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Chiral Synthesis *via* Organoboranes. 31. A Simple Synthesis of Enantiomerically Pure (*Z*)- and (*E*)-Alkenes, (*Z*)-RCH=CHR* and (*E*)-RCH=CHR*

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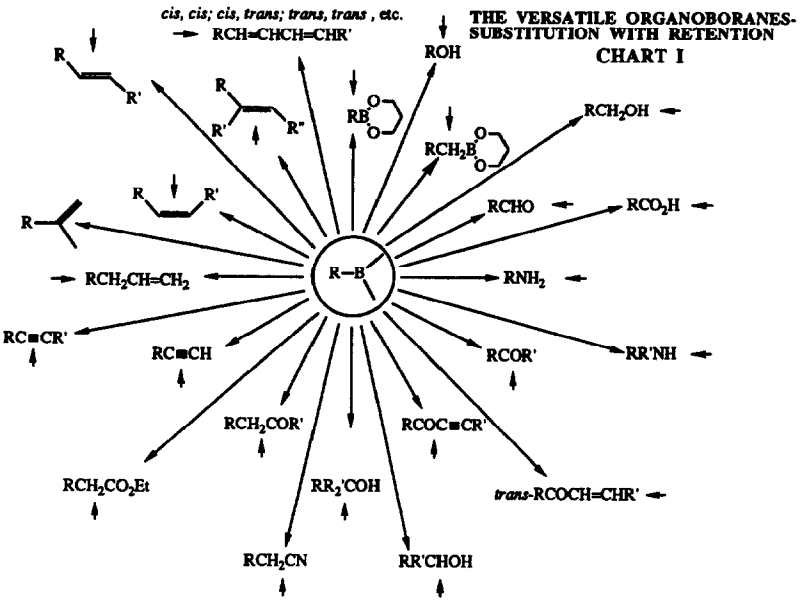
Abstract: The monoisopinocampheylorganylboranes, IpcR*BH, readily available in purities ≥99% ee by the asymmetric hydroboration of alkenes with monoisopinocampheylborane, $IpcBH_2$, are easily transformed into enantiomerically pure (≥99% ee) (*Z*)- and (*E*)-alkenes. The generality of the procedure was demonstrated by synthesizing four each (*Z*)- and (*E*)-alkenes. This new procedure makes the enantiomerically pure compounds readily available and contributes another stage to the completion of our goal of providing a truly general asymmetric synthesis of pure enantiomers.

The discovery of hydroboration in 1956 made organoboranes readily available.[2] A detailed systematic study of the chemistry of organoboranes revealed that these are among the most versatile intermediates available to the organic chemist interested in the synthesis.[3] A remarkable feature of the great majority of the substitution reactions of organoboranes is the fact that they proceed with complete retention of configuration of the organic group that is transferred from boron to some other element or group.[4] Representative conversions of organoboranes are summarized in Chart I. The small arrows, in Chart I, indicate the compounds that have already been synthesized.

It became evident that if it were possible to achieve asymmetric hydroboration of alkenes, thus placing optically active organo groups on boron, it might be possible to achieve the first general synthesis of pure enantiomers. Indeed, early in our hydroboration studies, we observed that hydroboration of α-pinene with borane proceeded to R_2BH (diisopinocampheylborane, Ipc_2BH) and then ceased. Apparently, the steric requirements of this group are so large that only two such bulky groups can attach themselves to boron. The formation of Ipc_2BH provided an optically active hydroborating reagent. However, the failure of this reagent to react with a third molecule of α-pinene made it clear that the reagent could be used only for the hydroboration of less hindered alkenes such as *cis*-2-butene. Thus treatment of *cis*-2-butene with Ipc_2BH, followed by oxidation, provided 2-butanol in very high optical purity.[5] To handle more hindered olefins, we required a reagent of lower steric requirements than Ipc_2BH. Accordingly, we prepared and tested optically pure monoisopinocampheylborane, $IpcBH_2$.[6] Indeed, asymmetric hydroboration of more hindered olefins with $IpcBH_2$, followed by crystallization, provided dialkylboranes, IpcR*BH, of ≥99% ee.[7] These dialkylboranes, IpcR*BH, upon treatment with acetaldehyde liberate the chiral auxiliary as α-pinene, readily recycled, and provide the corresponding boronate ester, $R^*B(OR)_2$, for utilization.[8] It occurred to us that the IpcR*BH intermediates, formed in the asymmetric hydroboration stage,[7] should be directly applicable to the synthesis of (*Z*)- and (*E*)-alkenes, providing an efficient, simple route to the asymmetric synthesis of these compounds. In this paper, we report on the utilization of the enantiomerically pure dialkylboranes, IpcR*BH, for an enantioselective synthesis of (*Z*)- and (*E*)-alkenes.



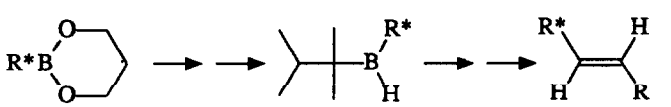
Results and Discussion

Zweifel observed that the treatment of the product from an acetylene and dicyclohexylborane with sodium methoxide and iodine gave the (*Z*)-alkenes.[9] Similarly, treatment of 1-halo-1alkyne with dicyclohexylborane followed by transfer of the alkyl group and protonolysis furnished the (*E*)-alkenes.[10] Two major disadvantages of this procedure is the fact that few dialkylboranes are readily synthesized and one of the two alkyl groups is wasted.

We overcame one of the difficulties by developing a general procedure for the synthesis of R_2BH[11]. But this procedure also resulted in the waste of one of the R groups. Use of thexylchloroborane, ThxBHCl, solved part of the problem.[12] However, in the iodination reaction, both RCH_2CH_2 and Thx migrated competitively. A general solution for the efficient synthesis of achiral (*Z*)- and (*E*)-olefins was then developed based on the hydroboration of 1-alkyne or 1-halo-1-alkyne with dibromoborane - dimethylsulfide ($BHBr_2.SMe_2$).[13]

Chiral (*Z*)- and (*E*)-alkenes have been synthesised earlier utilizing α-chiral terminal alkynes as precursors.[14] This procedure, however, in addition to giving variable ee's (29-89%) and poor yields (19-60%), is also limited by the availability of chiral alkynes.

Recently, we achieved the synthesis of enantiomerically pure thexylmonoalkylboranes and utilized them for the synthesis of *trans*-olefins, internal alkynes, and ketones in very high enantiomeric purities (eq 1).[15]



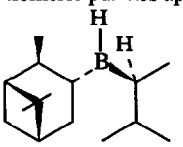
(1)

Although this procedure provides *trans*-olefins in high enantiomeric purities, it involves nine steps.

As part of our continuing research efforts to develop simple and practical methods for the enantioselective synthesis of organic compounds we recognized the possible utility and potential of the optically pure dialkylborane, IpcR*BH, produced by the hydroboration of prochiral olefin with $IpcBH_2$.[7] The potential of these optically active organoborane intermediates, IpcR*BH, has remained largely unexplored. We, therefore, decided to explore the utility of IpcR*BH for providing an efficient, general synthesis of chiral (*Z*)- and (*E*)-alkenes in high enantiomeric purities.

The optically active isopinocampheylalkylboranes, IpcR*BH, required for the synthesis of chiral alkenes, were prepared by asymmetric hydroboration of prochiral olefins with monoisopinocampheylborane, $IpcBH_2$, followed by crystallization.[7]

Utilizing the general procedure described above, the following representative dialkylboranes were prepared in enantiomeric purities approaching 100% ee.



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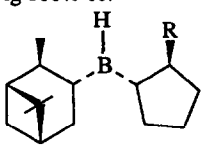
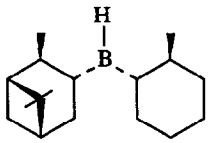


2: R = CH_3
3: R = Ph



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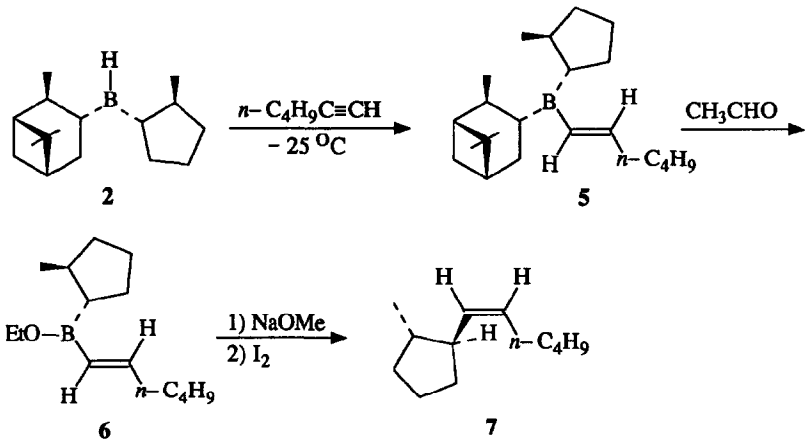
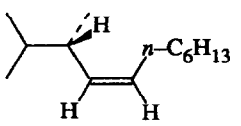
The enantiomeric purity of all these organoborane intermediates was established by capillary GC analysis of the appropriate derivatives of the alcohols obtained following alkaline hydrogen peroxide oxidation.[8]

Hydroboration of 1-hexyne with essentially 100% optically pure dialkylborane **2** at 25 °C for 2-3 h furnished the desired dialkylalkenylborane **5**. Treatment of this dialkylalkenylborane **5** with acetaldehyde at 0 °C results in the selective, facile elimination of the chiral auxiliary, providing the corresponding borinate **6**. The borinate **6**, on treatment with sodium methoxide, followed by iodination at 0 °C furnished the desired (*Z*)- alkene **7** in high enantiomeric purity and in good yield (Scheme I).

Scheme I



Using the general procedure described above, the following representative (*Z*)-alkenes were prepared in enantiomeric purities approaching 100% ee (Table I).



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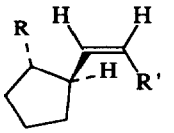

7: R = CH_3, R' = n–C_4H_9
9: R = Ph, R' = $-C(CH_3)_3$

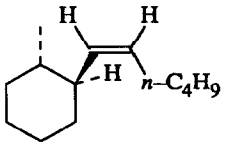

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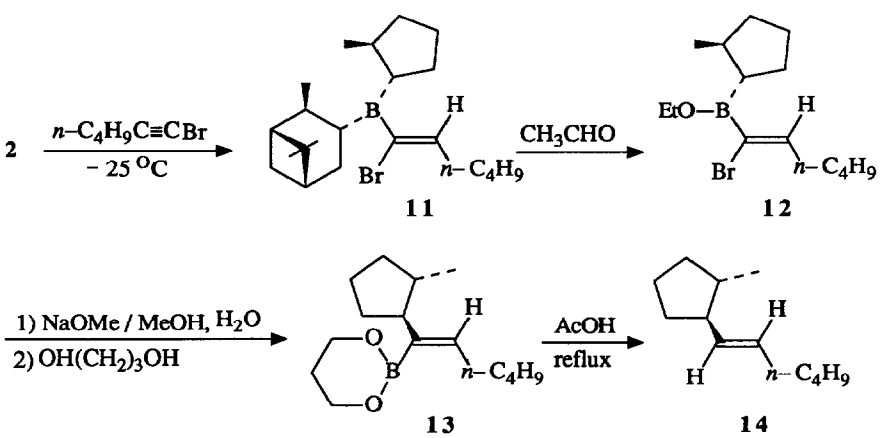
Table I. Synthesis of chiral (*Z*)-olefins.

olefin	configuration of olefin	% geometric purity[a]	$[\alpha]^{23}_D$ (c, MeOH)	yield % (isolated)	% ee
7	1'*S*, 2'*S*	≥ 99%	+ 25.1 (0.45)	70	≥ 99
8	*S*	≥ 99%	+ 28.5 (3.05)	65	≥ 99
9	1'*S*, 2'*S*	≥ 99%	+ 86.0 (2.5)	60	≥ 99
10	1'*S*, 2'*S*	≥ 99%	+ 35.7 (3.5)	68	≥ 99

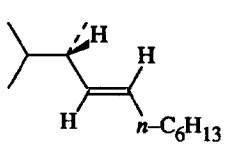
[a]Established by capillary GC.

Similarly, for the preparation of (*E*)-alkenes **14**, the dialkylborane **2** was treated with 1-bromo-1-hexyne at 0 °C for 2-3 h to furnish the desired α-bromoalkenyldialkylborane **11**. Hydroboration of 1-bromo-1-alkynes with IpcR*BH was very slow at –25 °C. Therefore, it was thought desirable to carry out the hydroboration at 0 °C. Elimination of the chiral auxiliary, followed by the treatment of the borinate **12** with sodium methoxide and protonolysis with acetic acid (reflux), furnished the desired (*E*)-alkene **14** in high enantiomeric purity and in good yield (Scheme II).

Scheme II



Using the general procedure described above, the following representative (*E*)-alkenes were prepared in enantiomeric purities approaching 100% ee (Table II).



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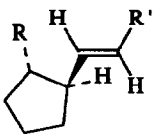

14: R = CH_3, R' = n–C_4H_9
16: R = Ph, R' = $-C(CH_3)_3$

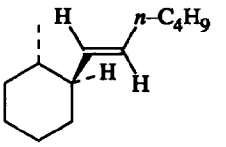

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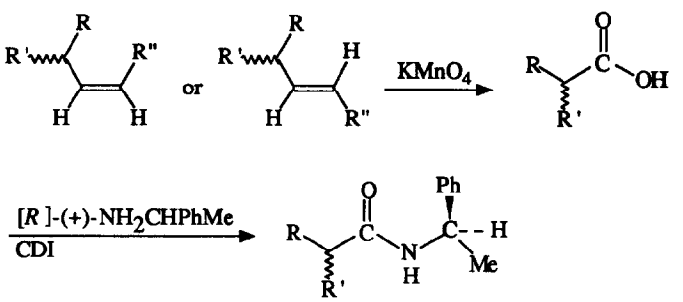
Table II. Synthesis of chiral (*E*)-olefins.

olefin	configuration of olefin	% geometric purity[a]	$[\alpha]^{23}_D$ (c, MeOH)	yield % (isolated)	% ee
14	1'*S*, 2'*S*	≥ 99%	+ 25.5 (4.9)	75	≥ 99
15	*S*	≥ 99%	+ 28.3 (2.0)	68	≥ 99
16	1'*S*, 2'*S*	≥ 99%	+ 86.8 (4.65)	63	≥ 99
17	1'*S*, 2'*S*	≥ 99%	+ 35.6 (4.05)	72	≥ 99

[a]Established by capillary GC.

Geometric purity of the alkenes was determined by resolving them on capillary GC. All the chiral (*Z*)- and (*E*)-alkenes prepared are new compounds. No direct method was found in the literature to establish their enantiomeric purities. Fortunately, the optical purities of these compounds could be established by oxidizing the alkenes with $KMnO_4$ to the corresponding carboxylic acids.[16] The acids were then coupled to (*R*)-(+)-α-methylbenzylamine in the presence of 1,1'-carbonyldiimidazole (CDI) to yield the diastereomeric amides (Scheme III).[17]

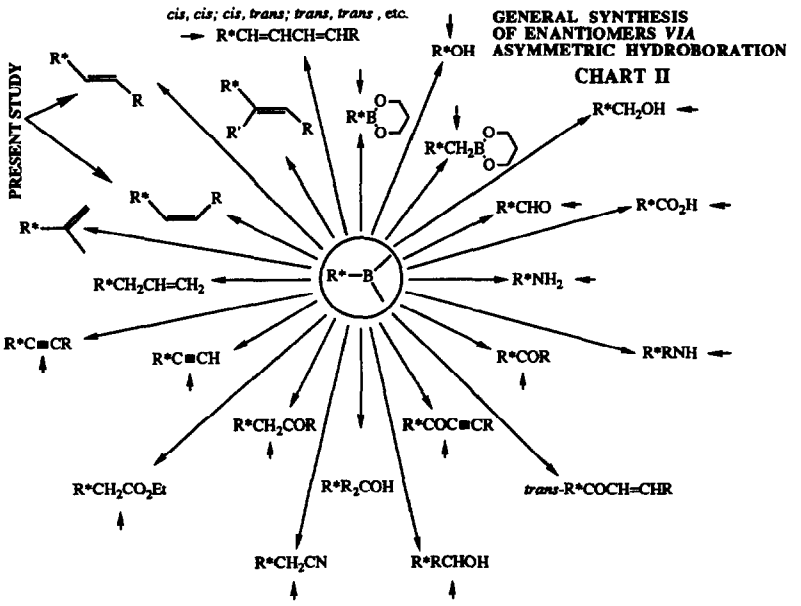
Scheme III



Each pair of diastereomeric amides was readily resolved by capillary GC (SPB-5, 30m). Racemic amides gave two peaks for the amides in a 1:1 ratio, thus assuring that no kinetic resolution had taken place.

Conclusion

An efficient, general synthesis of chiral (*Z*)- and (*E*)-alkenes of high enantiomeric purities has been achieved. In this study the chiral dialkylboranes, IpcR*BH, have been utilized for the synthesis of chiral (*Z*)- and (*E*)-olefins. Since chiral dialkylboranes, IpcR*BH, of either the (+)- or (−)- series are readily available in essentially pure enantiomeric form, we can now synthesise (+)- and (−)- chiral olefins of known absolute configuration and of consistently high geometric and enantiomeric purity. The arrows, in Chart II, indicate the compounds that have already been synthesized in pure enantiomeric form.



Experimental section

All operations were carried out under nitrogen atmosphere with oven-dried glassware. The ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The ^{1}H NMR spectra were scanned on a Varian T-60 and Varian 200 MHz spectrometers, and the ^{13}C spectra were obtained on a Varian 200 MHz instrument. The chemical shifts are relative to Me_4Si for ^{1}H and ^{13}C NMR spectra. IR and mass spectra were recorded on a Perkin-Elmer 137 and Finnegan GC/mass spectrometers respectively. Gas chromatographic analyses were carried out with a Hewlett-Packard 5750 chromatograph with a TC-detector. Optical rotations were measured on a Rudolph Polarimeter Autopol III to ± 0.01°, but rounded off to 0.1°. Capillary gas chromatographic analyses were carried out with a Hewlett-Packard 5890 chromatograph fitted with 50 m methylsilicone, 15 m supelcowax, or 30 m SPB-5 columns.

Materials. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Anhydrous diethyl ether (EE) was purchased from Mallinckrodt, Inc., and used directly. (−) Menthyl chloroformate was purchased from the

Aldrich Chemical Company. (*R*)-MTPA was purchased from the Aldrich Chemical Company, converted to the acid chloride and distilled.

Preparation of (*E*)-alkylvinylisopinocampheylboranes. The following procedure for the preparation of *B*-(1*S*, 2*S*-*trans*-methylcyclopentyl)-(*E*-1'-hexenyl)isopinocampheylborane (**5**) is representative. 1-Hexyne (0.98 g, 12 mmol) was added to the suspension of the dialkylborane **2** (2.33 g, 10 mmol) in 10 mL of EE at –25 °C. The reaction mixture was stirred for a period of 2 h at –25 °C. The disappearence of the solid (dialkylborane) and formation of a clear homogeneous solution indicated completion of the hydroboration. An aliquot drawn from the reaction mixture showed a peak at δ +72.0 in the ^{11}B NMR, indicating the formation of the desired dialkylalkenylborane **5.**

Preparation of (*E*)-alkylvinylborinates. The following procedure for the preparation of *B*-(ethoxy)-(1*S*, 2*S*-*trans*-methylcyclopentyl)-(*E*)-1'-hexenylborane (**6**) is representative. To an ice-cooled solution of the above dialkylalkenylborane (3.13 g, 10 mmol) in (EE), was slowly added acetaldehyde (0.53 g, 12 mmol). The reaction mixture was stirred vigorously at 0 °C for a further period of 30 min. An aliquot drawn from the reaction mixture showed a peak at δ +47.0 in the ^{11}B NMR, indicating elimination of the chiral auxiliary and formation of the corresponding borinate. Excess acetaldehyde, α-pinene and EE were pumped off at room temperature under vacuum (15 Torr) and then under high vacuum (0.01 Torr) to yield the corresponding borinate **6**. ^{1}H NMR (60 MHz, $CDCl_3$) 0.8-1.0 (m, 9H), 1.2 (m, 14H), 4.0 (q, *J*=6Hz, 2H), 5.7 (d, *J*=18Hz,1H), 6.55 (2t's, *J*=6Hz, 1H).

Preparation of (*Z*)-alkyl-α-bromovinylisopinocampheylboranes. The following procedure for the preparation of *B*-(1*S*, 2*S*-*trans*-methylcyclopentyl)-(*Z*-1'-bromohexenyl)-isopinocampheylborane (**11**) is typical. 1-Bromo-1-hexyne (1.93 g, 12 mmol) was added dropwise to a suspension of the dialkylborane **2** (2.33 g, 10 mmol) in EE (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. The disappearance of the solid dialkylborane and formation of a clear homogeneous solution indicated the completion of the hydroboration reaction. An aliquot drawn from the reaction mixture showed a peak at δ +68.0 in the ^{11}B NMR, indicating the formation of the desired dialkylalkenylborane **11.**

Preparation of (*Z*)-alkyl-α-bromovinylborinates. The following procedure for the preparation of *B*-(ethoxy)-(1*S*, 2*S*-*trans*-methylcyclopentyl)-*Z*-1'-bromohexenylborane (**12**) is representative. To an ice-cooled solution of the above dialkylalkenylborane (3.92 g, 10 mmol) in EE, was slowly added acetaldehyde (0.53 g, 12 mmol). The reaction mixture was stirred vigorously at 0 °C for 30 min. An aliquot drawn from the reaction mixture showed a peak at δ +45.0 in the ^{11}B NMR, indicating the elimination of the chiral auxiliary and formation of the corresponding borinate. Excess acetaldehyde, α-pinene and EE were pumped off at room temperature under vacuum (15 Torr) and then under high vacuum (0.01 Torr) to furnish the corresponding borinate **12.** ^{1}H NMR (60 MHz, $CDCl_3$) 0.8-1.0 (m, 9H), 1.2-2.2 (m, 14H), 4.0 (q, *J*=6Hz, 2H), 6.03 (t, *J*=6Hz, 1H).

Preparation of (*E*)-2-alkenyl-1,3,2-dioxaborinanes. The following procedure for the preparation of the boronate ester **13** is representative. To an ice-cooled solution of the above borinate **12** (3.0g, 10 mmol) in

EE (10 mL), was slowly added NaOMe/MeOH (2.3 mL, 10 mmol). The reaction mixture was then stirred at ambient temperature overnight. To this water (20 mL) was added. Aqueous and organic layers were separated. The aqueous portion was extracted with EE (3 x 25 mL). The combined ether portion was washed with water (10 mL), brine (5 mL) and dried. Removal of solvent furnished the desired boronic acid (2.0g) which was esterified in *n*-pentane with 1,3-propane diol (1.2g) to afford the desired boronate ester. This was further purified by distillation under reduced pressure to afford the pure boronate ester **13** in 90% yield (2.1g). bp. 68-70 °C (0.8 Torr)

^{1}H NMR (60 MHz, $CDCl_3$) 0.89 (d, *J*=3 Hz, 6H), 1.2-2.2 (m, 16H), 4.0 (t, *J*=6 Hz, 4H), 5.75 (t, *J*=7 Hz, 1H).

General procedure for the preparation of (*Z*)-alkenes. The following procedure for the preparation of (*Z*)-1-(1'*S*, 2'*S*-*trans*-methylcyclopentyl)-2-butylethylene (**7**) is representative. To an ice-cooled solution of the borinate **6** (2.2g, 10 mmol) in EE(10 mL) was added a solution of sodium methoxide in methanol (2.3 mL, 10 mmol) and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed under vacuum and methanol (10 mL) was added. The reaction mixture was then cooled to 0 °C followed by dropwise addition of iodine (2.54g, 10 mmol) in methanol (20 mL) over a period of 1 h. The reaction mixture was then stirred at room temperature for a further period of 3 h. Aqueous sodium thiosulfate solution was then added and the reaction mixture was extracted with pentane (3 x 25 mL), washed with water, brine and dried. Removal of solvent afforded the crude product whose ^{1}H NMR indicated the formation of the desired alkene along with some alkenyl iodide. Careful distillation gave the pure alkene **7** in 70% yield (1.16g); bp. 68-70 °C (3 Torr);

IR(neat) 2960, 2920, 1460 cm^{-1};

^{1}H NMR (200 MHz, $CDCl_3$) 0.8-1.0 (d & t, 6H), 1.1-2.4 (m, 14 H), 5.1-5.45 (m, 2H);

^{13}C NMR (200 MHz, $CDCl_3$) 134.7, 130.2, 46.6, 42.2, 34.6, 33.7, 32.5, 27.5, 23.8, 22.5, 18.7, 14.2;

M.S : 166 (3.47%) M^+, 110 (2.74%), 109 (6.73%), 95 (33.37%), 82 (100%), 81 (60.06%), 67 (85.67%), 55 (50.72%).

General procedure for the preparation of (*E*)-alkenes. The following procedure for the preparation of (*E*)-1-(1'*S*, 2'*S*-*trans*-methylcyclopentyl)-2-butylethylene (**14**) is representative. In a 100 mL r.b. flask fitted with a nitrogen inlet and a reflux condenser was placed the boronate ester **13** (2.24g, 8.9 mmol) and excess acetic acid (10 mL). The reaction mixture was heated under reflux for a period of 10-12 h. It was then diluted with water, washed with aq. sodium bicarbonate, water, brine and dried. Removal of solvent followed by distillation of the residue under reduced pressure afforded the pure alkene **14** in 75% yield (1.25g); bp. 68-70 °C (3 Torr);

IR(neat) 2960, 2920, 1460, 980 cm^{-1};

^{1}H NMR (200 MHz, $CDCl_3$) 0.8-1.0 (d & t, 6H), 1.1-2.4 (m, 14H), 5.1-5.5 (m, 2H);

^{13}C NMR (200 MHz, $CDCl_3$) 134.5, 130.2, 52, 41.2, 34.5, 33.3, 32.4, 32, 23.4, 22.3, 18.5, 14;

M.S : 166 (5.77%) M^+, 110 (2.08%), 109 (7.49%), 95 (29.77%), 82 (100%), 81 (46.8%), 67 (65.7%), 55 (25.18%).

(*Z*)-1-(1'S, 2'S-*trans*-methylcyclohexyl)-2-butylethylene (10). Yield 68%; bp. 62-64 °C (1.5 Torr);
IR(neat) 2940, 2840, 1460 cm^{-1};
^1H NMR (200 MHz, $CDCl_3$) 0.8-0.95 (d & t, 6H), 1.2-2.1 (m, 6H), 5.05-5.4 (m, 2H);
^{13}C NMR (200 MHz, $CDCl_3$) 135.7, 129.3, 43.5, 37.5, 35.2, 33.7, 32.2, 27.5, 26.7, 26.3, 22.5, 20.9, 14.1;
M.S. : 180 (10.19%) M^+, 110 (6.91%), 109 (16.22%), 97 (13.32%), 96 (91.93%), 95 (39.79%), 81 (100%), 67 (83.61%), 55 (72.77%).

(*S*)-(*Z*)-2,3-dimethyl-4-undecene (8). Yield 65%; bp. 58-60 °C (1.5 Torr);
IR (neat) 2940, 2840, 1460 cm^{-1};
^1H NMR (200 MHz, $CDCl_3$) 0.8-0.95 (d & t, 12H), 1.2-1.5 (bm, 9H), 1.95-2.2 (m, 3H), 5.1-5.4 (m, 2H);
^{13}C NMR (200 MHz, $CDCl_3$) 135, 129.2, 38, 33.5, 31.9, 30, 29.2, 27.6, 22.8, 20.2, 19.9, 18.6, 14.2;
M.S : 182 (9.48%) M^+, 139 (3.62%), 111 (2.75%), 97 (45.29%), 83 (98.85%), 69 (63.27%), 55 (100%).

(*Z*)-1-(*t*-butyl)-2-(1'*S*, 2'*S*-*trans*-phenylcyclopentyl)ethylene (9). Yield 60%; bp. 78-80 °C (0.7 Torr);
IR (neat) 3020, 2940, 2860, 1600, 1480, 1360 cm^{-1};
^1H NMR (200 MHz, $CDCl_3$) 0.9 (s,9H), 1.7-2.2 (m, 8H), 5.0-5.3 (m, 2H), 7.2 (s, 5H);
^{13}C NMR (200 MHz, $CDCl_3$) 140.1, 132.6, 128.4, 128.3, 128, 127.9, 54.1, 48.1, 34.5, 34.2, 31.4, 29.8, 24.4;
M.S : 228 (100%) M^+, 213 (2.8%), 172 (10.63%), 157 (40.24%), 144 (50.49%), 129 (34.74%), 95 (40.24%), 91 (74.65%), 81 (28.64%), 69 (38.62%), 55 (35.17%).

(*E*)-1-(1'*S*, 2'*S*-*trans*-methylcyclohexyl)-2-butylethylene (17). Yield 72%; bp. 62-64 °C (1.5 Torr);
IR (neat) 2940, 2840, 1460, 980 cm^{-1};
^1H NMR (200 MHZ, $CDCl_3$) 0.8-0.95 (d & t, 6H), 1.2-2.1 (m, 6H), 5.1-5.4 (m, 2H);
^{13}C NMR (200 MHz, $CDCl_3$) 135.8, 130, 49.1, 37.2, 35.4, 34.1, 32.4, 32.1, 26.7, 26.4, 22.3, 21, 14;
M.S : 180 (15.1%) M^+, 110 (8.94%), 109 (21.31%), 97 (13.52%), 96 (100%), 95 (43.26%), 81 (96.91%), 67 (71.63%), 55 (60.88%).

(*S*)-(*E*)-2,3-dimethyl-4-undecene (15). Yield 68%; bp. 58-60 °C (1.5 Torr);
IR (neat) 2950, 2920, 2840, 1460, 970 cm^{-1};
^1H NMR (200 MHZ, $CDCl_3$) 0.8-0.95 (d & t, 12H), 1.2-1.5 (m, 9H), 1.85-2.1 (m, 3H), 5.2-5.4 (m,2H);
^{13}C NMR (200 MHz, $CDCl_3$) 134.9, 129.6, 43.1, 33.2,32.8, 31.8, 29.8, 28.9, 22.7, 20, 19.7, 17.7, 14.1;
M.S : 182 (9.48%) M^+, 139 (3.6%), 97 (45.3%), 83 (98.6%), 69 (63.3%), 55 (100%).

(*E*)-1-(*t*-butyl)-2-(1'*S*, 2'*S*-*trans*-phenylcyclopentyl)ethylene (16). Yield 63%; bp. 78-80 °C (0.7 Torr); IR (neat) 3020, 2940, 2860, 1600, 1480, 1360, 980 cm^{-1};
^1H NMR (200 MHZ, $CDCl_3$) 0.9 (s, 9H), 1.7-2.4 (m, 8H), 5.2 (d, J=2Hz, 2H), 7.1-7.3 (m, 5H);

^{13}C NMR (200 MHz, $CDCl_3$) 145.4, 141.9, 128.5, 128.2, 127.8, 126.2, 53.2, 52, 34.6, 33.5, 32.9, 30, 24.3;
M.S : 228 (99.89%) M^+, 213 (3.25%), 172 (22.71%), 157 (59.49%), 144 (84.81%), 129 (51.11%), 95 (59.39%), 91 (100%), 81 (43.46%), 69 (75.53%), 55 (53.43%).

General procedure for the determination of optical purity of alkenes. The alkene was dissolved 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. The dark mixture was stirred at 25 °C for 24 h. Sodium bisulfite (solid) was added, in positions, until the mixture became colorless. The reaction mixture was acidified with 3 M HCl and then diluted with ether. Aqueous and organic layers were separated. The aqueous portion was saturated with NaCl and extracted three times with ether. The combined organic portion was washed with brine and dried over $MgSO_4$. The solvent was removed to get the residue, which was distilled under reduced pressure to get the carboxylic acid. The acid (0.02 mmol) was coupled to (*R*)-(+)-methylbenzylamine (0.02 mmol) in the presence of 1,1'-carbonyldiimidazole (0.02 mmol) in ether to give the desired amide. The crude amide was taken up in ether and analyzed by capillary GC.

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