### Catalytic Asymmetric Allylic Transfer Reactions for the Enantioselective Synthesis of Dienyl and Enynyl Alcohols

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Keywords: Allylation / Asymmetric catalysis / Alcohols / Lewis acids / Titanium

Efficient catalytic asymmetric allylic transfer reactions of achiral aldehydes with 2-ethynyl- and 2-ethenyl-2-propenyl-stannane promoted by BINOL- $Ti^{IV}$  complex with synergetic reagent are achieved for the synthesis of homoenynyl- and dienyl alcohols with high levels of enantioselectivity. The

#### Introduction

The availability of efficient synthetic methods for achieving absolute stereoselectivity in a catalytic process in the production of enantiomerically pure compounds is of considerable current interest in the field of synthetic chemistry.<sup>[1-3]</sup> In this regard, allylic transfer reactions provide excellent stereoselective routes for converting aldehydes into the corresponding alcohols.<sup>[4-7]</sup> In the light of widespread advances in catalytic methods for the synthesis of chiral substances, the allylic transfer reaction of carbonyl functionalities with chiral Lewis acid catalysts has led to significant developments in the area of synthetic chemistry.<sup>[8]</sup> Although there have been several elegant reports regarding reinforcing catalytic ability for practical use in the literature,<sup>[9,10]</sup> the scope of the catalytic allylic transfer reaction still remains in its application with structurally simple allyl systems. Recently, we reported two versions of the enantioselective synthesis of dienyl alcohols 1 based on an accelerating strategy.<sup>[11,12]</sup> Our approach involves the use of a BINOL-Ti<sup>IV</sup> complex as a chiral promoter along with *i*PrSBEt<sub>2</sub> as an accelerating synergetic reagent that has recently been shown to provide highly enantioselective versions of allylic transfer reactions of achiral aldehydes in the production of enantioenriched alcohols.<sup>[13-16]</sup> During the course of our research program aimed at finding new reagents and realizing useful and practical ways to expand the scope of allylic transfer reactions, we became quite interested in the addition of the dienyl moiety to one carbon homologated systems such as 2 and 3 (Scheme 1). The realization of an efficient method for the synthesis of 2 and 3 should be valuable because the structures are featured in many biologically relevant substances,<sup>[17]</sup> and many useful functional group transformations can be foreseen for enynyl and dienyl moieties.<sup>[18-20]</sup> With the notion that this investigation leads to the efficient synthesis of a number of optic-

 Department of Chemistry and BK-21 School of Molecular Science, Sungkyunkwan University, Suwon 440-746, Korea Fax: (internat.) +82-31/290-7075 E-mail: cmyu@chem.skku.ac.kr yields. The application of catalytic asymmetric dienylation in a single operation was exemplified by the enantioselective synthesis of naturally occurring (–)-Ipsdienol and (–)-Ipsenol.

range of enantioselectivity is 84-99% ee with good chemical

ally active alcohols, we set out to determine the scope with new allylic transfer reagents.



Scheme 1

#### **Results and Discussion**

The new reagent 4, a crucial compound in the present research, was prepared from commercially available 2methyl-1-buten-3-yne in a single operation, purified by distillation, and was found to be stable upon storage. Treatment of dilithiated 2-methyl-1-buten-3-yne, prepared according to a literature procedure,<sup>[21,22]</sup> with Bu<sub>3</sub>SnCl (0.8 equiv.) at -78 °C in THF for 30 min. then workup (quenching with pH 7 buffer solution at -78 °C followed by extraction with hexanes), afforded the crude product. After removal of baseline impurities by filtration through Et<sub>3</sub>N-pretreated silica gel with hexane as eluent, a final purification was effected by distillation (0.1 Torr, 88 °C, 64% yield). The stage was thus set for the allylic transfer reaction of 4 with aldehydes promoted by a Lewis acid catalyst. After examining several conditions based on our previous studies, [10-15]the following observations were made: (i) a control experiment revealed that the reaction proceeded only slowly in the absence of a synergetic reagent (10 mol-% catalyst, -20°C, 20 h, 32% yield); (ii) *i*PrSBEt<sub>2</sub> was found to be quite efficient in the catalytic process to speed up the reaction rate (with 5 mol-% BINOL-Ti<sup>IV</sup>, see Table 1);<sup>[23]</sup> (iii) a 1:1 mixture of BINOL and  $Ti(OiPr)_4$  in the presence of 4 Å molecular sieves proved to be the most efficient catalyst;<sup>[24-27]</sup> (iv) the reaction performed at -20 °C in PhCF<sub>3</sub> resulted in optimal chemical yields and enantioselectivities in comparison with other solvents such as CH<sub>2</sub>Cl<sub>2</sub> and toluene. Under optimal conditions, the allylic transfer reaction was carried out according to the following procedure: The red-brown mixture of (S)-BINOL-Ti<sup>IV</sup> complex (5

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mol-%) prepared from (S)-BINOL (0.05 equiv.) and freshly distilled Ti(O*i*Pr)<sub>4</sub> (0.05 equiv.) in PhCF<sub>3</sub> at 25 °C for 3 h was cooled to -20 °C, and 5 (R = PhCH<sub>2</sub>CH<sub>2</sub>) was added. To this mixture was added dropwise 4 (1.1 equiv.) in  $PhCF_3$ followed by 7 (1.2 equiv.) in PhCF<sub>3</sub> with a gas-tight syringe via a syringe pump over 1 h along the wall of the flask while keeping the temperature below -20 °C. After 7 h at -20°C, the mixture was quenched by the addition of a saturated aqueous NaHCO<sub>3</sub>. After work up, chromatography on silica gel gave 2a ( $R = PhCH_2CH_2$ ) in 83% yield with 93% ee. The reliability of the reaction was further examined with a variety of aldehydes of varying steric and electronic environments. Reactions are generally complete after 7 h at -20°C. As shown in Table 1, we observed that better chemical yields and enantioselectivities were obtained with lesshindered aldehydes, including alkynal, than with the more bulky cyclohexanecarboxaldehyde.

Table 1. Catalytic asymmetric enynylation of 4<sup>[a]</sup>



<sup>[a]</sup> All reactions were carried out at -20 °C in PhCF<sub>3</sub>. – <sup>[b]</sup> (*S*)-BINOL:Ti(O*i*Pr)<sub>4</sub> = 1:1 (5 mol-%). – <sup>[c]</sup> Yields refer to isolated and purified products. – <sup>[d]</sup> Enantiomeric excess were determined by preparation of (+)-MTPA ester derivatives, analysis by 500 MHz <sup>1</sup>H NMR spectroscopy, and comparison with corresponding diastereomers which were prepared from (*R*)-BINOL-Ti<sup>IV</sup> (all entries) and by HPLC analysis using chiral column (Chiracel OD-H, 5% *i*PrOH in hexanes, entries 4,5).

In the light of the above results for the catalytic asymmetric enynylation reaction, we turned our attention next to examine the use of this approach with a dienvltin reagent for the catalytic asymmetric dienylation reaction of aldehydes.<sup>[28]</sup> Treatment of  $8^{[29]}$  with 5 (R = PhCH<sub>2</sub>CH<sub>2</sub>, 1 equiv.) in the presence of (S)-BINOL-Ti<sup>IV</sup> (5 mol-%) followed by 7 in PhCF<sub>3</sub> for 5 h afforded the alcohol 3a (R = Ph CH<sub>2</sub>CH<sub>2</sub>) in 78% isolated yield and 97% ee. From Table 2 it can be seen that asymmetric dienvlation reactions were conducted on a variety of aldehydes under identical conditions to furnish alcohols 3 with excellent enantioselectivities. Reaction times and chemical yields were also dependent on the steric environment of the substrates. The absolute configuration of the predominating enantiomer for adducts was unambiguously established by comparison of values of specific rotations with those of previously known alcohols.[28]

The direct synthetic application of catalytic asymmetric dienylation was exemplified by the enantioselective syn-

Table 2. Catalytic asymmetric dienylation of 8<sup>[a]</sup>



Compound	5 (R)	h	Yield [%]	ee [%]
	PhCH <sub>2</sub> CH <sub>2</sub>	5	78	97
3b	nC <sub>6</sub> H <sub>13</sub>	5	81	93
3c	$cC_6H_{11}$	10	53	91
3d	Ph	5	88	93
3e	PhCH=CH	5	74	96
3f	PhC≡C	5	91	91

 $^{\left[ a\right] }$  All conditions were identical with the enynylation described in Table 1.

thesis of naturally occurring (-)-Ipsdienol and (-)-Ipsenol (Scheme 2), which are two of the aggregation pheromones isolated from the bark beetle *Ips. paraconfusus*.<sup>[30-33]</sup> Reaction of **8** with 3-methyl-2-butenal under identical conditions except with (*R*)-BINOL instead of (*S*)-BINOL afforded Ipsdienol **9** (68% yield; 93% *ee*;  $[\alpha]_D^{23} = -15.1$ , EtOH). Similarly, isovaleraldehyde was converted under the same conditions to Ipsenol **10** (77% yield; 99% *ee*;  $[\alpha]_D^{25} = -17.9$ , EtOH).

H,OH

H, OH

(-)-Ipsendiol (9)

(-)-Ipsenol (10)

Scheme 2

#### Conclusion

In summary, an efficient catalytic protocol for the enantioselective synthesis of enynyl and dienyl alcohols has been developed, based on the use of chiral Lewis acid and synergetic reagent. For this purpose, two tin reagents were prepared and proven to be efficient for allylic transfer reactions with achiral aldehydes. A variety of aldehydes were converted into the corresponding alcohols with high levels of enantioselectivity. We believe that the products can serve as synthetic intermediates for the synthesis of chiral substances by selective functional group transformations. Further studies on the scope of this reaction and related transformations are in progress.

### **Experimental Section**

**General Remarks:** All reactions were run in flame dried glassware under an atmosphere of nitrogen. Tetrahydrofuran (THF) was dried by refluxing over sodium and benzophenone until a permanent purple coloration was presented, and distilled prior to use.  $\alpha,\alpha,\alpha$ -Trifluorotoluene was distilled from CaH<sub>2</sub> prior to use. All liquid reagents purchased from Aldrich were distilled properly prior to use, unless otherwise indicated. Purification was conducted by flash column chromatography on silica gel (230-400 mesh), eluting with a mixture of hexane and ethyl acetate, unless otherwise stated. All reactions were monitored by thin layer chromatography carried out on Merck silica gel plate (60 F254) using UV light as visualizing agent and ethanolic anisaldehyde solution and heat as developing agent. FT-IR spectra were recorded on a Nicolet 205. <sup>1</sup>H NMR spectra were recorded on a Varian Unity Inova at 500 MHz in CDCl<sub>3</sub> as a solvent with TMS or residual chloroform as the internal standard. <sup>13</sup>C NMR spectra were measured on a Bruker AC-P200 at 50 MHz or on a Varian Unity Inova at 125 MHz in CDCl<sub>3</sub> as a solvent. EI-mass spectra were obtained on a VG-Instrument Trio 2000 system at 70 eV. Optical rotations were measured on a JASCO P-1020 digital polarimeter at ambient temperature. Enantiomeric ratios were determined by preparation of (+)-MTPA ester derivatives, analysis by 500 MHz <sup>1</sup>H NMR spectroscopy, and comparison with corresponding diastereomers which were prepared from (R)-BINOL-Ti<sup>IV</sup> and/or by HPLC analysis using a chiral column (Chiracel OD-H column, 5% iPrOH in hexanes, UV 254 nm, flow 1.0 mL/min.).

Tributyl(2-methylene-but-3-ynyl)stannane (4): To a solution of freshly distilled 2-methyl-1-buten-3-yne (2.3 mL, 1.60 g, 24 mmol) in dry THF (5 mL) were successively added BuLi (2.19 M in hexane, 22 mL, 48 mmol) and tBuOK (5.2 g, 48 mmol) in THF (50 mL) at -78 °C under nitrogen atmosphere. After an additional 30 min. at -78 °C, the temperature was allowed to rise to 0 °C, and the mixture was stirred at this temperature for 20 min. To the mixture was added a solution of anhydrous LiBr (4.2 g, 48 mmol) in THF(25 mL) at -20 °C, and the mixture was stirred for 20 min. at this temperature. After the mixture was cooled to -78 °C, precooled Bu<sub>3</sub>SnCl (5.20 mL, 6.24 g, 19.2 mmol) in THF (5 mL) was added with a cannula at the same temperature. After stirring for 30 min. at -78 °C, a buffer solution (pH = 7, 20 mL) was added to the reaction mixture. The mixture was extracted with hexane (ca. 150 mL  $\times$  2). After drying the combined organic solution over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvents were removed under reduced pressure. After removal of baseline impurities on a column with Et<sub>3</sub>Npretreated silica gel (ca 5 cm), distillation under reduced pressure afforded 4 (4.36 g, 12.3 mmol, 64%) as a colorless liquid: b.p.  $88-89 \text{ °C} (0.1 \text{ Torr}). - \text{TLC}: R_f = 0.67 \text{ (hexane)}. - \text{FR-IR (neat)}:$  $\tilde{v} = 3290, 3031, 2955, 2923, 1611, 1452, 1267, 913, 754, 700 \text{ cm}^{-1}$ .  $- {}^{1}H$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.79 - 0.95$  [m, 15 H, Sn(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>], 1.26-1.34 [m, 6 H, Sn(CH<sub>2</sub>CH<sub>2</sub>-1.44 - 1.54 $CH_2CH_3)_3],$ [m, 6 Η, Sn(CH<sub>2</sub>CH<sub>2</sub>- $CH_2CH_3$ ], 1.90 (d, J = 1.13 Hz, 2 H,  $SnCH_2C=CH_2$ ), 2.83 (s, 1 H, C=CH), 5.04 (s, 1 H, C=CHH), 5.10 (d, J = 1.13 Hz, 1 H, C= CH*H*).  $- {}^{13}$ C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 9.11, 13.73, 14.56,$ 26.98, 29.26, 73.04, 82.91, 123.83, 125.96. –  $C_{17}H_{32}Sn$  (355.13): calcd. C 57.49, H 9.08; found C 57.77, H 9.27.

(+)-(*3R*)-5-Methylene-1-phenylhept-6-yn-3-ol (2a): In a typical procedure for the allylic transfer reactions, a flame-dried flask containing (*S*)-BINOL (114.6 mg, 0.4 mmol) and activated powdered 4 Å molecular sieves (1.2 g) was evacuated, carefully purged with nitrogen three times and then charged with dry PhCF<sub>3</sub> (4 mL) followed by freshly distilled Ti(O*i*Pr)<sub>4</sub> (freshly prepared 0.5 M in PhCF<sub>3</sub>, 0.8 mL, 0.4 mmol). The reaction was allowed to proceed at 25 °C for 3 h. The red-brown mixture was cooled to -20 °C in a dry ice/CCl<sub>4</sub> bath, and hydrocinnamaldehyde (5, R = PhCH<sub>2</sub>CH<sub>2</sub>, 0.27 g, 2.0 mmol) in PhCF<sub>3</sub> (1.0 mL) was added. To this mixture was added dropwise tributyl(2-methylenebut-3-ynyl)stannane (4, 0.78 g, 2.2 mmol) in PhCF<sub>3</sub> (2 mL) followed by *i*PrSBEt<sub>2</sub> (7, 0.35 g, 2.4 mmol) in PhCF<sub>3</sub> (2 mL) with gas-tight syringe via a syringe pump over 1 h along the wall of the flask while keeping the temper-

ature below -20 °C. After stirring for 7 h at -20 °C, aqueous NaHCO<sub>3</sub> (5 mL) was added to the reaction mixture, and then diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The molecular sieves were removed by filtration, and the aqueous layer was extracted with CH2Cl2 (ca 20 mL  $\times$  2). After drying the combined organic solution over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvents were removed under reduced pressure. Column chromatography (SiO2, 15% EtOAc in hexanes) afforded 3 (R = PhCH<sub>2</sub>CH<sub>2</sub>, 0.334 g, 0.167 mmol, 83%) as a colorless liquid. TLC:  $R_f = 0.25$  (15:85, EtOAc/hexane).  $- [\alpha]_D^{22} = +30.6$  $(c = 1.55, \text{CHCl}_3; 93\% \text{ ee}). - \text{FT-IR}$  (neat):  $\tilde{v} = 3408, 3296, 2941,$ 2921, 1608, 1496, 1296, 912 cm<sup>-1</sup>. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.79 - 1.85$  (m, 3 H, PhCH<sub>2</sub>CH<sub>2</sub> and OH), 2.30 (dd, J = 8.65, 14.31 Hz, 1 H, HOCHCHHC=C), 2.40 (dd, J = 3.97, 14.31 Hz, 1 H, HOCHCHHC=C), 2.70 (ddd, J = 7.37, 9.07, 13.89 Hz,1 H, PhCHH), 2.84 (ddd, J = 6.52, 9.07, 13.32 Hz, 1 H, PhCHH), 2.94 (s, 1 H, C=CH), 3.93 (m, 1 H, HOCH), 5.41 (s, 1 H, C=CHH), 5.56 (d, J = 1.79 Hz, 1 H, C=CHH), 7.17–7.30 (m, 5 H, Ph). – <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 31.98$ , 38.30, 45.06, 69.23, 77.86, 83.60, 125.68, 125.76, 127.26, 128.31, 128.36, 141.93. - EI-MS:  $m/z = 200 [M^+]$ .  $- C_{14}H_{16}O (200.28)$ : calcd. C 83.96, H 8.05; found C 84.01, H 8.13. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 1.89$  (M = major), 2.02 (m = minor) (m, 2 H, PhCH<sub>2</sub>CH<sub>2</sub>); 5.16 (M), 5.22 (m) (s, 1 H, C=CHH)].

(+)-(5R)-3-Methyleneundec-1-yn-5-ol (2b): Compound 2b was obtained according to the above procedure for 2a as a colorless oil. Yield: 78%. – TLC:  $R_f = 0.33$  (15:85, EtOAc/hexane). –  $[\alpha]_D^{25} =$ +8.9 (c = 1.64, CHCl<sub>3</sub>; 94% *ee*). – FR-IR (neat):  $\tilde{v} = 3385$ , 3306, 2955, 2857, 1612, 1492, 1266, 1048, 909 cm<sup>-1</sup>. - <sup>1</sup>H NMR  $(500 \text{ MHz}, \text{ CDCl}_3)$ :  $\delta = 0.89$  (t,  $J = 6.81 \text{ Hz}, 3 \text{ H}, \text{ CH}_2\text{CH}_3$ ), 1.24-1.36 [m, 8 H, (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>], 1.46-1.50 (m, 2 H, HOCHCH<sub>2</sub>), 1.74 (d, J = 3.97 Hz, 1 H, OH), 2.24 (dd, J = 8.79, 13.61 Hz, 1 H, HOCHCHHC=C), 2.38 (dd, J = 3.97, 13.61 Hz, 1 H, HOCHCHHC=C), 2.94 (s, 1 H, C≡CH), 3.89 (m, 1 H, HOCH), 5.41 (s, 1 H, C=CHH), 5.56 (d, J = 1.70 Hz, 1 H, C=CHH). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.02, 22.56, 25.54, 29.24, 31.77, 36.71, 45.09, 69.78, 77.69, 83.72, 125.53, 128.73. - EI-MS: m/z =162 [M<sup>+</sup> - H<sub>2</sub>O]. - C<sub>12</sub>H<sub>20</sub>O (180.29): calcd. C 79.94, H 11.18; found C 79.71, H 11.10. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 1.89$  (M), 2.02 (m) (m, 2 H, PhCH<sub>2</sub>CH<sub>2</sub>); 2.24 (M), 2.37 (m) (dd, 1 H, OCHCHH); 2.37 (m), 2.55 (M) (dd, 1 H, OCHCHH); 5.06 (M), 5.22 (m) (s, 1 H, C=CHH)].

(+)-(1S)-1-Cyclohexyl-3-methylene-pent-4-yn-1-ol (2c): Compound 2c was obtained according to the above procedure for 2a as a colorless oil. Yield: 41%. – TLC:  $R_f = 0.33$  (15:85, EtOAc/hexane). –  $[\alpha]_{D}^{22} = +6.8$  (c = 0.87, CHCl<sub>3</sub>; 84% ee). - FR-IR (neat):  $\tilde{v} =$ 3385, 3306, 2955, 2857, 1612, 1492, 1266, 1048, 909 cm<sup>-1</sup>. - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.05 - 1.22$  (m, 6 H, cHex), 1.40-1.55 (m, 2 H, cHex), 1.65 (br s, 1 H, OH), 1.71-1.80 (m, 2 H, cHex), 1.83-1.88 (m, 1 H, cHex), 2.22 (dd, J = 9.64, 14.20 Hz, 1 H, HOCHCHHC=C), 2.38 (dd, J = 2.84, 14.20 Hz, 1 H, HOCHCH*H*C=C), 2.94 (s, 1 H, C≡C*H*), 3.66 (m, 1 H, HOC*H*), 5.41 (s, 1 H, C=CHH), 5.56 (d, J = 1.20 Hz, 1 H, C=CHH). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 22.23, 25.94, 28.24, 29.45, 29.64, 31.77, 45.11, 69.83, 76.84, 83.54, 125.51, 129.35. – EI-MS: m/z = 178 [M<sup>+</sup>]. - C<sub>12</sub>H<sub>18</sub>O (178.27): calcd. C 80.85, H 10.18; found C 80.47, H 10.40. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 2.46$  (M), 2.41 (m) (dd, 2 H, OCHCHH); 5.48 (M), 5.33 (m) (s, 1 H, C=CH)].

(+)-(1*S*)-3-Methylene-1-phenylpent-4-yn-1-ol (2d): Compound 2d was obtained according to the above procedure for 2a as a colorless oil. Yield: 91%. – TLC:  $R_f = 0.25$  (15:85, EtOAc/hexane). –  $[\alpha]_{25}^{25} = +20.4$  (c = 1.63, CHCl<sub>3</sub>; 97% *ee*). – FR-IR (neat):  $\tilde{v} =$ 

3381, 3290, 3031, 1611, 1452, 1050, 913, 754, 700 cm<sup>-1</sup>. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.19 (d, *J* = 3.11 Hz, 1 H, OH), 2.55–2.59 (m, 2 H, HOCHC*H*<sub>2</sub>C=C), 2.99 (s, 1 H, C=C*H*), 5.00 (ddd, *J* = 3.11, 5.95, 7.65 Hz, 1 H, HOC*H*), 5.39 (s, 1 H, C= *CH*H), 5.56 (d, *J* = 1.70 Hz, 1 H, C=CH*H*), 7.25–7.42 (m, 5 H, Ph). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 47.17, 72.26, 78.04, 83.47, 125.82, 126.00, 127.10, 127.64, 128.43, 143.48. – EI-MS: *m*/*z* = 107 [M<sup>+</sup> – C<sub>5</sub>H<sub>5</sub>]. – C<sub>12</sub>H<sub>12</sub>O (172.23): calcd. C 83.69, H 7.02; found C 83.55, H 7.38. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta$  = 2.46 (M), 2.59 (m) (dd, 1 H, HOCHC*H*HC=C); 6.21 (M), 6.29 (m) (dd, 1 H, OC*H*)].

(+)-(3S)-5-Methylene-1-phenylhept-1-en-6-yn-3-ol (2e): Compound 2e was obtained according to the above procedure for 2a as a colorless oil. Yield: 68%. – TLC:  $R_f = 0.19$  (15:85, EtOAc/hexane). –  $[\alpha]_{D}^{25} = +29.2$  (c = 0.85, CHCl<sub>3</sub>; 92% ee). - FR-IR (neat):  $\tilde{v} =$ 3583, 3422, 3298, 3054, 2956, 2925, 1611, 1448, 1266, 968 cm<sup>-1</sup>. -<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.94$  (d, J = 3.69 Hz, 1 H, OH), 2.45-2.53 (m, 2 H, HOCHCH<sub>2</sub>C=C), 2.98 (s, 1 H, C≡CH), 4.62 (m, 1 H, HOCH), 5.44 (s, 1 H, C=CHH), 5.59 (d, J = 1.14 Hz, 1 H, C=CHH), 6.25 (dd, J = 6.23, 15.87 Hz, 1 H, PhCH=CH), 6.66 (d, J = 15.87 Hz, 1 H, PhCH=CH), 7.23-7.40 (m, 5 H, Ph). -<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 45.20, 70.71, 77.99, 83.58,$ 125.56, 126.06, 126.48, 126.71, 127.64, 129.53 ,130.49, 131.00, 136.65. – EI-MS:  $m/z = 198 [M^+]$ . – C<sub>14</sub>H<sub>14</sub>O (198.26): calcd. C 84.81, H 7.12; found C 84.78, H 7.02. [Diagnostic <sup>1</sup>H NMR  $(CDCl_3, 500 \text{ MHz})$  of (+)-MTPA ester:  $\delta = 6.06 \text{ (M)}, 6.19 \text{ (m)} (dd,$ 1 H, PhCH=CH); 6.65 (M), 6.77 (n) (d, 1 H, PhCH=CH)].

(+)-(*3S*)-5-Methylene-1-phenylhepta-1,6-diyn-3-ol (2f): Compound 2f was obtained according to the above procedure for 2a as a colorless oil. Yield: 81%. – TLC:  $R_f = 0.23$  (15:85, EtOAc/hexane). –  $[a]_{D5}^{25} = +31.5$  (c = 1.10, CHCl<sub>3</sub>; 91% *ee*). – FR-IR (neat):  $\tilde{v} = 3583$ , 3422, 3298, 3054, 2956, 2925, 1611, 1448, 1266, 968 cm<sup>-1</sup>. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.64$  (br s, 1 H, OH), 2.68 (m, 2 H, HOCHCH<sub>2</sub>C=C), 2.98 (s, 1 H, C=CH), 4.90 (dd, J = 6.41, 6.41 Hz, 1 H, HOCH), 5.51 (s, 1 H, C=CHH), 5.63 (d, J = 1.22 Hz, 1 H, C=CHH), 7.26–7.45 (m, 5 H, Ph). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 45.35$ , 61.32, 78.12, 83.29, 85.47, 88.95, 122.48, 125.78, 126.53, 128.46. 129.62, 131.50. – EI-MS: m/z = 196 [M<sup>+</sup>]. – C<sub>14</sub>H<sub>12</sub>O (196.25): calcd. C 85.68, H 6.16; found C 85.55, H 6.11. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 2.59$  (M), 2.76 (m) (m, 2 H, OCHCH<sub>2</sub>); 6.03 (M), 6.08 (n) (dd, 1 H, OCHCH<sub>2</sub>)].

Tributyl(2-methylene-but-3-enyl)stannane (8): A flame-dried flask containing tBuOK (5.53 g, 49.2 mmol) was evacuated, carefully purged with nitrogen three times and then charged with dry THF (50 mL) followed by 2,2,6,6-tetramethylpiperidine (8.30 mL, 6.95 g, 49.2 mmol). The solution was cooled to -78 °C in a dry ice/acetone bath, and a solution of nBuLi (2.41 M in hexane, 20.5 mL, 49.4 mmol) was added over 10 min. while keeping the temperature below -50 °C. After stirring for 20 min. at -78 °C, freshly distilled 2-methylbuta-1,3-diene (4.8 mL, 3.27 g, 48 mmol) in THF (10 mL) was added over 10 min. during which time a deep red solution was formed. After stirring at -78 °C for 30 min., precooled Bu<sub>3</sub>SnCl (9.0 mL, 10.8 g, mL, 33.2 mmol) in THF (20 mL) was added with a cannula at -78 °C. After stirring for 20 min. at -78 °C, a buffer solution (pH = 7, 20 mL) was added at the same temperature. The mixture was extracted with hexane (ca. 150 mL  $\times$  2). After drying the combined organic solution over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvents were removed under reduced pressure. After removal of baseline impurities by column chromatography with Et<sub>3</sub>N-pretreated silica gel (ca. 5 cm) with hexane as eluent, distillation under reduced pressure afforded 8 (6.05 g, 16.9 mmol, 51%) as a colorless

liquid: b.p. 94–96 °C (0.1 Torr). – TLC:  $R_f = 0.90$  (85:15, hexane/ EtOAc). - FR-IR (neat):  $\tilde{v} = 2963, 2933, 1649, 1638, 1461, 987,$ 959, 897, 863 cm<sup>-1</sup>. - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta =$ 0.82-0.90 (m, 15 H, Sn(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.26-1.33 (m, 6 H,  $Sn(CH_2CH_2CH_2CH_3)_3),$ 1.44 - 1.50(m, 6 H.  $Sn(CH_2CH_2CH_2CH_3)_3$ , 1.90 (d, J = 0.85 Hz, 2 H,  $SnCH_2C=$  $CH_2$ ), 4.76 (d, J = 0.85 Hz, 1 H, C=CHH), 4.81 (s, 1 H, C=CHH), 5.05 (d, J = 10.50 Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 5.09 (d, J =17.29 Hz, 1 H,  $H_2C=C-CH=CHH$ , 6.37 (dd, J = 10.50, 17.29Hz, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>). - <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 9.28, 13.27, 13.45, 26.95, 28.95, 111.62, 112.50, 139.48, 146.11; Calcd. for C<sub>17</sub>H<sub>34</sub>Sn: calcd. C 57.17, H 9.60; found C 57.59, H 9.85.

(+)-(3R)-5-Methylene-1-phenyl-hept-6-en-3-ol (3a): Compound 3a was obtained according to the procedure for the synthesis of 2a except with 8 instead of 4. Yield: 78%. – TLC:  $R_f = 0.23$  (15:85, EtOAc/hexane).  $- \left[\alpha\right]_{D}^{24} = +31.05 \ (c = 1.70, \text{ EtOH}; 97\% \ ee). -$ FR-IR (neat):  $\tilde{v} = 3424, 3030, 2935, 1640, 1600, 1454, 993, 900$  $cm^{-1}$ . - <sup>1</sup>H NMR (500 MHz, CDCl<sub>2</sub>):  $\delta = 1.81 - 1.85$  (m, 2 H, PhCH<sub>2</sub>CH<sub>2</sub>), 2.18 (s, 1 H, OH), 2.28 (dd, J = 9.07, 14.17 Hz, 1 H, HOCHCHHC=C), 2.53 (ddd, J = 0.85, 3.69, 14.17 Hz, 1 H, HOCHCHHC=C), 2.71 (ddd, J = 7.37, 9.07, 13.89 Hz, 1 H, PhCHH), 2.85 (ddd, J = 6.80, 8.79, 13.89 Hz, 1 H, PhCHH), 3.80 (m, 1 H, HOCHCH), 5.09 (dd, J = 0.85, 1.14 Hz, 1 H, HHC=  $C-CH=CH_2$ ), 5.12 (d, J = 11.05 Hz, 1 H,  $H_2C=C-CH=CHH$ ), 5.16 (d, J = 1.14 Hz, 1 H,  $HHC=C-CH=CH_2$ ), 5.22 (d, J =17.57 Hz, 1 H,  $H_2C=C-CH=CHH$ ), 6.39 (dd, J = 17.57, 11.05 Hz, 1 H,  $H_2C=C-CH=CH_2$ ), 7.17–7.30 (m, 5 H, Ph). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 32.11$ , 38.78, 40.09, 69.08, 114.27, 118.38, 125.79, 128.37, 128.42, 138.44, 142.09, 143.01. - EI-MS:  $m/z = 202 [M^+]$ . - C<sub>14</sub>H<sub>18</sub>O (202.30): calcd. C 83.12, H 8.97; found C 82.98, H 8.91. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 2.46$  (M), 2.37 (m) (m, 2 H, OCHCH<sub>2</sub>); 6.35 (M), 6.29 (n) (m, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>)].

(+)-(5R)-3-Methylene-1-undecen-5-ol (3b): Compound 3b was obtained according to the procedure for the synthesis of 2a except with 8 instead of 4. Yield: 81%. – TLC:  $R_f = 0.44$  (15:85, EtOAc/ hexane).  $- [\alpha]_{D}^{24} = +6.35$  (c = 0.93, EtOH; 93% ee). - FR-IR (neat):  $\tilde{v} = 3449$ , 3409, 2927, 1655, 1631, 995, 903 cm<sup>-1</sup>. - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.86 - 0.90$  (m, 5 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.28-1.33 (m, 6 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.51 (m, 1 H, HOCHCH*H*CH<sub>2</sub>), 1.62 (d, J = 3.11 Hz, 1 H, OH), 1.67 (m, 1 H,  $HOCHCHHCH_2$ ), 2.21 (dd, J = 9.07, 13.89 Hz, 1 H, HOCHCHHC=CH<sub>2</sub>), 2.52 (ddd, J = 1.11, 3.69, 13.89 Hz, 1 H, HOCHCHHC=CH<sub>2</sub>), 3.74 (m, 1 H, HOCHCH), 5.09 (dd, J =1.11, 1.21 Hz, 1 H, HHC=C-CH=CH<sub>2</sub>), 5.11 (d, J = 10.78 Hz, 1 H,  $H_2C=C-CH=CHH$ ), 5.16 (d, J = 1.21 Hz, 1 H, HHC=C-CH=CH<sub>2</sub>), 5.25 (d, J = 17.58 Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 6.40 (dd, J = 10.78, 17.58 Hz, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>). - <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 14.05$ , 22.56 25.71, 29.35, 31.64, 37.24, 40.08, 69.67, 114.1, 114.2, 138.54, 143.27. - EI-MS: m/z =182 [M<sup>+</sup>]. - C<sub>12</sub>H<sub>22</sub>O: calcd. C 79.06, H 12.16; found C 79.11, H 12.03. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 2.46$  (M), 2.37 (m) (m, 2 H, OCHCH<sub>2</sub>); 5.21 (M), 5.33 (m) (m, 1 H, OCHCH<sub>2</sub>); 6.35 (M), 6.29 (m) (m, 1 H, H<sub>2</sub>C=C-CH= CH<sub>2</sub>)].

(-)-(*IS*)-1-Cyclohexyl-3-methylenepent-4-en-1-ol (3c): Compound 3c was obtained according to the procedure for the synthesis of 2a except with 8 instead of 4. Yield: 53%. – TLC:  $R_f = 0.38$  (15:85, EtOAc/hexane). –  $[\alpha]_D^{-5} = -4.25$  (c = 0.63, EtOH; 91% *ee*). – FR-IR (neat):  $\tilde{v} = 3405$ , 2926, 2854, 1650, 1600, 1450, 1029 cm<sup>-1</sup>. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.06-1.30$  (m, 6 H, *c*Hex), 1.41 (m, 1 H, *c*Hex), 1.59 (d, J = 2.84 Hz, 1 H, OH), 1.68 (m, 1 H,

cHex), 1.74–1.82 (m, 2 H, cHex), 1.89 (m, 1 H, cHex), 2.14 (dd, J = 10.20, 13.89 Hz, 1 H, HOCHCHH), 2.61 (dd, J = 4.55, 13.89 Hz, 1 H, HOCHCHH), 3.51 (m, 1 H, HOCHCH), 5.09 (d, J = 1.23 Hz, 1 H, HHC=C-CH=CH<sub>2</sub>), 5.11 (d, J = 11.05 Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 5.16 (d, J = 1.23 Hz, 1 H, HHC=C-CH= CH<sub>2</sub>), 5.23 (d, J = 17.57 Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 6.40 (dd, J = 11.05, 17.57 Hz, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ = 26.16, 28.44, 28.16, 29.03, 29.64, 36,83, 43.53, 73.36, 114.10, 118.19, 138.39, 143.60. – EI-MS: m/z = 180 [M<sup>+</sup>]. – C<sub>12</sub>H<sub>20</sub>O (180.29): calcd. C 79.94, H 11.08; found C 79.98, H 10.93. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester: δ = 5.06 (M), 4.93 (m) (s, 1 H, HHC=C); 6.35 (M), 6.28 (m) (dd, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>)].

(-)-(1S)-3-Methylene-1-phenyl-4-penten-1-ol (3d): Compound 3d was obtained according to the procedure for the synthesis of 2a except with 8 instead of 4. Yield: 88%. - TLC:  $R_f = 0.27$  (15:85, EtOAc/hexane).  $- [\alpha]_{D}^{25} = -24.08$  (c = 1.66, EtOH; 93% ee). -FR-IR (neat):  $\tilde{v} = 3408, 3386, 3087, 2927, 1595, 1453, 1094, 995,$ 903 cm<sup>-1</sup>. - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.13$  (s, 1 H, OH), 2.44 (dd, J = 7.68, 13.54 Hz, 1 H, HOCHCHH), 2.68 (dd, J =5.94,13.54 Hz, 1 H, HOCHCHH), 4.85 (m, 1 H, HOCHCH), 5.12 (d, J = 1.05 Hz, 1 H,  $HHC=C-CH=CH_2$ ), 5.14 (d, J = 11.01Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 5.18 (d, J = 1.05 Hz, 1 H, HHC= C-CH=CH<sub>2</sub>), 5.34 (d, *J* = 18.11 Hz, 1 H, H<sub>2</sub>C=C-CH=CH*H*), 6.43 (dd, J = 18.11, 11.01 Hz, 1H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>), 7.26-7.41 (m, 5 H, Ph).  $- {}^{13}$ C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 42.20, 72.19,$ 114.25, 118.80 125.75, 127.54, 128.41, 138.32, 142.73, 144.06. -EI-MS:  $m/z = 174 [M^+]$ . - C<sub>12</sub>H<sub>14</sub>O (174.24): calcd. C 82.72, H 8.10; found C 82.63, H 9.81. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 5.05$  (M), 4.87 (m) (s, 1 H, HHC=C); 6.08 (M), 6.15 (m) (dd, 1 H, OCHPh); 6.38 (M), 6.31 (m) (dd, 1 H,  $H_2C=C-CH=CH_2$ )].

(+)-(3S)-5-Methylene-1-phenylhepta-1,6-dien-3-ol (3e): Compound 3e was obtained according to the procedure for the synthesis of 2a except with **8** instead of **4**. Yield: 74%. – TLC:  $R_f = 0.27$  (15:85, EtOAc/hexane).  $- [\alpha]_{D}^{25} = +52.95$  (c = 1.45, EtOH; 96% ee). -FR-IR (neat):  $\tilde{v} = 3421, 3084, 3028, 2930, 1654, 1593, 1025, 966,$ 902 cm<sup>-1</sup>. - <sup>1</sup>H NMR (500 MHz, CDCl<sub>2</sub>):  $\delta = 2.04$  (s, 1 H, OH), 2.49 (dd, J = 8.50, 14.17 Hz, 1 H, HOCHCHH), 2.63 (dd, J =4.82, 14.17 Hz, 1 H, HOCHCHH), 4.47 (m, 1 H, HOCHCH), 5.15 (d, J = 1.13 Hz, 1 H,  $HHC=C-CH=CH_2$ ), 5.16 (d, J = 10.77Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 5.21 (d, J = 1.13 Hz, 1 H, HHC=  $C-CH=CH_2$ ), 5.32 (d, J = 17.57 Hz, 1 H,  $H_2C=CH-C=CH$ ), 6.26 (dd, J = 6.24, 15.87 Hz, 1 H, PhCH=CH), 6.43 (dd, J =17.57, 10.77 Hz, 1 H, H<sub>2</sub>C=CH-C=CH), 6.63 (d, J = 15.87 Hz, 1 H, PhCH=CH), 7.22-7.40 (m, 5 H, Ph). - <sup>13</sup>C NMR (50 MHz,  $CDCl_3$ ):  $\delta = 40.09, 70.73, 114.29, 118.81, 126.46, 127.59, 128.53,$ 130.19, 131.65, 136.74, 138.44, 142.36. – EI-MS:  $m/z = 200 \text{ [M^+]}$ . - C14H16O (200.28): calcd. C 83.96, H 8.05; found C 83.63, H 8.08. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 5.83$  (M), 5.91 (m) (dd, 1 H, OCH); 6.39 (M), 6.33 (m) (dd, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>); 6.59 (M), 6.68 (m) (d, 1 H, PhCH=CH)].

(+)-(*3S*)-5-Methylene-1-phenylhept-6-en-1-yn-3-ol (3f): Compound 3f was obtained according to the procedure for the synthesis of 2a except with 8 instead of 4. Yield: 91%. – TLC:  $R_f = 0.32$  (15:85, EtOAc/hexane). –  $[\alpha]_D^{23} = +57.5$  (c = 0.75, EtOH; 91% ee). – FR-IR (neat):  $\tilde{v} = 3408$ , 3386, 3087, 2927, 1595, 1453, 1094, 995, 903 cm<sup>-1</sup>. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.84$  (d, J = 3.89, 1 H, OH), 2.59 (dd, J = 7.66, 14.17 Hz, 1 H, HOCHCHH), 2.67 (ddd, J = 1.13, 5.66, 14.17 Hz, 1 H, HOCHCHH), 4.82 (m, 1 H, HOCHCH), 5.11 (d, J = 11.30 Hz, 1 H, H<sub>2</sub>C=C–CH=CHH), 5.16 (s, 1 H, H<sub>2</sub>C=C–CH=CHH), 5.19 (d, J = 1.13 Hz, 1 H,

*H*HC=C-CH=CH<sub>2</sub>), 5.34 (d, J = 18.21 Hz, 1 H, H*H*C= C-CH=CH<sub>2</sub>), 6.43 (dd, J = 18.21, 11.30 Hz, 1 H, H<sub>2</sub>C=C*H*-C= CH), 7.26-7.41 (m, 5 H). - <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ = 40.24, 61.49, 83.22, 85.89, 114.20, 119.30, 122.67, 128.26, 128.40, 131.67, 139.31, 141.40. - EI-MS: m/z = 198 [M<sup>+</sup>]. - C<sub>14</sub>H<sub>14</sub>O (198.26): calcd. C 84.81, H 7.12; found C 84.73, H 7.11. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester: δ = 5.67 (M), 5.73 (m) (dd, 1 H, OC*H*); 6.38 (M), 6.31 (m) (dd, 1 H, H<sub>2</sub>C= C-C*H*=CH<sub>2</sub>)].

(-)-(4R)-2-Methyl-6-Methyleneocta-2,7-dien-4-ol (9, Ipsdienol): Ipsdienol was obtained according to the procedure for the synthesis of 2a except with (R)-BINOL and 8 instead of 4. Yield: 68%. -TLC:  $R_f = 0.22$  (15:85, EtOAc/hexane).  $- [\alpha]_D^{23} = -15.1$  (c = 1.12, EtOH; 93% ee; ref.:<sup>[32]</sup> -13.2). - FR-IR (neat):  $\tilde{v} = 3440, 3080,$ 2970, 2850, 1800, 1665, 1630, 1590, 1385, 1250, 1020, 1005, 990  $cm^{-1}$ . - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.83 (s, 1 H, OH), 1.69 (d, J = 1.21 Hz, 3 H,  $CH_3MeC=C$ ), 1.73 (d, J = 1.21 Hz, 3 H,  $MeCH_3C=C$ ), 2.38 (dd, J = 8.11, 14.17 Hz, 1 H, HOCHCHH), 2.45 (dd, J = 5.18, 14.17 Hz, 1 H, HOCHCHH), 4.52 (m, 1 H, HOCHCH) 5.10 (d, J = 1.01 Hz, 1 H, HHC=C-CH=CH<sub>2</sub>), 5.12 (d, J = 10.54, 1 H, H<sub>2</sub>C=C-CH=CHH), 5.14 (d, J = 1.01 Hz, 1 H,  $HHC=C-CH=CH_2$ ), 5.21 (m, 1 H,  $Me_2C=CH$ ), 5.28 (d, J =17.53 Hz, 1 H,  $H_2C=CH-C=CH$ ), 6.41 (dd, J = 10.54, 17.53 Hz, 1 H, H<sub>2</sub>C=CH-C=CH). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 18.04, 25.39, 39.83, 66.45. 113.44, 118.15, 127.42, 134.4, 138.40, 149.3. – EI-MS:  $m/z = 152 [M^+]$ . – C<sub>10</sub>H<sub>16</sub>O (152.24): calcd. C 78.90, H 10.59; found C 78.67, H 10.44. [Diagnostic <sup>1</sup>H NMR  $(CDCl_3, 500 \text{ MHz})$  of (+)-MTPA ester:  $\delta = 6.32 \text{ (M)}, 6.28 \text{ (m)} \text{ (dd,}$  $1 \text{ H}, \text{H}_2\text{C}=\text{C}-\text{C}H=\text{C}\text{H}_2$ ].

(-)-(4S)-2-Methyl-6-methyleneoct-7-en-4-ol (10, Ipsenol): Ipsenol was obtained according to the procedure for the synthesis of 2a except with (R)-BINOL and 8 instead of 4. Yield: 77%. - TLC:  $R_f = 0.40$  (15:85, EtOAc/hexane).  $- [\alpha]_D^{25} = -17.9$  (c = 1.08, EtOH, 99% ee; ref.<sup>[33]</sup> –17.5). – FR-IR (neat):  $\tilde{v} = 3378$ , 3088, 2957, 2929, 2871, 1595, 1465, 1367, 900 cm<sup>-1</sup>. - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.91$  (d, J = 6.52 Hz, 3 H, CH<sub>3</sub>MeCH), 0.93 (d, J = 6.53 Hz, 3 H, MeCH<sub>3</sub>CH), 1.32 (m, 1 H,  $Me_2CHCHH$ ), 1.36 (ddd, J = 5.67, 8.79, 13.60 Hz, 1 H,  $Me_2CHCHH$ , 1.58 (d, J = 3.12 Hz, 1 H, OH), 1.83 (m, 1 H,  $Me_2CH$ ), 2.21 (dd, J = 9.07, 13.89 Hz, 1 H, HOCHCHHC=CH<sub>2</sub>), 2.50 (dd, *J* = 1.14, 3.40, 13.89 Hz, 1 H, HOCHC*H*HC=CH<sub>2</sub>), 3.72 (m, 1 H, HOCHCH), 5.10 (d, J = 0.55 Hz, 1 H, HHC=C-CH= CH<sub>2</sub>), 5.12 (d, J = 10.77 Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 5.17 (dd, J = 0.55, 1.14 Hz, 1 H,  $HHC=C-CH=CH_2$ ), 5.25 (d, J = 17.58Hz, 1 H, H<sub>2</sub>C=C-CH=CHH), 6.40 (dd, J = 10.77, 17.85 Hz, 1 H, H<sub>2</sub>C=C-CH=CH<sub>2</sub>). - <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) 22.25, 23.64, 24.87, 40.80, 46.68, 67.88, 114.59, 118.88, 139.07, 143.70. - EI-MS:  $m/z = 154 [M^+]$ . - C<sub>10</sub>H<sub>18</sub>O (154.25): calcd. C 77.87, H 11.76; found C 77.81, H 11.57. [Diagnostic <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of (+)-MTPA ester:  $\delta = 2.33$  (M), 2.41 (m) (dd, 1 H, HOCHCHHC=CH<sub>2</sub>); 6.31 (M), 6.36 (m) (dd, 1 H, H<sub>2</sub>C=C-CH= CH<sub>2</sub>), virtually no minor diastereomers were detected].

#### Acknowledgments

This research was supported by the Center for Molecular Design and Synthesis (CMDS) at KAIST founded by a funding from the Korea Science & Engineering Foundation (KOSEF Science Research Center program).

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Received August 24, 2000 [O00438]