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

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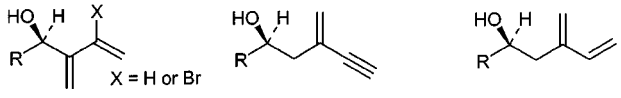
Efficient catalytic asymmetric allylic transfer reactions of achiral aldehydes with 2-ethynyl- and 2-ethenyl-2-propenylstannane promoted by BINOL-Ti^{IV} complex with synergetic reagent are achieved for the synthesis of homoenynyl- and dienyl alcohols with high levels of enantioselectivity. The range of enantioselectivity is 84–99% *ee* with good chemical yields. The application of catalytic asymmetric dienylation in a single operation was exemplified by the enantioselective synthesis of naturally occurring (–)-Ipsdienol and (–)-Ipsenol.

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.[1−3] In this regard, allylic transfer reactions provide excellent stereoselective routes for converting aldehydes into the corresponding alcohols.[4−7] 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.[8] Although there have been several elegant reports regarding reinforcing catalytic ability for practical use in the literature,[9,10] 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.[11,12] Our approach involves the use of a BINOL-Ti^{IV} complex as a chiral promoter along with *i*PrSBEt_2 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.[13−16] 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,[17] and many useful functional group transformations can be foreseen for enynyl and dienyl moieties.[18−20] With the notion that this investigation leads to the efficient synthesis of a number of optically active alcohols, we set out to determine the scope with new allylic transfer reagents.



1 **2** **3**

Scheme 1

Results and Discussion

The new reagent **4**, a crucial compound in the present research, was prepared from commercially available 2-methyl-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,[21,22] with Bu_3SnCl (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_3N-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_2 was found to be quite efficient in the catalytic process to speed up the reaction rate (with 5 mol-% BINOL-Ti^{IV}, see Table 1);[23] (iii) a 1:1 mixture of BINOL and Ti(O*i*Pr)$_4$ in the presence of 4 Å molecular sieves proved to be the most efficient catalyst;[24−27] (iv) the reaction performed at −20 °C in $PhCF_3$ resulted in optimal chemical yields and enantioselectivities in comparison with other solvents such as CH_2Cl_2 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^{IV} complex (5

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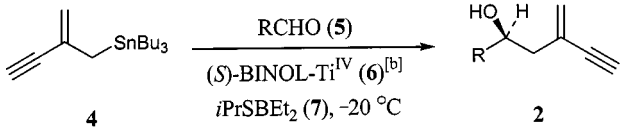
mol-%) prepared from (*S*)-BINOL (0.05 equiv.) and freshly distilled Ti(O*i*Pr)$_4$ (0.05 equiv.) in $PhCF_3$ at 25 °C for 3 h was cooled to −20 °C, and **5** (R = $PhCH_2CH_2$) was added. To this mixture was added dropwise **4** (1.1 equiv.) in $PhCF_3$ followed by **7** (1.2 equiv.) in $PhCF_3$ with 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 $NaHCO_3$. 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 less-hindered aldehydes, including alkynal, than with the more bulky cyclohexanecarboxaldehyde.

Table 1. Catalytic asymmetric enynylation of **4**[a]



4 **2**

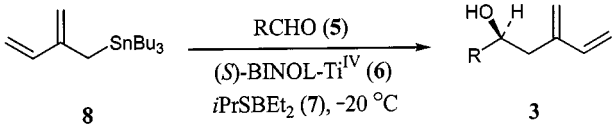
Compound	**5** (R)	h	Yield [%][c]	*ee* [%][d]
2a	$PhCH_2CH_2$	7	83	93
2b	nC_6H_{13}	7	78	94
2c	cC_6H_{11}	22	41	84
2d	Ph	9	91	97
2e	PhCH=CH	7	68	92
2f	PhC≡C	7	81	91

[a] All reactions were carried out at −20 °C in $PhCF_3$. − [b] (*S*)-BINOL:Ti(O*i*Pr)$_4$ = 1:1 (5 mol-%). − [c] Yields refer to isolated and purified products. − [d] Enantiomeric excess were determined by preparation of (+)-MTPA ester derivatives, analysis by 500 MHz ^{1}H NMR spectroscopy, and comparison with corresponding diastereomers which were prepared from (*R*)-BINOL-Ti^{IV} (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 dienyltin reagent for the catalytic asymmetric dienylation reaction of aldehydes.[28] Treatment of **8**[29] with **5** (R = $PhCH_2CH_2$, 1 equiv.) in the presence of (*S*)-BINOL-Ti^{IV} (5 mol-%) followed by **7** in $PhCF_3$ for 5 h afforded the alcohol **3a** (R = Ph CH_2CH_2) in 78% isolated yield and 97% *ee*. From Table 2 it can be seen that asymmetric dienylation 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 synthesis of naturally occurring (−)-Ipsdienol and (−)-Ipsenol (Scheme 2), which are two of the aggregation pheromones isolated from the bark beetle *Ips. paraconfusus*.[30−33] 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).

Table 2. Catalytic asymmetric dienylation of **8**[a]



8 **3**

Compound	**5** (R)	h	Yield [%]	*ee* [%]
3a	$PhCH_2CH_2$	5	78	97
3b	nC_6H_{13}	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

[a] All conditions were identical with the enynylation described in Table 1.

(−)-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. α,α,α-Trifluorotoluene was distilled from CaH_2 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 F_{254}) using UV light as visualizing agent and ethanolic anisaldehyde solution and heat as developing agent. FT-IR spectra were recorded on a Nicolet 205. ^{1}H NMR spectra were recorded on a Varian Unity Inova at 500 MHz in $CDCl_3$ as a solvent with TMS or residual chloroform as the internal standard. ^{13}C NMR spectra were measured on a Bruker AC-P200 at 50 MHz or on a Varian Unity Inova at 125 MHz in $CDCl_3$ 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 ^{1}H NMR spectroscopy, and comparison with corresponding diastereomers which were prepared from (*R*)-BINOL-Ti^{IV} and/or by HPLC analysis using a chiral column (Chiracel OD-H column, 5% *i*PrOH 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 *t*BuOK (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_3SnCl (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 × 2). After drying the combined organic solution over anhydrous Na_2SO_4, the solvents were removed under reduced pressure. After removal of baseline impurities on a column with Et_3N-pretreated 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 °C (0.1 Torr). − TLC: R_f = 0.67 (hexane). − FR-IR (neat): $\tilde{\nu}$ = 3290, 3031, 2955, 2923, 1611, 1452, 1267, 913, 754, 700 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79−0.95 [m, 15 H, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.26−1.34 [m, 6 H, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.44−1.54 [m, 6 H, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.90 (d, *J* = 1.13 Hz, 2 H, $SnCH_2C{=}CH_2$), 2.83 (s, 1 H, C≡C*H*), 5.04 (s, 1 H, C=C*H*H), 5.10 (d, *J* = 1.13 Hz, 1 H, C=CH*H*). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 $PhCF_3$ (4 mL) followed by freshly distilled $Ti(OiPr)_4$ (freshly prepared 0.5 M in $PhCF_3$, 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_4 bath, and hydrocinnamaldehyde (**5**, R = $PhCH_2CH_2$, 0.27 g, 2.0 mmol) in $PhCF_3$ (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 $PhCF_3$ (2 mL) followed by *i*PrSBEt_2 (**7**, 0.35 g, 2.4 mmol) in $PhCF_3$ (2 mL) with gas-tight syringe via a syringe pump over 1 h along the wall of the flask while keeping the temperature below −20 °C. After stirring for 7 h at −20 °C, aqueous $NaHCO_3$ (5 mL) was added to the reaction mixture, and then diluted with CH_2Cl_2 (20 mL). The molecular sieves were removed by filtration, and the aqueous layer was extracted with CH_2Cl_2 (ca 20 mL × 2). After drying the combined organic solution over anhydrous Na_2SO_4, the solvents were removed under reduced pressure. Column chromatography (SiO_2, 15% EtOAc in hexanes) afforded **3** (R = $PhCH_2CH_2$, 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, $CHCl_3$; 93% *ee*). − FT-IR (neat): $\tilde{\nu}$ = 3408, 3296, 2941, 2921, 1608, 1496, 1296, 912 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79−1.85 (m, 3 H, $PhCH_2CH_2$ and OH), 2.30 (dd, *J* = 8.65, 14.31 Hz, 1 H, HOCHC*H*HC=C), 2.40 (dd, *J* = 3.97, 14.31 Hz, 1 H, HOCHCH*H*C=C), 2.70 (ddd, *J* = 7.37, 9.07, 13.89 Hz,1 H, PhC*H*H), 2.84 (ddd, *J* = 6.52, 9.07, 13.32 Hz, 1 H, PhCH*H*), 2.94 (s, 1 H, C≡C*H*), 3.93 (m, 1 H, HOC*H*), 5.41 (s, 1 H, C=C*H*H), 5.56 (d, *J* = 1.79 Hz, 1 H, C=CH*H*), 7.17−7.30 (m, 5 H, Ph). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 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 ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 1.89 (M = major), 2.02 (m = minor) (m, 2 H, $PhCH_2CH_2$); 5.16 (M), 5.22 (m) (s, 1 H, C=C*H*H)].

(+)-(*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, $CHCl_3$; 94% *ee*). − FR-IR (neat): $\tilde{\nu}$ = 3385, 3306, 2955, 2857, 1612, 1492, 1266, 1048, 909 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.81 Hz, 3 H, CH_2CH_3), 1.24−1.36 [m, 8 H, $(CH_2)_4CH_3$], 1.46−1.50 (m, 2 H, $HOCHCH_2$), 1.74 (d, *J* = 3.97 Hz, 1 H, OH), 2.24 (dd, *J* = 8.79, 13.61 Hz, 1 H, HOCHCH*H*C=C), 2.38 (dd, *J* = 3.97, 13.61 Hz, 1 H, HOCHC*H*HC=C), 2.94 (s, 1 H, C≡C*H*), 3.89 (m, 1 H, HOC*H*), 5.41 (s, 1 H, C=CH*H*), 5.56 (d, *J* = 1.70 Hz, 1 H, C=C*H*H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 [$M^+ - H_2O$]. − $C_{12}H_{20}O$ (180.29): calcd. C 79.94, H 11.18; found C 79.71, H 11.10. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 1.89 (M), 2.02 (m) (m, 2 H, $PhCH_2CH_2$); 2.24 (M), 2.37 (m) (dd, 1 H, OCHCH*H*); 2.37 (m), 2.55 (M) (dd, 1 H, OCHC*H*H); 5.06 (M), 5.22 (m) (s, 1 H, C=C*H*H)].

(+)-(*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, $CHCl_3$; 84% *ee*). − FR-IR (neat): $\tilde{\nu}$ = 3385, 3306, 2955, 2857, 1612, 1492, 1266, 1048, 909 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05−1.22 (m, 6 H, *c*Hex), 1.40−1.55 (m, 2 H, *c*Hex), 1.65 (br s, 1 H, OH), 1.71−1.80 (m, 2 H, *c*Hex), 1.83−1.88 (m, 1 H, *c*Hex), 2.22 (dd, *J* = 9.64,14.20 Hz, 1 H, HOCHC*H*HC=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=CH*H*), 5.56 (d, *J* = 1.20 Hz, 1 H, C=C*H*H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. − $C_{12}H_{18}O$ (178.27): calcd. C 80.85, H 10.18; found C 80.47, H 10.40. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 2.46 (M), 2.41 (m) (dd, 2 H, OCHC*H*H); 5.48 (M), 5.33 (m) (s, 1 H, C=C*H*)].

(+)-(*1S*)-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). − $[\alpha]_D^{25}$ = +20.4 (*c* = 1.63, $CHCl_3$; 97% *ee*). − FR-IR (neat): $\tilde{\nu}$ =

3381, 3290, 3031, 1611, 1452, 1050, 913, 754, 700 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.19 (d, *J* = 3.11 Hz, 1 H, OH), 2.55–2.59 (m, 2 H, HOCHC*H*$_2$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=C*H*H), 5.56 (d, *J* = 1.70 Hz, 1 H, C=CH*H*), 7.25–7.42 (m, 5 H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 [$M^+ - C_5H_5$]. – $C_{12}H_{12}O$ (172.23): calcd. C 83.69, H 7.02; found C 83.55, H 7.38. [Diagnostic ^1H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 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, $CHCl_3$; 92% *ee*). – FR-IR (neat): $\tilde{\nu}$ = 3583, 3422, 3298, 3054, 2956, 2925, 1611, 1448, 1266, 968 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.94 (d, *J* = 3.69 Hz, 1 H, OH), 2.45–2.53 (m, 2 H, HOCHC*H*$_2$C=C), 2.98 (s, 1 H, C≡C*H*), 4.62 (m, 1 H, HOC*H*), 5.44 (s, 1 H, C=C*H*H), 5.59 (d, *J* = 1.14 Hz, 1 H, C=CH*H*), 6.25 (dd, *J* = 6.23, 15.87 Hz, 1 H, PhCH=C*H*), 6.66 (d, *J* = 15.87 Hz, 1 H, PhC*H*=CH), 7.23–7.40 (m, 5 H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. – $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.78, H 7.02. [Diagnostic ^1H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 6.06 (M), 6.19 (m) (dd, 1 H, PhCH=C*H*); 6.65 (M), 6.77 (n) (d, 1 H, PhC*H*=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). – $[\alpha]_D^{25}$ = +31.5 (*c* = 1.10, $CHCl_3$; 91% *ee*). – FR-IR (neat): $\tilde{\nu}$ = 3583, 3422, 3298, 3054, 2956, 2925, 1611, 1448, 1266, 968 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.64 (br s, 1 H, OH), 2.68 (m, 2 H, HOCHC*H*$_2$C=C), 2.98 (s, 1 H, C≡C*H*), 4.90 (dd, *J* = 6.41, 6.41 Hz, 1 H, HOC*H*), 5.51 (s, 1 H, C=C*H*H), 5.63 (d, *J* = 1.22 Hz, 1 H, C=CH*H*), 7.26–7.45 (m, 5 H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. – $C_{14}H_{12}O$ (196.25): calcd. C 85.68, H 6.16; found C 85.55, H 6.11. [Diagnostic ^1H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 2.59 (M), 2.76 (m) (m, 2 H, OCHC*H*$_2$); 6.03 (M), 6.08 (n) (dd, 1 H, OC*H*CH$_2$)].

Tributyl(2-methylene-but-3-enyl)stannane (8): A flame-dried flask containing *t*BuOK (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 *n*BuLi (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_3SnCl (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 × 2). After drying the combined organic solution over anhydrous Na_2SO_4, the solvents were removed under reduced pressure. After removal of baseline impurities by column chromatography with Et_3N-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): $\tilde{\nu}$ = 2963, 2933, 1649, 1638, 1461, 987, 959, 897, 863 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.90 (m, 15 H, Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$), 1.26–1.33 (m, 6 H, Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$), 1.44–1.50 (m, 6 H, Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$), 1.90 (d, *J* = 0.85 Hz, 2 H, SnC*H*$_2$C=CH$_2$), 4.76 (d, *J* = 0.85 Hz, 1 H, C=C*H*H), 4.81 (s, 1 H, C=CH*H*), 5.05 (d, *J* = 10.50 Hz, 1 H, H$_2$C=C–CH=CH*H*), 5.09 (d, *J* = 17.29 Hz, 1 H, H$_2$C=C–CH=CH*H*), 6.37 (dd, *J* = 10.50, 17.29 Hz, 1 H, H$_2$C=C–C*H*=CH$_2$). – ^{13}C NMR (50 MHz, $CDCl_3$): δ 9.28, 13.27, 13.45, 26.95, 28.95, 111.62, 112.50, 139.48, 146.11; Calcd. for $C_{17}H_{34}Sn$: 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). – $[\alpha]_D^{24}$ = +31.05 (*c* = 1.70, EtOH; 97% *ee*). – FR-IR (neat): $\tilde{\nu}$ = 3424, 3030, 2935, 1640, 1600, 1454, 993, 900 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.81–1.85 (m, 2 H, PhCH$_2$C*H*$_2$), 2.18 (s, 1 H, OH), 2.28 (dd, *J* = 9.07, 14.17 Hz, 1 H, HOCHC*H*HC=C), 2.53 (ddd, *J* = 0.85, 3.69, 14.17 Hz, 1 H, HOCHCH*H*C=C), 2.71 (ddd, *J* = 7.37, 9.07, 13.89 Hz, 1 H, PhC*H*H), 2.85 (ddd, *J* = 6.80, 8.79, 13.89 Hz, 1 H, PhCH*H*), 3.80 (m, 1 H, HOC*H*CH), 5.09 (dd, *J* = 0.85, 1.14 Hz, 1 H, H*H*C=C–CH=CH$_2$), 5.12 (d, *J* = 11.05 Hz, 1 H, H$_2$C=C–CH=C*H*H), 5.16 (d, *J* = 1.14 Hz, 1 H, *H*HC=C–CH=CH$_2$), 5.22 (d, *J* = 17.57 Hz, 1 H, H$_2$C=C–CH=CH*H*), 6.39 (dd, *J* = 17.57, 11.05 Hz, 1 H, H$_2$C=C–C*H*=CH$_2$), 7.17–7.30 (m, 5 H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. – $C_{14}H_{18}O$ (202.30): calcd. C 83.12, H 8.97; found C 82.98, H 8.91. [Diagnostic ^1H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 2.46 (M), 2.37 (m) (m, 2 H, OCHC*H*$_2$); 6.35 (M), 6.29 (n) (m, 1 H, H$_2$C=C–C*H*=CH$_2$)].

(+)-(*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): $\tilde{\nu}$ = 3449, 3409, 2927, 1655, 1631, 995, 903 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86–0.90 (m, 5 H, CH$_2$C*H*$_2$C*H*$_3$), 1.28–1.33 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$CH$_3$), 1.51 (m, 1 H, HOCHCH*H*CH$_2$), 1.62 (d, *J* = 3.11 Hz, 1 H, OH), 1.67 (m, 1 H, HOCHC*H*HCH$_2$), 2.21 (dd, *J* = 9.07, 13.89 Hz, 1 H, HOCHC*H*HC=CH$_2$), 2.52 (ddd, *J* = 1.11, 3.69, 13.89 Hz, 1 H, HOCHCH*H*C=CH$_2$), 3.74 (m, 1 H, HOC*H*CH), 5.09 (dd, *J* = 1.11, 1.21 Hz, 1 H, H*H*C=C–CH=CH$_2$), 5.11 (d, *J* = 10.78 Hz, 1 H, H$_2$C=C–CH=C*H*H), 5.16 (d, *J* = 1.21 Hz, 1 H, *H*HC=C–CH=CH$_2$), 5.25 (d, *J* = 17.58 Hz, 1 H, H$_2$C=C–CH=CH*H*), 6.40 (dd, *J* = 10.78, 17.58 Hz, 1 H, H$_2$C=C–C*H*=CH$_2$). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. – $C_{12}H_{22}O$: calcd. C 79.06, H 12.16; found C 79.11, H 12.03. [Diagnostic ^1H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 2.46 (M), 2.37 (m) (m, 2 H, OCHC*H*$_2$); 5.21 (M), 5.33 (m) (m, 1 H, OC*H*CH$_2$); 6.35 (M), 6.29 (m) (m, 1 H, H$_2$C=C–C*H*=CH$_2$)].

(−)-(*1S*)-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). – $[\alpha]_D^{25}$ = −4.25 (*c* = 0.63, EtOH; 91% *ee*). – FR-IR (neat): $\tilde{\nu}$ = 3405, 2926, 2854, 1650, 1600, 1450, 1029 cm^{-1}. – ^1H NMR (500 MHz, $CDCl_3$): δ = 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,

*c*Hex), 1.74−1.82 (m, 2 H, *c*Hex), 1.89 (m, 1 H, *c*Hex), 2.14 (dd, J = 10.20, 13.89 Hz, 1 H, HOCHC*H*H), 2.61 (dd, J = 4.55,13.89 Hz, 1 H, HOCHCH*H*), 3.51 (m, 1 H, HOC*H*CH), 5.09 (d, J = 1.23 Hz, 1 H, H*H*C=C−CH=CH_2), 5.11 (d, J = 11.05 Hz, 1 H, H_2C=C−CH=C*H*H), 5.16 (d, J = 1.23 Hz, 1 H, *H*HC=C−CH=CH_2), 5.23 (d, J = 17.57 Hz, 1 H, H_2C=C−CH=CH*H*), 6.40 (dd, J = 11.05, 17.57 Hz, 1 H, H_2C=C−C*H*=CH_2). − ^{13}C NMR (50 MHz, $CDCl_3$): 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^+]. − $C_{12}H_{20}O$ (180.29): calcd. C 79.94, H 11.08; found C 79.98, H 10.93. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 5.06 (M), 4.93 (m) (s, 1 H, *H*HC=C); 6.35 (M), 6.28 (m) (dd, 1 H, H_2C=C−C*H*=CH_2)].

(−)-(*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): $\tilde{\nu}$ = 3408, 3386, 3087, 2927, 1595, 1453, 1094, 995, 903 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.13 (s, 1 H, OH), 2.44 (dd, J = 7.68, 13.54 Hz, 1 H, HOCHC*H*H), 2.68 (dd, J = 5.94,13.54 Hz, 1 H, HOCHCH*H*), 4.85 (m, 1 H, HOC*H*CH), 5.12 (d, J = 1.05 Hz, 1 H, H*H*C=C−CH=CH_2), 5.14 (d, J = 11.01 Hz, 1 H, H_2C=C−CH=C*H*H), 5.18 (d, J = 1.05 Hz, 1 H, *H*HC=C−CH=CH_2), 5.34 (d, J = 18.11 Hz, 1 H, H_2C=C−CH=CH*H*), 6.43 (dd, J = 18.11, 11.01 Hz, 1H, H_2C=C−C*H*=CH_2), 7.26−7.41 (m, 5 H, Ph). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. − $C_{12}H_{14}O$ (174.24): calcd. C 82.72, H 8.10; found C 82.63, H 9.81. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 5.05 (M), 4.87 (m) (s, 1 H, *H*HC=C); 6.08 (M), 6.15 (m) (dd, 1 H, OC*H*Ph); 6.38 (M), 6.31 (m) (dd, 1 H, H_2C=C−C*H*=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): $\tilde{\nu}$ = 3421, 3084, 3028, 2930, 1654, 1593, 1025, 966, 902 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.04 (s, 1 H, OH), 2.49 (dd, J = 8.50, 14.17 Hz, 1 H, HOCHC*H*H), 2.63 (dd, J = 4.82, 14.17 Hz, 1 H, HOCHCH*H*), 4.47 (m, 1 H, HOC*H*CH), 5.15 (d, J = 1.13 Hz, 1 H, H*H*C=C−CH=CH_2), 5.16 (d, J = 10.77 Hz, 1 H, H_2C=C−CH=C*H*H), 5.21 (d, J = 1.13 Hz, 1 H, *H*HC=C−CH=CH_2), 5.32 (d, J = 17.57 Hz, 1 H, H_2C=CH−C=C*H*), 6.26 (dd, J = 6.24, 15.87 Hz, 1 H, PhCH=C*H*), 6.43 (dd, J = 17.57, 10.77 Hz, 1 H, H_2C=C*H*−C=CH), 6.63 (d, J = 15.87 Hz, 1 H, PhC*H*=CH), 7.22−7.40 (m, 5 H, Ph). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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 [M^+]. − $C_{14}H_{16}O$ (200.28): calcd. C 83.96, H 8.05; found C 83.63, H 8.08. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 5.83 (M), 5.91 (m) (dd, 1 H, OC*H*); 6.39 (M), 6.33 (m) (dd, 1 H, H_2C=C−C*H*=CH_2); 6.59 (M), 6.68 (m) (d, 1 H, PhC*H*=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): $\tilde{\nu}$ = 3408, 3386, 3087, 2927, 1595, 1453, 1094, 995, 903 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.84 (d, J = 3.89, 1 H, OH), 2.59 (dd, J = 7.66, 14.17 Hz, 1 H, HOCHC*H*H), 2.67 (ddd, J = 1.13, 5.66, 14.17 Hz, 1 H, HOCHCH*H*), 4.82 (m, 1 H, HOC*H*CH), 5.11 (d, J = 11.30 Hz, 1 H, H_2C=C−CH=C*H*H), 5.16 (s, 1 H, H_2C=C−CH=CH*H*), 5.19 (d, J = 1.13 Hz, 1 H, *H*HC=C−CH=CH_2), 5.34 (d, J = 18.21 Hz, 1 H, H*H*C=C−CH=CH_2), 6.43 (dd, J = 18.21, 11.30 Hz, 1 H, H_2C=C*H*−C=CH), 7.26−7.41 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$): 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^+]. − $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.73, H 7.11. [Diagnostic ^{1}H NMR ($CDCl_3$, 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_2C=C−C*H*=CH_2)].

(−)-(*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.:[32] −13.2). − FR-IR (neat): $\tilde{\nu}$ = 3440, 3080, 2970, 2850, 1800, 1665, 1630, 1590, 1385, 1250, 1020, 1005, 990 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.83 (s, 1 H, OH), 1.69 (d, J = 1.21 Hz, 3 H, C*H*$_3$MeC=C), 1.73 (d, J = 1.21 Hz, 3 H, MeC*H*$_3$C=C), 2.38 (dd, J = 8.11, 14.17 Hz, 1 H, HOCHC*H*H), 2.45 (dd, J = 5.18, 14.17 Hz, 1 H, HOCHCH*H*), 4.52 (m, 1 H, HOC*H*CH) 5.10 (d, J = 1.01 Hz, 1 H, H*H*C=C−CH=CH_2), 5.12 (d, J= 10.54, 1 H, H_2C=C−CH=C*H*H), 5.14 (d, J = 1.01 Hz, 1 H, *H*HC=C−CH=CH_2), 5.21 (m, 1 H, Me_2C=C*H*), 5.28 (d, J = 17.53 Hz, 1 H, H_2C=CH−C=C*H*), 6.41 (dd, J = 10.54, 17.53 Hz, 1 H, H_2C=C*H*−C=CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 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^+]. − $C_{10}H_{16}O$ (152.24): calcd. C 78.90, H 10.59; found C 78.67, H 10.44. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 6.32 (M), 6.28 (m) (dd, 1 H, H_2C=C−C*H*=CH_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.[33] −17.5). − FR-IR (neat): $\tilde{\nu}$ = 3378, 3088, 2957, 2929, 2871, 1595, 1465, 1367, 900 cm^{-1}. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (d, J = 6.52 Hz, 3 H, C*H*$_3$MeCH), 0.93 (d, J = 6.53 Hz, 3 H, MeC*H*$_3$CH), 1.32 (m, 1 H, Me_2CHC*H*H), 1.36 (ddd, J = 5.67, 8.79, 13.60 Hz, 1 H, Me_2CHCH*H*), 1.58 (d, J = 3.12 Hz, 1 H, OH), 1.83 (m, 1 H, Me_2C*H*), 2.21 (dd, J = 9.07, 13.89 Hz, 1 H, HOCHC*H*HC=CH_2), 2.50 (dd, J = 1.14, 3.40, 13.89 Hz, 1 H, HOCHC*H*HC=CH_2), 3.72 (m, 1 H, HOC*H*CH), 5.10 (d, J = 0.55 Hz, 1 H, H*H*C=C−CH=CH_2), 5.12 (d, J = 10.77 Hz, 1 H, H_2C=C−CH=C*H*H), 5.17 (dd, J = 0.55, 1.14 Hz, 1 H, *H*HC=C−CH=CH_2), 5.25 (d, J =17.58 Hz, 1 H, H_2C=C−CH=C*H*H), 6.40 (dd, J = 10.77, 17.85 Hz, 1 H, H_2C=C−C*H*=CH_2). − ^{13}C NMR (50 MHz, $CDCl_3$) 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^+]. − $C_{10}H_{18}O$ (154.25): calcd. C 77.87, H 11.76; found C 77.81, H 11.57. [Diagnostic ^{1}H NMR ($CDCl_3$, 500 MHz) of (+)-MTPA ester: δ = 2.33 (M), 2.41 (m) (dd, 1 H, HOCHC*H*HC=CH_2); 6.31 (M), 6.36 (m) (dd, 1 H, H_2C=C−C*H*=CH_2), virtually no minor diastereomers were detected].

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