This article was downloaded by: [University of Connecticut]
On: 09 September 2013, At: 01:02
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of Tri- and Disalicylaldehydes and Their Chiral Schiff Base Compounds

Hai-Bin Liu [a b], Mei Wang [a], Ying Wang [a], Lin Wang [a] & Li-Cheng Sun [a c]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning, China

[b] Department of Biology and Chemical Engineering, Liaoning Institute of Science and Technology, Benxi, Liaoning, China

[c] School of Chemical Science and Engineering, Royal Institute of Technology, Stockholm, Sweden

Published online: 04 Mar 2010.

To cite this article: Hai-Bin Liu , Mei Wang , Ying Wang , Lin Wang & Li-Cheng Sun (2010) Synthesis of Tri- and Disalicylaldehydes and Their Chiral Schiff Base Compounds, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:7, 1074-1081, DOI: 10.1080/00397910903040252

To link to this article: http://dx.doi.org/10.1080/00397910903040252

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [University of Connecticut] at 01:02 09 September 2013

Synthetic Communications®, 40: 1074–1081, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903040252

Taylor & Francis
Taylor & Francis Group

Downloaded by [University of Connecticut] at 01:02 09 September 2013

SYNTHESIS OF TRI- AND DISALICYLALDEHYDES AND THEIR CHIRAL SCHIFF BASE COMPOUNDS

Hai-Bin Liu,[1,2] Mei Wang,[1] Ying Wang,[1] Lin Wang,[1] and Li-Cheng Sun[1,3]

[1]*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning, China*

[2]*Department of Biology and Chemical Engineering, Liaoning Institute of Science and Technology, Benxi, Liaoning, China*

[3]*School of Chemical Science and Engineering, Royal Institute of Technology, Stockholm, Sweden*

A suitable procedure for convenient preparation of 1,3,5-tris(4-hydroxy-5-formylphenyl)-benzene (6) was exploited via 5-bromosalicylaldehyde as starting reactant. Among the obtained products, compound 6, 4-methoxy-3-formylphenylboronic acid (9), 1,3,5-tris(4-methoxy-5-formylphenyl)benzene (10), and 4-methoxy-4′-hydroxyl-3,3′-diformyl-1,1′-diphenyl (11) had not been reported previously. Two new chiral Schiff base ligands,* L1 *and* L2*, were obtained from the tri- or disalicylaldehydes.

Keywords: 5-Bromosalicylaldehyde; disalicylaldehyde; Schiff base ligands; trisalicylaldehyde

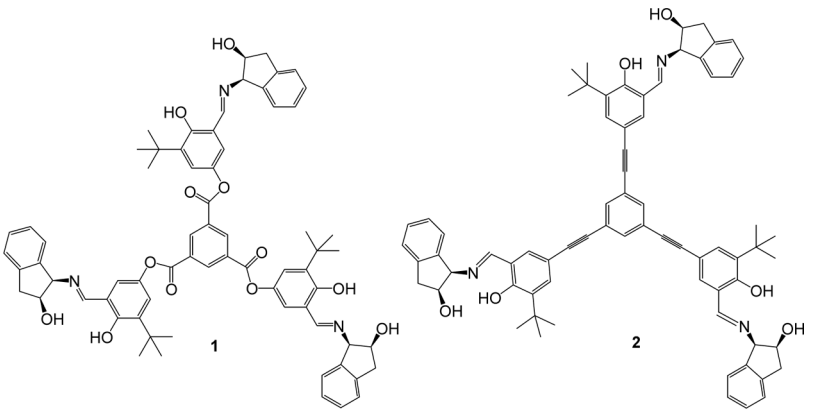
INTRODUCTION

Salicylaldehydes and their derivatives can be transformed to Schiff bases and salen compounds, which are important ligands and have been widely used in asymmetric catalysis.[1] Transition-metal complexes containing chiral Schiff bases or salen ligands can catalyze many enantioselective reactions, such as asymmetric oxidation of sulfides,[2] epoxidation of olefins,[3] cyclopropanation of styrene,[4] and asymmetric hetero-Diels–Alder reactions.[5] Monosalicylaldehydes and their Schiff base ligands have been widely studied, for example, 3-aryl-5-butylsalicylaldehydes were prepared in our group by the Suzuki–Miyaura coupling reaction, as well as 10 new Schiff base ligands,[6] which were applied to the asymmetric oxidation of aryl methyl sulfides to give good to excellent ee values (up to 90% ee).[7]

However, there are few reports concerning the synthesis of tri- or disalicylaldehydes and the catalytic reactions using their Schiff base ligands. In 2007, Suresh and coworkers prepared chiral Schiff base ligands **1** and **2** by condensation of two

Received March 24, 2009.

Address correspondence to Hai-Bin Liu, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, Liaoning, China. E-mail: haibin0616@163.com



Scheme 1. Schiff base ligands **1** and **2**.

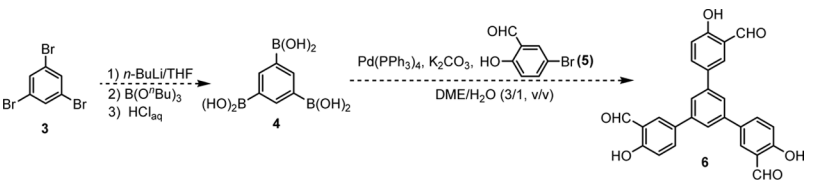
trisalicylaldehydes and chiral aminoalcohol, which catalyzed the asymmetric oxidation of thioanisole with good ee values (Scheme 1).[8]

In this article, we describe the synthesis of trisalicylaldehyde by hydroxyl protection and formyl protection, forming arylboronic acid, followed by Suzuki–Miyaura coupling reaction and hydroxyl deprotection. Moreover, disalicylaldehyde was prepared via the same method as the synthesis of trisalicylaldehyde.

RESULTS AND DISCUSSION

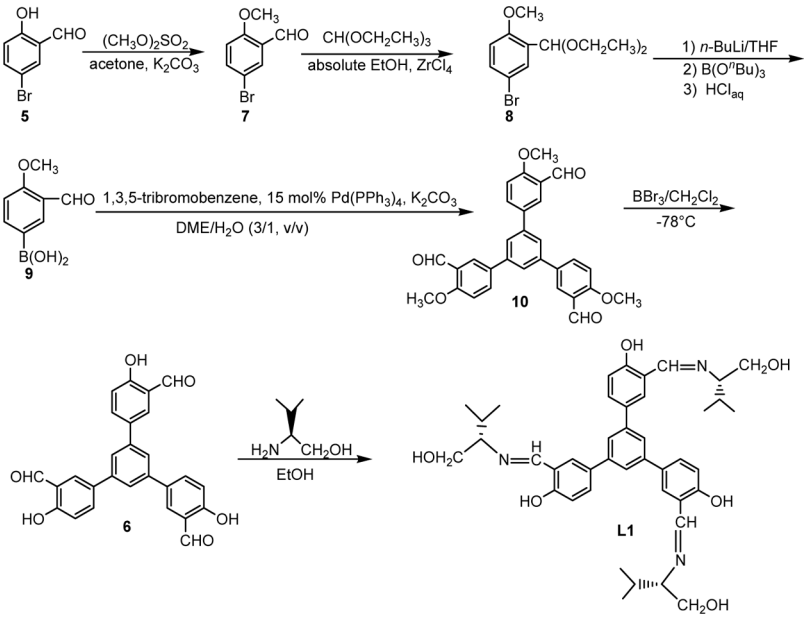
At first, we attempted to prepare trisalicylaldehyde **6** through the simple synthetic route as outlined in Scheme 2: 1,3,5-tribromobenzene transformed to 1,3,5-tribronic acid benzene **4** first, and then the Suzuki–Miyaura coupling reaction of **4** with 5-bromosalicylaldehyde **5** gave trisalicylaldehyde **6**. Unfortunately, all attempts at forming arylboronic acid **4** were unsuccessful, presumably because of the instability of the intermediate of **3** with *n*-BuLi.

Therefore, another synthetic route was designed to obtain trisalicylaldehyde **6**, shown in Scheme 3. Because phenol hydroxyl and formyl groups would be destroyed in the presence of a strong base, they need to be protected. Compound **7** was conveniently prepared in acetone for 10 h, and then it was reacted with triethylorthoformate in absolute EtOH and a catalytic amount of $ZrCl_4$ to obtain compound **8**. Lithiation of compound **8** with 1.2 equiv. of *n*-BuLi in tetrahydrofuran (THF) at $-78\,^{\circ}C$ followed by reaction with 2.0 equiv. of $B(O^nBu)_3$ and acidic hydrolysis



Scheme 2. The simple synthetic route of preparing trisalicylaldehyde **6**.

Downloaded by [University of Connecticut] at 01:02 09 September 2013



Scheme 3. Preparation of Schiff base **L1**.

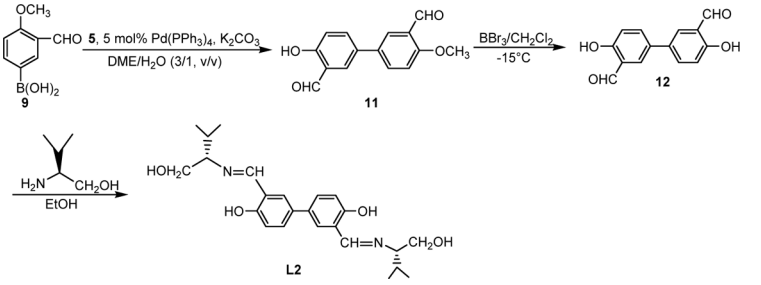
produced arylboronic acid **9** in 94% yield as a yellow needle crystal. Refluxing a solution of **9** and 1,3,5-tribromobenzene in mixed ethylene glycol dimethyl ether (DME) and water (3/1, v/v) in the presence of 15 mol% $Pd(PPh_3)_4$ and K_2CO_3 (6 equiv.) for 48 h provided trialdehyde **10** in 38% yield. Compound **10** was reacted with BBr_3 in CH_2Cl_2 at $-78\,^{\circ}C$ and then hydrolyzed to obtain trisalicylaldehyde **6**. In this step, the resulting mixture needed to be slowly and carefully added into chilled water and stirred continuously until two liquid layers formed. Therefore, trisalicylaldehyde **6** was transformed to the corresponding Schiff base **L1** in 36% yield as a salmon-pink solid by condensation with (*S*)-valinol.

According to the literature, there are some reports of the synthesis of disalicylaldehydes.[9] Using the method of preparing trisalicylaldehyde **6** as a base, we succeeded in synthesizing disalicylaldehyde **12** and its chiral Schiff base ligand **L2**. The synthesis of chiral Schiff base ligand **L2** is summarized in Scheme 4.

Compound **11** was obtained in 78% yield by taking advantage of the Suzuki–Miyaura coupling reaction with 5-bromosalicylaldehyde **5** (1 equiv.) and arylboronic acid **9** (1.2 equiv.) as reactants in mixed DME and water (3:1) at $90\,^{\circ}C$ for 6 h. Compound **11** was reacted with BBr_3 in CH_2Cl_2 at $-15\,^{\circ}C$ and then hydrolyzed to obtain disalicylaldehyde **12** as a light green solid in 67% yield. Thus, 2 equiv. of (*S*)-valinol and disalicylaldehyde **12** were dissolved in an appropriate volume of anhydrous ethanol and stirred for 12 h at $60\,^{\circ}C$. After flash-column chromatography and drying in vacuo, the chiral Schiff base ligand **L2** was obtained in 56% yield.

In conclusion, trisalicylaldehyde **6** and disalicylaldehyde **12** were successfully synthesized via 5-bromosalicylaldehyde as starting reactant. Among the obtained compounds, **6, 9, 10**, and **11** have not been reported previously. Two new chiral Schiff base ligands, **L1** and **L2**, have also been prepared. The application of the

Downloaded by [University of Connecticut] at 01:02 09 September 2013



Scheme 4. Preparation of Schiff base **L2**.

two new chiral Schiff base ligands is currently being explored for asymmetric oxidation of sulfides.

EXPERIMENTAL

General Procedures

Catalysts $Pd(PPh_3)_4$[10] and (*S*)-valinol[11] were obtained by literature procedures. Anhydrous THF was dried prior to use by distillation over sodium/benzophenone ketyl. Absolute ethanol was predried by 4-Å molecular sieves for 1 day and then distilled over sodium/diethyl phthalate. A mixture of DME/water was degassed before use for Suzuki–Miyaura coupling reactions. Melting points were measured on an XRc-1 melting-point apparatus and are uncorrected. NMR, mass spectroscopy (MS), and high-performance liquid chromatography (HPLC) spectra were recorded on Unity Inova 400-MHz or Brucker 400-MHz (with tetramethylsilane as internal standard), Hewlett 5973 or HP 1100 MSD, and Waters instruments, respectively. High-resolution mass spectra (HRMS) were obtained on a Micromass GCT-TOF mass spectrometer.

5-Bromo-2-methoxybenzaldehyde (7)

Dimethylsulfate (1.51 g, 12 mmol) was added to a mixture of 5-bromosalicylaldehyde (**5**) (2.0 g, 10 mmol) and solid K_2CO_3 (2.76 g, 20 mmol) in acetone (30 mL). The mixture was stirred at room temperature for 10 h before being quenched with H_2O (15 mL) and concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 (3×20 mL) and dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded the title compound as a white solid (2.0 g, 93%); mp 107–109 °C (lit.[12]: 113.5–116.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.37 (s, 3H, OCH_3), 6.88 (d, $J = 8.8$ Hz, 1H), 7.61 (dd, $J = 2.4$, 2.8 Hz, 1H), 7.89 (d, $J = 2.8$ Hz, 1H), 10.36 (s, 1H, C*H*O). EI-HRMS ($C_8H_7BrO_2$): calcd. 213.9629; found 213.9634.

4-Bromo-2-(diethoxymethyl)-1-methoxybenzene (8)

Triethylorthoformate (5.92 g, 40 mmol) and anhydrous $ZrCl_4$ (0.02 g, 0.1 mmol) were added to a suspension of 5-bromo-2-methoxybenzaldehyde (**7**)

Downloaded by [University of Connecticut] at 01:02 09 September 2013

(4.28 g, 20 mmol) in absolute EtOH (20 mL). The mixture was stirred at room temperature for several minutes until the solid was dissolved. The resulting mixture was purified by chromatography (petroleum ether/EtOAc, 2.5/1) to give the title compound as a light green liquid (5.64 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 [t, $J = 4.4$ Hz, 6H, $(OCH_2CH_3)_2$], 3.59 [m, 4H, $(OCH_2CH_3)_2$], 3.81 (s, 3H, OCH_3), 5.72 [s, 1H, $CH(OCH_2CH_3)_2$], 6.74 (d, $J = 8.8$ Hz, 1H), 7.36 (dd, $J = 2.4$, 2.4 Hz, 1H), 7.67 (d, $J = 2.4$ Hz, 1H); GC mass: 288.

4-Methoxy-3-formylphenylboronic Acid (9)

A solution of protected aldehyde 4-bromo-2-(diethoxymethyl)-1-methoxybenzene (**8**) (5.76 g, 20 mmol) in THF (30 mL) was cooled to −78 °C under argon. *n*-BuLi (2.9 M in hexanes, 8.3 mL, 24 mmol) was added dropwise over 30 min. The solution was stirred at −78 °C for 1 h before being quenched with $B(O^nBu)_3$ (9.2 g, 40 mmol). The yellow resulting solution was stirred at −78 °C for 2 h, allowed to warm slowly to room temperature, and was stirred overnight. The mixture was quenched with HCl (20 mL, 1 M) and extracted with Et_2O (3 × 20 mL). The organic layer was washed twice with H_2O (20 mL) and once with brine (15 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated, and the crude product was purified by recrystallization from ethanol to obtain 3.39 g of yellow solid in a yield of 94%. Mp 206–208 °C; ^{1}H NMR [400 MHz, $CD_3C(O)CD_3$]: δ 3.11 [s, 2H, $B(OH)_2$], 4.0 (s, 3H, OCH_3), 7.19 (d, $J = 8.8$ Hz, 1H), 8.13 (dd, $J = 2.0$, 2.0 Hz, 1H), 8.28 (d, $J = 3.6$ Hz, 1H), 10.45 (s, 1H, CHO); ^{13}C NMR [$CD_3C(O)CD_3$]: δ 55.6, 111.5, 124.3, 134.4, 142.4, 163.8, 189.1, 206.1. EI-HRMS ($C_8H_9O_4B$): calcd. 180.0590; found 180.0594.

1,3,5-Tris(4-methoxy-5-formylphenyl)benzene (10)

1,3,5-Tribromobenzene (0.78 g, 2.5 mmol), 4-methoxy-3-formylphenylboronic acid (**9**) (2.7 g, 15 mmol), K_2CO_3 (2.07 g, 15 mmol), and $Pd(PPh_3)_4$ (0.73 g, 0.37 mmol, 15 mol%) were added to a Schlenk flask with a stirring bar. The mixture was purged with argon. Degassed solvent of DME/water (3/1, v/v, 100 mL) was then added. The mixture was refluxed with stirring in the dark at 90 °C for 48 h under the protection of argon. The organic layer was then separated, and the water layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel, eluting with CH_2Cl_2 to give the title compound as a white solid (0.46 g, 38%). Mp 257–258 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 9H, OCH_3), 7.06 (d, $J = 8.4$ Hz, 3H), 7.65 (s, 3H), 7.84 (dd, $J = 2.8$, 2.4 Hz, 3H), 8.08 (d, $J = 2.0$ Hz, 3H), 10.48 (s, 3H, CHO). EI-HRMS ($C_{30}H_{24}O_6$): calcd. 480.1573; found 480.1577.

1,3,5-Tris(4-hydroxy-5-formylphenyl)benzene (6)

BBr_3 (1 M in CH_2Cl_2, 3.2 mL, 3.2 mmol) was added at −78 °C under nitrogen to a suspension of 1,3,5-tris(4-methoxy-5-formylphenyl)benzene (**10**) (0.3 g, 0.63 mmol) in dry CH_2Cl_2 (6 mL). After 10 min, the external temperature was raised

Downloaded by [University of Connecticut] at 01:02 09 September 2013

to −15 °C, and the dark brown suspension was stirred for 1 h. The resulting mixture was slowly poured into chilled water (10 mL) and stirred continuously until two liquid layers were formed. The aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (CC) (silica gel, CH_2Cl_2/MeOH, 100/1) afforded the title compound as a pale white solid (0.18 g, 66%); mp > 300 °C; ^{1}H NMR (400 MHz, DMSO): δ 7.15 (d, J = 8.4 Hz, 3H), 7.81 (s, 3H), 8.07 (d, J = 9.6 Hz, 3H), 8.11 (s, 3H), 10.35 (s, 3H, C*H*O), 10.93 (s, 3H, O*H*); ^{13}C NMR (DMSO): δ 117.9, 122.5, 123.0, 127.6, 131.4, 135.2, 140.5, 160.5, 191.8. EI-HRMS ($C_{27}H_{18}O_6$): calcd. 438.1103; found 438.1096.

Chiral Schiff Base Ligand L1

(*S*)-Valinol (0.48 g, 0.47 mmol) and 1,3,5-tris(4-hydroxy-5-formylphenyl)benzene (**6**) (0.8 g, 0.12 mmol) were dissolved in 4 mL of EtOH. The solution was stirred overnight at 60 °C. After the solvent was evaporated under reduced pressure, the residue was subject to flash-column chromatography on silica gel using CH_2Cl_2/CH_3OH (95/5) as eluent to give the title compound as a salmon-pink solid (0.27 g, 36%). Mp 129–132 °C; $[\alpha]_{589}^{21} = -284.5°$ (c 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 [t, 18H, CH(C*H*$_3$)$_2$], 1.98–1.91 [m, 3H, C*H*(CH$_3$)$_2$], 3.21–3.08 (m, 3H, N-C*H*), 3.94–3.70 (m, 6H,C*H*$_2$OH), 7.91 (s, 3H, C*H*=N), 7.28 (s, 3H), 6.63–6.61 (m, 9H), 14.15 (s, 3H, O*H*). EI-HRMS ($C_{42}H_{51}N_3O_6$): calcd. 693.3778; found 693.3771.

4-Methoxy-4′-hydroxyl-3,3′-diformyl-1,1′-diphenyl (11)

5-Bromosalicylaldehyde (**5**) (0.76 g, 3.80 mmol), 3-formyl-4-methoxyphenylboronic acid (**9**) (0.82 mg, 4.56 mmol), K_2CO_3 (0.79 g, 5.7 mmol), and $Pd(PPh_3)_4$ (0.22 g, 0.19 mmol, 5 mol%) were added to a Schlenk flask with a stirring bar. The mixture was purged with argon. Degassed solvent of DME/water (3/1, v/v, 35 mL) was then added. The mixture was refluxed with stirring at 90 °C for 6 h under the protection of argon. The organic layer was then separated, and the water layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel, eluting with CH_2Cl_2 to give the title compound as a light green solid (0.76 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H, OC*H*$_3$), 7.00–7.04 (m, 2H), 7.68–7.71 (m, 3H), 7.97 (d, J = 2.4 Hz, 1H), 9.91 (s, 1H, C*H*O), 10.46 (s, 1H, C*H*O), 10.94 (s, 1H, O*H*); EI-HRMS ($C_{15}H_{12}O_4$): calcd. 256.0736; found 256.0732.

4,4′-Diol-3,3′-diformyl-1,1′-diphenyl (12)

BBr_3 (1 M in CH_2Cl_2, 13.6 mL, 13.6 mmol) was added at −15 °C under nitrogen to a solution of 4-methoxy-4′-hydroxy-3,3′-biformyl-1,1′-biphenyl (**11**) (0.87 g, 3.4 mmol) in dry CH_2Cl_2 (10 mL). The dark brown suspension was stirred for 1 h. The resulting mixture was slowly poured into chilled water (30 mL) and stirred continuously until two liquid layers were formed. The aqueous phase was extracted with

Downloaded by [University of Connecticut] at 01:02 09 September 2013

Et_2O (3×20 mL). The combined organic layers were washed with water (2×20 mL) and brine, dried with $MgSO_4$, and concentrated under reduced pressure. Purification by CC (silica gel, CH_2Cl_2/MeOH, 95/5) afforded the title compound as a yellow solid (0.55 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, $J = 9.6$ Hz, 2H), 7.66–7.68 (m, 4H), 9.93 (s, 2H, C*H*O), 10.95 (s, 2H, O*H*). EI-HRMS ($C_{14}H_{10}O_4$): calcd. 242.0579; found 242.0576.

Chiral Schiff Base Ligand L2

(*S*)-Valinol (0.21 g, 2 mmol) and 4,4′-diol-3,3′-diformyl-1,1′-diphenyl (**12**) (0.24 g, 1 mmol) were dissolved in 4 mL of EtOH. The solution was stirred for 12 h at 60 °C. After the solvent was evaporated under reduced pressure, the residue was subject to flash-column chromatography on silica gel using petroleum ether/ethyl acetate (1/5) as eluent to give the title compound as a salmon-pink solid (0.23 g, 56%). Mp 88–90 °C; $[\alpha]_{589}^{21} = -51.7°$ (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, $J = 6.8$ Hz, 12H), 1.87–1.95 (m, 2H), 3.04–3.09 (m, 2H), 3.78–3.86 (m, 4H), 6.82 (d, $J = 8.4$ Hz, 2H), 7.04 (s, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 8.17 (s, 2H, C*H*=N), 13.91 (s, 2H); ^{13}C NMR ($CDCl_3$): 165.8 (*C*H=N), 161.5 (*C*-OH), 130.8, 130.6, 129.3, 118.4, 117.8, 77.8 (*C*H-N), 64.7 (CH_2OH), 30.4 [$CH(CH_3)_2$], 20.0 and 18.8 [2C, $CH(CH_3)_2$]. MS (API-ES): calcd. m/z 412.3, found 413.3 $[M + H]^+$, 435.2 $[M + Na]^+$.

ACKNOWLEDGMENTS

We are grateful to the Chinese National Natural Science Foundation (Grant Nos. 20471013 and 20633020), the Swedish Energy Agency, the Swedish Research Council, and the K&A Wallenberg Foundation for financial support of this work.

REFERENCES

1. Fernández, I.; Khiar, N. Recent developments in the synthesis and utilization of chiral sulfoxides. *Chem. Rev.* **2003**, *103*(9), 3651–3670.
2. (a) Vetter, A. H.; Berkessel, A. Schiff-base ligands carrying two elements of chirality: Matched–mismatched effects in the vanadium-catalyzed sulfoxidation of thioethers with hydrogen peroxide. *Tetrahedron Lett.* **1998**, *39*, 1741–1744; (b) Sun, J.; Zhu, C.; Dai, Z.; Yang, M.; Pan, Y.; Hu, H. Efficient asymmetric oxidation of sulfides and kinetic resolution of sulfoxides catalyzed by a vanadium–salan system. *J. Org. Chem.* **2004**, *69*, 8500–8503; (c) Zeng, Q.; Wang, H.; Wang, T.; Cai, Y.; Weng, W.; Zhao, Y. Vanadium-catalyzed enantioselective sulfoxidation and concomitant, highly efficient kinetic resolution provide high enantioselectivity and acceptable yields of sulfoxides. *Adv. Synth. Catal.* **2005**, *347*, 1933–1936.
3. (a) Zheng, X.; Jones, C. W.; Weck, M. Ring-expanding olefin metathesis: A route to highly active unsymmetrical macrocyclic oligomeric co-salen catalysts for the hydrolytic kinetic resolution of epoxides. *J. Am. Chem. Soc.* **2007**, *129*, 1105–1112; (b) Bobb, R.; Alhakimi, G.; Studnicki, L.; Chin, J. Stereoselective recognition of an aziridine with a Co(III) complex: A potential transition-state analogue for catalytic epoxidation. *J. Am. Chem. Soc.* **2002**, *124*, 4544–4545; (c) Angelino, M. D.; Laibinis, P. E. Synthesis and characterization of a polymer-supported salen ligand for enantioselective epoxidation.

Downloaded by [University of Connecticut] at 01:02 09 September 2013

Macromolecules **1998**, *31*, 7581–7587; (d) Kureshy, R. I.; Khan, N. H.; Jasra, R. V. Catalytic asymmetric epoxidation of non-functionalised alkenes using polymeric Mn(III) salen as catalysts and NaOCl as oxidant. *J. Mol. Catal. A: Chem.* **2004**, *218*, 141–146.

4. (a) Li, Z. N.; Liu, G. S.; Zheng, Z.; Chen, H. L. Cyclopropanation of styrene catalyzed by Cu-(chiral Schiff-base) complexes. *Tetrahedron: Asymmetry* **2000**, *56*, 7187–7191; (b) Katsuki, T. Chiral metallosalen complexes: Structures and catalyst tuning for asymmetric epoxidation and cyclopropanation. *Adv. Synth. Catal.* **2002**, *344*, 131–147.
5. (a) Schaus, S. E.; Brånalt, J.; Jacobsen, E. N. Asymmetric hetero-Diels–Alder reactions catalyzed by chiral (salen) chromium(III) complexes. *J. Org. Chem.* **1998**, *63*, 403–405; (b) Aikawa, K.; Irie, R.; Katsuki, T. Asymmetric hetero-Diels–Alder reaction using chiral cationic metallosalen complexes as catalysts. *Tetrahedron* **2001**, *57*, 845–851.
6. Liu, H.; Wang, M.; Wang, Y.; Gu, Q.; Sun, L. Synthesis of 3-aryl-5-*t*-butyl-salicylaldehydes and their chiral Schiff base compounds. *Synth. Commun.* **2007**, *37*, 3815–3826.
7. Liu, H.; Wang, M.; Wang, Y.; Yin, R.; Sun, L. Influence of substituents in the salicylaldehyde-derived Schiff bases on vanadium-catalyzed asymmetric oxidation of sulfides. *Appl. Organometal. Chem.* **2008**, *22*, 253–257.
8. Suresh, P.; Srimurugan, S.; Babu, B.; Pati, H. N. Asymmetric sulfoxidation of prochiral sulfides using aminoalcohol derived chiral C_3-symmetric trinuclear vanadium Schiff base complexes. *Tetrahedron: Asymmetry* **2007**, *18*, 2820–2827.
9. (a) Chang, Y. M.; Lee, S. H.; Cho, M. Y.; Yoo, B. W.; Rhee, H. J.; Lee, S. H.; Yoon, C. M. Homocoupling of aryl iodides and bromides using a palladium/indium bimetallic system. *Synth. Commun.* **2005**, *35*, 1851–1857; (b) Elizbarashvili, E.; Matitaishvili, T.; Topuria, K. Synthesis of macrocyclic polyazomethines. *J. Braz. Chem. Soc.* **2007**, *18*(6), 1254–1258; (c) Nising, C. F.; Friedrich, A.; Braese, S. The double oxa-Michael-aldol condensation: Straightforward access to dimeric tetrahydroxanthenones. *Synlett* **2007**, *19*, 2987–2990.
10. Coulson, D. R. Tetrakis(triphenylphosphine)palladlum. *Inorg. Synth.* **1972**, *13*, 121–125.
11. Bean, F. R.; Johnson, J. R. Derivatives of phenylboric acid, their preparation and action upon bacteria II: Hydroxyphenylboric acids. *J. Am. Chem. Soc.* **1932**, *54*, 4415–4425.
12. Laali, K. K.; Koser, J. G. F.; Subramanyam, J. S.; Forsyth, D. A. Substituent control of intramolecular hydrogen bonding in formyl-protonated *o*-anisaldehydes: A stable ion and semiempirical MO investigation. *J. Org. Chem.* **1993**, *58*, 1385–1392.

Downloaded by [University of Connecticut] at 01:02 09 September 2013