DOI: 10.1002/adsc.200900595

A Spirocyclic Chiral Borate for Catalytic Enantioselective Nozaki-Hiyama Allylation of Ketones

Xin-Ren Huang,[a] Chinpiao Chen,[a,*] Gene-Hsian Lee,[b] and Shie-Ming Peng[b]

[a] Department of Chemistry, National Dong Hwa University, Soufeng, Hualien 974, Taiwan, Republic of China
Fax: (+886)-3-863-0475; e-mail: chinpiao@mail.ndhu.edu.tw
[b] Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Received: August 25, 2009; Published online: November 24, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900595.

Abstract: A new class of chiral spirocyclic borate ligands **5a–d** with a rigid borocycle has been developed. The catalyst formed from chromium(II)-**5a** promotes the highly efficient enantioselective Nozaki–Hiyama allylation of alkyl and aryl ketones using allyl bromide. The scope of the present method is shown to be wide, and it affords an efficient access to chiral tertiary homoallylic alcohols.

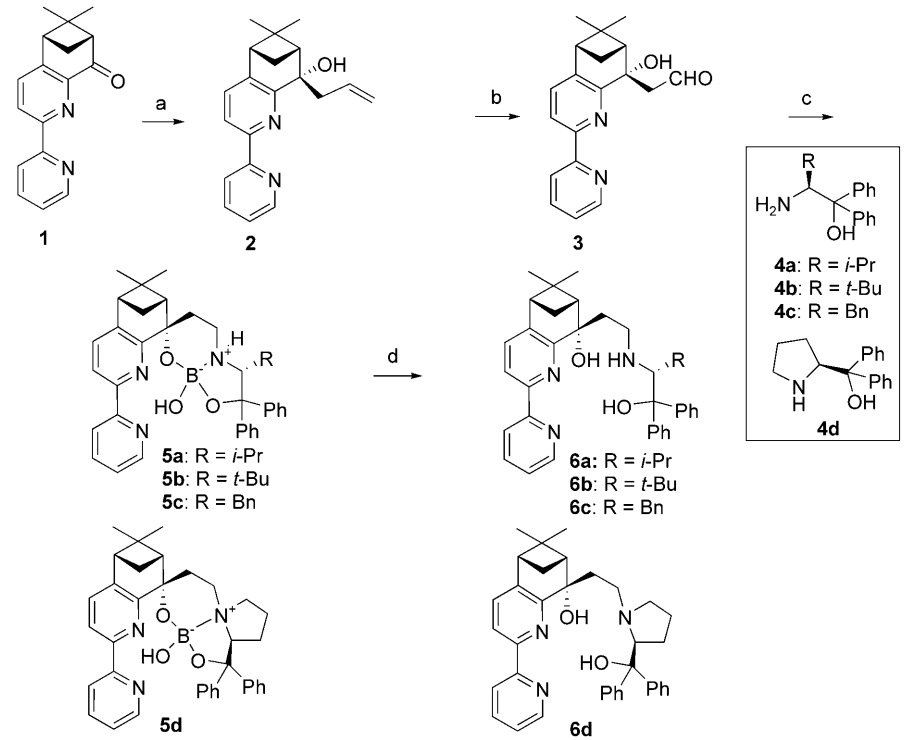
Keywords: aminoborates; bipyridyls; chromium catalysts; Nozaki–Hiyama allylation; spirocyclic borates

The use of organochromium species as reagents began in 1977 when Nozaki and Hiyama et al.[1] as well as Heathcock et al.[2] recognized that these species mediated Barbier–Grignard carbonyl additions, and so participated in carbon-carbon bond-forming reactions in organic solvents. Carbonyl allylations using allylchromium reagents (Nozaki–Hiyama reaction) rank among the foremost methods for natural product syntheses owing to the extreme chemoselectivity and substrate compatibility.[3] Organochromium reagents are easily prepared *in situ* by the oxidative addition of chromium(II) species to allyl, propargyl, aryl and vinyl halides or triflates (requiring catalytic amounts of Ni(II) salt for sp^2 carbon centers), and can be efficiently added to aldehydes to give the corresponding alcohols in favorable yields.[4] The original Nozaki–Hiyama–Kishi (NHK) reaction relies on the use of stoichiometric quantities of chromium(II) chloride. The catalytic redox system described by Fürstner et al. enabled the quantity of chromium salts to be reduced, making these reactions more valuable and environmentally benign.[5] The catalytic modification of this process has significantly improved the application of and permitted the design of chiral ligands for the enantioselective variations.[6] Chiral homoallyl alcohols with high levels of enantioselectivity have been synthesized by catalytic asymmetric addition of allylchromium reagents to carbonyl compounds.[7,8]

Like other enantioselective allyl fragment additions, the asymmetric Nozaki–Hiyama reaction has been successful for aldehyde allylation with a wide range of catalyst systems.[9,10] Recently, ketone allylations have been explored.[11] The development of new, effective chiral ligands for the Nozaki–Hiyama allylation of ketones is extremely intricate and needs a wide screening of chiral ligands. Recently, Sigman et al. elucidated a chromium-catalyzed enantioselective ketone allylation in which allyl bromides were used directly.[12] Herein, we report the synthesis of a chiral spirocyclic borate ligand that is effective in the chromium-catalyzed enantioselective allylation of alkyl and aryl ketones.

Chiral bipyridyl ligands derived from enantioenriched pinene allows for a variety of structural variations and affords moderate to high levels of enantiselectivities in different asymmetric transformations.[13] A chiral spirocyclic borate ligand which incorporates a rigid framework in the bipyridyl moiety for NH allylation was synthesized in a three-step process from ketone **1**[14] and amino alcohols **4a–d**.[15] Barbier-type allylation of ketone **1** stereoselectively formed homoallylic alcohol **2**.[16] Ozonolysis followed by reductive amination of the hydroxy aldehyde **3** with amino alcohols **4a–d** using sodium borohydride in acetic acid afforded spirocyclic borates **5a–5d** in 30–35% overall yield (Scheme 1). For comparison, the borates were converted to the corresponding boron-free amino alcohols (**6a–6d**) by stirring in acidic methanol. The formation of the borate ligands and their subsequent removal were followed by ^{11}B NMR.

In order to study the stereochemical diversity of the spiroborate ligand, a complete set of stereoiso-



Scheme 1. Synthesis of chiral spiroborate ligands. *Reactions conditions:* (a) allyl bromide, Zn, NH_4OAc, THF (82%); (b) O_3, CH_2Cl_2/MeOH, −78 °C, DMS (71%); (c) amino alcohol **4**, THF, $NaBH_4$, AcOH (45–60%); (d) MeOH, reflux.

mers was synthesized starting from the antipode of ketone **1** and both the enantiomers of amino alcohol **4a** (Figure 2). Interestingly the ligands **5a-1** and **5a-2** showed no borate formation in the structure as a result of unfavorable disposition of groups. X-ray crystallographic structures on the other hand reveal a tetracyclic skeleton with a rigid spirocyclic borate and unambiguously establish the absolute configuration of **5c** and **5c-3** as SRRS and RSSR, respectively (Figure 1).

Catalytic evaluation of the Cr(II)-ligand **5a** in the allylation of 1-(3-methoxyphenyl)-ethanone with allyl

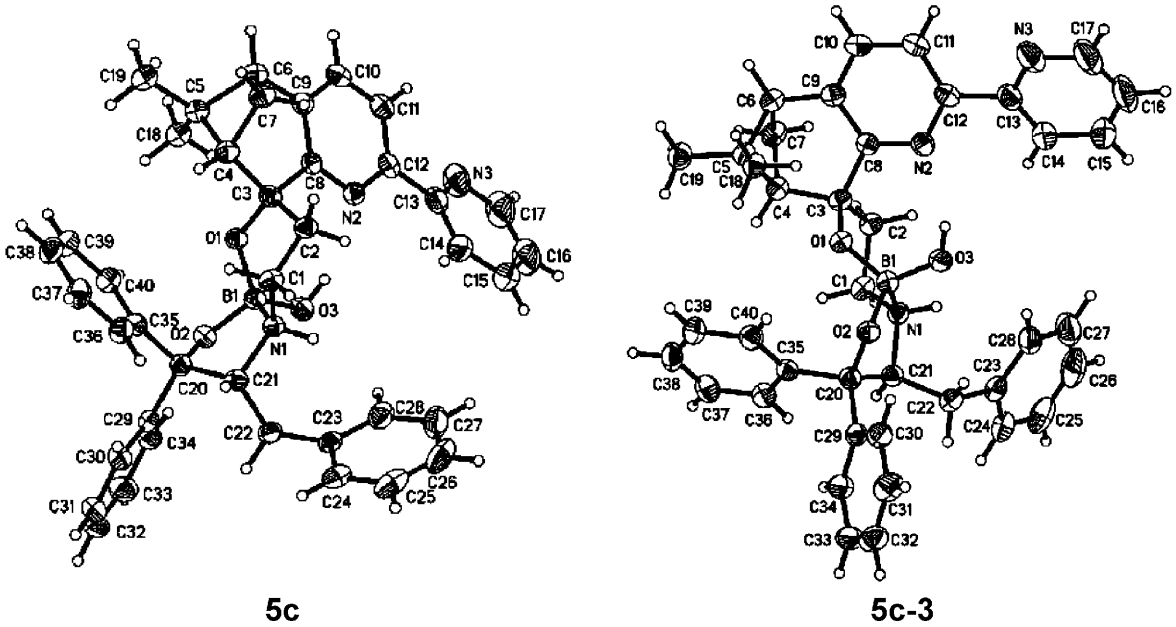


Figure 1. X-ray crystallographic structures of spiroborate **5c** (CCDC 713511) and enantiomer **5c-3** (CCDC 713512).

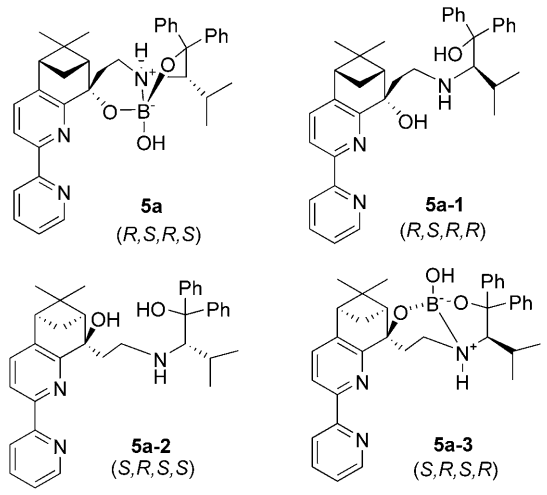
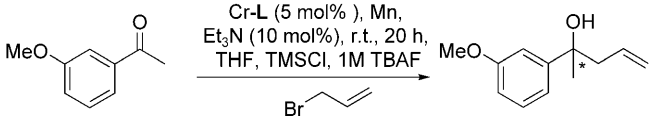


Figure 2. Stereochemical diversity of chiral spiroborate **5a**.

bromide following reported conditions formed (*R*)-2-(3-methoxyphenyl)-pent-4-en-2-ol with excellent enantioselectivity (93%) and in good isolated yield (85%). A similar level of asymmetric induction was found for the antipode **5a-3**. Diasteromeric ligands **5a-1** and **5a-2** with no rigid framework and presumably a different mode of coordination to the chromium center lowered the enantiomeric excess without any change in stereochemistry of the product (Table 1).

The corresponding boron-free ligand **6a** under identical conditions formed the (*S*)-tertiary alcohol in 59% *ee* and 70% isolated yield. Consequently the chirality of the bipyridyl moiety alongside the presence or absence of borate ring governs the stereochemical outcome of the allylation reaction. The steric influence of the chiral ligands **5b–d** and **6b–d**, respectively, on the asymmetric induction of the allylation of 1-(3-methoxyphenyl)-ethanone display a similar trend with the ligand containing isopropyl group in the amino alcohol moiety affording the highest selectivity. A pentacyclic ligand, expected to be formed from ligand **5d** with a proline module deviated from the usual trend, affording (*S*)-alcohol in 49% *ee*.

Table 1. Allyl bromide addition to 3-methoxyacetophenone in the presence of chiral spiroborates **5a–d** and boron-free ligands **6a–d**.



Entry	Ligand	Yield [%]	*ee* [%]	Configuration[a]
1	**6a**	70	59	*S*
2	**5a**	85	93	*R*
3	**5a-1**	80	33	*R*
4	**5a-2**	82	33	*S*
5	**5a-3**	86	89	*S*
6	**5b**	77	69	*R*
7	**6b**	78	3	*R*
8	**5c**	80	75	*R*
9	**6c**	79	3	*R*
10	**5d**	77	49	*S*
11	**6d**	85	10	*R*

[a] The *ee*% was determined on a Chiracel OD-H HPLC column.

The catalyst system was optimized using ligand **5a** with a Cr(II) complex formed *in situ* in the presence of various bases, allyl halides and solvents. Of the three tested allyl halides that comprised CrY_3, the allyl bromide and $CrBr_3$ combination afforded the best enantioselectivity. Similarly, THF at room temperature in the presence of triethylamine represented optimized conditions for the reaction (Table 2).

The extent of enantioselection for different ketones using Cr(II)-**5a** was explored under optimized reaction conditions (Table 3). Aryl ketones were excellent substrates for the transformation, as evidenced by a 74% yield and a 97% *ee* for the allylation of 1-(2-bromophenyl)-ethanone (Table 3, entry 6), and exceptional functionality tolerance as observed with halide-containing compounds. The nature and position of the substituent on the aryl ring had drastic effect on the enantioselective outcome of the reaction (Table 3, entry 1–13). The substrate scope demonstrated no straight correlation between the electronic nature of aryl group and enantioselectivity, although high yields of homoallylic alcohol was obtained in all the cases. Notably, similarly high levels of reactivity and enantioselectivity were observed for aliphatic ketones under identical reaction conditions (Table 3, entries 16 and 17). Modifying the aryl moiety or the methyl group of aryl methyl ketones resulted only in a very slight decrease in the asymmetric induction validating a broad substrate scope with the present catalyst system (Table 3, entries 14, 15, 18 and 19).

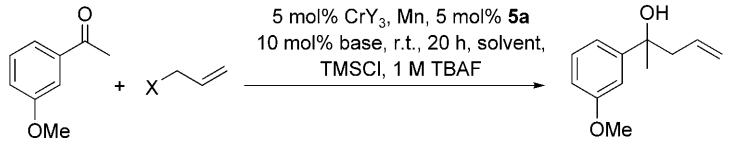
In summary, the chiral spiroborate ligand, (*S*,*R*,*R*,*S*)-**5a**, was demonstrated to promote efficient and highly enantioselective catalytic Nozaki–Hiyama reactions of alkyl and aryl ketones. The rigid framework of the ligand is essential for high stereoselection (up to 97% *ee*) and interestingly induced the opposite sense of enantioselectivity after the removal of borate ring. Further studies will be directed at the generality and functional group compatibility of this catalytic carbon-carbon bond forming process.

Experimental Section

Synthesis of 5a

To a solution of compound **3** (1.00 g, 3.2 mmol) in THF (20 mL) was added (*S*)-2-amino-3-methyl-1,1-diphenylbutan-1-ol (820 mg, 3.2 mmol), and the mixture was stirred at

Table 2. Optimization of reaction conditions for Nozaki–Hiyama allylation of 3-methoxyacetophenone.



Entry	X	Y	Base	*T* [°C]	Solvent	Yield [%][a]	*ee* [%][b]
1	Br	Cl	Et_3N	r.t.	CH_3CN	80	33
2	Br	Cl	Et_3N	r.t.	Deithyl ether	–	–
3	Br	Cl	Et_3N	r.t.	CH_2Cl_2	55	61
4	Br	Cl	Et_3N	r.t.	Toluene	68	19
5	Br	Cl	Et_3N	r.t.	Benzene	65	29
6	Br	Cl	Et_3N	r.t.	THF	83	91
7	Br	Cl	Et_3N	r.t.	DMF	75	3
8	Br	Cl	Et_3N	r.t.	Hexanes	–	–
9	Br	Cl	Et_3N	5	THF	63	93
10	Br	Cl	Et_3N	r.t.	THF	81	93
11	Br	Cl	Et_3N	60	THF	72	9
12	Br	Cl	Et_3N	r.t.	THF	83	91
13	Br	Cl	K_2CO_3	r.t.	THF	56	47
14	Br	Cl	DIPEA	r.t.	THF	85	87
15	Br	Cl	*t*BuOK	r.t.	THF	59	57
16	Br	Cl	Pyridine	r.t.	THF	75	73
17	Cl	Cl	Et_3N	r.t.	THF	77	3
18	Br	Cl	Et_3N	r.t.	THF	80	91
19	I	Cl	Et_3N	r.t.	THF	61	81
20	Cl	Br	Et_3N	r.t.	THF	75	71
21	Br	Br	Et_3N	r.t.	THF	84	93
22	I	Br	Et_3N	r.t.	THF	63	71

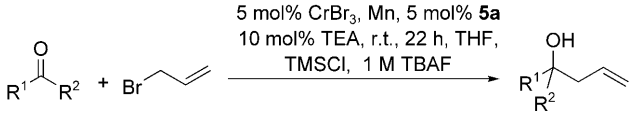
[a] Isolated yields.
[b] Enantiomeric ratio determined by HPLC equipped with a chiral stationary phase.

room temperature for 2 h. The solvent was removed under reduced pressure, and glacial acetic acid (20 mL) was added into the resultant residue. The reaction solution was cooled in an ice-bath, and sodium borohydride (1.20 g, 32.0 mmol) was added. After being stirred at room temperature for 2 h, a saturated sodium bicarbonate solution was added into the reaction solution until it became basic, which was then extracted with ethyl acetate. The combined extracts were dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure to yield a crude product which was purified by flash column chromatography on silica gel using ethyl acetate-hexane (1:4, 1:2) as the mobile phase to afford the pure compound **5a**; yield: 1.00 g (1.8 mmol, 56%); mp 223 °C; $[\alpha]_D^{25}$: +30° (*c* 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64–8.6 2 (d, *J* = 6.0 Hz, 1H), 8.40–8.38 (d, *J* = 9.0 Hz, 1H), 8.14–8.11 (d, *J* = 9.0 Hz, 1H), 8.68–8.65 (t, *J* = 9.0 Hz, 1H), 7.68–7.65 (d, *J* = 9.0 Hz, 1H), 7.28 (m, 2H), 7.23–7.07 (m, 5H), 3.97 (s, 1H), 3.76 (s, 1H), 3.10 (s, 1H), 2.87–2.83 (m, 1H), 2.67–2.65 (t, *J* = 6.0 Hz, 1H), 2.65–2.63 (m, 1H), 2.55–2.47 (m, 1H), 2.19–2.04 (m, 1H), 1.69–1.68 (d, *J* = 3.0 Hz, 1H), 1.31–1.28 (m, 2H), 1.26 (s, 3H), 1.10–1.07 (d, *J* = 9.0 Hz, 3H), 0.95–0.92 (d, *J* = 9.0 Hz, 3H), 0.72 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 160.5, 149.2, 148.6, 145.6, 142.2, 137.7, 134.5, 127.6, 126.8, 126.5, 126.0, 125,9, 123.4, 121.2, 120.1, 84.0, 76.6, 71.6, 50,0, 47.3, 46.2, 44.3, 42.3, 34.3, 32.5, 28.7, 26.6, 23.8, 26.6, 23.8, 21.8, 15.6; IR (KBr): ν = 3353, 3063, 2938, 1576, 1432, 1383, 1242, 1164, 1098, 1082, 1049, 1027, 846, 783, 746 cm^{-1}; MS-FAB: *m/z* = 556 ([M−H_2O]$^+$, 100), 512.4 (23); HR-MS: *m/z* = 556.3141 (M^+−OH), calcd. for $C_{36}H_{40}BN_3O_3$ (M^+): 573.3163.

Synthesis of 6a

To a solution of **5a** (57.4 mg, 0.1 mmol) in methanol (5 mL) was added 1 N HCl (5 mL), and stirred at room temperature for 2 h. Then methanol was removed, and a saturated sodium bicarbonate solution (5 mL) was added to the residue until it became basic. The resulting aqueous solution was extracted by diethyl ether (5 mL × 3), and the combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield a crude product which was purified by flash column chromatography on silica gel using ethyl acetate-hexane (1:4, 1:2) as the mobile phase to afford the pure compound **6a**; yield: 50.0 mg (0.09 mmol, 90%); mp: 90–92 °C $[\alpha]_D^{23.0}$: +3.0° (*c* 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65–8.64 (d, *J* = 4.0 Hz, 1H), 8.46–8.44 (d, *J* = 8.0 Hz, 1H), 8.17–8.15 (d, *J* = 8.0 Hz, 1H), 7.83–7.80 (t, *J* = 6.0 Hz, 1H), 7.69–7.67 (d, *J* = 8.0 Hz, 2H), 7.56–7.54 (d, *J* = 8.0 Hz, 2H), 7.36–7.34 (d, *J* = 8.0 Hz, 1H), 7.31–7.26 (m, 5H), 7.18–7.14 (m, 2H), 2.78 (s, 1H), 2.74–2.72 (t, *J* = 4.0 Hz, 1H), 2.67–2.62 (m, 2H), 2.29–2.20 (m, 1H), 2.17–2.14 (t, *J* = 6.0 Hz, 1H), 2.09–2.04 (m, 1H), 1.79–1.69 (m, 1H), 1.44 (s, 3H),

Table 3. Yields and enantioselectivities for the asymmetric allylation of alkyl and aryl ketones with Cr(II)-**5a**.



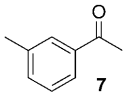
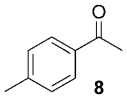
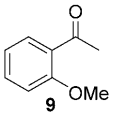
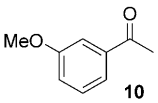
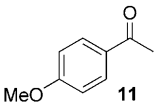
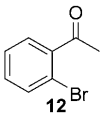
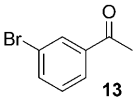
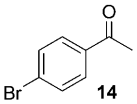
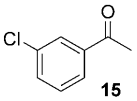
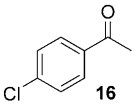
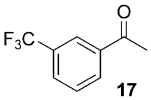
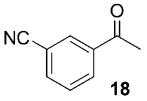
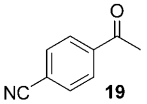
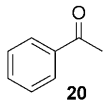
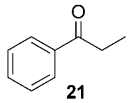
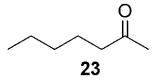
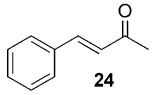
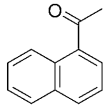
Entry	R^1 R^2	Yield [%]	*ee* [%][a]	[α] (*T*°C, *c* $CHCl_3$)
1	 **7**	79	73 (*R*)	+34.1 (27.2, 0.86)
2	 **8**	82	57 (*R*)[c]	+27.8 (25.0, 0.69)
3	 **9**	82	41 (*na*)	+12.3 (27.2, 0.9)
4	 **10**	83	93 (*na*)	+44.8 (27.2, 1.02)
5	 **11**	79	55 (*R*)	+43.9 (27.2, 1.23)
6	 **12**	74	97 (*na*)[b]	+23.0 (30.4, 1.27)
7	 **13**	87	89 (*R*)	+34.1 (30.4, 1.03)
8	 **14**	82	81 (*R*)	+35.6 (30.4, 1.48)
9	 **15**	82	81 (*na*)[b]	+28.8 (30.4, 1.43)
10	 **16**	73	82 (*R*)[c]	+41.6 (30.4, 1.18)
11	 **17**	70	93 (*S*)	–38.0 (24.6, 0.25)
12	 **18**	75	37 (*na*)	+12.2 (24.7, 0.45)
13	 **19**	73	27 (*na*)	+9.4 (24.8, 0.50)

Table 3. (Continued)

Entry	R^1 R^2	Yield [%]	*ee* [%][a]	[α] (*T*°C, *c* $CHCl_3$)
14	 **20**	75	73 (*R*)[b]	+21.2 (28.3, 0.52)
15	 **21**	76	60 (*R*)[b]	+13.3 (28.6, 0.61)
16	 **22**	68	75 (*S*)	−22.0 (24.6, 0.25)
17	 **23**	75	73 (*S*)	−10.0 (24.8, 0.26)
18	 **24**	77	77 (*R*)	+41.4 (24.6, 0.7)
19	 **25**	82	79 (*R*)	+43.5 (24.6, 1.22)

[a] The *ee* % was determined with a Chiracel OD-H HPLC column and the absolute configuration was assigned based on a comparison with the literature data.
[b] The *ee* % was determined by converting the homoallyl alcohols to diols.
[c] The *ee* % was determined using a Chiracel OJ HPLC column.

1.07–1.06 (d, $J=4.0$ Hz, 3H), 0.78–0.77 (d, $J=4.0$ Hz, 3H), 0.68 (s, 3H); MS-FAB: $m/z=547.00$ ($[M]^+$, 29.86), HR-MS: $m/z=547.3196$, calcd. for $C_{36}H_{41}N_3O_2$ (M^+): 547.3199.

Procedure for Catalytic Enantioselective Nozaki–Hiyama Allylation

Anhydrous THF (2 mL) was added to $CrBr_3$ (7.3 mg, 25.0 μmol) and Mn (42.0 mg, 750 μmol) in an inert atmosphere box, and the mixture was stirred for 1 h at room temperature. After ligand **5a** (14.0 mg, 24.4 μmol) and anhydrous NEt_3 (7.0 μL, 5.0 mg, 50 μmol) had been added, the suspension was stirred at room temperature for 1 hour. Finally, allyl bromide was added (65 μL, 90.9 mg, 750 μmol). After 1 h at room temperature, ketone (0.5 mmol) and Me_3SiCl (93 μL, 81.5 mg, 750 μmol) were added, and the suspension was stirred at room temperature for 20 h. Saturated aqueous $NaHCO_3$ was added. Following filtration and evaporation, the aqueous phase was extracted with Et_2O. After evaporation of the combined organic phases, the residue was dissolved in THF (2 mL). A TBAF solution (1.5 mL, 1.5 mmol, 1 M in THF) was added and the mixture was stirred until desilylation was complete (as verified by TLC). Saturated aqueous $NaHCO_3$ was added, and the solution was extracted using CH_2Cl_2, and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent and flash chromatography (hexane/EtOAc 4:1) gave (*R*)-1-phenyl-3-buten-1-ol as a pale-yellow oil; yield: 26.7 mg (180 mmol, 72%, 90% *ee*). The enantiomeric excess was determined by HPLC analysis using a chiral column (Chiralcel OD-H or OJ column, flow rate 0.25 mL min^{-1}).

Acknowledgements

We thank Dr. Sankareswaran Srimurugan for his helpful discussions (Postdoctoral fellowship awarded by National Science Council of the Republic of China, under Contract NSC 96-2811 M-259-001). The authors thank Ms. L. M. Hsu, at the Instruments Center, National Chung Hsing University, for her help in obtaining HR-MS, and the National Science Council of the Republic of China, for financially supporting this research under Contract NSC 97-2113 M-259-002-MY3.

References

[1] a) Y. Okude, S. Hirano, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **1977**, *99*, 3179–3180; b) Y. Okude, T. Hiyama, H. Nozaki, *Tetrahedron Lett.* **1977**, *18*, 3829–3832.
[2] C. T. Buse, C. H. Heathcock, *Tetrahedron Lett.* **1978**, *19*, 1685–1688.
[3] a) A. Fürstner, *Chem. Rev.* **1999**, *99*, 991–1045; b) M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, J. C. Palacios, *Chem. Soc. Rev.* **1999**, *28*, 169–177; c) L. A. Wess-

johann, G. Scheid, *Synthesis* **1999**, 1–36; d) K. Takai, H. Nozaki, *Proc. Jpn. Acad. Ser. B* **2000**, *76*, 123–131; e) G. C. Hargadena, P. J. Guirya, *Adv. Synth. Catal.* **2007**, *349*, 2407–2424.

[4] For reviews, see: a) A. S. K. Hashmi, *J. Prakt. Chem.* **1996**, *338*, 491–495; b) A. Fürstner, *Chem. Eur. J.* **1998**, *4*, 567–570.

[5] a) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 2533–2534; b) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 12349–21357.

[6] M. Bandini, P. G. Cozzi, P. Melchiorre, A. Umani-Ronchi, *Angew. Chem.* **1999**, *111*, 3558–3561; *Angew. Chem. Int. Ed.* **1999**, *38*, 3357–3359.

[7] a) M. Bandini, P. G. Cozzi, A. Umani-Ronchi, *Chem. Commun.* **2002**, 919–927; b) M. Lombardo, S. Licciulli, S. Morganti, C. Trombini, *Chem. Commun.* **2003**, 1762–1763; c) A. Berkessel, D. Menche, C. A. Sklorz, M. Schröder, I. Paterson, *Angew. Chem.* **2003**, *115*, 1062–1065; *Angew. Chem. Int. Ed.* **2003**, *42*, 1032–1035; d) A. Berkessel, M. Schröder, C. A. Sklorz, S. Tabanella, N. Vogl, J. Lex, J. M. Neudörfl, *J. Org. Chem.* **2004**, *69*, 3050–3056; e) I. Paterson, H. Bergmann, D. Menche, A. Berkessel, *Org. Lett.* **2004**, *6*, 1293–1295.

[8] a) H.-W. Choi, K. Nakajima, D. Demeke, F.-A. Kang, H.-S. Jun, Z.-K. Wan, Y. Kishi, *Org. Lett.* **2002**, *4*, 4435–4438; b) M. Inoue, T. Suzuki, M. Nakada, *J. Am. Chem. Soc.* **2003**, *125*, 1140–1141; c) K. Namba, Y. Kishi, *Org. Lett.* **2004**, *6*, 5031–5033; d) M. Inoue, M. Nakada, *Org. Lett.* **2004**, *6*, 2977–2980.

[9] a) Y. Yamamoto, *Acc. Chem. Res.* **1987**, *20*, 243–249; b) J. A. Marshall, *Chem. Rev.* **1996**, *96*, 31–47; c) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763–2793.

[10] a) A. L. Costa, M. G. Piazza, E. Tagliavini, C. Trombini, A. Umani-Ronchi, *J. Am. Chem. Soc.* **1993**, *115*, 7001–7002; b) G. E. Keck, K. H. Tarbet, L. S. Geraci, *J. Am. Chem. Soc.* **1993**, *115*, 8467–8468; c) A. Yanagisawa, H. Nakashima, A. Ishiba, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 4723–4724; d) M. Inoue, T. Suzuki, M. Nakada, *J. Am. Chem. Soc.* **2003**, *125*, 1140–1141; e) G. Xia, H. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 2554–2555; f) C. Chen, K. Tagami, Y. Kishi, *J. Org. Chem.* **1995**, *60*, 5386–5387.

[11] a) R. Wada, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 8910–8911; b) S. Lou, P. N. Moquist, S. E. Schaus, *J. Am. Chem. Soc.* **2006**, *128*, 12660–12661; c) S. Casolari, D. D′Addario, E. Tagliavini, *Org. Lett.* **1999**, *1*, 1061–1063; d) R. Hamasaki, Y. Chounan, H. Horino, Y. Yamamoto, *Tetrahedron Lett.* **2000**, *41*, 9883–9887; e) K. M. Waltz, J. Gavenonis, P. J. Walsh, *Angew. Chem.* **2002**, *114*, 3849–3852; *Angew. Chem. Int. Ed.* **2002**, *41*, 3697–3699; f) A. Cunningham, V. Mokal-Parekh, C. Wilson, S. Woodward, *Org. Biomol. Chem.* **2004**, *2*, 741–748; g) J. G. Kim, K. M. Waltz, I. F. Garcia, D. Kwiatkowski, P. J. Walsh, *J. Am. Chem. Soc.* **2004**, *126*, 12580–12585; h) Y.-C. Teo, J.-D. Goh, T.-P. Loh, *Org. Lett.* **2005**, *7*, 2743–2745; i) J. Lu, M.-L. Hong, S.-J. Ji, Y.-C. Teo, T.-P. Loh, *Chem. Commun.* **2005**, 4217–4218; j) A. J. Wooten, J. G. Kim, P. J. Walsh, *Org. Lett.* **2007**, *9*, 381–384; k) L. F. Tietze, K. Schiemann, C. Wegner, *J. Am. Chem. Soc.* **1995**, *117*, 5851–5852; l) S. Yamasaki, K. Fujii, R. Wada, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2002**, *124*, 6536–6537; m) M. Wadamoto, H. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 14556–14557; n) X. Zhang, D. Chen, X. Liu, X. Feng, *J. Org. Chem.* **2007**, *72*, 5227–5233; o) J. J. Miller, M. S. Sigman, *Angew. Chem.* **2008**, *120*, 783–786; *Angew. Chem. Int. Ed.* **2008**, *47*, 771–774; p) T. D. Haddad, L. C. Hirayama, P. Taynton, B. Singaram, *Tetrahedron Lett.* **2008**, *49*, 508–511.

[12] J. J. Miller, M. S. Sigman, *J. Am. Chem. Soc.* **2007**, *129*, 2752–2753.

[13] a) Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561–3571; b) P.-T. Lee, C. Chen, *Tetrahedron: Asymmetry* **2005**, *16*, 2704–2710; c) Y.-J. Chen, C. Chen, *Tetrahedron: Asymmetry* **2007**, *18*, 1313–1319; d) Y.-J. Chen, C. Chen, *Tetrahedron: Asymmetry* **2008**, *19*, 2201–2209.

[14] R.-X. Lin, C. Chen, *J. Mol. Catal. A: Chem.* **2006**, *243*, 89–98.

[15] Y. Wu, H. Yun, Y. Wu, K. Ding, Y. Zhou, *Tetrahedron: Asymmetry* **2000**, *11*, 3543–3552.

[16] C. Chen, W.-C. Dai, H.-G. Chang, *Org. Prep. Proced. Int.* **2002**, *34*, 471–475.

