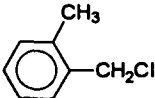
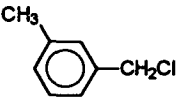

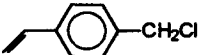

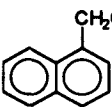
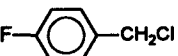
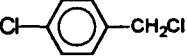
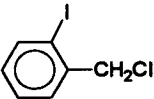




**Table 1.** (*R*)-*n*-Butylarylcarbinols (**2**) were prepared from (1*S*,2*S*,3*R*,5*S*)-(+)-pinanediol *n*-butylboronic ester and arylmethyl chlorides

Entry	Product <sup>a</sup>	ArCH <sub>2</sub> Cl	Reaction Time <sup>b</sup>	Yield (%) <sup>c</sup>	EE(%) <sup>d</sup>
1	<b>2a</b>	PhCH <sub>2</sub> Cl	0 min	72	71
2	<b>2a</b>	PhCH <sub>2</sub> Cl	10 min	77	72
3	<b>2a</b>	PhCH <sub>2</sub> Cl	60 min	73	71
4	<b>2b</b>		10 min	39	55
5	<b>2c</b>		10 min	64	79
6	<b>2d</b>		10 min	63	78
7	<b>2e</b> *		10 min	64	60
8	<b>2f</b>		10 min	68	45
9	<b>2g</b>		10 min	64	45
10	<b>2h</b>		10 min	69	69
11	<b>2i</b>		10 min	95	36
12	<b>2j</b> *		10 min	71	64

<sup>a</sup> All reaction products exhibited physical and spectral characteristics in accord with literature values. <sup>b</sup> Reaction time at -78 °C after adding lithium dicyclohexylamide. <sup>c</sup> Isolated yield. <sup>d</sup> Determined by <sup>1</sup>H NMR analysis of the corresponding Mosher's esters. \* Confirmed by HRMS.

chlorophenyl)methyl lithium at -78 °C for 10 min gave (*S*)-1-phenyl-1-pentanol in 75% chemical yield and 70% optical purity after oxidation; the reaction using (1*R*,2*R*)-(-)-1,2-dicyclohexyl-1,2-ethanediol *n*-butylboronic ester gave (*R*)-1-phenyl-1-pentanol in 70% optical purity. None of the desired 1-phenyl-1-pentanol was formed in reactions using the chiral boronic ester prepared from diethyl L-tartrate, presumably due to the higher acidity of the α-proton in the tartrate ester

compared to the benzylic proton in benzyl chloride which precluded the formation of the prerequisite ( $\alpha$ -chlorophenyl)methylolithium reagent.

Zinc chloride enhances both the chemical yield and the stereoselectivity of reactions involving chiral boronic esters with dichloromethylolithium reagents by influencing which of the two chlorines is displaced.<sup>1</sup> Not surprisingly, since there is only a single chlorine available, no improvement was noted in the present case upon the addition of zinc chloride.

The enantioface selectivity brought about by the chiral boronic ester provides a useful degree of enantioselectivity and is applicable to systems which might not tolerate the organometallic reagents required in the Matteson reaction sequence (Table 1, entries 11 and 12).<sup>11</sup> In addition, it offers the intriguing possibility that boronic esters containing chirality in both the alkyl group and in the ester might lead to enhanced diastereoselectivities via matched (versus mismatched) diastereochemical pairings.<sup>12</sup>

### Acknowledgements

We wish to thank the Department of Energy and the Robert H. Cole Foundation for support of this research.

### References

1. For reviews see: (a) Matteson, D. S. *Stereodirected Synthesis with Organoboranes*; Springer, Berlin, 1995, pp. 162–220. (b) Matteson D. S. *Chem. Rev.* **1989**, *89*, 1535. (c) Matteson, D. S. *Acc. Chem. Res.* **1988**, *21*, 294.
2. (a) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687. (b) Sadhu, K. M.; Matteson, D. S. *Tetrahedron Lett.* **1986**, *27*, 795. (c) Brown, H. C.; Phadke, A. S.; Rangaishenvi, M. V. *J. Am. Chem. Soc.* **1988**, *110*, 6263. (d) Soundararajan, R.; Li, G.; Brown, H. C. *Tetrahedron Lett.* **1994**, *35*, 8957. (e) Soundararajan, R.; Li, G.; Brown, H. C. *Tetrahedron Lett.* **1994**, *35*, 8961. (f) Brown, H. C.; Phadke, A. S.; Bhat, N. G. *Tetrahedron Lett.* **1993**, *34*, 7845.
3. (a) Matteson, D. S.; Majumdar, D. J. *Organomet. Chem.* **1980**, *184*, C41. (b) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 230. (c) Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236.
4. (a) Brown, H. C.; Ragaishenvi, M. V. *Tetrahedron Lett.* **1990**, *31*, 7113. (b) Brown, H. C.; Jayaraman, S. *J. Org. Chem.* **1993**, *58*, 6791.
5. (a) Kabalka, G. W.; Li, N.-S.; Yu, S. *Tetrahedron Lett.* **1995**, *36*, 8545. (b) Li, N.-S.; Yu, S.; Kabalka, G. W. *Organometallics* **1997**, *16*, 709. (c) Li, N.-S.; Yu, S.; Kabalka, G. W. *J. Organomet. Chem.* **1997**, *531*, 101.
6. (a) Ohkuma, T.; Ooka, H.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2675. (b) Rawson, D.; Meyer, A. I. *J. Chem. Soc., Chem. Commun.* **1992**, 494. (c) Zhang, X.; Kumobayashi, H.; Takaya, H. *Tetrahedron: Asymmetry* **1994**, *5*, 1179.
7. (a) Niwa, S.; Soai, K. *J. Chem. Soc., Perkin Trans 1* **1991**, 2717. (b) Nakajima, M.; Tomioka, K.; Koga, K. *Tetrahedron* **1993**, *49*, 9751. (c) Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka, M.; Kobayashi, S. *Tetrahedron* **1992**, *48*, 5691. (d) Urabe, H.; Yamakawa, T.; Sato, F. *Tetrahedron: Asymmetry* **1992**, *3*, 5. (e) Chibale, K.; Greeves, N.; Lyford, L.; Pease, J. E. *Tetrahedron: Asymmetry* **1993**, *4*, 2407.
8. Lithium dicyclohexylamide (1 mmol) was prepared in situ by metallating dicyclohexylamine (0.18 g, 0.20 mL, 1 mmol) in THF (1 mL) with *n*-BuLi (1 mmol; 0.63 mL, 1.6 M solution in hexane) at 0°C and was used immediately.
9. (+)-Pinanediol *n*-butylboronic ester (1 mmol) was prepared in situ by the reaction of *n*-butyldiisopropoxyborane (1 mmol) with (+)-pinanediol (1 mmol) in THF (1 mL) at rt for 30 min. After removing the solvent and isopropanol under reduced pressure, the residue was used without further purification. The <sup>1</sup>H NMR of the crude boronic ester [250 MHz NMR (CDCl<sub>3</sub>)  $\delta$ : 0.77 to 2.41 (*m*, 24 H, pinanyl with methyl resonance at  $\delta$  0.84, 1.29, 1.38 *n*-butyl), 4.25 (*dd*, 1H, *J*=1.87,

- $J=8.70$ . CHOB] is consistent with that reported in the literature: Matteson, D. S.; Ray, R.; Rocks, R. R.; Tsai, D. J. *Organometallics* **1983**, *2*, 1536.
10. Mazaleyrat, J.-P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585.
11. Benzylic chlorides containing strongly electron-withdrawing substituents (e.g.  $-\text{NO}_2$  and  $-\text{CO}_2\text{CH}_3$ ) generate significant amounts of coupling products, presumably due to the stability of the intermediate carbanions.
12. Masamune, S.; Choy, W.; Peterson, J. S.; Sita, L. F. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1.

(Received 10 April 1997; accepted 13 June 1997)