Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 60 (2004) 7427–7430
Tetrahedron

3,3′-Functionalized octahydro-BINOL: a facile synthesis and its high enantioselectivity in the alkyne addition to aldehydes

Lan Liu[a,b] and Lin Pu[a,*]

[a]*Department of Chemistry, University of Virginia, Charlottesville, VA 22904-4319, USA*
[b]*School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China*

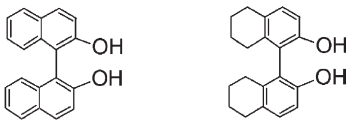
Received 8 April 2004; revised 17 May 2004; accepted 19 May 2004

Available online 10 June 2004

Abstract—A facile synthesis of an enantiomerically pure 3,3′-bismorpholinylmethyl H_8-BINOL ligand has been developed. This compound in combination with Et_2Zn and $Ti(O^iPr)_4$ is found to catalyze the highly enantioselective reaction of phenylacetylene with aromatic aldehydes. The enantioselectivity of this catalytic process for the reactions of *ortho*-substituted benzaldehydes is significantly higher than that based on H_8-BINOL.

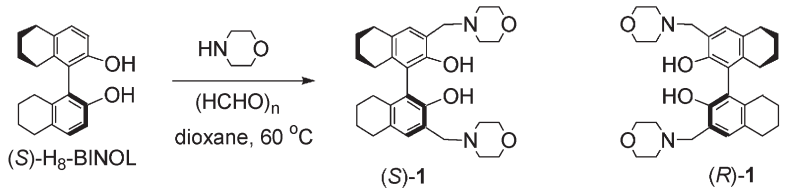
1. Introduction

Application of 1,1′-bi-2-naphthol (BINOL) and its derivatives in asymmetric catalysis has been extensively studied.[1–3] Recently, catalysts[4] based on the partially hydrogenated BINOL ligand, H_8-BINOL,[5] have also been investigated. In a few cases, the partially hydrogenated BINOL has shown improved chiral induction over BINOL. This improved enantioselectivity is attributed to the increased steric interaction between the two partially hydrogenated naphthalene rings in H_8-BINOL. Considering the extremely rich chemistry of functionalized BINOLs, we envision that functionalized H_8-BINOL should also exhibit interesting properties in catalysis as well as in other applications. Especially, introduction of 3,3′-substituents to H_8-BINOL may lead to ligands of high enantioselectivity for asymmetric reactions as demonstrated by many 3,3′-substituted BINOL ligands. However, very few functionalized H_8-BINOL ligands have been synthesized and studied.[4c–e] Herein, we report our discovery of a facile synthesis of an enantiomerically pure 3,3′-bisaminomethyl H_8-BINOL. This compound has shown high enantioselectivity in the catalytic asymmetric alkyne addition to aromatic aldehydes, especially to the *ortho*-substituted benzaldehydes.



BINOL H_8-BINOL

We conducted the reaction of the enantiomerically pure (*S*)-H_8-BINOL[5] with paraformaldehyde and morpholine in dioxane at 60 °C.[6] This one-pot process led to the formation of (*S*)-3,3′-bis (morpholin-4-ylmethyl)-H_8-BINOL, (*S*)-**1**, in 65% yield (Scheme 1). The specific optical rotation of (*S*)-**1**, $[\alpha]_D$, was −15.5 (c=1.0, $CHCl_3$). The ^1H NMR spectrum of (*S*)-**1** gave a singlet at δ 10.37 for the two hydroxyl groups, indicating a C_2 symmetric structure probably with intramolecular hydrogen bonds between the hydroxyl groups



(*S*)-H_8-BINOL (*S*)-**1** (*R*)-**1**

Scheme 1. Synthesis of the enantiomerically pure 3,3′-bismorpholinylmethyl H_8-BINOL.

Keywords: Asymmetric catalysis; H_8-BINOL; Alkyne addition; Propargylic alcohols.
* Corresponding author. Tel.: +1-4349246953; fax: +1-4349243710; e-mail address: lp6n@virginia.edu

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.05.049

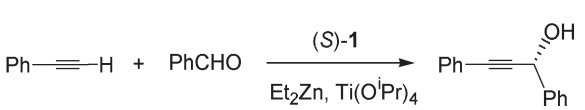
Table 1. Results for the reaction of phenylacetylene with benzaldehyde in the presence of (*S*)-**1**, $Ti(O^iPr)_4$ and Et_2Zn

Entry	(*S*)-**1** (mol%)	PhCCH (equiv.)	Et_2Zn (equiv.)	$Ti(O^iPr)_4$ (mol%)	Solvent	*T* (°C)	Yield (%)	ee (%)
1	2	4	4	100	THF (3 mL)	rt	25	81
2	5	4	4	100	THF (3 mL)	rt	64	83
3	10	4	4	100	THF (3 mL)	rt	93	83
4	20	4	4	100	THF (3 mL)	rt	95	84
5	40	4	4	100	THF (3 mL)	rt	90	85
6	20	4	4	100	CH_2Cl_2 (3 mL)	rt	96	82
7	20	4	4	100	Ether (3 mL)	rt	60	84
8	20	4	4	100	Toluene (3 mL)	rt	85	84
9	10	4	4	100	THF (3 mL)	0	85	83
10	10	2	2	100	THF (3 mL)	rt	63	86
11	10	1.5	1.5	100	THF (3 mL)	rt	58	83
12	20	2	2	50	THF (3 mL)	rt	45	83
13	20	2	2	100	THF (3 mL)	rt	77	84
14	20	2	2	200	THF (3 mL)	rt	89	84
15	20	2	2	100	THF (1 mL)	rt	38	83
16	20	2	2	100	THF (6 mL)	rt	65	84

and the adjacent morpholine nitrogens. The optical purity of (*S*)-**1** was determined to be >99% by HPLC analysis on the Daicel Chiralcel OD column. The enantiomer of (*S*)-**1**, (*R*)-**1**, was also prepared by starting with (*R*)-H_8-BINOL. The specific optical rotation of (*R*)-**1**, $[\alpha]_D$, was +15.5 (c=1.0, $CHCl_3$).

Compound (*S*)-**1** is an axially chiral ligand with a C_2 symmetric bis(aminoalcohol) structure. Since both chiral amino alcohols and the axially chiral BINOL compounds have exhibited excellent chiral inductions in many Lewis-acid catalyzed asymmetric reactions, (*S*)-**1** should also be potentially useful in asymmetric catalysis. We used (*S*)-**1** to catalyze the asymmetric alkynylzinc addition to aldehydes.[7] This reaction can produce chiral propargylic alcohols that are of great utility in organic synthesis. We first explored the conditions for the reaction of phenylacetylene with benzaldehyde in the presence of (*S*)-**1**, Et_2Zn and $Ti(O^iPr)_4$ (Scheme 2). As shown by the results summarized in Table 1, (*S*)-**1** catalyzed this reaction with good enantioselectivity which did not change significantly with respect to the reaction conditions. Increasing the amount of (*S*)-**1** from 2 to 40 mol% greatly increased the yield of the propargylic alcohol but not the ee (entries 1–5). Solvent and temperature also showed little effect on the enantioselectivity (entries 6–9). Decreasing the amount of Et_2Zn and phenylacetylene to 2 equiv. decreased the yield of the product (entry 10). Increasing the amount of $Ti(O^iPr)_4$ from 50 to 200 mol% increased the yield (entries 12–14). Increasing or decreasing the amount of the solvent led to reduction in yield (entries 15 and 16). The configuration of the propargylic alcohol product was R as determined by comparing it with the literature.[8]

We have applied the conditions of entry 3 in Table 1 to the reaction of phenylacetylene with a variety of aldehydes and the results are summarized in Table 2. In general, (*S*)-**1** showed high enantioselectivity for the reaction of the alkyne



Scheme 2. Reaction of phenylacetylene with benzaldehyde catalyzed by (*S*)-**1**.

with aromatic aldehydes. Earlier, Chan and coworkers found that H_8-BINOL in combination with $Ti(O^iPr)_4$ and Me_2Zn catalyzed the reaction of phenylacetylene with certain aromatic aldehydes with high enantioselectivity at 0 °C.[4j] Under these conditions, however, the reaction of an *ortho*-substituted benzaldehyde was not very good. Using H_8-BINOL could only give 76% ee for the reaction of phenylacetylene with *o*-chlorobenzaldehyde. In contrast, the 3,3′-functionalized H_8-BINOL ligand (*S*)-**1** catalyzed the same reaction with 97% ee (entry 2, Table 2). This ligand was also found to be good for the asymmetric reaction of other *ortho*-substituted benzaldehydes with ee's in the range of 89–98% (entries 2–8, Table 2).

In summary, a novel 3,3′-functionalized H_8-BINOL has been synthesized by a one-pot reaction of H_8-BINOL with paraformaldehyde and morpholine. A preliminary study of this ligand in the asymmetric alkyne addition to aldehydes has demonstrated the potential of this ligand in asymmetric catalysis. In the presence of (*S*)-**1**, high enantioselectivity

Table 2. Asymmetric reactions of phenylacetylene with aromatic aldehydes in the presence of (*S*)-**1**, Et_2Zn and $Ti(O^iPr)_4$[a]

Entry	Aldehyde	Isolated yield (%)	ee (%)
1	PhCHO	93	83
2	*o*-ClPhCHO	88	97
3	*o*-MeOPhCHO	76	93
4	*o*-EtOPhCHO	83	92
5	*o*-MePhCHO	88	89
6[b]	*o*-NO_2PhCHO	62	98
7	*o*-BrPhCHO	84	97
8	2,4,5-Trimethylbenzaldehyde	68	96
9	*m*-MeOPhCHO	93	86
10	*p*-BrPhCHO	86	87
11	*p*-FPhCHO	50	86
12	*m*-MePhCHO	98	91
13	*p*-MePhCHO	86	83
14	*p*-MeOPhCHO	99	85
15	1-Naphthylaldehyde	85	83
16[c]	2,6-Dichlorobenzaldehyde	62	86
17[d]	$CH_3(CH_2)_6CHO$	76	67

[a] Unless indicated otherwise, reactions were conducted by stirring (*S*)-**1**:Et_2Zn:PhCCH:$Ti(O^iPr)_4$:RCHO=0.1:4:4:1:1 at room temperature in THF for 4 h.
[b] 2 equiv. of Et_2Zn and 2 equiv. of PhCCH were used.
[c] The reaction time was 6 h.
[d] 20 mol% (*S*)-**1** was used.

has been observed for the reaction of phenylacetylene with aromatic aldehydes, especially with the *ortho*-substituted benzaldehydes. Application of this ligand to other asymmetric reactions is currently under investigation.

2. Experimental

2.1. General data

All reactions were carried out under nitrogen. Unless otherwise specified, all the reagents were purchased from Aldrich Chemical Co. and used directly. Diethylzinc (95%) was purchased from Strem. Toluene was distilled over sodium under nitrogen. Methylene chloride, diethyl ether and tetrahydrofuran were dried by passing through activated alumnia columns under nitrogen. All the solvents were stored over 4 Å molecular sieves before use. Deuterated chloroform was stored over 4 Å molecular sieves before use. NMR spectra were obtained using the Varian-300 MHz spectrometer. Mass spectra were recorded either at atmospheric pressure chemical ionization (APCI) or at electrospray ionization (ESI) mode. HPLC analyses were carried out with the Waters 600 by using the Daicel Chiralcel OD column and eluting with 10% *i*-PrOH in hexane at 1.0 mL/min unless otherwise indicated, and were detected at 254 nm by the Waters 486. The optical rotations were measured on the JASCO DIP-1000 Polarimeter.

2.2. Synthesis and characterization of (*S*)-1

Paraformaldehyde (6.0 g, 0.20 mol) was placed in a round bottom flask equipped with a reflux condenser. Morpholine (17.6 g, 0.20 mol) was added dropwise over 0.5 h with rigorous stirring. Since this was a strongly exothermic reaction, the addition rate was adjusted in order to keep the oil bath temperature at ~60 °C. After the addition, the reaction mixture was heated at 60 °C for ca. 12 h until the solution became clear. H_8-BINOL (3.0 g, 0.010 mol) and dioxane (10 mL) were added and the solution was stirred at 60 °C for additional 8 h. The solvent was then removed by roto-evaporation. The residue was dissolved in CH_2Cl_2 (50 mL), washed with 1 M HCl (3×10 mL) and water (3×10 mL), and dried over Na_2SO_4. After roto-evaporation, the crude material was purified by using ethylacetate/hexane (3:1) to elute through a short silicon gel column. This gave (*S*)-**1** as colorless crystals (3.3 g) in 65% yield. Mp 215.5–216.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.37 (s, 2H), 6.73 (s, 2H), 3.83–3.57 (m, 12H), 2.72–2.13 (m, 16H), 1.72–1.56 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.71, 135.5, 128.4, 127.1, 123.6, 117.4, 66.3, 61.6, 52.5, 28.9, 26.9, 22.9, 22.8. $[\alpha]_D=-15.5$ (c=1.0, $CDCl_3$). Anal. Calcd for $C_{30}H_{39}N_2O_4$: C, 72.84; H, 8.56; N, 5.66. Found: C, 73.22; H, 8.20; N, 5.66. MS (FIA-ESI) m/z 493.0 (M^+, 100).

2.3. General procedure for the phenylacetylene addition to aldehydes catalyzed by (*S*)-1

In a 10 mL round-bottom flask, phenylacelylene (1.0 mmol, 113 μL) was dissolved in THF (3 mL) at room temperature. Et_2Zn (1.0 mmol, 110 μL), $Ti(O^iPr)_4$ (74 μL, 0.25 mmol), (*S*)-**1** (12.3 mg, 0.025 mmol) and an aldehyde (0.25 mmol) were then added sequentially. After the resulting reaction mixture was stirred at room temperature for 4 h, a saturated ammonium chloride solution was added to quench the reaction. The mixture was extracted with methylene chloride (3×5 mL) and the organic solution was concentrated under vacuum. The residue was purified by passing through a short silica gel column eluted with methylene chloride/hexane (1:1) which afforded the pure propargylic alcohol product.

2.3.1. 1,3-Diphenylprop-2-yn-1-ol.[8] 86% yield. 87% ee determined by HPLC analysis. Retention time: t_{major}=24.0 min and t_{minor}=13.3 min.

2.3.2. 1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-ol.[9] 88% yield. 97% ee determined by HPLC analysis. Retention time: t_{major}=14.0 min and t_{minor}=12.0 min.

2.3.3. 1-(2,6-Dichlorophenyl)-3-phenylprop-2-yn-1-ol. 62% yield. 87% ee determined by HPLC analysis. Retention time: t_{major}=12.2 min and t_{minor}=8.9 min. $[\alpha]_D^{24}=+3.67$ (c=1.26, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.36–7.17 (m, 6H), 6.60 (d, 1H, J=10.2 Hz), 3.40 (d, 1H, J=10.2 Hz). The large coupling constant observed here between the hydroxyl proton and the methine proton is probably due to the intramolecular hydrogen bond between the hydroxyl group and one of the two chlorine atoms at the 2,6-positions. This intramolecular hydrogen bond allows the hydroxyl proton and the methine proton to form an antiperiplanar conformation as shown by a PCSpartan-Semi-Empirical AM1 calculation and it significantly increases the coupling constant. ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 134.7, 132.1, 130.0, 129.5, 128.9, 128.5, 122.6, 86.9, 86.5, 61.7. MS (FIA-APCI) m/z 258.4 (M^+-H_2O, 100).

2.3.4. 1-(2-Nitrophenyl)-3-phenylprop-2-yn-1-ol.[10] 62% yield. 98% ee determined by HPLC analysis. Retention time: t_{major}=16.0 min and t_{minor}=20.6. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26–7.80 (m, 2H), 7.77–7.74 (m, 2H),7.51–7.15(m, 5H), 5.80 (s, 1H), 2.63 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 147.6, 132.0, 130.7, 129.3, 128.7, 127.7, 124.51, 124.1, 122.0, 87.8, 87.7, 64.2.

2.3.5. 1-(2,4,5-Trimethylphenyl)-3-phenylprop-2-yn-1-ol. 68% yield. 96% ee determined by HPLC analysis. Retention time: t_{major}=34.8 min and t_{minor}=13.4. $[\alpha]_D^{24}=-20.9$ (c=1.38, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.53 (m, 3H), 7.39–7.36 (m, 3H), 7.05 (s, 1H), 5.84 (d, 1H, J=4.8 Hz), 2.95 (d, 1H, J=4.8 Hz), 2.44 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 134.9, 133.4, 131.4, 130.8, 127.6, 127.4, 121.8, 88.0, 85.3, 61.9, 28.9, 18.5, 17.5. MS (FIA-APCI) m/z 232.5 (M^+-H_2O, 100). (The starting material contained ~7% 5-bromo-1,2,4-trimethylbenzene which could not be completely removed from the product.)

2.3.6. 1-(2-Ethoxyphenyl)-3-phenylprop-2-yn-1-ol. 83% yield. 92% ee determined by HPLC analysis. Retention time: t_{major}=18.4 min and t_{minor}=12.5 min. $[\alpha]_D^{24}=+2.92$ (c=1.38, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.60 (m, 1H), 7.50–7.47 (m, 2H),7.31–7.24 (m, 4H), 7.04–6.9(m, 2H), 5.85 (d, 1H, J=4.5 Hz), 4.40–4.03 (m, J=6.9 Hz, 2H), 3.29 (d, 1H, J=4.5 Hz), 1.51–1.46 (t, 3H,

J=5.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 132.0, 129.9, 129.2, 128.6, 128.5, 128.3, 123.1. 121.1, 122.1, 88.7, 86.1, 64.3, 62.3, 15.2. MS (FIA-APCI) m/z 234.8 [M^+-H_2O, 100].

2.3.7. 1-(2-Bromophenyl)-3-phenylprop-2-yn-1-ol.[10] 84% yield. 97% ee determined by HPLC analysis. Retention time: t_{major}=24.3 min and t_{minor}=20.0 min (eluted with 5% *i*-PrOH in hexane at 1.0 mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87–7.84 (m, 1H), 7.61–7.58 (m, 1H), 7.50–7.46 (m, 2H), 7.42–7.19 (m, 5H), 6.02 (d, 1H, J=4.5 Hz), 2.62 (d, 1H, J=4.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 133.3, 132.0, 130.2, 128.9, 128.5, 128.2, 123.1, 122.5, 87.9, 87.1, 64.9.

2.3.8. 1-(2-Methoxyphenyl)-3-phenylprop-2-yn-1-ol.[11] 76% yield. 93% ee determined by HPLC analysis. Retention time: t_{major}=22.1 min and t_{minor}=18.4 min.

2.3.9. 1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-ol.[11] 93% yield. 86% ee determined by HPLC analysis. Retention time: t_{major}=40.4 min and t_{minor}=21.9 min.

2.3.10. 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-ol.[9] 99% yield. 85% ee determined by HPLC analysis. Retention time: t_{major}=39.6 min and t_{minor}=16.8 min.

2.3.11. 1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol.[11] 50% yield. 86% ee determined by HPLC analysis. Retention time: t_{major}=35.7min and t_{minor}=11.6 min.

2.3.12. 1-(3-Methylphenyl)-3-phenylprop-2-yn-1-ol.[11] 98% yield. 91% ee determined by HPLC analysis. Retention time: t_{major}=34.4 min and t_{minor}=13.8 min.

2.3.13. 1-(2-Methylphenyl)-3-phenylprop-2-yn-1-ol.[11] 88% yield. 89% ee determined by HPLC analysis. Retention time: t_{major}=27.7 min and t_{minor}=11.8 min.

2.3.14. 1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol.[10] 86% yield. 87% ee determined by HPLC analysis. Retention time: t_{major}=43.9 min and t_{minor}=12.3 min.

2.3.15. 1-(4-Methylphenyl)-3-phenylprop-2-yn-1-ol.[11] 86% yield. 87% ee determined by HPLC analysis. Retention time: t_{major}=28.6 min and t_{minor}=13.1 min.

2.3.16. 1-Naphthalen-1-yl-3-phenylprop-2-yn-1-ol.[11] 86% yield. 87% ee determined by HPLC analysis. Retention time: t_{major}=44.4 min and t_{minor}=19.8 min.

2.3.17. 1-Phenyldec-1-yn-3-ol.[9] 76% yield. 67%ee determined by HPLC analysis. Retention time: t_{major}=7.6 min and t_{minor}=17.6 min.

2.4. General procedure for the preparation of the racemic propargylic alcohols

All the racemic propargylic alcohols were prepared for the HPLC analysis according to the following procedure. A solution of an alkyne (0.75 mmol) in tetrahydrofuran (3 mL) in a 25 mL flask was cooled to −78 °C with a dryice/acetone bath. *n*-BuLi (1.6 M in hexanes, 0.7 mmol) was then added and the reaction mixture was brought to room temperature and stirred for 3 h. An aldehyde (0.5 mmol) was added and the mixture was stirred for additional 8 h. The reaction was quenched with ice, and the resulting mixture was extracted with methylene chloride. After the organic solution was dried over magnesium sulfate, the solvent was removed by roto-evaporation and the residue was passed through a short silica gel column and eluted with methylene chloride/hexane (1:1) to afford the product.

Acknowledgements

L.L. thanks the support from the National Natural Science Foundation of China (Grant20202015). Partial support of this work from the National Institute of Health (R01GM58454/R01EB002037) is gratefully acknowledged.

References and notes

1. Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494.
2. Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155–3211.
3. Kočovskú, P.; Vyskočil, S.; Smrčina, M. *Chem. Rev.* **2003**, *103*, 3213–3245.
4. (a) A review: Au-Yeung, T. L.-L.; Chan, S.-S.; Chan, A. S. *Adv. Synth. Catal.* **2003**, *345*, 537–555. (b) Iida, T.; Yamamoto, N.; Matsunaga, S.; Woo, H.-G.; Shibasaki, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2223–2226. (c) Reetz, M. T.; Merk, C.; Naberfeld, G.; Rudolph, J. N. G.; Goddard, R. *Tetrahedron Lett.* **1997**, *38*, 5273–5276. (d) Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1452–1456. (e) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, P. J.; Hoveyda, A. H. *Organometallics* **2002**, *21*, 409–417. (f) Long, J.; Hu, J.; Shen, X.; Ji, B.; Ding, K. *J. Am. Chem. Soc.* **2002**, *124*, 10–11. (g) Wang, B.; Feng, X.; Huang, Y.; Liu, H.; Cui, X.; Jiang, Y. *J. Org. Chem.* **2002**, *67*, 2175–2182. (h) Chan, A. S. C.; Zhang, F.-Y.; Yip, C.-W. *J. Am. Chem. Soc.* **1997**, *119*, 4080–4081. (i) Zhang, F.-Y.; Chan, A. S. C. *Tetrahedron: Asymmetry* **1997**, *8*, 3651–3655. (j) Lu, G.; Li, X.; Chan, W. L.; Chan, A. S. C. *J. Chem. Soc., Chem. Commun.* **2002**, 172–173. (k) Waltz, K. M.; Carroll, P. J.; Walsh, P. J. *Organometallics* **2004**, *23*, 127–134.
5. Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930–1946.
6. The reaction of 2,2′-biphenol with paraformaldehyde and morpholine was reported: Fabris, F.; Lucchi, O. D.; Lucchini, V. *J. Org. Chem.* **1997**, *62*, 7156–7164.
7. Reviews: (a) Pu, L. *Tetrahedron* **2003**, *59*, 9873–9886. (b) Pu, L.; Yu, H. B. *Chem. Rev.* **2001**, *101*, 757–824.
8. Corey, E. J.; Cimprich, K. A. *J. Am. Chem. Soc.* **1994**, *116*, 3151–3152.
9. Gao, G.; Moore, D.; Xie, R.-G.; Pu, L. *Org. Lett.* **2002**, *4*, 4143–4146.
10. Lu, G.; Li, X.; Zhou, Z.; Chan, W. L.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2001**, *12*, 2147–2152.
11. Moore, D.; Pu, L. *Org. Lett.* **2002**, *4*, 1855–1857.