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Tetrahedron
Tetrahedron 63 (2007) 5319–5322

Enantioselective allylation of aldehydes catalyzed by new bifunctional bisoxazoline–metal complexes

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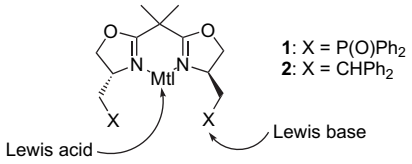
Received 30 August 2006; revised 22 February 2007; accepted 23 February 2007
Available online 25 February 2007

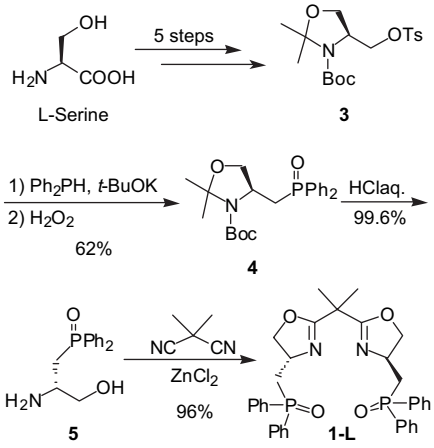
Abstract—The asymmetric allylation reactions of aldehydes catalyzed by a 10 mol % bisoxazoline complex bearing a phosphine oxide moiety, which was newly designed and synthesized from L-serine, afforded the corresponding homoallylic alcohols in 48–74% yields with 39–86% ee. The reaction proceeds with the dual activation of the aldehyde and allylsilane by the Lewis acid and base of the catalyst. The evidence for the activation of the allylsilane was clarified by the ^{31}P NMR spectra.

1. Introduction

The asymmetric allylation of aldehydes is an important process to obtain chiral homoallylic alcohols, and numerous methodologies have already been reported.[1] Allyltributylstannane is well known as an allylation reagent for the asymmetric allylation of aldehydes.[2] These allylations proceed through activation of the carbonyl group catalyzed by a Lewis acid. Furthermore, some examples of the asymmetric allylation using allyltrimethylsilane[3] or allyltrimethoxysilane[4] have been developed to produce the corresponding homoallylic alcohols with high enantioselectivities. On the other hand, in 1999, Shibasaki et al. reported the cyanosilylation of aldehydes with trimethylsilylcyanide using a Lewis acid–Lewis base bifunctional catalyst to give cyanohydrines with high yields and excellent enantioselectivities.[5] This reaction proceeded via the dual activation system in which the metal acted as a Lewis acid to activate the carbonyl group, and the phosphine oxide acted as a Lewis base to activate the silicon. On the basis of these concepts, we prepared a novel bisoxazoline derivative catalyst bearing a Lewis acid (metal) and a Lewis base (phosphine oxide). In this paper, we describe the asymmetric allylations of allyltrichlorosilane to aldehydes catalyzed by the Zn(II)–bisoxazoline complex **1**.



The novel bisoxazoline derivative ligand **1-L** was synthesized using L-serine. Oxazolidine **3** prepared from L-serine was treated with diphenylphosphine in the presence of *tert*-BuOK in THF, followed by oxidation with hydrogen peroxide to give the phosphinoylmethyloxazolidine **4** in 62% yield. The oxazolidine **4** was deprotected, and then the resulting amino alcohol reacted with dimethylmalononitrile catalyzed by zinc chloride[6] to afford phosphinoylmethylbisoxazoline **1-L** (PM-BOX) in a 96% yield (Scheme 1).



Scheme 1. Synthesis of bisoxazoline derivative ligand.

Keywords: Dual activation catalyst; Bisoxazoline–zinc complex; Asymmetric allylation.
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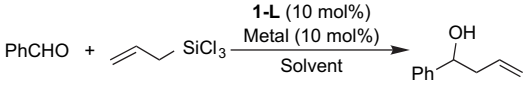
doi:10.1016/j.tet.2007.02.104

First, the metal complex catalyzed asymmetric allylations of benzaldehyde with allyltrichlorosilane in the presence of 10 mol % PM-BOX **1-L** in CH_2Cl_2 at room temperature were investigated. When $Ti(O^iPr)_4$ and Et_2AlCl as Lewis acids were used, the reactions hardly proceeded (Table 1, entries 1 and 2). Using $Cu(OTf)_2$, the reaction gave the homoallylalcohol in 22% yield with an 63% ee along with about 40% recovered benzaldehyde containing a small amount of benzoic acid (entry 3). The PM-BOX–ZnI_2 system produced a good enantioselectivity, and the combination of PM-BOX–$ZnCl_2$ showed a lower yield with a good enantioselectivity (Table 1, entries 4 and 7). The reaction using $Zn(OTf)_2$ instead of ZnI_2 at room temperature produced a racemic product (Table 1, entry 5). The reaction at 0 °C in THF gave the product in 22% yield with 47% ee (Table 1, entry 6). The reaction at −78 °C did not occur at all. From entries 4–9 in Table 1, it can be seen that the combination of PM-BOX–ZnI_2 in a coordinating solvent, such as THF, is the most matched one to give the product in up to 74% yield with an 86% ee. The catalytic loading amount of 5 mol % widely decreased the yield, but the ee only slightly decreased (51% yield, 77% ee). When the other allylic reagents, such as the allyltrimethylsilane and allyltrimethoxysilane, were employed, the homoallylic alocohols were only slightly obtained. The allylations of aldehydes with allyltrichlorosilane in the absence of ZnI_2 in THF at room temperature for 24 h afforded a trace amount of the product.

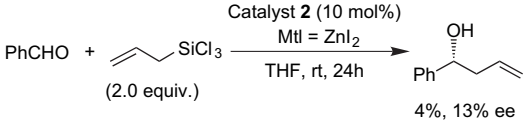
The reaction catalyzed by the benzhydrylmethylbisoxazoline–ZnI_2 complex **2** instead of PM-BOX–ZnI_2 gave the product in only 4% yield along with a 13% ee (Scheme 2).

Table 1. Effects of metals and solvents on chemical yield and enantioselectivity[a]



Entry	Metal	Solvent	Time (h)	Yield[b] (%)	ee[c] (%)
1	$Ti(O^iPr)_4$	CH_2Cl_2	24	1	nd[d]
2	Et_2AlCl	CH_2Cl_2	24	Trace	nd[d]
3	$Cu(OTf)_2$	CH_2Cl_2	24	22	63
4	ZnI_2	CH_2Cl_2	24	65	67
5	$Zn(OTf)_2$	CH_2Cl_2	1	61	5
6[e]	$Zn(OTf)_2$	THF	24	22	47
7	$ZnCl_2$	CH_2Cl_2	24	38	84
8	ZnI_2	THF	24	74	86
9	$ZnCl_2$	THF	24	30	80

[a] The reaction was carried out using allyltrichlorosilane (2.0 equiv) and benzaldehyde (1 equiv) with PM-BOX (10 mol %) and metal (10 mol %) at room temperature.
[b] Yield of isolated product.
[c] Determined by HPLC analysis.
[d] Not determined.
[e] Reaction was performed in THF at 0 °C.



Scheme 2. Effects of phosphine oxide (Lewis base) on chemical yield and enantioselectivity.

To clarify the interaction between the diphenylphosphinoyl moiety and the allyltrichlorosilane, the ^{31}P NMR was measured. ^{31}P NMR spectrum of the PM-BOX–ZnI_2 complex indicated a peak at 29.9 ppm, and that of an equimolar mixture of the complex and allylsilane appeared at 44.5 ppm (Fig. 1).

Finally, we investigated the catalytic enantioselective addition of allyltrichlorosilane to typical aromatic, aliphatic, and α,β-unsaturated aldehydes in the presence of a 10 mol % PM-BOX–ZnI_2 complex. These results are summarized in Table 2. The allylation of the *p*-nitro and *p*-chlorobenzaldehyde gave similar results as those of the benzaldehyde in terms of enantioselectivity (Table 2, entries 2 and 3). On the other hand, the reaction with *p*-methoxybenzaldehyde gave a product with a low chemical yield and enantioselectivity (Table 2, entry 4). The aliphatic aldehyde provided a homoallylic alcohol with a moderate yield and enantioselectivity compared with the aromatic aldehydes (Table 2, entry 5). For the reaction with the α,β-unsaturated aldehyde, the 1,2-addition reaction exclusively occurred (Table 2, entry 6).

In conclusion, we described that the PM-BOX–ZnI_2 complex, easily prepared from the inexpensive L-serine, was effective as a bifunctional catalyst for the asymmetric allylation of aldehydes with allyltrichlorosilane. Although the reaction mechanism was not completely revealed, we assumed a dual activation pathway based on the ^{31}P NMR

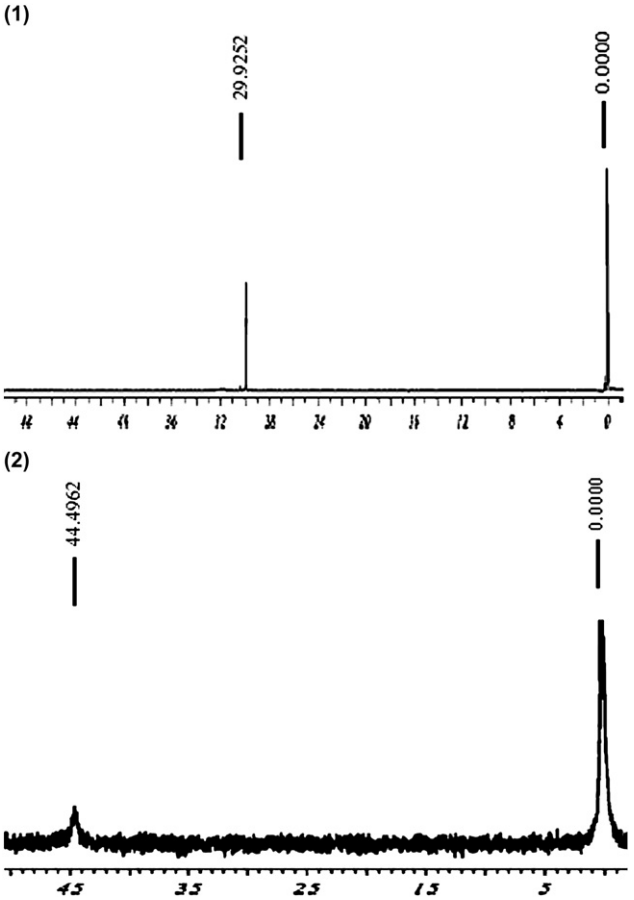


Figure 1. ^{31}P NMR spectra of (1) PM-BOX–ZnI_2 complex and (2) PM-BOX–ZnI_2+allyltricholorosilane.

Table 2. Asymmetric allylation of aldehydes catalyzed by PM-BOX–ZnI_2 complex[a]

Entry	Aldehyde	Yield[b] (%)	ee[c] (%)	*R*/*S*
1	C_6H_5CHO	74	86	*R*
2	*p*-$NO_2C_6H_4CHO$	73	79	*R*
3	*p*-ClC_6H_4CHO	65	76	*R*
4	*p*-$MeOC_6H_4CHO$	52	39	*R*
5	$C_6H_5CH_2CH_2CHO$	48	68	S
6	(*E*)-$C_6H_5CH{=}CHCHO$	54	64	*R*

[a] The reaction was carried out using allyltrichlorosilane (2.0 equiv) and aldehyde (1 equiv) with PM-BOX (10 mol %) and zinc iodide (10 mol %) at room temperature for 24 h in THF.
[b] Yield of isolated product.
[c] Determined by HPLC analysis.

spectrum, which showed the interaction of oxygen atom of phosphine oxide and allyltrichlorosilane. A study of the reaction mechanism and further application of the PM-BOX–metal complex to the other asymmetric reactions are currently underway in our laboratory.

2. Experimental section

2.1. General

NMR spectra were recorded on a BRUKER DRX-400 spectrometer, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR. Chemical shifts were reported in δ from TMS as the internal standard for the ^{1}H and ^{13}C NMR spectra. ^{31}P chemical shifts were recorded relative to the signal for 85% phosphoric acid, which was used as the external reference. Flash column chromatography was carried out on silica gel 60 (Cica-MERCK). The enantiomeric excess was determined by HPLC analysis. In general, reactions were carried out in dry solvents under N_2 atmosphere, unless noted otherwise. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) and chlorobenzene (PhCl) were distilled from calcium hydride. Other reagents were purified by usual methods. (*S*)-*N*-*tert*-Butoxycarbonyl-4-[[(4′-methylbenzenesulfonyl)oxy]methyl]-2,2-dimethyloxazolidine **3** was synthesized via a literature procedure.[7]

2.1.1. (*S*)-*N*-*tert*-Butoxycarbonyl-4-(diphenylphosphinoylmethyl)-2,2-dimethyloxazolidine (4). To a solution of diphenylphosphine (7.4 g, 40 mmol) in THF (100 mL) was added *tert*-BuOK (4.5 g, 40 mmol) at 0 °C. After stirring for 1 h at room temperature, to this reaction mixture was dropwise added **3** (7.0 g, 18.2 mmol) in THF (100 mL) at 0 °C. After completion of the reaction, water was added. The solvent was then removed, and any remaining material was dissolved in CH_2Cl_2 (100 mL). To the resulting solution was added a 30% aqueous solution of H_2O_2 (20 mL) at 0 °C, and stirred for 0.5 h at the same temperature. The reaction mixture was then diluted with water and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated under reduced pressure. The residual crude product was purified by column chromatography on silica gel (hexane/EtOAc=1/1) to afford **4** (4.7 g, 62% yield) as a white solid: mp 126–128 °C; IR 2975, 1682, 1430, 1380, 1180, 730, 710, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.60 (m, 15H), 2.31–2.60 (m, 1H), 3.09–3.15 (m, 1H), 3.93–3.97 (br, 1H), 4.11–4.16 (br, 1H), 4.34–4.42 (br, 1H), 7.38–7.54 (m, 6H), 7.67–7.82 (m, 3H), 7.97–7.98 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 28.5, 32.1 (J_{CP}=67.1 Hz), 53.5, 67.1, 80.2, 128.2–130.4, 152.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5; IR (KBr) 3200, 1715, 1410, 1200, 1102 cm^{-1}; $[\alpha]_D^{25}$ −14.8 (*c* 1.0, $CHCl_3$).

2.1.2. (*S*)-2-Amino-3-(diphenylphosphinoylmethyl)propan-1-ol (5). To a solution of the protected intermediate **4** (3.49 g, 8.4 mmol) in THF (35 mL) was added 2 N aq HCl (35 mL). The reaction mixture was stirred under reflux for 5 h, cooled to room temperature, and neutralized by 2 N aq NaOH. The aqueous layer was extracted with CH_2Cl_2, the combined organic layers were dried over Na_2SO_4, and then concentrated under reduced pressure. The residual crude product was purified by column chromatography on silica gel (EtOAc/MeOH=1/1) to afford **5** (2.3 g, 99.6% yield) as a yellow syrup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36–2.40 (m, 2H), 2.93 (br, 3H), 3.18–3.24 (m, 1H), 3.40–3.48 (m, 2H), 7.45–7.56 (m, 6H), 7.73–7.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6 (d, J_{CP}=70.1 Hz), 48.7, 67.7, 128.7–132.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.1; IR (neat) 3400, 2950, 1615, 1469, 1200 cm^{-1}; $[\alpha]_D^{25}$ +9.23 (*c* 1.0, $CHCl_3$).

2.1.3. 2,2′-Bis[(*S*)-(4-diphenylphosphinoylmethyl)-2-oxazolin-2-yl]propane (1-L). To a solution of dimethylmalononitrile (0.15 g, 1.6 mmol) in PhCl (10 mL) was added a solution of **5** (1.3 g, 4.7 mmol) in PhCl (10 mL) and $ZnCl_2$ (0.64 g, 4.7 mmol). The reaction mixture was stirred under reflux for 24 h, cooled to room temperature, and quenched with a solution of ethylenediamine (4 mL) in water (20 mL). The mixture was then stirred for 1 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4, and then concentrated under reduced pressure. The residual crude product was purified by column chromatography on silica gel (EtOAc/MeOH=8/1) to afford **1-L** (0.94 g, 96% yield) as a white solid: mp 168–170 °C; IR 1650, 1430, 1180, 1160, 1118, 740, 710, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 6H), 2.30–2.39 (m, 2H), 2.87–2.93 (m, 2H), 4.26–4.37 (m, 6H), 7.43–7.54 (m, 12H), 7.70–7.79 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 36.1 (J_{CP}=68.6 Hz), 38.5, 61.1, 73.4, 128.6–134.0, 169.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4; IR (KBr) 3440, 1660, 1450, 1190, 1130 cm^{-1}; $[\alpha]_D^{25}$ +21.3 (*c* 1.0, $CHCl_3$); HRMS (EI): calcd for $C_{35}H_{37}O_4N_2P_2$ (M^++1) 611.2229, found 611.2229. Anal. Calcd for $C_{35}H_{36}N_2P_2$: C, 68.84; H, 5.94; N, 4.59. Found: C, 68.35; H, 6.06; N, 4.53.

2.2. General procedure for reactions of allyltrichlorosilane with aldehydes

2.2.1. Synthesis of (*R*)-1-phenyl-3-buten-1-ol (entry 1 in Table 2). A mixture of ZnI_2 (24 mg, 0.074 mmol) and PM-BOX (45 mg, 0.074 mmol) was dissolved in dry THF (4 mL) under an argon atmosphere, and then stirred at room temperature for 2 h. To the resulting solution was dropwise added benzaldehyde (78.5 mg, 0.74 mmol) and then allyltrichlorosilane (0.21 mL, 1.48 mmol) at room temperature. The mixture was stirred for 24 h at this temperature

and then quenched with an aqueous saturated $NaHCO_3$ solution. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4, then concentrated under reduced pressure. The residual crude product was purified by column chromatography on silica gel (hexane/EtOAc=10/1) to afford the homoallylic alcohol (80.2 mg, 74% yield) as a colorless oil. The enantiomeric excess was determined by a chiral HPLC analysis: IR (neat) 3400 (br), 3080, 3050, 2950, 2820, 1620, 1605, 1500, 1455, 1050, 1000, 920, 760, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (br, 1H), 2.45–2.55 (m, 2H), 4.71–4.75 (m, 1H), 5.12–5.19 (m, 2H), 5.75–5.86 (m, 1H), 7.25–7.37 (m, 5H); $[\alpha]_D^{27}$ +46.5 (*c* 1.0, CH_2Cl_2) [lit.[8] $[\alpha]_D$ +45.6 (*c* 0.92, CH_2Cl_2)]; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=98/2, flow rate=1.0 mL/min): t_R=14.7 min, t_S=16.5 min.

2.2.2. (*R*)-1-(*p*-Nitrophenyl)-3-buten-1-ol (entry 2 in Table 2). IR (neat) 3400 (br), 3075, 2980, 2900, 2850, 1640, 1600, 1510, 1340, 1100, 1050, 915, 850, 710, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 1H), 2.42–2.49 (m, 1H), 2.53–2.60 (m, 1H), 4.86 (dt, 1H, *J*=7.8, 3.3 Hz), 5.15–5.21 (m, 2H), 5.73–5.84 (m, 1H), 7.56 (d, 2H, *J*=8.9 Hz), 8.19 (d, 2H, *J*=8.9 Hz); $[\alpha]_D^{25}$ +51.5 (*c* 1.0, $CHCl_3$) [lit.[9] $[\alpha]_D$ –33.2 for (*S*) (*c* 0.5, $CHCl_3$)]; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH=20/1, flow rate=0.4 mL/min): t_R=45.8 min, t_S=48.1 min.

2.2.3. (*R*)-1-(*p*-Chlorophenyl)-3-buten-1-ol (entry 3 in Table 2). IR (neat) 3380 (br), 3075, 2970, 2900, 1640, 1590, 1490, 1410, 1090, 1040, 1010, 910, 860, 810, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 1H), 2.41–2.53 (m, 2H), 4.72 (m, 1H), 5.13–5.18 (m, 2H), 5.73–5.83 (m, 1H), 7.27–7.33 (m, 4H); $[\alpha]_D^{25}$ +47.3 (*c* 1.0, $CHCl_3$) [lit.[9] $[\alpha]_D$ –60.6 for (*S*) (*c* 1.5, $CHCl_3$)]; HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH=98/2, flow rate=0.7 mL/min): t_S=23.2 min, t_R=25.1 min.

2.2.4. (*R*)-1-(*p*-Methoxyphenyl)-3-buten-1-ol (entry 4 in Table 2). IR (neat) 3450 (br), 3080, 3020, 2950, 2920, 2850, 1640, 1615, 1590, 1520, 1470, 1440, 1300, 1250, 1180, 1040, 920, 830, 810, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (br, 1H), 2.50 (t, 2H, *J*=12.6 Hz), 3.79 (s, 3H), 4.67 (t, 1H, *J*=6.4 Hz), 5.10–5.17 (m, 2H), 5.74–5.82 (m, 1H), 6.86–6.88 (m, 2H), 7.25–7.28 (m, 2H); $[\alpha]_D^{25}$ +21.9 (*c* 1.0, $CHCl_3$) [lit.[2] $[\alpha]_D$ –48.0 for (*S*) (*c* 1.0, $CHCl_3$)]; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=20/1, flow rate=0.5 mL/min): t_R=21.1 min, t_S=23.7 min.

2.2.5. (*S*)-1-Phenyl-5-hexen-3-ol (entry 5 in Table 2). IR (neat) 3350 (br), 3050, 3010, 2920, 2850, 1630, 1590, 1485, 1440, 1060, 1030, 980, 900, 850, 730, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 1H), 1.73–1.81 (m, 2H), 2.14–2.21 (m, 1H), 2.28–2.35 (m, 1H), 2.64–2.68 (m, 1H), 2.70–2.84 (m, 1H), 3.64–3.70 (m, 1H), 5.14 (d, 2H, *J*=12.9 Hz), 5.76–5.86 (m, 1H), 7.16–7.29 (m, 5H); $[\alpha]_D^{25}$ –6.63 (*c* 1.0, $CHCl_3$) [lit.[2] $[\alpha]_D$ +1.8 for (*R*) (*c* 0.9, $CHCl_3$)]; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=20/1, flow rate=0.5 mL/min): t_S=17.6 min, t_R=25.5 min.

2.2.6. (1*E*,3*R*)-1-Phenyl-1,5-hexadien-3-ol (entry 6 in Table 2). IR (neat) 3400 (br), 3100, 3050, 3000, 2850, 1645, 1605, 1580, 1500, 1450, 1140, 970, 920, 875, 750, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (br, 1H), 2.38–2.43 (m, 2H), 4.37 (dd, 1H, *J*=13.0, 6.8 Hz), 5.10–5.21 (m, 2H), 5.82–5.89 (m, 1H), 6.25 (dd, 1H, *J*=15.9, 6.3 Hz), 6.59 (d, 1H, *J*=15.7 Hz); $[\alpha]_D^{25}$ +5.98 (*c* 0.5, $CHCl_3$) [lit.[2] $[\alpha]_D$ –36.9 for (*S*) (*c* 1.06, $CHCl_3$)]; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH=20/1, flow rate=1 mL/min): t_R=12.1 min, t_S=20.4 min.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (C) No. 17550098 and The 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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