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The Use of *B*-[(*E*)-3-(Diphenylamino)allyl]diisopinocampheylborane as a Reagent for the Stereoselective Synthesis of *anti*-β-Diphenylamino Alcohols and *trans*-1-Diphenylamino-2-(1-hydroxyalkyl) cyclopropanes

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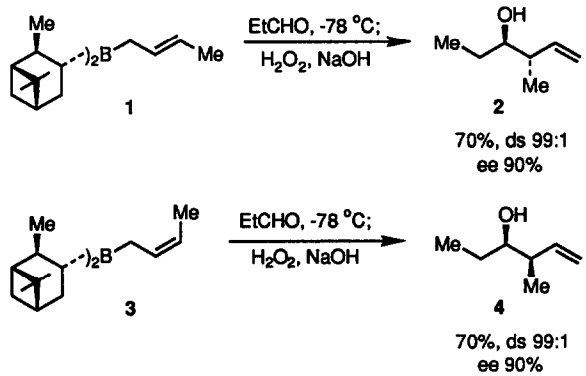
ABSTRACT : *anti*-β-Amino alcohols and *trans*-1-amino-2-(1-hydroxyalkyl) cyclopropanes have been produced with high relative and absolute stereocontrol in a simple one-pot process *via* the reaction of aldehydes with *B*-[(*E*)-3-(diphenylamino)allyl]-diisopinocampheylborane and a subsequent alkaline hydrogen peroxide work-up.

Introduction

1,2-Amino alcohols and vicinal diamines are common structural units that occur in legions of natural products.[1] There are two distinct strategies that may be employed to elaborate compounds containing such functionality. Firstly, amino alcohol or diamine entities may be introduced into molecules without any change in the carbon skeleton. These methods require, for example, the oxyamination of alkenes or the ring opening of epoxides with nitrogen centred nucleophiles.[2] Methods for the generation of amino alcohol moieties with the simultaneous construction of the interconnecting carbon-carbon bond are less frequently used in asymmetric syntheses. Recently, Shibasaki and coworkers reported[3] that lanthanum t-butoxide and (S)-(-)-binaphthol formed an efficient catalyst for the asymmetric Henry reaction[4] of aliphatic aldehydes with nitromethane to form β-nitro alcohols (73-90% ee). Additionally, Taguchi has utilised zirconocene-mediated methodology for the coupling of aldehydes with chiral aldimines to generate *syn*-amino alcohol derivatives.[5] Brown and coworkers have introduced several allyl- and crotyl-boranes that convert aldehydes into homoallylic alcohols.[6] These methods, which are exemplified by the transformations in Scheme 1, are particularly useful for the preparation of 4-hydroxy- and 4-hydroxy-3-methyl-1-alkenes. In all cases, the products were formed with both excellent relative and absolute stereochemical control. In an adaptation of this chemistry, we have introduced *B*-{(*E*)-3-[(diisopropylamino)dimethylsilyl]allyl}diisopinocampheylborane as a reagent for the synthesis of *anti*-vicinal diols.[7] Herein we now report a convergent enantioselective method for the preparation of *anti*-β-diphenylamino alcohols[8] and quite surprisingly, *trans*-diphenylamino cyclopropanemethanol derivatives using related organoboron chemistry.

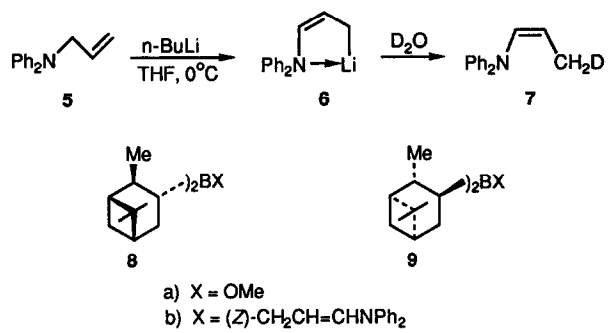
SCHEME 1



Results and Discussion

The original objective of our studies was to extend the Brown organoboron methodology to the preparation of amino alcohols from aldehydes. We expected that the Z-specific lithiation of allyl-(diphenylamine), metathesis with *B*-methoxydiisopinocampheylborane and reaction with aldehydes should provide, on work-up, various *syn*-amino alcohols. Following the Eisch precedent,[9] allyl(diphenylamine) was lithiated by reaction with n-butyllithium in THF at 0 °C. In order to confirm the relative geometry of the intermediate organolithium species, the anion was quenched with an excess of D_2O. Inspection of the ^1H NMR spectrum of the product was consistent with formulation as the *cis*-monodeuterio-enamine **7** (δ 1.09 (m, 2H), 4.84 (app q, 1H, *J* ~8Hz), 5.95 (d, 1H, *J* =8.4Hz)). This result is fully in accord with formulation of the intermediate organolithium species as the chelate **6**. On this basis, we expected that metathetic exchange of chelate **6** with the methoxyboranes **8a** and **9a** should provide the corresponding *(Z)*-alkenylboranes **8b** and **9b** and ultimately *syn*-β-hydroxy diphenylamines on reaction with aldehydes. These expectations proved to be unfounded.

SCHEME 2

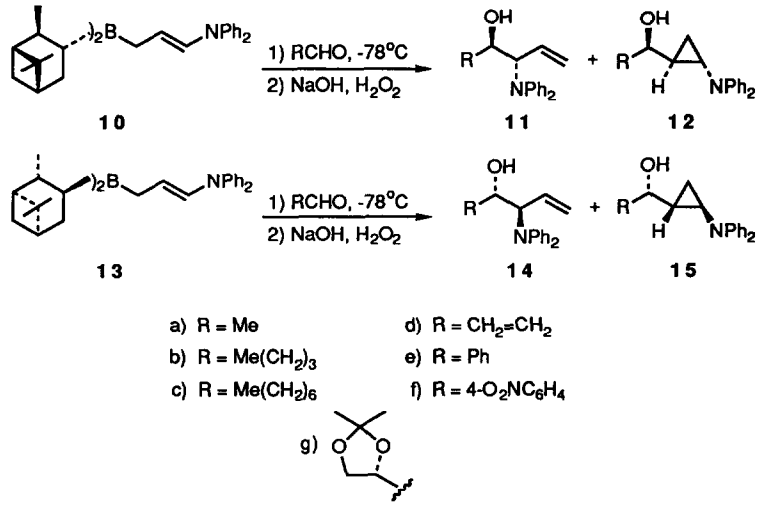


Chelate **6** was allowed to react with an equivalent of (-)-*B*-methoxydiisopinocampheylborane (**8a**) followed by the addition of boron trifluoride-diethyl ether. Without isolation, the resultant allylborane was allowed to react with acetaldehyde to give, on alkaline hydrogen peroxide work up, *(2R, 3S)*-3-

(diphenylamino)-4-penten-2-ol (**11a**) (40%). In the same way, the *(2S, 3R)*-isomer **14a** was prepared from the antipodal methoxyborane **9a** (41%). These masked aldol reactions were extended to a range of aldehydes to produce both antipodes of the *anti*-β-diphenylamino alcohols **11** and **14** (Scheme 3, the Table).

In all cases, the yields of β-diphenylamino alcohol products **11** and **14** were only modest (28-48%). However, the reactions all proceeded with excellent *anti*-relative stereochemical control (diastereoselectivity ≥ 95:5) and this was readily apparent from the ^{1}H and ^{13}C NMR spectra. Additionally in each case, the absolute stereochemistry of reaction was also outstanding. This was determined by converting all the β-diphenylamino alcohols **11** and **14** into their corresponding *(R)-O*-methyl mandelates[10] or *(R)*-(+)-Mosher esters.[11] Comparisons of the ^{1}H NMR spectra of each diastereoisomeric pair of esters **16** and **17** (**a-d**) or **18** and **19** clearly show that the enantiomeric excesses in all reactions were at least 95%. Entries 13 and 14 in the Table[12] illustrate reactions with matched and mismatched stereochemical biases. The *anti*-relative stereocontrol for these two samples was consistantly very good, however, absolute stereochemical control was clearly lower in the mismatched example.

SCHEME 3



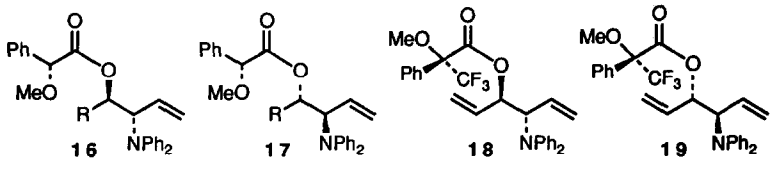
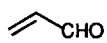
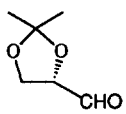


Table Reactions of Aldehydes with Boranes **10** and **13**

Entry	Aldehyde	Borane	Products (%)[a]	
1	CH_3CHO	**10**	**11a**(40)	**12a**(27)
2		**13**	**14a**(41)	**15a**(28)
3	$CH_3(CH_2)_3CHO$	**10**	**11b**(43)	**12b**(25)
4		**13**	**14b**(40)	**15b**(25)
5	$CH_3(CH_2)_6CHO$	**10**	**11c**(46)	**12c**(24)
6		**13**	**14c**(47)	**15c**(25)
7		**10**	**11d**(45)	(b)
8		**13**	**14d**(47)	(b)
9	PhCHO	**10**	**11e**(48)	**12e**(15)
10		**13**	**14e**(47)	**15e**(12)
11	p-NO_2PhCHO	**10**	(b)	**12f**(11)
12		**13**	(b)	**15f**(10)
13		**10**	**11g**(23),**14g**(6)	**12g**(19),**15g**(4)
14		**13**	**14g**(28)	**15g**(26)

a All products were formed with diasteriomeric excesses of ≥95:5 and enantiomeric excesses of ≥95%.

b Product present, but not isolated

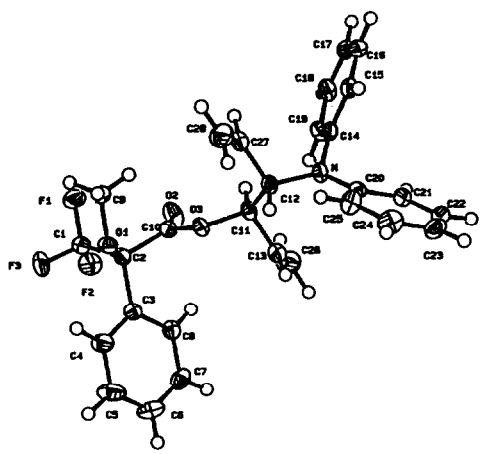
The assignments of both relative and absolute stereochemistries in these reactions needed substantiation. Thus we sought to confirm both by an X-ray crystallographic study. Fortunately, we were able to secure suitable crystals of the (*R*)-(+)-Mosher ester **18**. The results, which will be published in full elsewhere,[13] are summarised in Figure 1. It is clear from this structure that the relative stereochemistry was *anti* and that the absolute stereochemistry of reaction was fully consistent with all other Brown homologation reactions.[6,7] This study unequivocally established both the relative and absolute stereochemistry of alcohol **11d** and, by implication, all the other β-diphenylamino alcohols in the Table. It is thus apparant that, although the organolithium reagent **6** had the *(Z)*-geometry, lithium boron exchange was accompanied by a *cis* to *trans* isomerisation to produce **10** or **13**. Possibly this is in consequence of facile rearrangement via a 1,3-boratropic shift[6] or in consequence of the enaminic character of allylboranes bearing nitrogen substituents (*vide infra*).

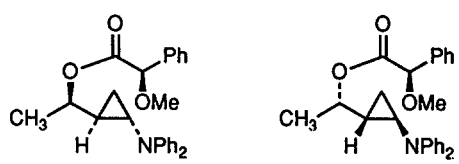
A second product (10-27%) was formed in all of the reactions of aldehydes with the allylboranes **10** and **13**. Both spectroscopic data and an X-ray crystallographic study were fully consistent with formulation of these substances as the cyclopropylamine derivatives **12** and **15** (Scheme 3). All these side products were obtained essentially as single diastereoisomers (diastereoselectivity ≥ 95:5) and this was readily apparent from their respective ^1H and ^{13}C NMR spectra. In one case, **12f**, the structure of the product was unequivocally established by X-ray crystallography. The results, which will be published in full elsewhere,[14] are summarised in Figure 2. Additionally, in at least two cases, the absolute stereochemistry of cyclopropane

formation was outstanding. This was determined by converting the cyclopropane-methanol derivatives **12a** and **15a** into their corresponding (*R*)-*O*-methyl mandelates.[10] Comparison of the ^{1}H NMR spectra of the diastereoisomeric ester pair **20** and **21** clearly show that the enantiomeric excesses in this reaction was at least 95%. Unfortunately, neither of these two esters nor the corresponding (*R*)-Mosher esters[11] were obtained as crystalline materials suitable for further X-ray crystallographic studies. Indeed, in all the examples in the Table, ester derivatives of **12** and **15** were particularly unstable and readily decomposed, on standing, to intractable mixtures of products. Tentatively, the absolute stereochemistry of the cyclopropane derivatives **12a** and **15a** were assigned by comparisons of the ^{1}H NMR spectra for the esters **20** and **21**. Thus ester **20** showed *inter alia* δ 1.16 (3H, d, J =6.3Hz) whereas ester **21** showed δ 1.01 (3H, d, J =6.4Hz). On the basis of the Trost analysis,[10] these spectroscopic characteristics are consistent with the absolute stereochemical assignments given in Scheme 3 and the Table. All the other cyclopropane derivatives were assumed to have the same absolute stereochemistries.

FIGURE 1

Molecular Structure of *(3R,4S)*-4-(Diphenylamino)-1,5-hexadien-3-yl *(2R)*-2-Methoxy-2-phenyl-3,3,3-trifluoropropanoate (18)





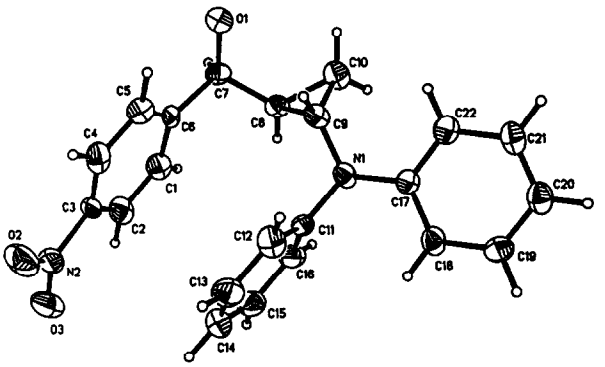
20 **21**

Several attempts were made to maximize the yield of the cyclopropane species at the expense of the diphenylamino alcohols. All these experiments proved to be futile. Reactions carried out above -78 °C

showed an unacceptable loss of diastereoselectivity and enantioselectivity. Modifications to reaction time, solvent concentration, solvent character, addition rate and reaction scale all resulted in approximately the same product ratio with only a small effect on the overall and relative yields of products. The most influential reaction component appeared to be the electronic character of the aldehyde. Yields of cyclopropanated products **12** and **15** from aromatic aldehydes were consistently less that those from alkyl aldehydes (Table).

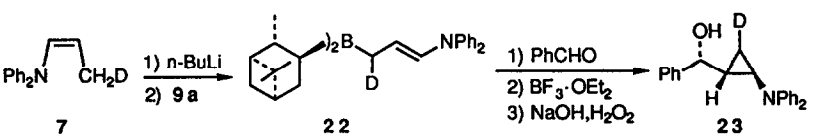
FIGURE 2

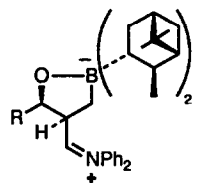
Molecular Structure of *(1S,2S)*-1-(Diphenylamino)-2-(*(1S)*-hydroxy-1-(4-nitrophenyl)methyl)cyclopropane (12f)



An attempt was made to clarify the mechanism of this unusual cyclopropanation chemistry. Thus we sought to examine the conversion of the monodeuterioenamine **7** into the corresponding cyclopropane (Scheme 4). Deprotonation of **7** with n-BuLi in THF and tetramethylethylenediamine (TMEDA) followed by addition of the methoxyborane **9a** and boron trifluoride etherate gave a solution presumably containing the allylborane derivative **22**. Subsequent addition of benzaldehyde gave, on alkaline hydrogen peroxide work up, the D-incorporated product (**23**) (10%). Examination of the ^1H NMR spectrum of this product showed D-incorporation to be exclusively in the 3 position of the cyclopropane ring. It is therefore reasonable to speculate that the cyclopropanemethanol derivatives **12** and **15** were formed via an enamine mechanism (Scheme 4) and the intermediacy of adduct **24**.

SCHEME 4





24

This study further demonstrates the utility of pinene-derived compounds in asymmetric synthesis. The direct conversion of aldehydes into enantiomerically pure amino alcohols via an experimentally simple one-pot process should find considerable use in synthesis. Work is currently in progress to determine if this methodology is applicable to other suitably protected allylamines for the synthesis of biologically active β-amino alcohols.

Experimental

n-Butyllithium was purchased as a solution in hexanes from Aldrich. TMEDA was purchased from Aldrich and was stored under argon, over potassium hydroxide pellets. Dichloromethane was freshly distilled from calcium hydride. THF was distilled over sodium benzophenone ketyl. 2,3-*O*-Isopropylidene-D-glyceraldehyde was prepared and freshly distilled prior to use[12]. Benzaldehyde was purchased from Aldrich and redistilled as needed. All other reagents were used directly as purchased.

T.l.c. was performed on Merck Kieselgel 60 F-254 glass plates. The chromatograms were initially examined under U.V. light and then developed with a vanillin solution and visualised by heating with a heat gun. Column chromatography was achieved under medium pressure using Merck Kieselgel 60 (230-400) mesh.

All reactions were run in oven dried glassware. Low temperature reactions were maintained by use of a CryoCool CC-80II. All NMR spectra were recorded using $CDCl_3$ with TMS as an internal standard. Elemental analyses were conducted by the Imperial College Microanalytical Service or by G.D. Searle & Company, Skokie, Illinois. High resolution mass spectra were recorded at the Department of Chemistry, Northwestern University, Evanston, Illinois and at the SERC Mass Spectrometry Service Centre, Swansea, UK. X-Ray crystal data were acquired at the Department of Chemistry, Northwestern University, Evanston, Illinois and the Department of Chemistry, Colorado State University.

Lithiation and Deuteration of Allyldiphenylamine (5) Allyldiphenylamine (**5**) (2.1 g, 10.0 mmol) and TMEDA (1.5 mL, 10.0 mmol) were dissolved in dry THF (15 mL) and cooled to 0 °C. n-BuLi (2.5 M, 4 mmol) was added to the solution over 5 min after which the solution was allowed to stir for 3h. The lithiated species (**6**) was quenched by addition of D_2O (5 mL) and then stirred at room temperature for 0.5 h. The reaction solution was concentrated by rotary evaporation and purified by Kugelrohr distillation to afford the crude deuterium-labelled product (**7**) (1.88 g, 89%) as a yellow liquid: ^1H NMR δ (200 MHz, $CDCl_3$) 1.09 (2H, m), 4.84 (1H, app q, J ~8 Hz), 5.95 (1H, d, J =8.4 Hz), 6.83-7.16 (10H, m); MS (EI) m/z (70eV) 210 ($M^{+\cdot}$, 33), 167 (9), 131 (7), 117 (8), 104 (87), 91 (20), 77 (100), 51 (83) and 39 (43).

Preparation of *(2R, 3S)*-3-(Diphenylamino)-4-penten-2-ol (11a) and *(1S, 2S)*-1-(Diphenylamino)-2-((*1R*)-1-hydroxyethyl)cyclopropane (12a). To a solution of allyldiphenylamine (**5**) (1.05 g, 5.00 mmol) in dry THF (10 mL) at 0 °C was added TMEDA (0.75 mL, 5.00 mmol) and n-BuLi (2.5 M, 2.0 mL). The solution was stirred at 0 °C for 3 h and subsequently cooled to -78 °C. The burgundy-red solution was treated with (-)-*B*-methoxydiisopinocampheylborane (**8a**) (1.58 g, 5.00 mmol) in dry THF (5 mL) and maintained at -78 °C for 2 h. To this solution was added $BF_3{\cdot}OEt_2$ (0.82 mL, 6.65 mmol) immediately followed by ethanal (0.22 g, 5.00 mmol) in dry THF (1 mL). The reaction mixture was kept at -78 °C for 3 h and was allowed to warm to 0 °C after which aqueous NaOH (2.5 M, 2.0 mL) and 30% H_2O_2 (2 mL) were added. The reaction mixture was stirred at room temperature for 12 h. The mixture was diluted with diethyl ether (30 mL) and separated from the aqueous layer. The organic solution was dried ($MgSO_4$), concentrated *in vacuo*, and the residue was purified by flash chromatography (silica gel, 4:1 hexanes-EtOAc) to yield the amino alcohol products **11a** (0.51 g, 40%) and **12a** (0.34 g, 27%).

Amino alcohol **11a** was obtained as a colorless oil: $[\alpha]_D$ +37.9° (CH_2Cl_2, c = 0.9); IR (neat) 3381, 3036, 2943, 2927, 2855, 1588, and 1498 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 1.20 (3H, d, *J* =6.1 Hz), 3.85 (1H, m), 4.25 (1H, t, *J* =7.2 Hz), 5.35 (2H, m), 5.70 (1H, m), 7.06 (6H, m), 7.27 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 20.0, 67.1, 70.7, 119.7, 123.1, 124.0, 129.5, 134.3, 147.7; MS (EI) *m/z* (70 eV) 253 ($M^{+\cdot}$, 11), 208 (100), 167 (7), 104 (6), 91 (4), 77 (8) and 43 (3). Anal. calc. for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.35; H, 7.66; N, 5.40%. A sample of **11a** (0.025 g, 0.100 mmol), (*R*)-*O*-methyl mandelic acid (0.033 g, 0.200 mmol) and 4-dimethylaminopyridine (5 mg) were dissolved in dry CH_2Cl_2 (10 mL). 1,3-Dicyclohexylcarbodiimide (0.041 g, 0.200 mmol) in dry CH_2Cl_2 (2 ml) was added and the course of reaction was monitored by TLC (silica gel, 10:1 hexanes-EtOAc). After 1 h, the entire mixture was directly chromatographed on silica gel and eluted with CH_2Cl_2. Evaporation gave the crude ester **16a** (0.041 g, 98%) as a colourless oil: ^1H NMR δ (200 MHz, $CDCl_3$) 1.26 (3H, d, *J* =6.3 Hz), 3.34 (3H, s), 4.60 (1H, m), 4.65 (1H, s), 4.91 (1H, m), 5.16 (2H, m), 5.50 (1H, m), 6.56 (2H, m), 6.93 -7.19 (13H, m). This material was used directly, without any further purification, for the determination of the enantioselectivity of reaction.

The cyclopropanamine derivative **12a** was obtained as a crystalline solid: m.p. 70-72 °C ($CHCl_3$); $[\alpha]_D$ +25.6° (CH_2Cl_2, c = 0.55); IR ($CHCl_3$) 3562, 3373, 3061, 3021, 2960, 2923, 2875, 1586 and 1491 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 0.87 (1H, m), 0.97 (1H, m), 1.10 (3H, d, *J* =6.4 Hz), 1.24 (1H, m), 2.66 (1H, m), 3.45 (1H, m, *J* =6.4 Hz), 6.98 (6H, m), 7.27 (4H, m); ^{13}C NMR δ (125.8 MHz, $CDCl_3$) 14.5, 22.7, 30.0, 37.3, 69.4, 121.8, 122.2, 129.2, 148.3; MS (EI) *m/z* (70eV) 253 ($M^{+\cdot}$, 19), 208 (94), 167 (21), 119 (50), 91 (32), 77 (100) and 51 (43). Anal. calc. for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.53; H, 7.89; N, 5.46%. Esterification with (*R*)-*O*-methyl mandelic acid gave **20** (52 mg, 94%) as a yellow oil: ^1H NMR δ (270 MHz, $CDCl_3$) 0.66-2.01 (2H, m), 1.16 (3H, d, *J* =6.3 Hz), 2.37 (1H, m), 3.20 (1H, m) 3.40 (3H, s), 4.71 (1H, s), 4.75 (1H, m) and 6.89-7.44 (15H, m).

Preparation of Amino Alcohols 11 and 14 and Cyclopropane Derivatives 12 and 15. Condensation of various aldehydes with the boranes **10** and **13** following the procedure above were used to prepare the following derivatives. In each case esterification with (*R*)-*O*-methyl mandelic acid or (*R*)-Mosher acid was used to determine enantioselectivities of reaction.

***(2S, 3R)*-3-(Diphenylamino)-4-penten-2-ol (14a).** yield 41% (0.52 g); $[\alpha]_D$ - 38.6° (CH_2Cl_2, c = 0.7); IR (neat) 3381, 3036, 2943, 2927, 2855, 1588, 1498 and 1454 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 1.20 (3H, d, *J* =6.1 Hz), 3.85 (1H, m), 4.25 (1H, t, *J* =7.2 Hz), 5.35 (2H, m), 5.70 (1H, m), 7.03 (6H, m), 7.27 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 19.9, 67.1, 70.6, 119.7, 123.0, 124.0, 129.4, 134.3, 147.6; MS (EI) *m/z* (70 eV) 253 ($M^{+\cdot}$, 28), 208 (100), 167 (15), 104 (27), 91 (18), 77 (42) and 43 (7). Anal. calc. for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.47; H, 7.54; N, 5.38%. Mandelate ester (**17a**): ^1H NMR δ (300 MHz, $CDCl_3$) 1.21 (3H, d, *J* =6.3 Hz), 3.37 (3H, s,), 4.46 (1H, m), 4.55 (1H, s), 5.15 (2H, m), 5.41 (1H, m), 5.79 (1H, m), 6.92 (6H, m) and 7.30 (9H, m).

***(1R, 2R)*-1-(Diphenylamino)-2-((*1S*)-1-hydroxyethyl)cyclopropane (15a).** yield 28% (0.35 g); m.p. 70-72 °C ($CHCl_3$); $[\alpha]_D$ -26.1° (CH_2Cl_2, c = 0.8 mg/ml); IR ($CHCl_3$) 3562, 3373, 3063, 3021, 2960, 2923, 2875, 1586, and 1491 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 0.86 (1H, m), 0.97 (1H, m), 1.10 (3H, d, *J* =6.4 Hz), 1.16 (1H, m), 2.66 (1H, m), 3.45 (1H, m, *J* =6.4 Hz), 6.99 (6H, m), 7.26 (4H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 14.4, 22.7, 29.9, 37.3, 69.2, 121.8, 122.2, 129.2, 148.4; MS (EI) *m/z* (70eV) 253 ($M^{+\cdot}$, 19), 208 (94), 167 (21), 119 (50), 91 (32), 77 (100) and 51 (43). Anal. calc. for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.57; H, 7.92; N, 5.45%. Mandelate ester (**21**): ^1H NMR δ (270 MHz, $CDCl_3$) 0.65-1.91 (2H, m), 1.01 (3H, d, *J* =6.4 Hz), 2.67 (1H, m), 3.41 (3H, s), 4.73 (1H, s), 4.75 (1H, m) and 6.90-7.45 (15H, m).

***(3S, 4R)*-3-(Diphenylamino)-1-octen-4-ol (11b).** yield 43% (0.64 g); $[\alpha]_D$ +35.3° (CH_2Cl_2, c = 0.6); IR (neat) 3384, 3044, 2943, 2855, 1589, 1495, 1453 and 1265 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 0.87 (3H, m), 1.10-1.75 (6H, m), 3.91 (1H, m), 4.34 (1H, t, *J* =7.2 Hz), 5.27 (2H, m), 5.96 (1H, m), 6.95 (6H, m), 7.25 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 14.3, 22.9, 28.3, 34.0, 67.6, 72.0, 119.8, 122.4, 123.4, 129.4, 134.7, 147.5; MS (EI) *m/z* (70 eV) 295 ($M^{+\cdot}$, 10), 234 (10), 208 (100), 167 (17), 119(26), 104 (25), 77 (49) and 41 (35). Anal. calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.25; H, 8.53; N, 4.54%. Mandelate ester (**16b**): ^1H NMR δ (300 MHz, $CDCl_3$) 0.77 (2H, t, *J* = 6.8 Hz), 1.18 (5H, m), 1.59 (1H, m), 1.92 (1H, m), 3.38 (3H, s), 4.37 (1H, t, *J* = 8.7 Hz), 4.70 (1H, s), 4.80 (2H, m), 5.34 (1H, m), 5.55 (1H, m) and 6.85-7.42 (15H, m).

***(3R, 4S)*-3-(Diphenylamino)-1-octen-4-ol (14b).** yield 40% (0.59 g); $[\alpha]_D$ -34.9° (CH_2Cl_2, c = 1.9); IR (neat) 3385, 3044, 2925, 2854, 1589, 1495, 1453 and 1265 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 0.88 (3H, m), 1.10-1.75 (6H, m), 3.91 (1H, m), 4.34 (1H, t, *J* =7.2 Hz), 5.27 (2H, m), 5.97 (1H, m), 6.95 (6H, m), 7.25 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 14.3, 22.9, 28.3, 34.0, 67.6, 72.0, 119.8, 122.4, 123.4, 129.4, 134.7, 147.6; MS (EI) *m/z* (70 eV) 295 ($M^{+\cdot}$, 14), 234 (4), 208 (100), 167 (14), 119(23), 104 (21), 77 (36) and 41 (18). Anal. calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.38; H, 8.62; N, 4.67%. Mandelate ester (**17b**): ^1H NMR δ (300 MHz, $CDCl_3$) 0.61 (2H, t, *J* =7.5 Hz), 0.84-1.95 (7H, m), 3.37 (3H, s), 4.46 (1H, t, *J* =8.1 Hz), 4.56 (1H, s), 5.14 (2H, m), 5.32 (1H, m), 5.85 (1H, m) and 6.89-7.40 (15H, m).

***(1S, 2S)*-1-(Diphenylamino)-2-((*1R*)-1-hydroxypentyl)cyclopropane (12b).** yield 25% (0.37 g); $[\alpha]_D$ +16.6° (CH_2Cl_2, c = 0.9); IR ($CHCl_3$) 3364, 3035, 3016, 2945, 2925, 2854, 1589 and 1495 cm^{-1}; ^1H NMR δ (270 MHz, $CDCl_3$) 0.84-1.47 (12H, m), 2.70 (1H, m, *J* =3.3 Hz), 3.33 (1H, m), 6.99 (6H, m), 7.26 (4H, m); ^{13}C NMR δ (125.8 MHz, $CDCl_3$) 13.9, 14.1, 22.7, 27.1, 28.4, 36.6, 37.2, 72.7, 121.7, 122.1, 129.1, 148.3;

MS (EI) *m/z* (70eV) 295 ($M^{+\cdot}$, 14), 234 (13), 208 (100), 169 (12), 119 (200), 104 (15), 77 (24) and 41 (7). Anal. calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 80.99; H, 8.65; N, 4.71%.

***(1R, 2R)*-1-(Diphenylamino)-2-((*1S*)-1-hydroxypentyl)cyclopropane (15b).** yield 25% (0.37 g); $[\alpha]_D$ -16.3° (CH_2Cl_2, c = 0.9); IR ($CHCl_3$) 3364, 3035, 3016, 2945, 2916, 2854, 1588 and 1492 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 0.84-1.47 (12H, m), 2.70 (1H, m, *J* =3.3 Hz), 3.33 (1H, m), 6.99 (6H, m), 7.26 (4H, m); ^{13}C NMR δ (125.8 MHz, $CDCl_3$) 14.0, 14.1, 22.7, 27.2, 28.4, 36.7, 37.3, 72.6, 121.8, 122.1, 129.1, 148.4; MS (EI) *m/z* (70eV) 295 ($M^{+\cdot}$, 12), 234 (35), 208 (100), 169 (31), 119 (24), 104 (22), 77 (45) and 41 (26). Anal. calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.50; H, 8.59; N, 4.75%.

***(3S, 4R)*-3-(Diphenylamino)-1-undecen-4-ol (11c).** yield 46% (0.78 g); $[\alpha]_D$ +30.7° (CH_2Cl_2, c = 2.7); IR (neat) 3389, 3037, 2925, 2855, 1589, 1494, 1452 and 1263 cm^{-1}; 1H NMR δ (200 MHz, $CDCl_3$) 0.85 (3H, m), 1.11-1.78 (12H, m), 3.90 (1H, m), 4.34 (1H, t, *J* =7.5 Hz), 5.25 (2H, m), 5.93 (1H, m), 6.96 (6H, m), 7.24 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 14.3, 22.9, 26.1, 29.5, 29.8, 32.0, 34.3, 67.6, 72.0, 119.8, 122.4, 123.5, 129.4, 134.7, 147.6; MS (EI) *m/z* (70 eV) 337 ($M^{+\cdot}$, 12), 238 (5), 208 (100), 169 (12), 119 (24), 77 (25) and 41 (17). Anal. calc. for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 81.54; H, 9.30; N, 4.08%. Mandelate ester (**16c**): ^1H NMR δ (300 MHz, $CDCl_3$) 0.83 (2H, t, *J* =7.0 Hz), 1.22 (11H, m), 1.60 (1H, m), 1.89 (1H, m), 3.38 (3H, s), 4.37 (1H, t, *J* =8.4 Hz), 4.70 (1H, s), 4.75 (2H, m), 5.34 (1H, m), 5.51 (1H, m) and 6.80-7.73 (15H, m).

***(3R, 4S)*-3-(Diphenylamino)-1-undecen-4-ol (14c).** yield 47% (0.79 g); $[\alpha]_D$ -31.4° (CH_2Cl_2, c = 1.2); IR (neat) 3388, 3037, 2925, 2855, 1589, 1494 and 1452 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 0.86 (3H, m), 1.11-1.78 (12H, m), 3.90 (1H, m), 4.34 (1H, t, *J* =7.5 Hz), 5.25 (2H, m), 5.93 (1H, m), 6.96 (6H, m), 7.24 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 14.3, 22.9, 26.1, 29.5, 29.8, 32.0, 34.3, 67.6, 72.0, 119.8, 122.4, 123.5, 129.4, 134.7, 147.6; MS (EI) *m/z* (70 eV) 337 ($M^{+\cdot}$, 11), 234 (32), 208 (100), 169 (21), 119 (20), 77 (50) and 41 (44). Anal. calc. for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 81.69; H, 9.28; N, 4.05%. Mandelate ester (**17c**): ^1H NMR δ (200 MHz, $CDCl_3$) 0.78-1.95 (15H, m), 3.53 (3H, s), 4.62 (1H, t, *J* =7.1 Hz), 5.18 (2H, m), 5.23 (1H, s), 5.57 (1H, m), 5.89 (1H, m) and 6.92-7.71 (15H, m).

***(1S, 2S)*-1-(Diphenylamino)-2-((*1R*)-1-hydroxyoctyl)cyclopropane (12c).** yield 24% (0.40 g); $[\alpha]_D$ +16.3° (CH_2Cl_2, c = 1.0); IR ($CHCl_3$) 3694, 3449, 3047, 2980, 2950, 2930, 2855, 1589 and 1491 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 0.87 (3H, m), 0.99 (1H, m), 1.14-1.40 (14H, m), 2.68 (1H, m, *J* =3.3 Hz), 3.33 (1H, m), 6.99 (6H, m), 7.27 (4H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 14.2, 22.7, 25.2, 28.5, 29.3, 29.7, 31.9, 37.0, 37.3, 72.7, 121.8, 122.2, 129.2, 148.4; MS (EI) *m/z* (70eV) 319 ($M^{+\cdot}$-H_2O , 26), 234 (100), 206 (27), 169 (55), 167 (40), 128 (17), 115 (15), 77 (43) and 43 (51). Anal. calc. for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 81.69; H, 9.40; N, 4.12%.

***(1R, 2R)*-1-(Diphenylamino)-2-((*1S*)-1-hydroxyoctyl)cyclopropane (15c).** yield 25% (0.42 g); $[\alpha]_D$ -17.6° (CH_2Cl_2, c = 1.1); IR ($CHCl_3$) 3695, 3449, 3049, 2980, 2950, 2932, 2854, 1588 and 1491 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 0.88 (3H, m), 1.00 (1H, m), 1.15-1.36 (14H, m), 2.69 (1H, m, *J* =3.3 Hz), 3.31 (1H, m), 6.99 (6H, m), 7.27 (4H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 14.1, 22.7, 25.2, 28.5, 29.2, 29.7, 31.9, 37.0, 37.3, 72.7, 121.8, 122.2, 129.2, 148.4 ; MS (EI) *m/z* (70eV) 319 ($M^{+\cdot}$-H_2O, 27), 234 (100), 206 (24), 169

(36), 167 (34), 128 (15), 77 (24), 43 (26) and 41 (30). Anal. calc. for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 81.62; H, 9.35; N, 4.14%.

***(3R, 4S)*-4-(Diphenylamino)-1,5-hexadien-3-ol (11d).** yield 45% (0.60 g); $[\alpha]_D$ +11.7° (CH_2Cl_2, c = 1.9); IR ($CHCl_3$) 3089, 3041, 3030, 2933, 2861, 1585 and 1497 cm^{-1}; ^1H NMR δ (200 MHz, $CDCl_3$) 4.46 (2H, m, *J* =5.8 Hz), 5.25 (4H, m), 5.95 (2H, m), 6.93 (6H, m), 7.21 (4H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 67.4, 72.6, 116.3, 119.3, 122.2, 123.3, 129.2, 134.4, 138.4, 147.3; MS (EI) *m/z* (70eV) 265 ($M^{+\cdot}$, 20), 237 (42), 208 (100), 169 (21), 130 (13), 104 (27), 77 (58) and 39 (12). Anal. calc. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.10; H, 7.34; N, 5.19%. Mosher ester (**18**): ^1H NMR δ (270 MHz, $CDCl_3$) 3.38 (3H, s), 4.64 (1H, m), 5.17 (4H, m), 5.78 (2H, m), 6.89 (6H, m) and 7.32 (9H, m).

***(3S, 4R)*-4-(Diphenylamino)-1,5-hexadien-3-ol (14d).** yield 47% (0.62 g); $[\alpha]_D$ -11.4° (CH_2Cl_2, c = 1.8); IR ($CHCl_3$) 3089, 3041, 3030, 2933, 2861, 1585 and 1497 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 4.48 (2H, m, *J* =5.8 Hz), 5.17 (1H, m), 5.30 (3H, m), 5.96 (2H, m), 6.94 (6H, m), 7.23 (4H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 67.4, 72.7, 116.4, 119.4, 122.2, 123.3, 129.2, 134.4, 138.4, 147.3; MS (EI) *m/z* (70eV) 265 ($M^{+\cdot}$, 20), 237 (26), 208 (100), 169 (34), 130 (15), 104 (25), 77 (53) and 51 (26). Anal. calc. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.36; H, 7.36; N, 5.23%. Mosher ester (**19**): ^1H NMR δ (300 MHz, $CDCl_3$) 3.50 (3H, s), 4.67 (1H, t, *J* =7.5 Hz), 5.09 (2H, m), 5.38 (2H, m), 5.71 (1H, m), 5.88 (2H, m) and 6.88-7.50 (15H, m).

***(1R, 2S)*-2-(Diphenylamino)-1-phenyl-3-buten-1-ol (11e).** yield 48% (0.76 g); $[\alpha]_D$ +13.7° (CH_2Cl_2, c = 0.6); IR ($CHCl_3$) 3551, 3419, 3087, 3033, 2980, 2920, 1588, 1495 and 1455 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 4.66 (1H, t ,*J* =6.8 Hz), 5.15 (1H, d, *J* =6.8 Hz), 5.27 (2H, m), 6.18 (1H, m), 6.80 (4H, d, *J* =8.5 Hz), 6.92 (2H, t, *J* =7.2 Hz), 7.20 (9H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 69.3, 73.8, 119.4, 121.9, 123.0, 126.9, 127.8, 128.2, 129.1, 134.0, 141.9, 147.4; MS (EI) *m/z* (70eV) 315 ($M^{+\cdot}$, 2), 209 (25), 208 (100), 193 (12), 169 (33), 130 (8), 104 (12), 91 (9), 77 (18) and 51 (4). Anal. calc. for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.81; H, 6.93; N, 4.31%. Mandelate ester (**16d**): ^1H NMR δ (300 MHz, $CDCl_3$) 3.32 (3H, s), 4.68 (1H, m), 4.69 (1H, s), 4.87 (2H, m), 5.74 (1H, m), 6.27 (1H, d, *J* =7.3 Hz) and 6.85-7.41 (15H, m).

***(1S, 2R)*-2-(Diphenylamino)-1-phenyl-3-buten-1-ol (14e).** yield 47% (0.74 g); $[\alpha]_D$ -13.1° (CH_2Cl_2, c = 1.5); IR ($CHCl_3$) 3551, 3419, 3087, 3033, 2980, 2920, 1588, 1495 and 1455 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 4.67 (1H, t, *J* =6.8 Hz), 5.15 (1H, d, *J* =6.8 Hz), 5.28 (2H, m), 6.18 (1H, m), 6.81 (4H, d, *J* =8.5), 6.93 (2H, t, *J* =7.2 Hz), 7.20 (9H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 69.3, 73.8, 119.3, 121.8, 123.0, 126.8, 127.8, 128.2, 129.1, 134.0, 141.9, 147.4; ; MS (EI) *m/z* (70eV) 315 ($M^{+\cdot}$, 4), 209 (25), 208 (100), 193 (13), 167 (5), 130 (8), 104 (12), 91 (8), 77 (17) and 51 (4). Anal. calc.for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.59; H, 6.99; N, 4.38%. Mandelate ester (**17d**): ^1H NMR δ (300 MHz, $CDCl_3$) 3.35 (3H, s), 4.56 (1H, s), 4.71 (1H, m, *J* =7.2 Hz), 5.16 (1H, m), 6.00 (1H, m), 6.29 (1H, d, *J* = 7.2 Hz) and 6.72-7.29 (15H, m).

***(1S, 2S)*-1-(Diphenylamino)-2-((*1S*)-1-hydroxy-1-(phenyl)methyl)cyclo-propane (12e).** yield 15% (0.24 g); m.p. 115-116 °C (hexane); $[\alpha]_D$ +15.5° (CH_2Cl_2, c = 0.8); IR ($CHCl_3$) 3554, 3366, 3059, 3029, 2940, 2871, 1584 and 1490 cm^{-1}; ^1H NMR δ (300 MHz, $CDCl_3$) 0.97 (1H, m), 1.13 (1H, m), 1.53 (1H, m), 2.81

(1H, m), 4.35 (1H, d, J =7.1 Hz), 6.85-7.30 (15H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 15.2, 30.1, 37.2, 76.2, 121.7, 122.1, 126.6, 128.2, 128.8, 129.2, 143.3, 148.0; MS (EI) *m/z* (70eV) 315 ($M^{+\cdot}$, 2), 297 (64), 209 (20), 208 (100), 193 (12), 169 (12), 129 (12), 104 (56), 91 (23), 77 (73) and 51 (22). Anal. calc. for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.79; H, 6.47; N, 4.49%.

***(1R, 2R)*-1-(Diphenylamino)-2-((*1R*)-1-hydroxy-1-(phenyl)methyl)cyclo-propane (15e).** yield 12% (0.19 g); m.p. 114-116 °C (hexane); $[\alpha]_D$ -15.8° (CH_2Cl_2, c = 0.6); IR ($CHCl_3$) 3554, 3366, 3059, 3029, 2940, 2871, 1584 and 1490 cm^{-1}; ^{1}H NMR δ (300 MHz, $CDCl_3$) 0.95 (1H, m, J =3.3 Hz), 1.14 (1H, m, J =6.2 Hz), 1.52 (1H, m), 2.80 (1H, m, J =3.3 Hz), 4.35 (1H, d, J =7.1 Hz), 6.82-7.30 (15H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 15.2, 30.1, 37.2, 76.2, 121.7, 122.1, 126.6, 128.2, 128.8, 129.2, 143.3, 148.0; MS (EI) *m/z* (70eV) 315 ($M^{+\cdot}$, 2), 297 (65), 209 (20), 208 (100), 193 (14), 169 (14), 129 (14), 104 (63), 91 (22), 77 (79) and 51 (24). Anal. calc. for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.82; H, 6.58; N, 4.32%.

***(1S, 2S)*-1-(Diphenylamino)-2-((*1S*)-1-hydroxy-1-(4-nitrophenyl)methyl)-cyclopropane (12f).** yield 11% (0.20 g); m.p. 160-161 °C (MeOH); $[\alpha]_D$ +5.3° (CH_2Cl_2, *c = 0.6*); IR ($CHCl_3$) 3544, 3425, 3059, 3029, 2940, 2861, 1598, 1584 and 1489 cm^{-1}; ^{1}H NMR δ (300 MHz, $CDCl_3$) 0.98 (1H, m, J =5.3 Hz), 1.09 (1H, m, J =6.1 Hz), 1.45 (1H, m), 2.90 (1H, m, J =3.4 Hz), 4.45 (1H, m, J =3.4 Hz), 6.97 (6H, m), 7.26 (4H, m), 7.47 (2H, m), 8.15 (2H, m); ^{13}C NMR δ (125.8 MHz, $CDCl_3$) 14.9, 30.1, 38.3, 74.8, 121.9, 122.6, 123.9, 126.7, 129.4, 147.6, 148.4, 150.5; MS (EI) *m/z* (70eV) 360 ($M^{+\cdot}$, 1), 342 (21), 326 (3), 209 (19), 208 (100), 193 (11), 169 (17), 119 (14), 104 (41), 91 (14), 77 (59) and 51 (19). Anal. calc. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.05; H, 5.28; N, 7.75%.

***1R 2R*)-1-(Diphenylamino)-2-((*1R*)-1-hydroxy-1-(4-nitrophenyl)methyl)-cyclopropane (15f).** yield 10% (0.18 g); m.p. 160-161 °C (MeOH); $[\alpha]_D$ -5.2° (CH_2Cl_2, c = 1.5); IR ($CHCl_3$) 3544, 3423, 3056, 3029, 2939, 2861, 1598, 1584 and 1489 cm^{-1}; ^{1}H NMR δ (300 MHz, $CDCl_3$) 0.98 (1H, m, J =5.3 Hz), 1.09 (1H, m, J =6.1 Hz), 1.45 (1H, m), 2.93 (1H, m, J =3.4 Hz), 4.44 (1H, m, J =3.4 Hz), 7.00 (6H, m), 7.25 (4H, m), 7.46 (2H, m), 8.15 (2H, m); ^{13}C NMR δ (125.8 MHz, $CDCl_3$) 15.0, 30.1, 38.4, 74.8, 122.0, 122.7, 123.9, 126.7, 129.5, 147.6, 148.4, 150.6 ; MS (EI) *m/z* (70eV) 360 ($M^{+\cdot}$, 1), 342 (13), 326 (2), 209 (19), 208 (100), 193 (10), 169 (14), 119 (12), 104 (31), 91 (12), 77 (44) and 51 (14). Anal. calc. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 72.97; H, 5.58; N, 7.72%.

***(4S)*-2,2-Dimethyl-4-((*1S, 2S*)-1-hydroxy-2-(diphenylamino)-3-buten-1-yl)-1,3-dioxolane (11g).** yield 29% (0.49 g, (of a 3.8:1 diastereomeric mixture with **14g**)), $[\alpha]_D$ +15.9° (CH_2Cl_2, c = 1.8); IR ($CHCl_3$) 3468, 3060, 3029, 2985, 2935, 2890, 1598 and 1494 cm^{-1}; 1H NMR δ (300 MHz, $CDCl_3$) 1.34 (3H, s), 1.46 (3H, s), 3.92 (1H, d, J =5.7 Hz), 4.15 (1H, m), 4.66 (1H, m), 5.31 (2H, m), 5.87 (1H, m), 6.98 (6H, m), 7.24 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 25.4, 26.9, 63.6, 66.0, 72.9, 76.9, 109.4, 119.9, 122.6, 123.4, 129.7, 133.7, 147.3; MS (EI) *m/z* (70eV) 339 ($M^{+\cdot}$, 21), 281 (17), 238 (23), 209 (38), 208 (77), 206 (35), 169 (35), 104 (26), 77 (60) and 43 (100). Anal. calc. for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.27; H, 7.42; N, 4.10%.

***(4S)*-2,2-Dimethyl-4-((*1R, 2R*)-1-hydroxy-2-(diphenylamino)-3-buten-1-yl)-1,3-dioxolane (14g).** yield 28% (0.47 g); $[\alpha]_D$ -40.0° (CH_2Cl_2, c = 1.9); IR ($CHCl_3$) 3464, 3062, 3027, 2983, 2935, 2890, 1598 and 1494 cm^{-1}; ^{1}H NMR δ (300 MHz, $CDCl_3$) 1.36 (3H, s), 1.46 (3H, s), 3.83 (1H, t, J =7.7 Hz), 3.96 (2H, m),

4.43 (1H, m), 4.56 (1H, m), 5.30 (2H, m), 6.11 (1H, m), 6.99 (6H, m), 7.23 (4H, m); ^{13}C NMR δ (75.1 MHz, $CDCl_3$) 25.6, 26.6, 65.8, 66.3, 69.8, 75.1, 109.6, 118.6, 122.2, 123.1, 129.4, 135.3, 147.5; MS (EI) *m/z* (70eV) 339 ($M^{+\cdot}$, 13), 281(14), 238 (23), 209 (31), 208 (80), 206 (38), 169 (25), 104 (29), 77 (57) and 43 (100). Anal. calc. for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.21; H, 7.29; N, 4.30%.

***(4S)*-2,2-Dimethyl-4-{*(1S)*-hydroxy-[*(1S,2S)*-(diphenylamino)cyclopropyl]methyl}-1,3 dioxolane (12g).** yield 23% (0.39 g, (of a 4.7:1 diastereomeric mixture)); $[\alpha]_D$ +16.4° (CH_2Cl_2, c = 1.7); IR ($CHCl_3$) 3467, 3060, 2985, 2935, 2891, 1589 and 1495 cm^{-1}; ^{1}H NMR δ (270 MHz, $CDCl_3$) 0.90 (2H, m), 1.12 (1H, m), 1.38 (3H, s), 1.46 (3H, s), 2.83 (1H, m) 3.38 (1H, m), 3.89 (1H, dd, *J* = 22.2, 7.0 Hz), 3.94 (1H, dd, *J* =21.9, 6.9 Hz), 4.12 (1H, m), 7.06 (2H, m), 7.14 (4H, m), 7.31 (4H, m); ^{13}C NMR δ (125.8 MHz, $CDCl_3$) 13.3, 24.6, 25.1, 26.3, 37.5, 64.3, 72.8, 78.0, 108.9, 121.7, 122.1, 129.0, 148.1; MS (EI) *m/z* (70eV) 339 ($M^{+\cdot}$, 14), 281 (17), 238 (36), 209 (35), 208 (100), 206 (48), 169 (14), 104 (25), 77 (37) and 43 (45). HRMS calc. for $C_{21}H_{25}NO_3$: ($M^{+\cdot}$), 339.1834. Found: ($M^{+\cdot}$), 339.1834.

***(4S)*-2,2-Dimethyl-4-{*(1R)*-hydroxy-[*(1R,2R)*-(diphenylamino)cyclopropyl]-methyl}-1,3-dioxolane (15g).** yield 26% (0.44 g); $[\alpha]_D$ -41.9° (CH_2Cl_2, c = 1.6); IR ($CHCl_3$) 3467, 3060, 2985, 2937, 2890, 1589 and 1495 cm^{-1}; ^{1}H NMR δ (270 MHz, $CDCl_3$) 0.97 (2H, m), 1.12 (1H, m), 1.28 (3H, s), 1.37 (3H, s), 2.76 (1H, m, *J* =3.2 Hz), 3.41 (1H, t, *J* =7.1 Hz), 3.53 (1H, m, *J* =3.0 Hz), 3.74 (1H, t, *J* =7.2 Hz), 3.88 (1H, m, *J* =3.0 Hz), 7.00 (6H, m), 7.26 (4H, m); ^{13}C NMR δ (67.5 MHz, $CDCl_3$) 14.2, 24.0, 25.0, 26.4, 36.4, 64.1, 71.0, 78.3, 108.8, 121.7, 122.2, 129.1, 148.2; MS (EI) *m/z* (70eV) 339 ($M^{+\cdot}$, 16), 281 (19), 238 (37), 209 (32), 208 (100), 206 (39), 169 (27), 104 (18), 77 (28) and 43 (26). HRMS calc. for $C_{21}H_{25}NO_3$: ($M^{+\cdot}$), 339.1834. Found: ($M^{+\cdot}$), 339.1830.

Preparation of *(1R, 2R)*-1-(*(1R)*-1-Hydroxybenzyl)-2-(diphenylamino)-3-[^{2}H]-cyclopropane (23). To a solution of the deuterium-labelled enamine (**7**) (1.05 g, 5.00 mmol) in dry THF (10 mL) at 0 °C was added TMEDA (0.75 mL, 5.00 mL) and n-BuLi (2.5 M, 2.0 mL). The solution wad stirred for 2 h and subsequently cooled to -78 °C. The anionic solution was treated with (+)-*B*-methoxydiisopinocampheyl-borane (**9a**) (1.58 g, 5.00 mmol) in dry THF (5 mL) and maintained at -78 °C for 2 h. To this solution was added $BF_3{\cdot}OEt_2$ (0.82 mL, 6.65 mmol) followed imediately by benzaldehyde (0.53 g, 5.00 mmol) in dry THF (1 mL). The reaction temperature was held at -78 °C for 3 h and then gradually allowed to warm to room temperature. Aqueous NaOH (2.5 M, 2.0 mL) and 30% H_2O_2 (2 mL) were added and the reaction mixture stirred for 12 h at room temperature. The reaction mixture was diluted with diethyl ether (25 mL) and separated from the aqueous layer. The organic solution was dried ($MgSO_4$) and concentrated in vacuo. The remaining residue was purified by column chromatography (silica gel, 2:1 hexanes-EtOAc) to give the amino alcohol **23** (0.16 g, 10%) as a white solid: m. p. 114-116 °C (hexane); ^{1}H NMR δ (300 MHz, $CDCl_3$) 0.95 (0.5H, m), 1.14 (0.5H, m), 1.49 (1H, m), 2.80 (1H, m), 4.35 (1H, d, *J* =7.2 Hz) and 6.81-7.31 (15H, m).

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