2d': pale yellow liquid; IR (neat) 3360 and 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1–2.8 (2 H, m, 3-H), 2.34 (1 H, br s, NH), 3.18 (3 H, s, 4-COOMe), 3.33 (1 H, dd, J_{4-3} = 5.6 and J_{4-5} = 7.8 Hz, 4-H), 3.73 (3 H, s, 2-COOMe), 4.27 (1 H, dd, J_{2-3} = 8.7 and 4.4 Hz, 2-H), 4.70 (1 H, d, J_{5-4} = 7.8 Hz, 5-H), and 7.22 (5 H, br s, Ph); ^{13}C NMR ($CDCl_3$) δ 32.12 (t, 3-C), 49.42 (d, 4-C), 51.24, 52.30 (each q, COOMe), 59.30 (d, 2-C), 64.53 (d, 5-C), 127.07, 127.66, 128.18 (each d, Ph), 140.30 (s, Ph), 173.12, and 176.03 (each s, COOMe); MS, m/z (rel intensity) 263 (M^+, 36), 204 (base peak), 177 (32), 145 (13), 144 (50), and 117 (46); HRMS calcd for $C_{14}H_{17}NO_4$ (M) 263.1157, found m/z 263.1150.

2d'': pale yellow liquid; IR (neat) 3350 and 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2–2.4 (2 H, m, 3-H), 2.38 (1 H, br s, NH), 2.91 (1 H, dt, J_{4-3} = 9.0, 8.3, J_{4-5} = 8.3 Hz, 4-H), 3.59 (3 H, s, 4-C), 3.73 (3 H, s, 2-COOMe), 4.01 (1 H, dd, J_{2-3} = 8.0 and 6.2 Hz, 2-H), 4.40 (1 H, d, J_{5-4} = 8.3 Hz, 5-H), and 7.2–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 34.59 (t, 3-C), 51.36 (d, 4-C), 52.00, 52.36 (each q, COOMe), 59.42 (d, 2-C), 66.83 (d, 5-C), 127.07, 128.01, 128.83 (each d, Ph), 141.42 (s, Ph), 174.07, and 174.84 (each s, COOMe); MS, m/z (rel intensity) 263 (M^+, 29), 204 (base peak), 177 (49), 145 (12), 144 (49), and 117 (40); HRMS calcd for $C_{14}H_{17}NO_4$ (M) 263.1157, found m/z 263.1157.

Chiral Synthesis via Organoboranes. 17. Preparation of α-Chiral α'-Alkynyl Ketones of High Enantiomeric Excess from Optically Pure Organyl(1-alkynyl)borinic Esters

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Optically pure alkynylborinic esters R*BC≡CR''(OR') are cleanly obtained at low temperatures from optically pure boronic esters R*B(OR')$_2$ and a lithium acetylide followed by treatment of the "ate" complex LiR*BC≡CR''(OR')$_2$ with ethereal hydrogen chloride. These borinic esters react with α,α-dichloromethyl methyl ether, DCME, in the presence of a hindered base to yield, after hydrogen peroxide oxidation, α-chiral α'-alkynyl ketones R*COC≡CR'' which exhibit the same high enantio- and stereoselectivity of the chiral boronic esters. β-Heterosubstituted (1-alkynyl)borinic esters, such as $\overline{CH_2OCH_2CH_2}CBC{\equiv}CR''(OR')$, despite their sensitivity to elimination reactions, can be similarly converted into the corresponding ketones in excellent yields. This development considerably expands the range of applicability of the "DCME" reaction.

Alkynyl ketones in general and optically active alkynyl ketones in particular are potentially interesting intermediates for the synthesis of natural products.[1] α-Chiral α'-alkynyl ketones have been prepared from optically active acyl halides and alkynes in the presence of cuprous iodide and $Pd(PPh_3)_2Cl_2$.[2] α-Chiral-amino α'-alkynyl ketones have been similarly obtained from α-amino acid derivatives and metalloacetylides.[3] However, these methods, in addition to involving considerable racemization in certain cases, are not general and are seriously restricted by the availability of the starting carboxylic acid unit. Organoborane routes to 1-alkynyl ketones include reaction of a lithium acetylide with a carboxylic acid anhydride in the presence of boron trifluoride etherate,[4a] hydroboration sequences with thexylborane,[4b] selective hydroboration of conjugated diynes with dialkylboranes,[4c] and reaction of iodine with "ate" complexes obtained from lithium organylacetylides and triorganylboranes.[4d] These methods, however, do not lend themselves readily to the synthesis of optically active 1-alkynyl ketones. Our approach to the preparation of these ketones is based on chiral organoboron chemistry.

Chiral organoboranes have emerged as an important class of asymmetric reagents for the preparation of a variety of compounds, usually with very high enantiomeric excess.[5] Among chiral organoboranes, optically pure boronic esters[6] are particularly suited for carbon–carbon bond-forming reactions[7] with elaboration into useful organic compounds.[8] Recently we have used optically pure boronic esters in a general synthesis of enantiomerically pure α-chiral acyclic ketones.[9] We have now extended our studies and report our results on the preparation of the title compounds via the "DCME" reaction of chiral (1-alkynyl)borinic esters.[10]

Results and Discussion

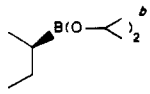
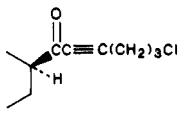
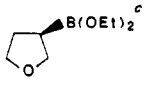
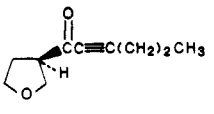
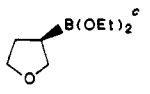
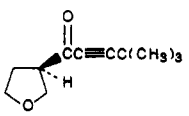
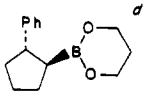
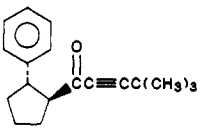
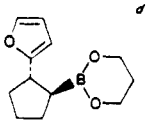
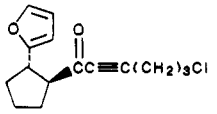
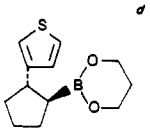
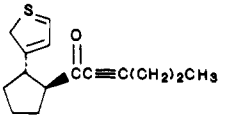
We have previously demonstrated that lithium acetylides react with boronic esters in a reversible manner, low temperatures favoring the formation of the ate complex (eq 1).[10]

$$R^*B(OR')_2 + LiC{\equiv}CR'' \underset{\text{room temperature}}{\overset{-78\ ^\circ C}{\rightleftharpoons}} LiR^*BC{\equiv}CR''(OR')_2 \quad (1)$$

(1) Suzuki, K.; Ohkuma, T.; Miyazawa, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1986**, *27*, 373.
(2) Giacomalli, G.; Rosini, C.; Caporusso, A. M.; Palla, F. *J. Org. Chem.* **1983**, *48*, 4887.
(3) Cupps, T. L.; Boutin, R. H.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 3972.
(4) (a) Brown, H. C.; Racherla, U. S.; Singh, S. M. *Tetrahedron Lett.* **1984**, *25*, 2411. (b) Brown, H. C.; Bhat, N. G.; Basavaiah, D. *Synthesis* **1983**, 885. (c) Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068. (d) Yamada, K.; Miyaura, N.; Itoh, M.; Suzuki, A. *Synthesis* **1977**, 679.
(5) Brown, H. C.; Jadhav, P. K.; Singaram, B. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986.
(6) Brown, H. C.; Singaram, B. *J. Am. Chem. Soc.* **1984**, *106*, 1797.
(7) Brown, H. C.; Imai, T.; Desai, M. C.; Singaram, B. *J. Am. Chem. Soc.* **1985**, *107*, 4980.
(8) (a) Matteson, D. S.; Sadhu, K. M.; Peterson, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 810 and references cited therein. (b) For recent reviews, see: Srebnik, M.; Ramachandran, P. V. *Aldrichimica Acta* **1987**, *20*, 9. (c) Matteson, D. S. *Synthesis* **1986**, 923.
(9) Brown, H. C.; Srebnik, M.; Bakshi, R. K.; Cole, T. E. *J. Am. Chem. Soc.* **1987**, *109*, 5420.
(10) For a general discussion of the preparation and characterization of this class of compounds, see: Brown, H. C.; Srebnik, M. *Organometallics* **1987**, *6*, 629.

0022-3263/88/1953-1391$01.50/0

Table I. α-Chiral α'-Alkynyl Ketones Obtained from DCME Reaction of the Corresponding Borinic Esters

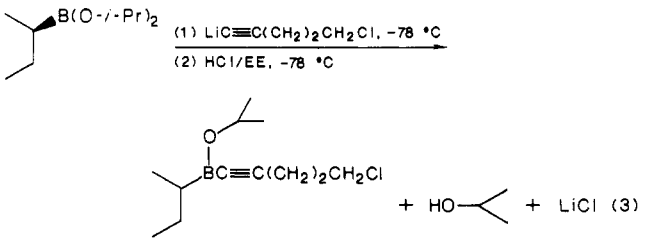
boronic ester[a]	lithium acetylide	ketone	$[\alpha]_D$ (c)[e]	% ee[f]	abs config	% yield[g]
	$LiC{\equiv}C(CH_2)_3Cl$	 **1**	−12.84 (1.89)	>99	*R*	65
	$LiC{\equiv}C(CH_2)_2CH_3$	 **2**	+4.87 (0.4)	>99	*R*	73
	$LiC{\equiv}CC(CH_3)_3$	 **3**	+7.54 (0.44)	>99	*R*	68
	$LiC{\equiv}CC(CH_3)_3$	 **4**	+123.91 (2.08)	>99	1*S*,2*S*	68
	$LiC{\equiv}C(CH_2)_3Cl$	 **5**	+105.34 (2.30)	>99	1*S*,2*S*	70
	$LiC{\equiv}C(CH_2)_2CH_3$	 **6**	+92.53 (2.08)	>99	1*S*,2*S*	72

[a] All boronic esters were obtained by hydroboration of olefins with (+)-α-pinene. [b] Reference 6. [c] Reference 23. [d] Reference 24. [e] All rotations were taken in methanol. [f] See text. [g] After column chromatography.

These alkynyl ate complexes can be cleanly decomposed at low temperatures with ethereal hydrogen chloride (eq 2). Applying this methodology to the reaction of (*R*)-

$$LiR^*BC{\equiv}CR''(OR')_2 \xrightarrow[-78\ °C]{HCl/EE} R^*BC{\equiv}CR''(OR') + HOR' + LiCl \quad (2)$$

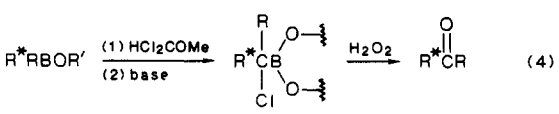
(−)-(1-methypropyl)diisopropoxyborane with 1-lithio-5-chloropentyne at −78 °C, followed by treatment with ethereal hydrogen chloride at the same temperature, cleanly produced the (1-alkynyl)borinic ester (δ +40.0) (eq 3).



(3)

After removal of volatiles and precipitated lithium chloride the borinate was of sufficient purity to be used directly in the next step.

Borinic esters can be converted into ketones by reaction with DCME in the presence of base followed by oxidation (eq 4).[9,11] The preferred base for this conversion is lithium



(4)

tert-butoxide.[9] Using this base, which has the advantage of being readily removed by aqueous workup, we prepared a series of α-chiral ketones from the corresponding chiral borinic esters.[9] However, when we attempted to apply LiO-*t*-Bu to the DCME reaction of (1-alkynyl)borinates, the α-chloro borinic esters were obtained in low yields. Instead we obtained primarly the starting chiral boronic esters (δ +30–31) (eq 5). It is known that the boron carbon

$$R^*BC{\equiv}CR''(OR') + HCl_2COMe + LiO\text{-}t\text{-}Bu \rightarrow R^*BOR'(O\text{-}t\text{-}Bu) \quad (5)$$

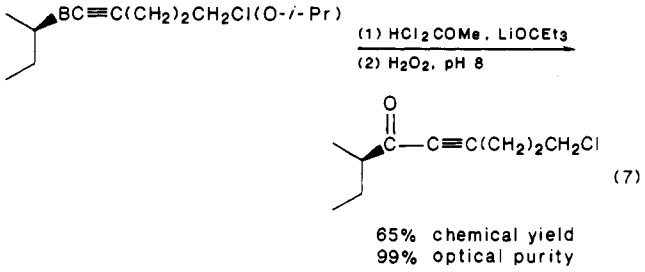
triple bond is labile. Apparently, under the conditions of the DCME reaction (1 equiv of DCME, 2 equiv of base), LiO-*t*-Bu coordinates with the alkynylborinate to form an ate complex, which then decomposes by preferential expulsion of a lithium acetylide (eq 6). This is in agreement

$$R^*BC{\equiv}CR''(OR') + LiO\text{-}t\text{-}Bu \rightleftarrows LiR^*BC{\equiv}CR''(OR')(O\text{-}t\text{-}Bu) \rightleftarrows R^*BOR'(O\text{-}t\text{-}Bu) + LiC{\equiv}CR'' \quad (6)$$

with our earlier observations on the reversible nature of such ate complex formation (eq 1).[10] A base of greater steric demands which would not competitively coordinate with the (alkynyl)borinic ester was clearly needed. We had previously observed that lithium triethylcarboxide, LiO-CEt_3, does not coordinate to simple borinic esters.[11,12] We,

(11) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876.
(12) For instance, LiO-*t*-Bu complexes with PhBMe(O-*i*-Pr) to the extent of 92%, while $LiOCEt_3$ shows no coordination within the detection limits of ^{11}B NMR. Brown, H. C.; Srebnik, M.; Cole, T. E., unpublished results.

therefore, tried this base in the "DCME reaction" of (1-alkynyl)borinates. Indeed, when ((*R*)-(−)-2-methylpropyl)(5-chloro-1-hexynyl)isopropoxyborane was treated with DCME in the presence of 2 equiv of $LiOCEt_3$, the α-chloro boronic ester intermediate (δ +27) was cleanly produced. Subsequent oxidation with hydrogen peroxide in pH 8 phosphate buffered solution furnished (*R*)-(−)-3-methyl-4-oxo-9-chloro-5-nonyne, 1 (eq 7). The 1-alkynyl

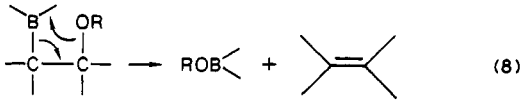


(7)

65% chemical yield
99% optical purity

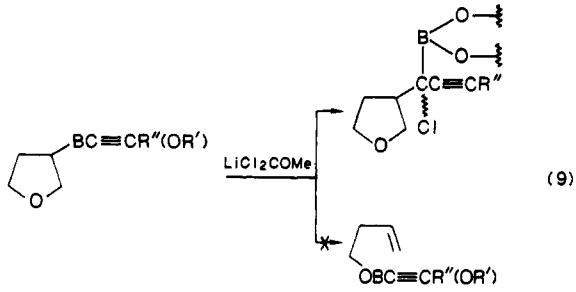
ketones are susceptible to attack by hydrogen peroxide under strongly alkaline conditions to give a variety of products, presumably due to initial oxirene formation.[13] To avoid this pitfall, we carried out the hydrogen peroxide oxidations in a phosphate buffered solution. In addition, under these conditions no racemization of the base-sensitive α-chiral ketones occurred. The results are summarized in Table I.

Organoboranes containing electronegative donor groups, i.e., OR, in the β-position readily undergo a facile cis elimination (eq 8).[14] Fortunately, we did not encounter



(8)

such difficulties. Thus the "DCME reaction" of (1-alkynyl)(3-tetrahydrofuryl)borinates proceeded smoothly to furnish the α-chloro boronic esters (δ +27–28), which were oxidized to the ketones as described above (Table I, entries 2 and 3). Apparently, under the conditions of the "DCMe reaction" migration of the organyl groups is preferred over the facile cis elimination[14] (eq 9). This constitutes the first



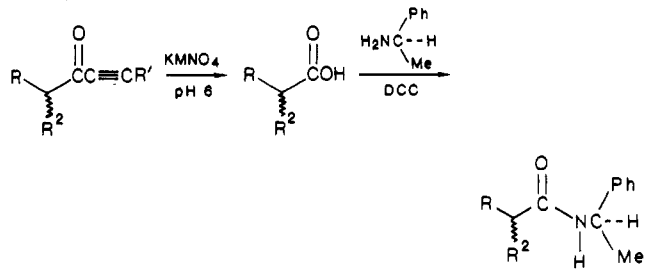
(9)

example of facile migration of β-heterosubstituted boronates. This favorable turn of events greatly extends the scope of the "DCME reaction". This may also pave the way for using these heterocyclic boronic esters in other carbon–carbon bond-forming reactions, i.e., Matteson's homologation procedure.[8c]

The stereochemistry and absolute configuration of the ketones are determined in the asymmetric hydroboration step of the prochiral alkenes and reflect the geometries of the boronic and borinic esters. In this study, (+)-α-pinene was used. Since (−)-α-pinene is also readily available both enantiomeric ketones are equally accessible.

(13) Kropf, H.; Scroder, R. *Liebigs Ann. Chem.* **1976**, 2325.
(14) Brown, H. C.; Vara Prasad, J. V. N. *J. Org. Chem.* **1985**, *50*, 3002.

Scheme I



The optical purity of the ketones was determined as follows. The ynones were oxidized to the carboxylic acids with potassium permanganate. The acids were coupled to (*S*)-(−)-methylbenzylamine in the presence of DCC to yield the diastereomeric amides[3] (Scheme I). Each pair of diastereomeric amides was readily resolvable by capillary GC (methylsilicone, 50 m). Racemic acids gave amides in a 1:1 ratio, thus proving that no kinetic resolution had taken place. In addition, ketones with two adjacent chiral centers (Table I, entries 4, 5, and 6) were also shown to be diastereomerically pure both by ^{13}C NMR and capillary GC analysis. In control experiments the cyclic ketones (Table I, entries 4, 5, and 6) were equilibrated in sodium methoxide for 24 h. Analysis by capillary GC indicated 5–10% epimerization. (The low value presumably is due to the fact that the trans isomers we used are the more stable thermodynamically.)

Applications and Conclusion

Optically active isoxazoles have been obtained by cyclization of α-chiral α'-alkynyl ketones.[15] Kishi[16] has prepared chiral β-halovinyl ketones, themselves versatile intermediates in organic synthesis,[17] from α-chiral acetylenic ketones. Both the acetylenic and carbonyl units serve as convenient handles for further elaborations. Thus the reduction of the carbonyl moiety of certain α-chiral alkynyl ketones with $LiAlH_4$ furnishes the *threo* propargylic alchohols in high selectivity.[1] In turn, chiral propargylic alcohols have been converted into a multitude of useful derivatives.[18]

Reactions which have been applied to achiral 1-alkynyl ketones should also find applicability to chiral ketones, for example, in the Pictet-Spengler reaction for the preparation of tetrahydro-β-carbolines,[19] stereoselective lithium cuprate addition to α,β-unsaturated ketones,[20] and the preparation of pyrrole derivatives,[21] to name but a few possibilities.

Clearly, α-chiral α'-alkynyl ketones are of growing importance in organic synthesis. We have developed a convenient preparation of this class of chiral compounds from

(15) Falorni, M.; Lardicci, L.; Giacomelli, G. *Gazz. Chim. Ital.* **1987**, *117*, 7.
(16) Cheon, S. H.; Christ, W. J.; Hawkins, L. D.; Jin, H.; Kishi, Y.; Taniguchi, M. *Tetrahedron Lett.* **1986**, *27*, 4759.
(17) Sheng, H.; Lin, S.; Huang, Y. Z. *Tetrahedron Lett.* **1986**, *27*, 4893 and references cited therein.
(18) (a) For intramolecular pericyclic reactions of acetylenic alcohols, see: Viola, A.; Collins, J. J.; Filipp, N. *Tetrahedron* **1981**, *37*, 3765. (b) Pauson-Khand reaction: Montana, A.; Moyana, A.; Pericas, M. A.; Serratosa, F. *Tetrahedron* **1985**, *41*, 5995. Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861. (c) Conversion to allenes: Colas, Y.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 845. (d) Conversion to α,β-unsaturated alcohols: Takai, K.; Kuroda, T.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *26*, 5585.
(19) Vercauteren, J.; Lavaud, C.; Levy, J.; Massoit, G. *J. Org. Chem.* **1984**, *49*, 2279.
(20) Fleming, I.; Perry, D. A. *Tetrahedron* **1981**, *37*, 4027.
(21) Utimoto, K.; Miwa, H.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 4277.

optically pure boronic esters via the "DCME reaction" of the derived alkynyl borinates. The ketones are obtained in uniformly high enantiomeric excess, 99%, with known absolute configuration and high chemical purity and yields. This reaction sequence is also applicable to β-heterosubstituted boronic esters, further extending the utility of this methodology.

Experimental Section

The reaction flask and other glass equipment were stored in an oven at 150 °C overnight and assembled in a stream of dry nitrogen gas. Syringes were assembled and fitted with needles while hot and cooled in a stream of dry nitrogen gas. Special experimental techniques used in handling air-sensitive materials are described in detail elsewhere.[22]

Spectra. ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The chemical shifts are in δ relative to BF_3·OEt_2. ^1H NMR (60 MHz) spectra were recorded on a Varian T-60 spectrophotometer. IR and mass spectra were recorded on Perkin-Elmer 137 and Finnegan GC/mass spectrometers, respectively. Optical rotations were measured on a Rudolph Autopol III polarimeter.

GC Analysis. All GC analyses were carried out with a Hewlett-Packard 5850 chromatograph coupled to a Hewlett-Packard 3390A integrator, using a 50-m methylsilicone column.

Materials. Anhydrous ethyl ether available from Mallinckrodt was stored over 4-Å molecular sieves under nitrogen and used without further purification. *n*-Butyllithium purchased from Alfa was estimated according to the standard procedure. α,α-Dichloromethyl methyl ether (DCME) (Aldrich) was distilled from CaH_2 and stored under nitrogen. All boronic esters were prepared according to the literature procedure.[23,24]

General Procedure for the Preparation of Chiral Ketones. A typical example is the preparation of **(1*S*,2*S*)-(+)-1-(*trans*-2-phenylcyclopentyl)-1-oxo-4,4-dimethyl-2-butyne (4).** In a 100-mL flask equipped with magnetic stirring bar and a connecting tube leading to a mercury bubbler was placed 2.3 g (10 mmol) of 2-([1*S*,2*S*]-*trans*-2-phenylcyclopentyl)-1,3,2-dioxaborinane in 10 mL of ether. To it was added 12.5 mmol of lithum 3,3-dimethylbutyne (prepared from 12.5 mmol of 3,3-dimethyl-1-butyne in 12.5 mL of EE and 12.5 mmol of *n*-butyllithium at −78 °C) dropwise at −78 °C. The reaction mixture was stirred at −78 °C for 2 h and quenched with 3.75 mL (4 M) hydrogen chloride in diethyl ether. After 0.5 h, the reaction mixture was slowly warmed to room temperature. During this period a white solid, LiCl, formed. After stirring the reaction mixture for 0.5 h at room temperature, the supernatant ether layer was transferred to another flask by a double-ended needle. The solid was washed with 2 × 10 mL of ether. The borinate (^{11}B NMR δ 40.68) thus obtained was freed of solvent at reduced pressure. The borinate was taken in 10 mL of ether and cooled to 0 °C. To it was added 1.8 mL (20 mmol) of α,α-dichloromethyl methyl ether, followed by 23.95 mL (1.67 M, 40 mmol) of lithium triethylcarboxide. After 0.5 h, the ice bath was removed and the stirring was continued for 2 h (^{11}B NMR δ 16.2). To the reaction mixture was added an excess of pH 8 phosphate buffer, followed by H_2O_2. The reaction mixture was stirred overnight. The organic layer was removed and the aqueous layer was extracted with 3 × 15 mL of ether. The combined organic layer was concentrated and triethylcarbinol was removed under reduced pressure (1 mm). The crude residue was subjected to column chromatography to yield pure ketone, 1.73 g, 68% yield: bp 150–155 °C (0.4 mmHg); $[\alpha]^{22}_D$ +123.04° (*c* 2.08, MeOH); IR (neat) 2202, 1708, 1666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (s, 5 H), 3.25 (m, 2 H), 2.4–1.06 (m, 6 H), 1.2 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 190.3, 144.1, 128.5, 127.4, 126.3, 78.9, 66.0, 61.6, 49.2, 35.8, 30.1, 29.8, 27.7, 25.4; electron impact mass spectrum, *m/e* (relative intensity) 257 (23.5), 256 (7.8), 255 (100), 254 (32.0), 239 (3.3), 197 (4.6), 149 (1.2).

(*R*)-(−)-3-Methyl-4-oxo-9-chloro-5-nonyne (1) was prepared from diisopropyl 2-butyl boronate: yield 65%, $[\alpha]^{25}_D$ −12.84° (*c* 1.89, MeOH); IR (neat) 2213, 1671 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 191.98, 92.20, 80.53, 49.99, 43.28, 30.53, 25.81, 16.44, 15.47, 11.44; chemical ionization mass spectrum, *m/e* (relative intensity) 187 (100, M + H); electron impact mass spectrum, *m/e* (relative intensity) 187 (2, M + H), 129 (100).

(*R*)-(+)-1-(3-Tetrahydrofuryl)-1-oxo-2-hexyne (2) was prepared from diethyl 3-tetrahydrofuryl boronate: yield 73%; bp 77–79 °C (0.6 mmHg); $[\alpha]^{25}_D$ +4.87° (*c* 0.9, MeOH); IR (neat) 2205, 1735, 1705, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60–4.16 (m, 4 H), 2.50–0.73 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 69.5, 68.4, 53.0, 30.9, 29.7, 28.8, 22.0, 18.7, 13.5; chemical ionization mass spectrum, *m/e* (relative intensity) 181 (100, M + H); electron impact mass spectrum, *m/e* (relative intensity) 181 (24, M + H), 109 (100), 99 (62).

(*R*)-(+)-1-(3-Tetrahydrofuryl)-1-oxo-4,4-dimethyl-2-butyne (3) was prepared as reported in general procedure using diethyl 3-tetrahydrofuryl boronate: yield 68%; bp 75–78 °C (0.6 mmHg); $[\alpha]^{25}_D$ +7.54° (*c* 0.44, MeOH); IR (neat) 2208, 1720, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.20–3.60 (m, 4 H), 2.50–2.00 (m, 3 H), 1.20 (s, 9 H); chemical ionization mass spectrum, *m/e* (relative intensity) 181 (100, M + H), 157 (28); electron impact mass spectrum, *m/e* (relative intensity) 181 (31, M + H), 137 (39), 109 (100), 99 (42), 81 (79).

(1*S*,2*S*)-(+)-1-(*trans*-2-Furylcyclopentyl)-1-oxo-6-chloro-2-hexyne (5) was prepared from propanediyl *trans*-2-furylcyclopentyl boronate: yield 70%; bp 170–175 °C (0.5 mmHg); $[\alpha]^{22}_D$ +105.34° (*c* 2.30, MeOH); IR (neat) 2214, 1710, 1668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 1 H), 6.15 (m, 2 H), 3.50 (m, 2 H),2.60–1.65 (m, 6 H), 1.60–0.8 (m, 6 H); ^{13}C NMR ($CDCl_3$) 157.1, 141.2, 110, 104.6 92.3, 80.2, 59.0, 43.2, 41.4, 32.3, 30.5, 29.5, 25.0, 16.5; electron impact mass spectrum, *m/e* (relative intensity) 267 (43), 266 (14), 265 (100).

(1*S*,2*S*)-(+)-1-(*trans*-3-Thienylcyclopentyl)-1-oxo-2-hexyne (6) was prepared from propanediyl *trans*-3-thienylcyclopentyl boronate: yield 72%; bp 145–150 °C (0.5 mmHg); $[\alpha]^{22}_D$ +92.53° (*c* 2.08, MeOH); IR (neat) 2211, 1724, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90–6.90 (m, 3 H), 3.50 (m, 1 H), 2.40–1.30 (m, 2 H), 1.25–0.8 (m, 7 H); ^{13}C NMR ($CDCl_3$) 190.3, 143.2, 127, 125.6, 119.8, 95.3, 80.4, 61.1, 44, 34.7, 29.8, 25, 21.3, 20.9, 13.5; electron impact mass spectrum, *m/e* (relative intensity) 248 (18.2), 247 (100), 237 (15.4), 211 (12.7), 179 (8.4), 151 (5.7).

General Procedure for the Determination of Optical Purity of Ketones. The ketone was dissolve in acetone (10 mL/mmol) at 0 °C and then treated dropwise with an aqueous solution of $KMnO_4$ (300 mol %) in 15 mL of 1 M phosphate buffer, pH 6.0. The dark mixture was stirred at 20 °C for 20 h and then filtered through a Celite pad which was subsequently washed with aqueous NaOH (1 M). The combined filtrate and washes were washed once with ether, acidified with 20% HCl, saturated with NaCl, and extracted with ether (3 × 5 mL), and the extracts were dried. Filtration and removal of solvent gave the corresponding acid. The acid (0.02 mmol) was coupled to (*S*)-(−)-α-methylbenzylamine (0.02 mmol) in the presence of DCC (0.02 mmol) in THF to give the desired amide. The crude amide was taken up in ether and analyzed by capillary GC.

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Registry No. **1**, 113163-05-6; **1** (boronic ester), 113163-02-3; **2**, 113163-06-7; **2** (boronic ester), 100858-36-4; **3**, 113163-07-8; **4**, 113163-08-9; **4** (boronic ester), 97235-26-2; **5**, 113163-09-0; **5** (boronic ester), 113163-03-4; **6**, 113163-10-3; **6** (boronic ester), 113163-04-5; DCME, 4885-02-3; (*R*)-EtCh(Me)B(OPr-*i*)C≡C-$(CH_2)_3Cl$, 113163-11-4; $Et_3COB(OPr\text{-}i)CCl(CHMeEt)C{\equiv}C\text{-}(CH_2)_3Cl$, 113163-12-5; $LiC{\equiv}C(CH_2)_3Cl$, 63220-92-8; $LiC{\equiv}C(CH_2)_2CH_3$, 18643-50-0; $LiC{\equiv}CC(CH_3)_3$, 37892-71-0.

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