Tetrahedron xxx (2014) 1–4

Contents lists available at ScienceDirect

Tetrahedron

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

# Synthesis of quinazoline based chiral ligands and application in the enantioselective addition of phenylacetylene to aldehydes

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ARTICLE INFO

*Article history:*
Received 26 June 2014
Received in revised form 8 August 2014
Accepted 27 August 2014
Available online xxx

*Keywords:*
Quinazolines
Quinazolinones
Phenylacetylene
Asymmetric alkynylation
Propargylic alcohol
Diethylzinc and organozinc addition

ABSTRACT

Five novel 4-phenylquinazolinols were synthesised in three steps. Their application as ligands in the titanium tetraisopropoxide promoted catalytic enantioselective addition of phenylacetylene to a variety of aldehydes gave propargylic alcohols. Under the optimised reaction conditions, the best enantioselectivity was obtained using L-lactic acid derived 4-phenylquinazolinol and apart from the cyclohexylcarbaldehyde derivative, 16 propargylic alcohols were then synthesised in moderate to excellent enantiomeric excess from 53% to 97%.



## 1. Introduction

Catalytic asymmetric C–C bond formation is an intense research area in the field of modern organic chemistry.[1] Among the variety of nucleophilic reactions, the asymmetric alkynylzinc addition to aldehydes has been a particularly significant method for the synthesis of propargylic alcohols, which are very useful precursors for various organic compounds involving natural products, pharmaceuticals and macromolecules.[2] In 1994, Ishizaki and Hoshino published the first asymmetric alkynylzinc reagents addition to aldehydes in the presence of chiral pyridyl alcohol ligand **1**[3] (Fig. 1). After this seminal report, many chiral ligands such as Salen,[4] pyridyl,[5] amino alcohol,[6–8] BINOL[9–11] and sulfonamide alcohols[10,12–14] and its derivatives[15,16] have been emerged to obtain high enantioselectivity in C–C bond forming reactions. In 2000, Carreira and coworkers discovered a highly enantioselective alkynylzinc addition to aldehydes.[17] This result was based on a stoichiometric approach using $Zn(OTf)_2$ and *N*-methylephedrine. A year later they came up with a catalytic version of this approach.[18] Another efficient method was reported by Pu et al. using BINOL derivatives and $Et_2Zn$ with $Ti(O^iPr)_4$.[19] In the last decades, many types of catalytic asymmetric reactions have been carried out with various heterocyclic ligands containing nitrogen such as pyridyl alcohols **1**–**3**,[20] quinazolinone[21,22] and quinazoline alcohols **4a**–**e**[23] (Fig. 1).

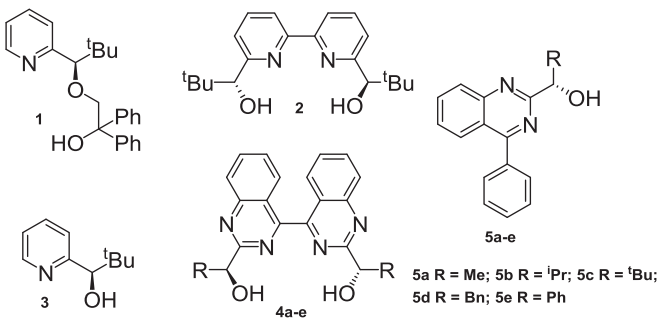


**Fig. 1.** Structure of some chiral heterocyclic ligands containing nitrogen (**1**–**4**) and evaluated ligands (**5a**–**e**).

In our previous report,[23] we synthesised a series of (1*S*,1′*S*)-4,4′-biquinazoline alcohols **4a**–**e** from commercially available chiral α-hydroxy acids and α-amino acids in a few steps. Their application as ligands in enantioselective phenylacetylene addition to aldehydes furnished good yields with moderate enantioselectivities. In this respect, we describe here the synthesis of a series of quinazoline alcohols **5a**–**e** containing a phenyl group at their 4-position. The addition of phenylacetylene to aromatic aldehydes was then

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http://dx.doi.org/10.1016/j.tet.2014.08.067
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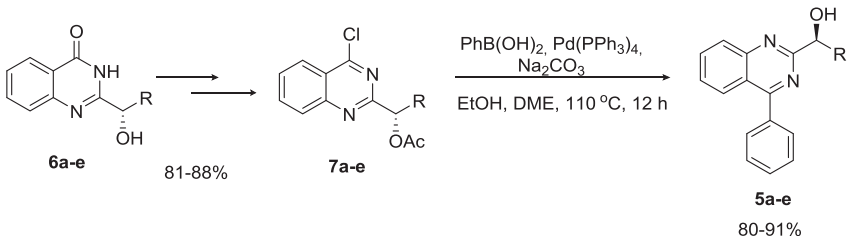
studied with the aim of determining the catalytic effects of these ligands.

## 2. Results and discussion

The quinazolinones **6a**–**e** were prepared from α-hydroxy acids and α-amino acids in four steps in high yields and without a need for chromatography (Scheme 1).[23] Enantiomerically pure quinazolinones **6a**–**e** were treated with $Ac_2O$ in the presence of pyridine as a base to protect the alcohols followed by exposing them to $POCl_3$ and *N*,*N*-diethyl aniline in order to obtain chloroquinazolines **7a**–**e** (Scheme 1).



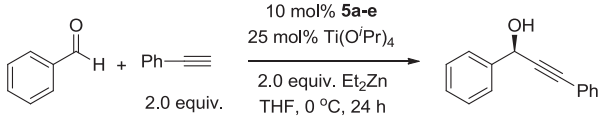

**Scheme 1.**

With chloroquinazolines **7a**–**e** in hand, the synthesis of chiral 4-phenylquinazoline alcohols was carried out via Suzuki coupling reactions with phenylboronic acid in the presence of 2 mol % of $Pd(PPh_3)_4$ at reflux. Except for **5d** (72% ee), the other chiral 4-phenylquinazolines **5a**–**c** and **5e** were obtained in enantiopure form (99% ee) and high yields (80–91%).

First of all, we carried out the alkynylation of benzaldehyde in the presence of 10 mol % of ligand **5a** both with and without $Ti(O^iPr)_4$ in dry THF at 0 °C under nitrogen atmosphere for 24 h. As can be seen in Table 1, in the absence of $Ti(O^iPr)_4$ the reaction yield was moderate but the enantioselectivity too low (Table 1, entry 1). Pleasingly, the loading of 25% $Ti(O^iPr)_4$ into the reaction conditions increased both enantiomeric excess and yield enormously (Table 1, entry 2). However a rise in ees and yields was not observed substantially when 10 and 40 mol % $Ti(O^iPr)_4$ was used (Table 1, entries 3 and 4). To identify the appropriate ligand, the synthesised quinazolines **5a**–**e** were then examined in the condition mentioned above. Although the better differentiated *tert*-leucine derived chiral centre containing ligand **5c** gave the least enantioselectivity (Table 1, entry 6), interestingly, the least bulky chiral centre bearing one **5a** was still the best ligand choice (Table 1, entry 2). Additionally, 1,3-diphenylprop-2-yn-1-ol was accomplished between 45 and 60% enantioselectivities (Table 1, entries 5, 7 and 8) with the other ligands (**5b**, **5d** and **5e**). In order to seek a more efficient catalytic system, we studied the effect of several reaction parameters such as the choice of solvent, the reaction temperature and the amount of the chiral ligand used. As a result of increasing the amount of ligand from 10 to 15 mol %, the ees remained the same. However, decreasing the amount of the ligand to 5 mol %, diminished slightly the reaction ees and yields.

After these observations we turned our attention to solvent screening in order to improve ees. No matter, which solvent was used, we could not get any better enantioselectivity apart from in THF. Decreasing the reaction temperature from 0 °C to −10 °C led to an increase in ee, but it reduced the reaction yield (Table 2, entry 9). Extending the reaction time from 24 to 40 h allowed us to increase the reaction yield from 65 to 89% (Table 2, entry 10).

**Table 1**
Asymmetric alkynylation of benzaldehyde catalysed by **5a**–**e**




| Entry | Ligand (mol %) | ee[a] (%) | Yield[b] (%) | Config.[f] |
|---|---|---|---|---|
| 1 | 5a (10)[c] | 14 | 64 | *R* |
| **2** | **5a (10)** | **78** | **98** | **R** |
| 3 | 5a (10)[d] | 70 | 90 | *R* |
| 4 | 5a (10)[e] | 77 | 91 | *R* |
| 5 | 5b (10) | 45 | 70 | *R* |
| 6 | 5c (10) | 4 | 75 | *R* |
| 7 | 5d (10) | 54 | 93 | *R* |
| 8 | 5e (10) | 60 | 80 | *R* |
| 9 | 5a (15) | 78 | 90 | *R* |
| 10 | 5a (5) | 74 | 87 | *R* |

[a] Determined by chiral HPLC (Chiralcel OD-H).
[b] Isolated yields.
[c] Without $Ti(O^iPr)_4$.
[d] $Ti(O^iPr)_4$: 10 mol %.
[e] $Ti(O^iPr)_4$: 40 mol %.
[f] The absolute configurations of adducts were assigned in accordance with literature.[24]

**Table 2**
Reaction optimisation for asymmetric alkynylation of benzaldehyde

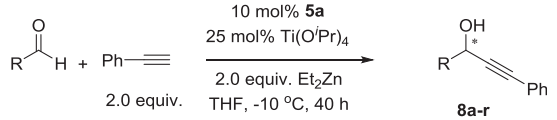
| Entry | Solvent | Temp (°C) | ee[a] (%) | Yield[b] (%) | Config.[c] |
|---|---|---|---|---|---|
| 1 | Hexane | 0 | 17 | 17 | *R* |
| 2 | THF | 0 | 78 | 98 | *R* |
| 3 | Diethyl ether | 0 | 51 | 75 | *R* |
| 4 | Dichloromethane | 0 | 27 | 96 | *R* |
| 5 | Chloroform | 0 | 7 | 38 | *R* |
| 6 | Toluene | 0 | 54 | 71 | *R* |
| 7 | 1,4-Dioxane | 0 | 35 | 70 | *R* |
| 8 | THF | 25 | 70 | 95 | *R* |
| 9 | THF | −10 | 84 | 65 | *R* |
| **10** | **THF** | **−10**[d] | **84** | **89** | **R** |
| 11 | THF | −20 | 80 | 50 | *R* |

[a] Determined by chiral HPLC (Chiralcel OD-H).
[b] Isolated yields.
[c] The absolute configurations of adducts were assigned in accordance with literature.[24]
[d] The reaction was conducted for 40 h.

The addition of phenylacetylene to a series of aldehydes was carried out under the optimised reaction conditions (THF as a solvent, 10% **5a**, 25% $Ti(O^iPr)_4$ at −10 °C for 40 h) (Table 2, entry 10). As shown in Table 3, 17 aldehydes were then converted into their propargylic alcohols in good to excellent yields (67–98%). While propargylic alcohols derived from aromatic aldehydes (Table 3, entries 1–13) gave highly enantioselective results up to 97%, aliphatic ones afforded moderate enantioselectivities (from 53 to 76% ee). Interestingly, among the aldehydes tested in the reaction, the

Please cite this article in press as: Karakaya, I.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.08.067

**Table 3**
Enantioselective addition of phenylacetylene to aldehydes using ligand **5a**




| Entry | Aldehyde | Product | ee[a] (%) | Yield[b] (%) | Config.[c] |
|---|---|---|---|---|---|
| 1 | Benzaldehyde | **8a** | 84 | 89 | *R*[24] |
| 2 | 2-Methoxybenzaldehyde | **8b** | 88 | 75 | *R*[25] |
| 3 | 3-Methoxybenzaldehyde | **8c** | 75 | 98 | *R*[26] |
| 4 | 4-Methoxybenzaldehyde | **8d** | 86 | 73 | *R*[24] |
| 5 | 2-Chlorobenzaldehyde | **8e** | 78 | 67 | *R*[27] |
| 6 | 3-Chlorobenzaldehyde | **8f** | 83 | 96 | *R*[24] |
| 7 | 4-Chlorobenzaldehyde | **8g** | 87 | 95 | *R*[24] |
| 8 | 3-Bromobenzaldehyde | **8h** | 80 | 78 | *R*[28] |
| 9 | 4-Bromobenzaldehyde | **8i** | 97 | 76 | *R*[24] |
| 10 | 3-Methylbenzaldehyde | **8j** | 91 | 98 | *R*[24] |
| 11 | 4-Methylbenzaldehyde | **8k** | 89 | 77 | *R*[24] |
| 12 | 1-Naphthaldehyde | **8l** | 91 | 94 | *R*[25] |
| 13 | Furfural | **8m** | 88 | 85 | *R*[29] |
| 14 | Crotonaldehyde | **8n** | 76 | 74 | NA |
| 15 | Propionaldehyde | **8o** | 53 | 68 | *R*[30] |
| 16 | Isobutyraldehyde | **8p** | 67 | 70 | *R*[31] |
| 17 | Cyclohexanecarbaldehyde | **8r** | 13 | 82 | *S*[31] |

[a] Determined by chiral HPLC (Chiralcel OD-H).
[b] Isolated yields.
[c] The absolute configurations of adducts were assigned in accordance with literature.

cyclohexanecarbaldehyde corresponding adduct accomplished neither a good enantioselectivity nor the same sense of stereoselectivity.

## 3. Conclusions

In summary, we successfully prepared novel chiral quinazolinols (**5a**–**e**) from commercially available starting materials in a few steps. Among these ligands, quinazolinol **5a** exhibited high catalytic activity and asymmetric induction in the alkynylation of aldehydes. It is of note that the best enantioselectivity (75%) of propargylic alcohols obtained in our earlier report[23] is the worst one in this present work for aromatic aldehydes. Application of these ligands in other catalytic enantioselective reactions is currently under investigation in our laboratory.

## 4. Experimental section

### 4.1. General procedure 1 for the preparation of (*S*)-1-(4-phenylquinazolin-2-yl)ethanol 5a

To a solution of (*S*)-1-(4-chloroquinazolin-2-yl)ethyl acetate **7a** (5.00 g, 19.90 mmol) in DME (15 mL) and ethanol (15 mL) were added phenylboronic acid (2.55 g, 20.94 mmol), $Pd(PPh_3)_4$ (454 mg, 0.39 mmol) and $Na_2CO_3$ (22 mL, 2 M in water). The resulting mixture was then refluxed for 12 h, cooled to room temperature and diluted with dichloromethane (150 mL). The mixture was washed with water (3×75 mL). The organic layer was dried over $Na_2SO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/EtOAc, 7:1), and then crystallised on addition of ethanol to give (*S*)-1-(4-phenylquinazolin-2-yl)ethanol **5a** as a colourless solid (4.48 g, 90%). Mp: 85–87 °C; $[\alpha]_D$ +7.5 (*c* 3.2, $CH_2Cl_2$); ee: 99%; retention time 6.9 min, Chiralcel OD-H, 90:10 *n*-hexane/*i*-PrOH, flow rate of 1 mL/min, 254 nm; IR (KBr, $cm^{-1}$) 3232, 3048, 2978, 2909, 1613, 1486, 1132, 1107; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.13 (d, *J*=8.8 Hz, 1H), 8.09 (d, *J*=8.4 Hz, 1H), 7.93–7.57 (m, 7H), 5.17–5.16 (m, 1H), 4.6 (s, 1H), 1.71 (d, *J*=6.7 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 168.9, 167.3, 150.7, 137.0, 134.0, 130.2, 130.0, 128.6, 128.4, 127.3, 127.2, 121.8, 69.8, 23.4; HRMS calculated for $C_{16}H_{14}N_2O$: 251.1186. Found: 251.1187.

### 4.2. (*S*)-2-Methyl-1-(4-phenylquinazolin-2-yl)propan-1-ol 5b

General procedure 1 was followed using (*S*)-1-(4-chloroquinazolin-2-yl)-2-methylpropyl acetate **7b** (4.50 g, 16.10 mmol), phenylboronic acid (2.06 g, 16.95 mmol), $Pd(PPh_3)_4$ (371 mg, 0.32 mmol) and $Na_2CO_3$ (16 mL, 2 M in water) in a solution in mixture of DME (15 mL) and ethanol (15 mL). The crude product was purified by column chromatography (hexane-EtOAc, 7:1), and then crystallised on addition of ethanol to give (*S*)-2-methyl-1-(4-phenylquinazolin-2-yl)propan-1-ol **5b** as a colourless solid (4.08 g, 91%). Mp: 69–70 °C; $[\alpha]_D$ −5.29 (*c* 1.7, $CH_2Cl_2$); ee: 99%; retention time 5.1 min, Chiralcel OD-H, 90:10 *n*-hexane-*i*-PrOH, flow rate of 1 mL/min, 254 nm; IR (KBr, $cm^{-1}$) 3455, 3061, 2959, 2928, 1613, 1487, 1143, 1019; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.12 (d, *J*=7.5 Hz, 1H), 8.08 (d, *J*=8.4 Hz, 1H), 7.94–7.58 (m, 7H), 4.92 (dd, *J*=5.6, 3.4 Hz, 1H), 4.46 (d, *J*=5.6 Hz, 1H), 2.54–2.46 (m, 1H), 1.17 (d, *J*=7.0 Hz), 0.77 (d, *J*=6.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 168.6, 166.1, 150.5, 137.1, 133.9, 130.1, 128.6, 128.4, 127.4, 127.2, 121.7, 34.0, 19.9, 15.4, 0.02; HRMS calculated for $C_{16}H_{14}N_2O$: 279.1499. Found: 279.1503.

### 4.3. (*S*)-2,2-Dimethyl-1-(4-phenylquinazolin-2-yl)propan-1-ol 5c

General procedure 1 was followed using (*S*)-1-(4-chloroquinazolin-2-yl)-2,2-dimethylpropyl acetate **7c** (2.30 g, 7.85 mmol), phenylboronic acid (1.01 g, 8.24 mmol), $Pd(PPh_3)_4$ (180 mg, 0.157 mmol) and $Na_2CO_3$ (17.3 mL, 2 M in water) in a solution in mixture of DME (15 mL) and ethanol (15 mL). The crude product was purified by column chromatography (hexane/EtOAc, 7:1), and then crystallised on addition of ethanol to give (*S*)-2,2-dimethyl-1-(4-phenylquinazolin-2-yl)propan-1-ol **5c** as a colourless solid (1.84 g, 80%). Mp: 101–103 °C; $[\alpha]_D$ +7.08 (*c* 2.4, $CH_2Cl_2$); ee: 99%; retention time 5.0 min, Chiralcel OD-H, 90:10 *n*-hexane/*i*-PrOH, flow rate of 1 mL/min, 254 nm; IR (KBr, $cm^{-1}$) 3459, 3062, 2957, 2866, 1614, 1565, 1546, 1487, 1391, 1068; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.15 (d, *J*=8.4 Hz, 1H), 8.10 (d, *J*=8.5 Hz, 1H), 7.92–7.58 (m, 7H), 4.73 (d, *J*=7.6 Hz, 1H), 4.47 (d, *J*=7.6 Hz, 1H), 1.06 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 167.4, 165.3, 150.5, 137.1, 133.8, 130.1, 130.1, 128.6, 127.3, 127.1, 121.8, 80.9, 30.9, 26.3; HRMS calculated for $C_{16}H_{14}N_2O$: 293.1655. Found: 293.1653.

### 4.4. (*S*)-Phenyl(4-phenylquinazolin-2-yl)methanol 5d

General procedure 1 was followed using (*S*)-(4-chloroquinazolin-2-yl)(phenyl)methyl acetate **7d** (5.40 g, 17.26 mmol), phenylboronic acid (2.20 g, 18.12 mmol), $Pd(PPh_3)_4$ (396 mg, 0.34 mmol) and $Na_2CO_3$ (7.8 mL, 2 M in water) in a solution in mixture of DME (6 mL) and ethanol (6 mL). The crude product was purified by column chromatography (hexane/EtOAc, 10:1), and then crystallised on addition of ethanol to give (*S*)-2,2-dimethyl-1-(4-phenylquinazolin-2-yl)propan-1-ol **5d** as a colourless solid (4.58 g, 85%). Mp: 102–106 °C; $[\alpha]_D$ +54.33 (*c* 2.0, $CH_2Cl_2$); ee: 72%; retention time 8.9 min (major), 11.7 min (minor), Chiralcel OD-H, 90:10 *n*-hexane/*i*-PrOH, flow rate of 1 mL/min, 254 nm; IR (KBr, $cm^{-1}$) 3423, 3058, 1613, 1565, 1547, 1389, 1058; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.19–7.31 (m, 14H), 6.10 (d, *J*=6.3 Hz, 1H), 5.29 (d, *J*=6.3 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 168.9, 165.2, 150.7, 142.5, 136.9, 134.1, 130.2, 130.2, 128.6, 128.5, 128.2, 127.6, 127.5, 127.2, 126.9, 121.9, 75.5; HRMS calculated for $C_{16}H_{14}N_2O$: 313.1342. Found: 313.1335.

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### 4.5. (*S*)-2-Phenyl-1-(4-phenylquinazolin-2-yl)ethanol 5e

General procedure 1 was followed using (*S*)-1-(4-chloroquinazolin-2-yl)-2-phenylethyl acetate **7e** (5.00 g, 15.30 mmol), phenylboronic acid (1.96 g, 16.06 mmol), $Pd(PPh_3)_4$ (352 mg, 0.31 mmol) and $Na_2CO_3$ (15 mL, 2 M in water) in a solution in mixture of DME (20 mL) and ethanol (20 mL). The crude product was purified by column chromatography (hexane/EtOAc, 6:1), and then crystallised on addition of ethanol to give (*S*)-2-phenyl-1-(4-phenylquinazolin-2-yl)ethanol **5e** as a colourless solid (4.24 g, 85%). Mp: 66–68 °C; $[\alpha]_D$ −70.74 (*c* 2.7, $CH_2Cl_2$); ee: 99%; retention time 6.2 min, Chiralcel OD-H, 90:10 *n*-hexane/*i*-PrOH, flow rate of 1 mL/min, 254 nm; IR (KBr, $cm^{-1}$) 3430, 3058, 1613, 1565, 1547, 1389, 1058; $^1H$ NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.12 (d, *J*=8.7 Hz, 1H), 8.06 (d, *J*=8.4 Hz, 1H), 7.92–7.23 (m, 12H), 5.36–5.29 (m, 1H), 4.48 (d, *J*=5.8 Hz, 1H), 3.51 (dd, *J*=13.8, 3.95 Hz, 1H), 3.17 (dd, *J*=13.8, 7.64 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 168.7, 165.7, 150.7, 138.2, 137.0, 134.0, 130.2, 130.08, 129.7, 128.6, 128.5, 128.1, 127.4, 127.2, 126.2, 121.83, 74.24, 43.59; HRMS calculated for $C_{16}H_{14}N_2O$: 327.1499. Found: 327.1485.

### 4.6. Typical procedure for catalytic asymmetric addition of phenylacetylene to aldehydes

Under nitrogen atmosphere, phenylacetylene (1.96 mmol) and diethylzinc (1.96 mmol, 1 M in hexane) were dissolved in freshly distilled THF (3 mL) and refluxed for 1 h. The resulting solution was brought to ambient temperature and following that a solution of chiral ligand **5a** (0.098 mmol) in THF (3 mL) was added. After stirring for 30 min, $Ti(O^iPr)_4$ (0.25 mmol) was added to the solution and stirred for a further 1 h. Finally, the mixture was cooled to −10 °C and aldehyde (0.98 mmol in 2 mL THF) was added. After stirring for 40 h at −10 °C under a nitrogen atmosphere, the reaction was then quenched with saturated ammonium chloride (10 mL). The aqueous phase was extracted with ethyl acetate (3×20 mL), washed with brine (3×20 mL), dried with anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc/hexane 9:1) to give the desired product. The enantiomeric excess was determined by chiral HPLC using Chiralcel OD-H column.

### Acknowledgements

We would like to thank to Gokhan Bilsel at TUBITAK UME for the HRMS measurements.

### Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.08.067.

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