  Bull. Chem. Soc. Jpn., 61, 93—100 (1988)

Invited Paper

Chiral Synthesis via Organoboranes. 11. Hydroboration. 82. Asymmetric Hydroboration of 1-Heteroarylcycloalkenes with Monoisopinocampheylborane. Synthesis of *trans*-2-Heteroarylcycloalkyl Boronates and Derived Alcohols of Very High Enantiomeric Purity

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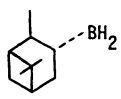
(Received May 28, 1987)

The hydroboration of representative 1-heteroarylcycloalkenes with monoisopinocampheylborane ($IpcBH_2$) was investigated systematically to establish the degree of asymmetric induction during hydroboration. The hydroboration of 1-heteroarylcyclopentene with $IpcBH_2$ at −25 °C proceeded cleanly to afford the corresponding dialkylboranes. These dialkylboranes, upon treatment with acetaldehyde and then oxidation, afforded the corresponding *trans*-2-heteroarylcycloalkanols of 85—86% ee. Similarly, 1-heteroarylcyclohexenes, upon hydroboration with $IpcBH_2$, followed by acetaldehyde treatment and oxidation, gave the corresponding alcohols in ca. 90% ee. The dialkylboranes or alkylboronic acids derived from 1-heteroarylcyclopentenes and $IpcBH_2$ can be recrystallized to furnish materials approaching 100% ee. From such dialkylboranes or alkylboronic acids, the corresponding boronates of ca. 100% ee were prepared and isolated. These are proving to be highly versatile synthetic intermediates for organic synthesis.

Asymmetric hydroboration, since its discovery in 1961,[2)] proved to be a highly efficient reaction in synthetic organic chemistry.[3)] Recently there has been intense interest in developing efficient methods for the preparation of organic compounds of high enantiomeric purities.[4)] Of these procedures, asymmetric hydroboration is highly promising as a method for preparation of chiral compounds containing various functional groups.[5)]

Monoisopinocampheylborane (**1**, $IpcBH_2$) hydroborates *trans*- and trisubstituted olefins with optical induction ranging from 53% to 100% ee.[6)] The dialkylboranes derived from $IpcBH_2$ and trisubstituted olefins were crystallized to materials approaching 100% ee.[7)] Recently heterocyclic olefins containing a double bond inside the ring were hydroborated with diisopinocampheylborane (**2**, Ipc_2BH) with quantitative asymmetric induction.[8,9a)] Masamune and coworkers[10)] have recently synthesized an asymmetric hydroborating agent, *trans*-2,5-dimethylborolane (**3**)



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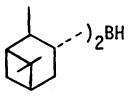

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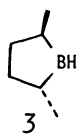


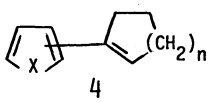
3

possessing a C_2 symmetry, which hydroborates *cis*-, *trans*- and trisubstituted olefins with an asymmetric induction ranging from 93—97% ee.

The wide range of biological activity, e.g., antitumor, carcinogenic, microbial growth inhibitor, plant growth inhibitor, antifeedant and antiflammatory displayed by a number of compounds possessing the furan and thiophene moiety has stimulated considerable effort to synthesize them.[11)] In continuation of our studies on the asymmetric hydroboration of heterocyclic olefins,[8,9)] various 1-heteroarylcycloalkenes were selected for study. This paper describes a systematic study of the hydroboration of 1-heteroarylcycloalkenes with $IpcBH_2$ to synthesize various chiral heterocyclic compounds.

Results and Discussion

In this study we consistently used monoisopinocampheylborane ($IpcBH_2$, 100% ee) from 92% ee (+)-α-pinene. A stock solution of $IpcBH_2$ was prepared from the TMED adduct of $IpcBH_2$ and boron trifluoride etherate in ethyl ether.[12)] Representative 1-heteroarylcycloalkenes (**4**) were selected for the



4

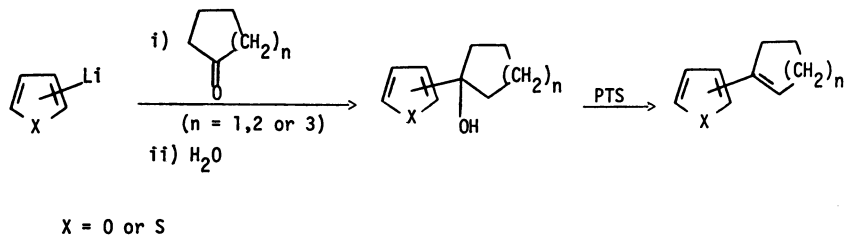
X = O or S

n = 1, 2 or 3

study. These alkenes, **4**, hitherto unreported, were prepared by the dehydration of the corresponding tertiary alcohols obtained from the addition of the heteroaryllithium to the cyclic ketone (Scheme 1). The olefins thus obtained were characterized by spectra and were 97—100% pure by GC examination.

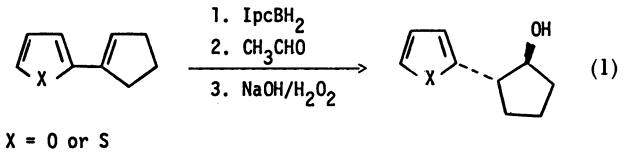
Hydroboration of 1-Heteroarylcycloalkenes with $IpcBH_2$. All of these representative olefins were hydroborated with an equimolar quantity of $IpcBH_2$. The reaction was monitored by quenching aliquots with methanol, followed by ^{11}B NMR spectra of the sample.

Hydroboration of 1-(2-Furyl)cycloalkenes. 2-Furylcycloalkenes of varying ring size were hydroborated



Scheme 1.

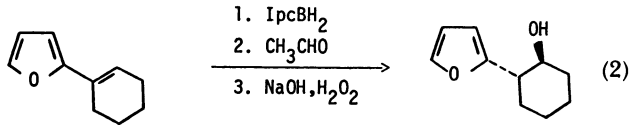
with $IpcBH_2$ in order to study the effect of ring size on asymmetric induction during hydroboration. The hydroboration of 1-(2-furyl)cyclopentene with (−)-$IpcBH_2$ [derived from (+)-α-pinene] proceeded smoothly at −25 °C in ethyl ether. The dialkylborane obtained was treated with acetaldehyde, then oxidation with alkaline hydrogen peroxide afforded *trans*-2-(2-furyl)cyclopentanol in excellent yield (Eq. 1, X=O).



(1)

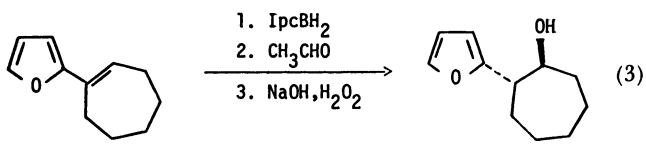
The optical purity of the alcohol by capillary GC analysis of its corresponding MTPA ester[13] was found to be of 86%.

The hydroboration of 1-(2-furyl)cyclohexene with (−)-$IpcBH_2$ proceeded slowly at −25 °C, achieving a 65% conversion in 10 days. The dialkylborane thus obtained was treated with acetaldehyde, followed by oxidation, affording *trans*-2-(2-furyl)cyclohexanol in 90% ee (Eq. 2). By increasing the temperature, i.e., to



(2)

0 °C, employed during hydroboration, 80% of the olefin could be hydroborated. However, the optical purity of the alcohol obtained after oxidation is lower, i.e., 80% ee. Similarly, 1-(2-furyl)cycloheptene could be hydroborated at −25 °C easily. Treatment with acetaldehyde, followed by oxidation, gave *trans*-2-(2-furyl)cycloheptanol in excellent yield (Eq. 3), with an

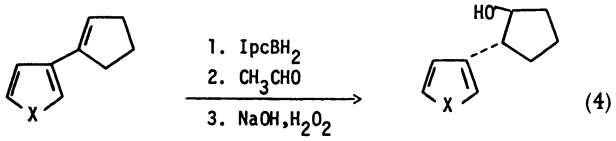


(3)

optical purity of the alcohol of 86%.

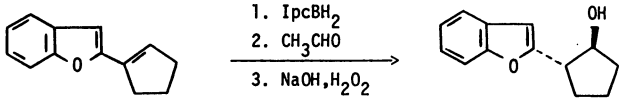
The asymmetric induction during hydroboration of 1-heteroarylcycloalkenes with $IpcBH_2$ increases slightly from the five-membered ring to the six-membered ring. The asymmetric induction in the seven-membered ring is, as expected, similar to that of the five-membered ring. Since the hydroboration of these cyclopentenes and cyclohexenes gave products with excellent asymmetric induction, various 1-heteroarylcyclopentenes and -cyclohexenes were hydroborated with $IpcBH_2$.

Hydroboration of 1-Heteroarylcyclopentenes. The hydroboration of 1-(3-furyl)cyclopentene with $IpcBH_2$ could be achieved at −25 °C. The dialkylborane obtained on treatment with acetaldehyde and then oxidation afforded *trans*-2-(3-furyl)cyclopentanol in 85% ee (Eq. 4, X=O). Similarly, 1-(2-thienyl)cyclopentene and 1-(3-thienyl)cyclopentene were hydroborated with $IpcBH_2$. The asymmetric induction during hydroboration was found to be 86% ee in both cases (Eqs. 1 and 4, X=S).



(4)

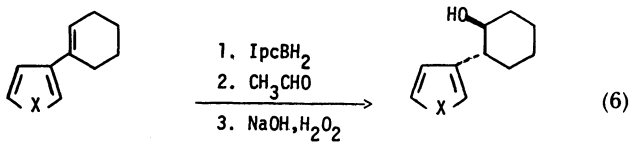
The hydroboration of 1-(2-benzofuryl)cyclopentene proceeded slowly at −25 °C. The dialkylborane was treated with acetaldehyde, followed by oxidation with alkaline hydrogen peroxide, giving *trans*-2-(2-benzofuryl)cyclopentanol in 85% ee (Eq. 5).



(5)

These results demonstrate the remarkable consistency in the asymmetric induction of these heterocyclic cyclopentenes during hydroboration with $IpcBH_2$. No significant change was observed in the asymmetric induction achieved during hydroboration with $IpcBH_2$, either by changing the heteroatom in the heterocycle (O or S), or by changing the position of the cyclopentene ring (2- or 3-position), or by altering substituents on the heteroaryl ring.

Hydroboration of 1-Heteroarylcyclohexenes. The hydroboration of 1-(3-furyl)cyclohexene proceeded similar to that of 1-(2-furyl)cyclohexene at −25 °C. The dialkylborane was treated with acetaldehyde and then oxidized to obtain *trans*-2-(3-furyl)cyclohexanol in 90% ee (Eq. 6, X=O). Similarly, 1-(3-thienyl)-



(6)

X = O or S

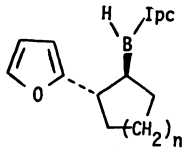
cyclohexene (Eq. 6, X=S) upon hydroboration with $IpcBH_2$, followed by acetaldehyde treatment, gave the boronic ester. Oxidation then afforded the corresponding *trans*-alcohol in 83% ee. The results are summarized in Table 1.

The absolute configuration of all product alcohols is not known. It was already established that $IpcBH_2$ attacks preferentially from one enantiotopic face of the alkene, realizing the alcohols of the same absolute configuration. Thus, the remarkable consistency of $IpcBH_2$ providing alcohols of the same absolute configuration was used to assign the absolute configurations of all of these alcohols. They are shown in Table 1.

Upgrading the Optical Purities of Boranes. In all of the above examples, only 83—90% of asymmetric induction could be achieved. It is highly desirable to have materials approaching 100% ee. We selected the 2-heteroarylcyclopentylboranes to study upgrading to materials of essentially 100% ee.

The above mentioned *trans*-2-heteroarylcyclopentylisopinocampheylboranes[14] were found to be solids at −25 °C in ethyl ether. For example, *trans*-2-(2-furyl)cyclopentylisopinocampheylborane (**4**), obtained via hydroboration of 1-(2-furyl)cyclopentene with $IpcBH_2$ at −35 °C, crystallized in a well-defined form in 65% yield. The dialkylborane on oxidation produced *trans*-2-(2-furyl)cyclopentanol of essentially 100% optical purity.

Similarly, the selective crystallization of *trans*-2-(3-furyl)cyclopentylisopinocampheylborane (**5**) at −35 °C provided material of only 90% ee. However, a second crystallization in ethyl ether at 0 °C gave material approaching 100% ee.



4, n = 1
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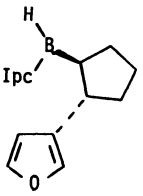

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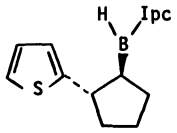
trans-2-(2-Thienyl)cyclopentylisopinocampheylborane (**6**) from 1-(2-thienyl)cyclopentene and $IpcBH_2$ showed unusual behavior. Although it is a dimer like the others (as evidenced by IR absorption at 1542 cm^{-1}), the major enantiomer accumulated in the mother liquor. The crystallized dialkylborane, **6**, showed reduced optical purity of only 7%. The dialkylborane in the mother liquor showed an optical purity of only 90%. It was further upgraded to 94% by cooling the reaction mixture to −78 °C, followed by the removal of crystalline borane. However, a



6

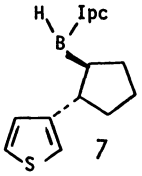


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Table 1. Asymmetric Hydroboration of 1-Heteroarylcycloalkenes with (−)-$IpcBH_2$[a]

Olefin	Product	Reaction temp °C	Reaction time Days	Isolated yield[b] %	$[\alpha]_D$ in degrees	% ee[c]	Absolute configuration
1-(2-Furyl)cyclopentene	*trans*-2-(2-Furyl)cyclopentanol	−25	4	82	+75.6 (*c* 2.2, MeOH)	86	1S, 2S
1-(2-Furyl)cyclohexene	*trans*-2-(2-Furyl)cyclohexanol	−25	10	70	+53.04 (*c* 1.8, MeOH)	90	1S, 2S
1-(2-Furyl)cycloheptene	*trans*-2-(2-Furyl)cycloheptanol	−25	4	80	+30.04 (*c* 2.4, MeOH)	86	1S, 2S
1-(3-Furyl)cyclopentene	*trans*-2-(3-Furyl)cyclopentanol	−25	4	84	+52.3 (*c* 2.2, MeOH)	85	1S, 2R
1-(3-Furyl)cyclohexene	*trans*-2-(3-Furyl)cyclohexanol	−25	10	77	+37.6 (*c* 2.1, MeOH)	90	1S, 2R
1-(2-Thienyl)cyclopentene	*trans*-2-(2-Thienyl)cyclopentanol	−25	4	86	+60.95 (*c* 2.3, MeOH)	86	1S, 2S
1-(3-Thienyl)cyclopentene	*trans*-2-(3-Thienyl)cyclopentanol	−25	3	89	+63.7 (*c* 2.05, MeOH)	86	1S, 2R
1-(3-Thienyl)cyclohexene	*trans*-2-(3-Thienyl)cyclohexanol	−25	10	84	+31.93 (*c* 1.45, MeOH)	83	1S, 2R
1-(2-Benzofuryl)cyclopentene	*trans*-2-(2-Benzofuryl)-pentanol	−25	10	71	+48.6 (*c* 2.74, MeOH)	85	1S, 2S

a) The reagent was prepared from (+)-α-pinene $[\alpha]_D^{25}$ +47.2 (neat), 92% ee and BMS. b) Based on the amount of olefin. c) Determined by capillary GC analysis of the corresponding Mosher ester.

material of ca. 99% optical purity could be obtained by crystallizing its *trans*-2-(2-thienyl)cyclopentylboronic acid. *trans*-2-(3-Thienyl)cyclopentylisopinocampheylborane (**7**) crystallized at −35 °C, similar to **4**, to produce a material approaching 100% ee.

Further, in the case of *trans*-2-(2-furyl)cyclohexylisopinocampheylborane (**8**) and *trans*-2-(2-furyl)cycloheptylisopinocampheylborane (**9**), the dimer, $(R^*BHIpc)_2$, was not crystalline. The products are readily converted into boronic acid, $R^*B(OH)_2$, by treatment with acetaldehyde, followed by hydrolysis. A simple crystallization of these boronic acids in ether/pentane provided material of high optical purity. The corresponding *trans*-alcohols obtained after oxidation of these pure dialkylboranes or alkyl boronic acid were characterized and the results are summarized in Table 2.

Isolation of *trans*-3-Heteroarylcycloalkylboronates of High Enantiomeric Purities. Chiral alkylboronic esters containing only one alkyl group attached to boron are highly promising intermediates for asymmetric synthesis proceeding through boron

Table 2. *trans*-2-Heteroarylcycloalkanols of High Enantiomeric Purity

Heterocycloalkanols	Yield %	$[\alpha]_D$ in degree	% ee[a)]	Absolute configuration
trans-2-(2-Furyl)cyclopentanol	70	+88.2 (*c* 2.325, MeOH)	99	1S, 2S
trans-2-(3-Furyl)cyciopentanol	60	+60.6 (*c* 2.29, MeOH)	99	1S, 2R
trans-2-(2-Thienyl)cyclopentanol	64	+70.6 (*c* 2.35, MeOH)	99	1S, 2S
trans-2-(3-Thienyl)cyclopentanol	65	+73.01 (*c* 2.32, MeOH)	99	1S, 2R
trans-2-(2-Furyl)cyclohexanol	55	+58.2 (*c* 1.8, MeOH)	98	1S, 2S
trans-2-(2-Furyl)cycloheptanol	70	+34.9 (*c* 2.4, MeOH)	99	1S, 2S

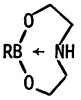
a) Determined by capillary GC analysis of the corresponding Mosher ester.

Table 3. Diethyl *trans*-2-Heteroarylcycloalkylboronates of High Enantiomeric Purity

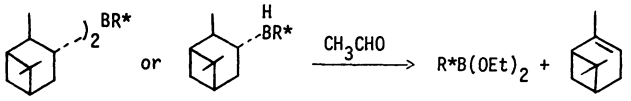
Boronic ester $R^*B(OEt)_2$	Yield %	$[\alpha]_D$ in degree	% ee	Absolute configuration	^{11}B NMR chemical shift δ[a)]
Diethyl *trans*-2-(2-furyl)cyclopentylboronate	60	+51.58 (*c* 2.52, EtOH)	99	1S, 2S	+31.4
Diethyl *trans*-2-(3-furyl)cyclopentylboronate	50	+41.34 (*c* 2.38, EtOH)	99	1S, 2R	+31.4
Diethyl *trans*-2-(2-thienyl)cyclopentylboronate	64	+36.10 (*c* 2.535, EtOH)	99	1S, 2S	+30.9
Diethyl *trans*-2-(3-thienyl)cyclopentylboronate	50	+46.72 (*c* 2.50, EtOH)	99	1S, 2R	+31.4
Diethyl *trans*-2-(2-furyl)cyclohexylboronate	35	+36.2 (*c* 2.10, EtOH)	98	1S, 2S	+31.3
Diethyl *trans*-2-(2-furyl)cycloheptylboronate	45	+24.6 (*c* 2.40, EtOH)	99	1S, 2S	+31.7

a) Relative to $EE\cdot BF_3$ ($\delta=0$).

Table 4. Diethanolamine *trans*-2-Heteroarylcycloalkylboronates of High Optical Purity

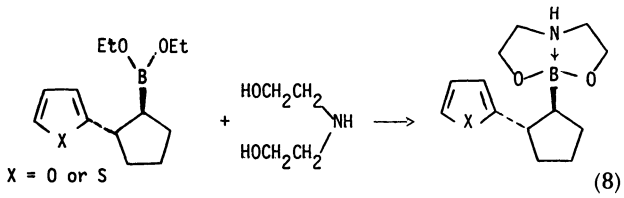
Boronic ester 	Yield %	Mp θ_m/°C	% ee	Absolute configuration	*m/z* M^+ 1
Diethanolamine *trans*-2-(2-furyl)-cyclopentylboronate	80	101—102	99	1S, 2S	250
Diethanolamine *trans*-2-(3-furyl)-cyclopentylboronate	85	160—161	99	1S, 2R	250
Diethanolamine *trans*-2-(2-thienyl)-cyclopentylboronate	85	128—130	99	1S, 2S	250
Diethanolamine *trans*-2-(3-thienyl)-cyclopentylboronate	86	153—154	99	1S, 2R	250
Diethanolamine *trans*-2-(2-furyl)-cyclohexylboronate	87	152—153	98	1S, 2S	264
Diethanolamine *trans*-2-(2-furyl)-cycloheptylboronare	90	157—158	99	1S, 2S	278

chemistry.[5,15,16] Previously, Brown, Jadhav and Desai[17] established the clean elimination of α-pinene from Ipc_2BR^* and IpcBHR* by treatment with acetaldehyde, giving $R^*B(OEt)_2$ without loss of optical activity (Eq. 7). A similar procedure provided



(7)

trans-2-heteroarylcycloalkylboronates. Simple distillation provided a pure boronate, characterized by ^{11}B NMR and ^1H NMR. The results are summarized in Table 3. From these esters, optically pure crystalline chelate esters stable in air were prepared by treating the ethyl boronates with diethanolamine (Eq. 8). From such derivatives, the corresponding boronic



(8)

acid can be easily regenerated by treating with hydrochloric acid.[18] These crystalline compounds showed a correct M^+ ion in the mass spectra. The results are summarized in Table 4.

Conclusion

The present method provides a simple and efficient method for the preparation of various *trans*-2-heteroarylcycloalkanols of high enantiomeric purity. Due to the availability of both enantiomers of α-pinene, both enantiomers of the heterocycles can be synthesized. The chiral auxiliary, α-pinene, can be recovered and recycled. The isolation of heterocyclic boronates of 100% ee provides a simple route to synthesize various heterocycles containing different functional groups in essentially 100% ee. The synthetic implications of such optically pure boronates are described elsewhere.[5] Moreover, using the known chemistry, these heterocycles can be converted to various other compounds.

Experimental

The reaction flasks 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.[19]

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

GC Analysis. All GC analyses were carried out with a Hewlett Packard 5750 chromatograph using (a) 12 ft×0.125 in column packed with 10% Carbowax 20 M on Chromosorb W (100—120 mesh) or (b) 12 ft×0.125 in column packed with 10% SE-30 on Chromosorb W (100—120 mesh). For preparative GC, either (c) a 6 ft×0.5 in column packed with 20% Carbowax 20 M on Chromosorb W (60—80 mesh) or (d) a 6 ft×0.5 in column packed with 20% SP-2100 on Chromosorb W (60—80 mesh) was used.

Materials. Borane-methyl sulfide (BMS) purchased from Aldrich Chemical Company was estimated according to the standard procedure.[19] (+)-α-Pinene $[\alpha]_D^{23}$ +47.2° (neat) was purchased from Aldrich Chemical Company and distilled from a small excess of LAH. Anhydrous ethyl ether available from Mallinckrodt, Inc. was used directly. *N,N,N',N'*-Tetramethylethylenediamine (TMED) was distilled over excess calcium hydride. Tetrahydrofuran (THF) was distilled over anhydrous benzophenone ketyl and stored under nitrogen atmosphere in an ampule. The bis adduct of monoisopinocampheylborane with tetramethylethylenediamine (TMED·2IpcBH$_2$) and generation of (−)-IpcBH$_2$ of 100% ee from it was done as reported in the literature.[12]

Preparation of 1-Heteroarylcycloalkenes. Preparation of Tertiary Alcohols. Tertiary alcohols were prepared according to a similar procedure reported in the literature.[20] To a cooled (0 °C) solution of 16.32 g (240 mmol) of furan and ether (200 mL) was added *n*-BuLi in hexane, 76.8 mL (176 mmol) dropwise. The resulting mixture was stirred at 0 °C for 1 h, after which was added an ethereal solution of the corresponding ketone (152 mmol). After being stirred overnight, the reaction mixture was quenched with water (10 mL). The ether layer was decanted, dried ($MgSO_4$) and the solvent was removed under reduced pressure.

Preparation of 1-Heteroarylcycloalkenes. The crude alcohol taken in 100 mL benzene was treated with catalytic amount of *p*-toluenesulfonic acid for about 30 min at 40—50 °C. The benzene layer was dried over anhydrous K_2CO_3 and distilled to give the required olefins in 80—90% overall yield and >97% GC pure.

1-(2-Furyl)cyclopentene. Bp 60—61°/3.5 mmHg, n_D^{21} 1.5400, IR (neat in cm^{-1}) 2953, 2928, 2847, 1481, 1331, 992, 950, 914, 793, 732. ^1H NMR ($CDCl_3$) δ=1.75—2.80 (6H, m), 5.90—6.45 (3H, m), 7.35 (1H, m). Mass spectrum *m/z* 134 (M^+).

1-(2-Furyl)cyclohexene. Bp 76—77°/2.5 mmHg, n_D^{21} 1.5242, IR (neat in cm^{-1}), 2931, 2860, 2837, 1490, 1437, 1154, 1021, 1005, 793, 732. ^1H NMR ($CDCl_3$) δ=1.40—2.60 (8H, m), 6.10—6.60 (3H, m), 7.30 (1H, m). Mass spectrum *m/z* 148 (M^+).

1-(2-Furyl)cycloheptene. Bp 70—72 °C/1.0 mmHg, n_D^{21} 1.5380, IR (neat in cm^{-1}) 2920, 2851, 1447, 1354, 1156, 1015, 790, 730. ^1H NMR ($CDCl_3$) δ=1.40—2.45 (10H, m), 6.05—6.40 (3H, m), 7.30 (1H, m). Mass spectrum *m/z* 162 (M^+).

1-(2-Thienyl)cyclopentene. Bp 68—70°/0.2 mmHg, n_D^{21} 1.5940, IR (neat in cm^{-1}) 2951, 2925, 2894, 2844, 1434, 1330, 1256, 852, 822, 798, 694. ^1H NMR ($CDCl_3$) δ=1.80—2.80 (6H, m), 6.0 (1H, m), 6.80—7.15 (3H, m). Mass spectrum *m/z* 150 (M^+).

1-(2-Benzofuryl)cycloheptene. Mp 72—73 °C, IR (KBr in cm^{-1}) 2948, 2945, 2891, 1446, 1437, 1251, 791, 746. ^1H NMR ($CDCl_3$) δ=1.8—2.25 (2H, m), 2.30—2.90 (4H, m), 6.3—6.6

(2H, bs), 7.1—7.7 (4H, m). Mass spectrum m/z 184 (M^+).

Preparation of 1-(3-Furyl/3-Thienyl)cycloalkenes. Following the general procedure used to prepare 3-furyl- or 3-thienyl-substituted cycloalkenes, 3-bromofuran or 3-bromothiophene (120 mmol) was taken in a 250-mL flask along with 150 mL of ether. It was cooled to −78 °C under N_2 and n-BuLi (144 mmol) was added dropwise. The reaction mixture was stirred at −78 °C for 1 h after which was added the corresponding ketone (120 mmol) slowly. It was further stirred 1 h at −78 °C, warmed to room temperature and quenched with water (10 mL). The ether layer was decanted, dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product directly taken in benzene (100 mL) and treated with catalytic amount of p-toluenesulfonic acid for 30 min at 40—50 °C. The benzene layer was dried over anhydrous K_2CO_3 and distilled to give the corresponding olefins in 75—90% overall yield.

1-(3-Furyl)cyclopentene. Bp 88—90°/3.0 mmHg, n_D^{21} 1.5080, IR (neat on cm^{-1}) 2955, 2871, 1732, 1506, 1449, 1157, 1046, 1022, 1005, 905, 873, 784. ^1H NMR ($CDCl_3$) δ=1.35—2.80 (6H, m), 5.90 (1H, m), 6.55 (1H, m), 7.40 (2H, m). Mass spectrum m/z 134 (M^+).

1-(3-Furyl)cyclohexene. Bp 58—60°/0.3 mmHg, n_D^{21} 1.5100, IR (neat in cm^{-1}) 2990, 2920, 1580, 1480, 1190, 1170, 1090, 1070, 1000, 950, 905, 810, 760. ^1H NMR ($CDCl_3$) δ=1.30—2.40 (8H, m), 6.0 (1H, m), 6.50 (1H, m), 7.30 (2H, m). Mass spectrum m/z 148 (M^+).

1-(3-Thienyl)cyclopentene. Mp 59—60 °C. IR (Nujol in cm^{-1}) 2904, 2676, 1745, 1716, 1515, 1464, 1419, 1377, 1318, 1294, 1083, 1035, 954, 866, 838, 770, 722. ^1H NMR ($CDCl_3$) δ=1.80—2.80 (6H, m), 5.95 (1H, m), 6.80—7.25 (3H, m). Mass spectrum m/z 150 (M^+).

1-(3-Thienyl)cyclohexene. Bp 78—84°/0.05 mmHg, n_D^{21} 1.5650. IR (neat in cm^{-1}) 2927, 2857, 2833, 1447, 1435, 869, 841, 770, 714, 633. ^1H NMR ($CDCl_3$) δ=1.30—2.50 (8H, m), 6.15 (1H, m), 6.90—7.30 (3H, m). Mass spectrum m/z 164 (M^+).

Hydroboration of 1-(2-Furyl)cyclopentene. In a 250-mL flask equipped with septum inlet, magnetic stirring bar and a connecting tube leading to a mercury bubbler was placed 30 mL (25 mmol) of $IpcBH_2$ in ethyl ether and this was cooled to −25 °C. To the reaction flask was added with stirring 3.35 g (25 mmol) of 1-(2-furyl)cyclopentene over a period of 5 min. The reaction mixture was allowed to stir at −25 °C for 4 days. After completing the reaction (^{11}B NMR), the reaction flask was brought to 0 °C and 5.6 mL (10 mmol) of acetaldehyde was added dropwise and stirred at 25 °C for 6 h. Excess acetaldehyde was removed under reduced pressure (25 °C, 15 mmHg, 1 h) and to it 10 mL of THF was added. The boronate thus obtained was oxidized with 25 mL of 3 M sodium hydroxide and 3.7 mL of 30% H_2O_2. The reaction mixture was stirred at 25 °C for 5 h. The aqueous layer was saturated with potassium carbonate and extracted with 3×25 mL of ether, dried over $MgSO_4$ and the ether evaporated. The residue was passed through silica-gel column. The pentane eluent removed α-pinene, 5% ether in pentane removed unreacted olefins whereas the ether·pentane (20:80) afforded the alcohol, which, upon distillation, yielded 3.1 g of (1*S*,2*S*)-*trans*-2-(2-furyl)cyclopentanol, by 67—70°/0.02 mmHg, 82% isolated yield. GC purity >98%. It was further purified by preparative GC column c to furnish a GC pure material $[\alpha]_D^{23}$ +76.66° (*c* 2.215, MeOH), n_D^{21} 1.5065, 86% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3358, 2959, 2975, 1594, 1504, 1451, 1147, 1069, 1045, 1010, 992, 800. ^1H NMR ($CDCl_3$) δ=1.80 (6H, m), 2.40 (1H, s), 3.0 (1H, m), 4.20 (1H, m), 6.0 (1H, m), 6.2 (1H, m), 7.25 (1H, m). Mass spectrum m/z 152 (M^+).

Hydroboration of 1-(2-Furyl)cyclohexene. With the usual experimental setup, 3.70 g (25 mmol) of 1-(2-furyl)cyclohexene was added dropwise to 35 mL (25 mmol) of $IpcBH_2$ in ethyl ether at −25 °C. The contents were stirred for 10 days at −25 °C and (5.6 mL) of acetaldehyde was added dropwise and stirred further for 6 h at room temperature. The boronate thus obtained was oxidized, worked up as usual, and purified by column chromatography as described in earlier cases to give 2.9 g of pure (1*S*,2*S*)-(+)-*trans*-2-(2-furyl)cyclohexanol, bp 75—80°/0.02 mmHg, 70% isolated yield. It was further purified by preparative GC column c to give GC pure material $[\alpha]_D^{23}$ +53.04 (*c* 1.795, MeOH), n_D^{21} 1.5080, 90% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 2931, 2858, 1591, 1448, 1170, 1146, 1122, 1060, 1009, 921, 802, 730. ^1H NMR ($CDCl_3$) δ=1.30—2.25 (8H, m), 2.40 (2H, m), 3.60 (1H, m), 6.0—6.40 (2H, m), 7.35 (1H, m). Mass spectrum m/z 166 (M^+).

Hydroboration of 1-(2-Furyl)cycloheptene. With the usual experimental setup, 4.05 g (25 mmol) of 1-(2-furyl)cycloheptene was added dropwise to 35 mL (25 mmol) of (−)-$IpcBH_2$ at −25 °C. The reaction mixture was stirred at −25 °C for 4 days. To the dialkylborane thus obtained was added 5.6 mL of acetaldehyde and the contents stirred 5 h at 25 °C. The excess of acetaldehyde was pumped off and the reaction mixture oxidized and worked up as described above to give 3.6 g of (1*S*,2*S*)-(+)-*trans*-2-(2-furyl)cycloheptanol, bp 78—80°/0.01 mmHg, 80% isolated yield. $[\alpha]_D^{21}$ +30.04 (*c* 2.43, MeOH), n_D^{21} 1.5115, 86% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3400, 2928, 2860, 1502, 1457, 1444, 1146, 1046, 1024, 1010, 729. ^1H NMR ($CDCl_3$) δ=1.70 (10H, m), 2.0 (1H, s), 2.80 (1H, m), 3.85 (1H, m), 6.10 (1H, m), 6.30 (1H, m), 7.30 (1H, m). Mass spectrum m/z 180 (M^+).

Hydroboration of 1-(2-Thienyl)cyclopentene. With the usual experimental setup, 3.75 g (25 mmol) of 1-(2-thienyl)cyclopentene was added dropwise to 35 mL (25 mmol) of (−)-$IpcBH_2$ at −25 °C. The reaction mixture was stirred for 4 days at −25 °C. The dialkylborane thus obtained was worked up as usual, as described above, to give 3.6 g of distilled (1*S*,2*S*)-(+)-*trans*-2-(2-thienyl)cyclopentanol, bp 88—91°/0.02 mmHg, 86% isolated yield. n_D^{21} 1.5600. It was further purified by preparative GC to give pure product $[\alpha]_D^{22}$ 60.95 (*c* 2.3, MeOH), 86% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3363, 2956, 2872, 1439, 1339, 1237, 1081, 1037, 824, 694. ^1H NMR ($CDCl_3$) δ=1.70—2.40 (7H, m), 3.10 (1H, m), 4.10 (1H, m), 6.80—7.30 (3H, m). Mass spectrum m/z 168 (M^+).

Hydroboration of 1-(3-Furyl)cyclopentene. With the usual experimental setup, 3.35 g of 1-(3-furyl)cyclopentene was added dropwise to 35.7 mL (25 mmol) of (−)-$IpcBH_2$ in ethyl ether at −25 °C. The contents after stirring for 4 days at −25 °C were worked up as usual and purified as described above to give 3.17 g of (1*S*,2*R*)-(+)-*trans*-2-(3-furyl)cyclopentanol, bp 75—80°/0.05 mmHg, 84% isolated yield. $[\alpha]_D^{22}$ +52.3 (*c* 2.2, MeOH), 85% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3357, 2956, 2874, 1500, 1468, 1450, 1340, 1161, 1090, 1064, 1025, 814, 726. ^1H NMR ($CDCl_3$) δ=1.60—2.30 (6H, m), 2.70 (2H, m), 4.05 (1H, m), 6.35 (1H,

bs), 7.40 (2H, m). Mass spectrum *m/z* 152 (M^+).

Hydroboration of 1-(3-Thienyl)cyclopentene. With the usual experimental setup, 3.75 g (25 mmol) of 1-(3-thienyl)cyclopentene (in 5 mL of ether) was added dropwise to 30 mL (25 mmol) of (−)-IpcBH$_2$ at −25 °C. After stirring for 3 days at −25 °C, it was treated with acetaldehyde and worked up as described above to give 3.75 g of (1*S*,2*S*)-(+)-*trans*-2-(3-thienyl)cyclopentanol, bp 90—91 °C/0.04 mmHg, 89% isolated yield. It was further purified by preparative GC column c to give GC pure product n_D^{21} 1.5620, $[\alpha]_D^{22}$ +63.7 (*c* 2.05, MeOH), 86% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3357, 2955, 2871, 1449, 1411, 1082, 1045, 844, 776, 645. ^{1}H NMR ($CDCl_3$) δ=1.4—2.35 (7H, m), 2.90 (1H, m), 4.0 (1H, m), 6.70—7.30 (3H, m). Mass spectrum *m/z* 168 (M^+).

Hydroboration of 1-(2-Benzofuryl)cyclopentene. With the usual experimental setup, 4.6 g (25 mmol) of 1-(2-benzofuryl)cyclopentene in 5 mL of ether was added dropwise to 30 mL (25 mmol) of (−)-IpcBH$_2$ at −25 °C. The reaction mixture was stirred at −25 °C for 10 days and worked up as described above to give 3.6 g of (1*S*,2*S*)-(+)-*trans*-2-(2-benzofuryl)cyclopentanol, bp 115—120 °C/0.02 mmHg isolated yield 71%, $[\alpha]_D^{22}$ +48.6° (*c* 2.74, MeOH), 85% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3381, 2954, 2872, 1476, 1450, 1439, 1260, 1177, 1054, 787, 768, ^{1}H NMR ($CDCl_3$) δ=1.40—2.40 (6H, m), 2.90—3.40 (2H, m), 4.10—4.70 (2H, m), 6.60—7.10 (4H, m).

Hydroboration of 1-(3-Furyl)cyclohexene. With the usual experimental setup, 3.7 g (25 mmol) of 1-(3-furyl)cyclohexene was added dropwise to 35 mL (25 mmol) of (−)-IpcBH$_2$ at −25 °C. The reaction mixture was stirred at −25 °C for 10 days and worked up, purified as described above to give 3.2 g of (1*S*,2*R*)-(+)-*trans*-2-(3-furyl)cyclohexanol, bp 85—90 °C/0.02 mmHg, 77% isolated yield. It was further purified by capillary GC column c to give GC pure alcohol $[\alpha]_D^{22}$ +37.6° (*c* 2.11, MeOH), 90% ee by capillary GC of its Mosher ester. IR (neat in cm^{-1}) 3427, 2929, 2856, 1498, 1447, 1344, 1159, 1119, 1059, 1025, 736. ^{1}H NMR ($CDCl_3$) δ=1.20—2.0 (9H, m), 2.15 (1H, s), 4.0 (1H, m), 6.45 (1H, bs), 7.40 (2H, m). Mass spectrum *m/z* 166 (M^+).

Hydroboration of 1-(3-Thienyl)cyclohexene. With the usual experimental setup, 4.1 g (25 mmol) of 1-(3-thiethyl)-cyclohexene was added dropwise to 35 mL (25 mmol) of (−)-IpcBH$_2$ in ether at −25 °C. The contents, after being stirred for 10 days at −25 °C, were treated with excess acetaldehyde, worked up as usual to give 3.82 g of (1*S*,2*R*)-(+)-*trans*-2-(3-thienyl)cyclohexanol, bp 95—100 °C/0.02 mmHg, 84% isolated yield. It was further purified by preparative GC to give GC pure product $[\alpha]_D^{20}$ +31.93° (*c* 1.450, MeOH), 83% ee by capillary GC of its Mosher ester. IR (Nujol in cm^{-1}) 3272, 2928, 1465, 1378, 1350, 1232, 1063, 787, 722. ^{1}H NMR ($CDCl_3$) δ=1.30—2.0 (8H, m), 2.20 (1H, s), 2.60 (1H, m), 3.50 (1H, m), 6.80—7.45 (3H, m). Mass spectrum *m/z* 182 (M^+).

General Procedure for Upgrading and Isolation of Boronic Esters of High Optical Purity. Diethyl *trans*-2-(2-Furyl)cyclopentylboronate. A 250-mL round-bottom flask equipped with a sidearm, magnetic stirring bar and gas lead was flushed with nitrogen. In this flask 70 mL (50 mmol) of (−)-IpcBH$_2$ was taken and cooled to −35 °C. To it was added 6.7 g (50 mmol) of 1-(2-furyl)cyclopentene dropwise with magnetic stirring. The flask was maintained at −35 °C without stirring for 4 days. A white crystalline solid separated out. The supernatant liquid was removed by double-ended needle and the crystals were washed with cold ether (3×20 mL). The solid was dried under vacuum (ca. 15 mmHg) at 0 °C. It was then suspended in 20 mL of ether and treated with excess acetaldehyde (6 mL). The reaction mixture was stirred at room temperature for 5 h and (^{11}B NMR δ=30.97) showed the absence of dialkylborane. The excess of acetaldehyde pumped off and the residue distilled to give (+)-diethyl (1*S*,2*S*)-*trans*-2-(2-furyl)cyclopentylboronate, 7.05 g, bp 65—70°/0.02 mmHg, 60% isolated yield. $[\alpha]_D^{22}$ +51.58° (*c* 2.52, EtOH), >99% ee. ^{1}H NMR ($CDCl_3$) δ=1.20 (6H, m), 1.60—2.25 (7H, m), 3.25 (1H, m), 3.85 (4H, q), 5.90 (1H, m), 6.20 (1H, m), 7.25 (1H, m). A part of the sample was oxidized with NaOH, H_2O_2 to give the *trans*-2-(2-furyl)cyclopentanol which was further purified by preparative GC. $[\alpha]_D^{23}$ +88.2° (*c* 2.325, MeOH), >99% ee by capillary GC of its Mosher ester.

Diethyl *trans*-2-(3-Furyl)cyclopentylboronate. With the usual experimental setup, 6.7 g (50 mmol) of 3-furylcyclopentene was added dropwise to 70 mL (50 mmol) of IpcBH$_2$ at −35 °C. The flask was maintained at −35 °C without stirring for 4 days. The white crystalline solid separated out. The supernatant liquid was removed by double-ended needle and the crystals were washed with (3×20 mL) of cold ether. The solid was redissolved in 25 mL of ether at room temperature in about 10 min. A part of the solution (0.5 mL) was oxidized with NaOH and H_2O_2 and the optical purity checked by capillary GC of its Mosher ester showed 90% ee. The remaining whole solution was kept in a cold room for slow crystallization at 0 °C for 24 h. The white crystalline needles separated out. The supernatant liquid was removed by double-ended needle and the crystals washed with ice cold ether (3×5 mL). The crystals were dried under vacuum and treated with excess acetaldehyde. The usual workup as described above gave 5.9 g required boronate, bp 76—80°/0.04 mmHg, 50% yield. $[\alpha]_D^{22}$ +41.34° (*c* 2.38, EtOH), >99% ee. ^{1}H NMR ($CDCl_3$) δ=0.9—1.3 (6H, m), 1.4—2.0 (7H, m), 3.0 (1H, m), 3.8 (4H, q), 6.25 (1H, m), 7.20 (2H, m). A part of the diethyl *trans*-2-(3-furyl)cyclopentylboronate was oxidized to give the corresponding alcohol $[\alpha]_D^{22}$ +60.6° (*c* 2.29, MeOH), >99%ee by capillary GC of its Mosher ester.

Diethyl *trans*-2-(3-Thienyl)cyclopentylboronate. With the usual experimental setup as described above, diethyl *trans*-2-(3-thienyl)cyclopentylboronate was obtained bp 90—91°/0.05 mmHg, 50% isolated yield. $[\alpha]_D^{24}$ +46.72° (*c* 2.5, EtOH), >99% ee. ^{11}B NMR δ=31.42, ^{1}H NMR ($CDCl_3$) δ=0.9—1.4 (6H, m), 1.6—2.40 (7H, m), 3.15 (1H, m), 3.80 (4H, m), 6.8—7.4 (3H, m) its corresponding alcohol $[\alpha]_D^{22}$ +73.01° (*c* 2.3175, MeOH), >99% ee.

Diethyl *trans*-2-(2-Thienyl)cyclopentylboronate. With the usual experimental setup, 7.5 g (50 mmol) of 1-(2-thienyl)cyclopentene was added dropwise to 70 mL (50 mmol) of IpcBH$_2$ at −35 °C. The flask was maintained at −35 °C for 4 days without stirring and further kept at −78 °C for 5 h. The mother liquor containing the pure enantiomer was removed carefully without any crystalline particle and treated with excess of acetaldehyde (8 mL). The reaction mixture was stirred at room temperature for 5 h (^{11}B NMR δ=30.78) showed the absence of dialkylborane. The excess acetaldehyde and solvent was pumped off and the residue was taken up in 100 mL of pentane. The pentane layer was extracted with 3×25 mL of ether. The ether layer

was washed with water, dried over anhydrous $MgSO_4$ and the solvent removed to give *trans*-2-(2-thienyl)cyclopentylboronic acid, 7.15 g, 80% yield, 94% ee. It was crystallized with ether pentane at room temperature to give 5.7 g of pure boronic acid, 64% yield, which, upon treatment with ethanol, afforded the corresponding boronate, bp 85—90°/0.25 mmHg, 64% yield, $[\alpha]_D^{23}$ +36.10° (*c* 2.54, EtOH), 99% ee. ^1H NMR ($CDCl_3$) δ=0.9—1.4 (6H, m), 1.5—2.5 (7H, m), 3.20 (1H, m), 3.90 (4H, m), 6.7—7.10 (3H, m). The above boronate, upon oxidation, gave *trans*-2-thienylcyclopentanol $[\alpha]_D^{21}$ +70.6° (*c* 2.30, MeOH) >99% ee.

Diethyl *trans*-2-(2-Furyl)cyclohexylboronate. With the usual experimental setup, 7.4 g (50 mmol) of 1-(2-furyl)-cyclohexene was added dropwise to 70 mL (50 mmol) of $IpcBH_2$ in THF at −25 °C. The contents were stirred for 10 days at −25 °C and acetaldehyde (11.2 mL) was added dropwise and stirred further for 6 h at room temperature. The excess acetaldehyde and solvent were pumped off and the residue taken up in 100 mL of pentane. The pentane layer was extracted with 3×20 mL of 3 M sodium hydroxide. The alkaline solution was neutralized with 6 M HCl and extracted with 3×25 mL of ether. The ether layer was washed with water, dried over anhydrous $MgSO_4$ and solvent removed to afford 5.82 g of *trans*-2-(2-furyl)cyclohexylboronic acid, 60% yield, $[\alpha]_D^{22}$ +40.0° (*c* 1.05, CH_2Cl_2), 90% ee. The white crystalline boronic acid dissolved in ether pentane (2:3), 25 mL and kept at room temperature for slow crystallization. The supernatant liquid was removed by double-ended needle and crystals washed with cold ether pentane mixture (3×5 mL). After the usual workup, it gave 3.8 g of boronic acid, yield, 40%. $[\alpha]_D^{22}$ +44.5° (*c* 1.1, CH_2Cl_2). It was treated with ethanol to give its diethyl *trans*-2-(2-furyl)cyclohexylboronate, bp 100—105°/0.8 mmHg, $[\alpha]_D$ +36.2° (*c* 2.1, EtOH). ^1H NMR ($CDCl_3$) δ=0.9—1.35 (6H, m), 1.50—2.3 (9H, m), 3.2 (1H, m), 3.6—4.0 (4H, m), 6.2 (2H, q), 7.2 (1H, m). The boronate was oxidized to give the corresponding alcohol $[\alpha]_D^{22}$ +58.2° (*c* 1.8, MeOH) >98% ee by capillary GC of its Mosher ester.

Diethyl *trans*-2-(2-Furyl)cycloheptylboronate. With the usual experimental setup as described above, *trans*-2-(2-furyl)cycloheptylboronic acid was obtained 9 g, 87% yield. The solid was dissolved in ether pentane (2:3) 25 mL at room temperature. A part of the solution (0.5 mL) was oxidized with $NaOH/H_2O_2$ and the optical purity checked by capillary GC of its Mosher ester showed 86% ee. The remaining solution was crystallized and recrystallized at 0 °C for 24 h. The white crystalline needles separated out. The crystals were filtered and washed with pentane to give pure boronic acid, 4.7 g, 45% yield. It was treated with ethanol to give diethyl *trans*-2-(2-furyl)cycloheptylboronate, bp 120—125°/0.9 mmHg, $[\alpha]_D^{22}$ +24.6 (*c* 2.4, EtOH). ^1H NMR ($CDCl_3$) δ=0.9—1.3 (6H, m), 1.4—2.0 (11H, m), 3.1 (1H, m), 3.65—4.0 (4H, q), 5.9 (1H, m), 6.2 (1H, m) and 7.3 (1H, m). A part of the diethyl *trans*-2-(2-furyl)cycloheptylboronate was oxidized to give the corresponding alcohol $[\alpha]_D$ +34.9° (*c* 2.4, MeOH) >99% ee by capillary GC of its Mosher ester.

General Procedure for the Preparation of Diethanolamine *trans*-2-Heteroarylcycloalkylboronate. Ethyl heteroarylcycloalkylboronate (5 mmol) prepared as described above was taken in 15 mL of ether. To it 0.52 mL (5.4 mmol) of diethanolamine in 5 mL of 2-propanol was added and the reaction mixture was stirred at 25 °C for 1 h. A crystalline solid formed. It was filtered and removed by filtration and washed with 5 mL of cold ether. The results are shown in Table 4.

We wish to thank the National Institutes of Health (GM 10937-23) for their financial support.

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