 (d, 2H, J=8.2 Hz), 7.11 (d, 2H, J=8.2 Hz), 6.91 (d, 2H, J=8.4 Hz), 6.59–6.66 (m, 5H), 5.59 (br, 1H), 5.16 (br, 1H), 4.53 (br, 1H), 3.82 (m, 1H), 3.74 (s, 3H), 1.23 (d, 3H, J=6.1 Hz), 0.97 (d, 3H, J=6.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.8, 144.9, 136.2, 134.9, 134.2, 133.3, 130.8, 130.6, 130.4, 127.4, 122.7, 121.1, 119.3, 115.6, 114.6, 86.2, 69.1, 63.3, 23.9, 23.0; HRMS: calcd for: $C_{25}H_{25}BrClNO_4$: 518.0728; found: 518.0730 $[M+H]^+$.

4.2.17. Methyl 2-(3-bromophenyl)-3-(2-hydroxyphenylamino)-2-isopropoxy-3-phenylpropanoate. Compound ***4o***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.38–7.40 (d, 2H), 7.13–7.22 (m, 4H), 6.96–6.99 (m, 2H), 6.54–6.69 (m, 4H), 5.69 (br, 1H), 5.15 (br, 1H), 4.57 (br, 1H), 3.84 (m, 1H), 3.73 (s, 3H), 1.18 (d, 3H, J=6.1 Hz), 0.98 (d, 3H, J=6.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.1, 145.3, 137.6, 135.4, 134.4, 130.9, 130.4, 129.1, 127.4, 127.2, 122.5, 121.1, 119.4, 116.1, 114.6, 86.5, 68.9, 64.2, 52.1, 23.9, 23.0; HRMS: calcd for: $C_{30}H_{24}BrNO_3$: 484.1118; found: 484.1117 $[M+H]^+$.

4.2.18. Methyl 3-(2-hydroxyphenylamino)-2-isopropoxy-2-(4-methoxyphenyl)-3-(4-nitrophenyl) propanoate. Compound ***4p***. Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (d, 2H, J=8.8 Hz), 7.18–7.22 (m, 4H), 6.80 (d, 2H, J=8.8 Hz), 6.61–6.70 (m, 3H), 6.48–6.49 (m, 2H), 5.35 (br, 1H), 5.30 (d, 1H, J=10.9 Hz), 4.70 (d, 1H, J=10.9 Hz), 3.86 (m, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 1.22 (d, 3H, J=5.9 Hz), 0.96 (d, 3H, J=5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 172.0, 159.6, 147.2, 146.2, 144.8, 133.9, 130.2, 130.1, 127.3, 122.2, 119.3, 115.3, 114.7, 112.9, 86.2, 68.9, 63.7, 55.2, 52.2, 23.9,

23.0; HRMS: calcd for: $C_{26}H_{28}N_2O_7$: 481.1969; found: 481.1965 $[M+H]^+$.

Acknowledgements

This work was supported by National Science Foundation of China (Grant No. 20772033) and Shanghai Pujiang Program (No. 07pzl4033).

Supplementary data

The spectroscopic data (^1H, ^{13}C spectroscopic data) of the compounds shown in Table 2 are included in the Supplementary data. This material is available free of charge via the Internet at Website. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.07.049.

References and notes

1. (a) Scott, J. W. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; John Wiley & Sons: New York, NY, 1989; Vol. 19, pp 209–226; (b) Marek, I. *Titanium and Zirconium in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2002.
2. (a) Kopf-Maier, P. In *Metal Ions in Biology and Medicine*; Collery, P., Poirier, L. A., Manfait, M., Etienne, J. C., Eds.; John Libbey Eurotext: Paris, 1990; pp 457–461, pp 465–467, pp 505–507; (b) Bischoff, H.; Berger, M. R.; Keppler, B. K.; Schmihl, D. *J. Cancer Res. Clin. Oncol.* **1987**, *113*, 446–450; (c) Keppler, B. K.; Heim, M. E. *Drugs Future* **1988**, *13*, 637–652; (d) Fruhauf, S.; Zeller, W. J. *Cancer Res.* **1991**, *51*, 2943–2948; (e) Fruhauf, S.; Zeller, W. *J. Cancer Chemother. Pharmacol.* **1991**, *27*, 301–307; (f) Whitehead, J. In *Metals and their Compounds in the Environment*; Merian, E., Ed.; Chemie: Weinheim, Germany, 1991; pp 1261–1267.
3. (a) Sharpless, K. B. *Chem. Br.* **1986**, *22*, 38–44; (b) Berrisford, D. J.; Bolm, C.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1059–1070; (c) Seebach, D.; Marti, R. E. *Helv. Chim. Acta* **1996**, *79*, 1710–1740.
4. (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524; (b) Lenoir, D. *Synthesis* **1989**, 883–897; (c) Pons, J. M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295–4312; (d) Wong, H. N. C. *Acc. Chem. Res.* **1989**, *22*, 145–152; (e) McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281–286.
5. For reviews, see: (a) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807–832; (b) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763–2794; (c) Brunel, J. M. *Chem. Rev.* **2007**, *107*, PR1–PR45; (d) Xia, Q.-H.; Ge, H.-Q.; Ye, C.-P.; Liu, Z.-M.; Su, K.-X. *Chem. Rev.* **2005**, *105*, 1603–1662; (e) North, M.; Usanov, D. L.; Young, C. *Chem. Rev.* **2008**, *108*, 5146–5226.
6. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley & Sons: New York, NY, 1998.
7. For reviews of this area, see: (a) Padwa, A.; Hornbuckle, S. *Chem. Rev.* **1991**, *91*, 263–309; (b) Ye, T.; Mckervey, M. A. *Chem. Rev.* **1994**, *94*, 1091–1160; (c) Li, A. H.; Dai, L. X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341–2372; (d) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577–6605.
8. (a) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489–3492; (b) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, *38*, 2365–2369; (c) Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277–2280; (d) Wulfman, D. S.; Peace, B. W. *Tetrahedron Lett.* **1972**, 3903–3906; (e) Wulfman, D. S.; Thinh, N. V.; McDaniel, R. S.; Peace, B. W.; Jones, M. T.; Heitsch, C. W. *J. Chem. Soc., Dalton Trans.* **1975**, 522–529; (f) Trost, B. M.; Hammen, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 962–964; (g) Breau, L.; Durst, T. *Tetrahedron: Asymmetry* **1991**, *2*, 367–370; (h) Solladié-Cavallo, A.; Adib, A.; Schmitt, M.; Fischer, J.; DeGan, D. *Tetrahedron: Asymmetry* **1992**, *3*, 1597–1620; (i) Breau, L.; Ogilvie, W. W.; Durst, T. *Tetrahedron Lett.* **1990**, *31*, 35–38; (j) Furukawa, N.; Sugihara, Y.; Fujihara, H. *J. Org. Chem.* **1989**, *54*, 4222–4224; (k) Kamigata, N.; Nakamura, Y.; Kikuchi, K.; Ikemoto, I.; Shimizu, T.; Matsuyama, H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1721–1728; (l) March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952; (m) Alt, M.; Maas, G. *Tetrahedron* **1994**, *50*, 7435–7444; (n) Doyle, M. P.; Forbes, D. C.; Protopopova, M. N.; Stanley, S. A.; Vasbinder, M. M.; Xavier, K. R. *J. Org. Chem.* **1997**, *62*, 7210–7215; (o) Jiang, B.; Zhang, X.; Luo, Z. *Org. Lett.* **2002**, *4*, 2453–2455; (p) Lu, C.; Chen, Z.; Liu, H.; Hu, W.; Mi, A. *Org. Lett.* **2004**, *6*, 3071–3074; (q) Torssel, S.; Somfai, P. *Adv. Synth. Catal.* **2006**, *348*, 2421–2430.
9. (a) Doyle, M. P.; Hu, W.; Timmons, D. J. *Org. Lett.* **2001**, *3*, 933–935; (b) Davies, H. M. L.; DeMeese, J. *Tetrahedron Lett.* **2001**, *42*, 6803–6805; (c) Muthusamy, S.; Gunanathan, C.; Nethaji, M. *Synlett* **2004**, 639–642.
10. (a) Ito, K.; Yoshitake, M.; Katsuki, T. *Heterocycles* **1996**, *42*, 305–317; (b) Ito, K.; Yoshitake, M.; Katsuki, T. *Chem. Lett.* **1995**, 1027–1028; (c) Ito, K.; Katsuki, T. *Chem. Lett.* **1994**, 1857–1860; (d) Ito, K.; Yoshitake, M.; Katsuki, T. *Tetrahedron* **1996**, *52*, 3905–3920; (e) Doyle, M. P.; Ene, D. G.; Forbes, D. C.; Tedrow, J. S. *Tetrahedron Lett.* **1997**, *38*, 4367–4370.
11. (a) Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811–10843; (b) Zhu, S.-F.; Chen, C.; Cai, Y.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2008**, *47*, 932–934; (c) Chen, C.; Zhu, S.-F.; Liu, B.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2007**, *129*, 12616–12617; (d) Maier, T. C.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 4594–4595.
12. (a) Wang, Y.; Zhu, Y.; Chen, Z.; Mi, A.; Hu, W.; Doyle, M. *Org. Lett.* **2003**, *5*, 3923–3926; (b) Wang, Y.; Chen, Z.; Mi, A.; Hu, W. *Chem. Commun.* **2004**, 2486–2487; (c) Huang, H.; Wang, Y.; Chen, Z.; Hu, W. *Adv. Synth. Catal.* **2005**, *347*, 531–534; (d) Lu, C.; Liu, H.; Chen, Z.; Hu, W.; Mi, A. *Org. Lett.* **2005**, *7*, 83–86; (e) Lu, C.; Liu, H.; Chen, Z.; Hu, W.; Mi, A. *Chem. Commun.* **2005**, 2624–2626; (f) Huang, H.; Guo, X.; Yang, L.; Hu, W. *Angew. Chem., Int. Ed.* **2007**, *46*, 1337–1339; (g) Guo, X.; Huang, H.; Yang, L.; Hu, W. *Org. Lett.* **2007**, *9*, 4721–4723; (h) Zhang, X.; Huang, H.; Guo, X.; Guan, X.; Yang, L.; Hu, W. *Angew. Chem., Int. Ed* **2008**, *47*, 6647–6649; (i) Yue, Y.; Guo, X.; Chen, Z.; Yang, L.; Hu, W. *Tetrahedron Lett.* **2008**, *49*, 6862–6865; (j) Xu, X.; Zhou, J.; Yang, L.; Hu, W. *Chem. Commun.* **2008**, 6564–6566.
13. Muthusamy, S.; Krishnamurthy, J. *Tetrahedron Lett.* **2007**, *48*, 6692–6695.
14. For ethereal oxonium ylide chemistry promoted by $Ti(OR)_4$, see: (a) Sawada, Y.; Mori, T.; Oku, A. *Chem. Commun.* **2001**, 1086–1087; (b) Sawada, Y.; Mori, T.; Oku, A. *J. Org. Chem.* **2003**, *68*, 10040–10045.
15. (a) Doyle, M. P.; Yan, M.; Hu, W.; Gronenberg, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 4692–4693; (b) Hansen, K. B.; Finney, N. S.; Jacobsen, E. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 676–678; (c) Galliford, C. V.; Beenan, M. A.; Nguyen, S. T.; Scheidt, K. A. *Org. Lett.* **2003**, *5*, 3487–3490.