Combining Pd- and Chiral Organocatalysis for the Enantioselective Deconjugative Allylation of Enals via Dienamine Intermediates

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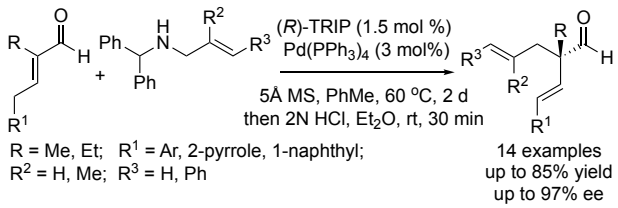
Supporting Information Placeholder

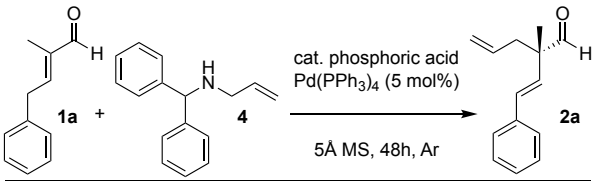


ABSTRACT: A catalytic enantioselective deconjugative allylation of enals is reported. A variety of enals underwent this transformation in high yield and ee, and products can be readily transformed into γ-allyl enals via a Cope rearrangement without erosion of ee. This transformation was used to install the quaternary stereocenter in (*S*)-bakuchiol, enabling completion of a concise formal synthesis.

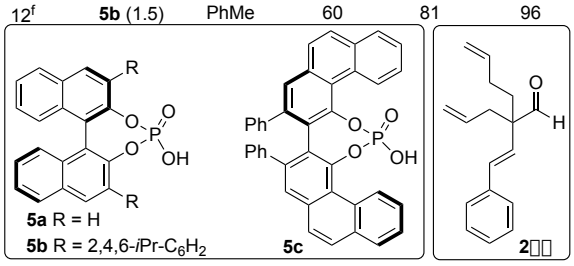
While recent years have seen the combination of enamine- and metal-catalysis facilitate access to novel synthetic building blocks,[1] examples of cooperative dienamine- and metal-catalysis are rare.[2] In contrast to organocatalytic reactions involving enamine intermediates, there is no uniform model for catalyst control of regio- or enantioselectivity in reactions of dienamine intermediates,[3] which likely contributes to the dearth of metal co-catalyzed asymmetric transformations of the latter. For example, whereas organo- and transition metal-catalyzed enantioselective α-allylation of aldehydes and ketones is now well established,[4] there are only two such reports of catalytically generated di- or trienamine intermediates.[2c,f] In both reports, cyclic substrates strongly biased reaction regiochemistry. We sought to examine the combination of dienamine- and metal-catalysis with linear enal substrates.

A considerable number of reaction conditions were evaluated,[5] including many chiral primary and secondary amine catalysts, allylic alcohol and acetate substrates, as well as different Pd sources, however none gave results superior to an adaptation of List's conditions,[4a] in terms of product yield, regioselectivity, and enantioselectivity. Subjecting linear enal (2*E*)-4-phenyl-2-butenal to List's conditions for α-allylation of α-branched aldehydes (i.e., Table 1, entry 1),[4a] however, gave only α-bis-allylated product, **2ααα**, the formation of which could not be suppressed. Switching to the corresponding enal with an α-Me group (**1a**), these conditions provided exclusively α-allylated product **2a**, but only in small quantities (entry 1). Temperatures up to the boiling point of MTBE were examined but still provided the product in low yields (entries 2-3). The

Table 1. Reaction Optimization.[a]



entry	cat. (mol %)	solvent	T (°C)	yield (%)[b]	ee (%)[c]
1	**5a** (3)	MTBE	40	9	6
2	**5a** (3)	MTBE	50	18	nd
3	**5a** (3)	MTBE	55	32	nd
4	**5a** (3)	PhMe	55	48	nd
5	**5a** (3)	PhMe	60	56	racemic
6	**5a** (3)	PhMe	70	63	racemic
7	**5b** (3)	PhMe	60	70	96
8	***ent*-5b** (3)	PhMe	60	77	-96
9	**5c** (3)	PhMe	60	61	20
10[d]	**5b** (3)	PhMe	60	64	98
11[e]	**5b** (3)	PhMe	40	59	96
12[f]	**5b** (1.5)	PhMe	60	81	96



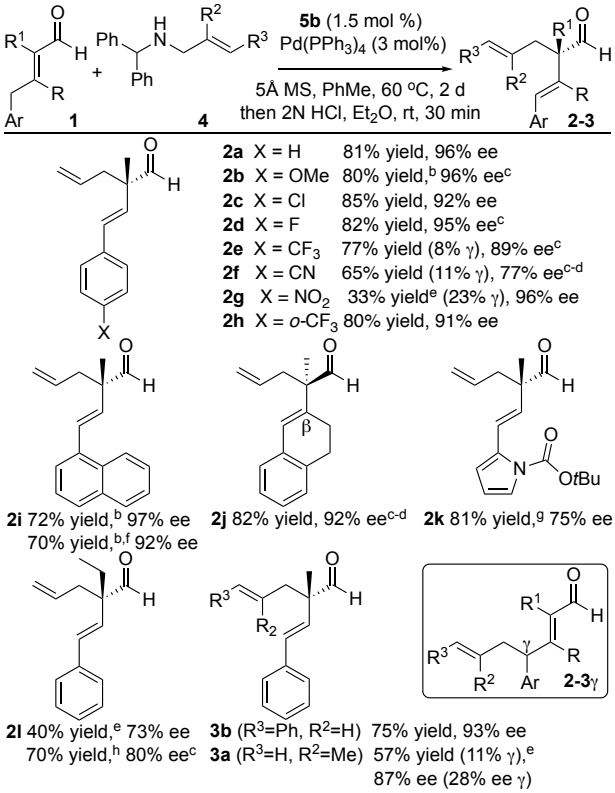
[a] Reaction conditions: **1a** (0.34 mmol), **4** (0.34 mmol), cat. phosphoric acid, $Pd(PPh_3)_4$ (5 mol %), 5Å MS (250 mg), solvent (1 mL), Ar, 48 h. [b] Isolated yield. [c] ee determined by chiral phase HPLC. [d] **4** (2 equiv) used. [e] Reaction time = 5 d. [f] $Pd(PPh_3)_4$ (3 mol %) used.

yield was further improved by changing reaction solvents to toluene (entry 4).[4b] Raising the temperature brought product yields up to moderate levels (entries 5-6). The use of TRIP (**5b**) gave the best results in terms of both reaction yield and ee (entry 5 vs. 7-9). Increasing the equivalents of **4** led to lower product yields, as did lower reaction temperatures, which also did not improve the ee (entries 10-11). Finally, reducing the catalytic loading of both Pd and phosphoric acid afforded product in 81% yield and 96% ee (entry 12).

After reaction optimization, enals with different α- and aryl groups, and differentially substituted *N*-allyl benzhydrylamines, were evaluated (Scheme 1). Enals containing phenyl groups bound to atoms with lone pairs gave results similar to that with an unsubstituted phenyl group (**2a-d**), however a longer reaction time was required for the strongly electron releasing OMe-substituted substrate. Competitive γ-allylation occurred for enals with phenyl groups containing *para* electron withdrawing substituents (**2e-g**), probably due to the higher negative charge density on the γ-carbon of their corresponding dienamines. For the *p*-NO_2 substrate, the γ-allylated product formed in significant quantities (1.4:1 α:γ) but was racemic. *Ortho* substitution was tolerated (**2h**), as was a 1-naphthyl group (**2i**), although a longer reaction time was required for the latter. The reaction with **2i** could also be readily scaled up. A substrate with β,β-disubstitution was also amenable to this transformation (**2j**). A heteroaromatic group resulted in a reduced ee (**2k**). When R^1 was changed from Me to Et, a loss in both reactivity and ee occurred, and the corresponding product (**2l**) was generated in 40% yield and 73% ee, with 40% of starting material remaining after 4 d. Substituting the isopropyl groups on the TRIP catalyst with less hindered Me groups proved most effective at improving the yield and ee of **2l** to 70% and 80%,[5] respectively, which is a strategy that might be amenable to other allylations that utilize catalytic phosphoric acids in conjunction with enamine- and Pd-catalysis.[4b,e,g] Additionally, β-methallylation provided non-trivial quantities of γ-product, which was formed in low ee (**3a**). A cinnamyl product (**3b**) was formed in a high yield and ee similar to the corresponding allyl product (**2a**). Under these conditions, the cyclic enal substrate employed by Jørgensen to promote γ-allylation formed a complex mixture of products (not shown).[2c] Finally, several enal substrates were unreactive, including enals with a γ-Bn instead of a γ-Ph, a disubstituted γ-carbon, R^1 = Ph, along with cyclohexyl enals in which the α,β-unsaturation was exo- (i.e., cyclohexylidene) and endocyclic.

To demonstrate the synthetic utility of this deconjugative allylation, which generates quaternary chiral centers, a brief synthesis of (*S*)-bakuchiol methyl ether (**8**) was completed (Scheme 2).[6] Starting from the opposite enantiomer of product **2b**, which was obtained using (*S*)-TRIP in the deconjugative allylation, Wittig olefination provided triene **6**. Hydroboration of the least hindered terminal alkene, followed by Dess-Martin oxidation afforded aldehyde **7**. Another Wittig olefination completed this concise, protecting group-free synthesis of (*S*)-

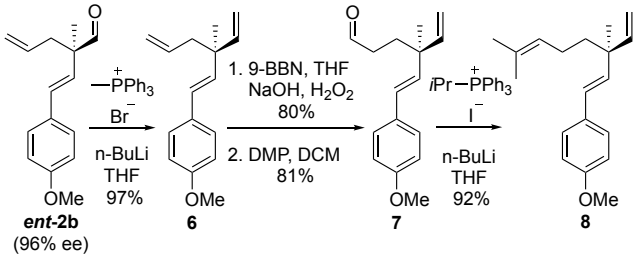
Scheme 1. Substrate Scope.[a]



[a] Yield = isolated yield. ee determined by chiral phase HPLC. [b] Reaction time = 6 d. [c] ee of corresponding alcohol. [d] (*S*)-TRIP used. [e] Reaction time = 4 d. [f] Reaction run on tenfold (3.40 mmol) scale. [g] H_2O used instead of 2N HCl in 2nd step. [h] (*R*)-3,3'-bis(2,4,6-trimethylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (**5d**) used instead of TRIP.

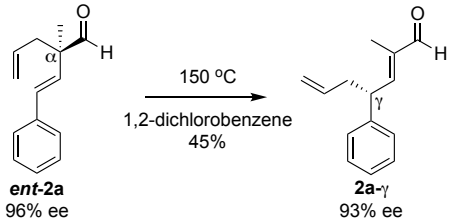
bakuchiol methyl ether in 4 steps and 58% yield from ***ent*-2b**. Comparison of the α_D of **8** with the literature value confirmed the configurational assignment of ***ent*-2b** and, by analogy, all products **2** and **3**.[6b]

Scheme 2. Formal Synthesis of (*S*)-(+)-Bakuchiol.[6c]



Finally, although the corresponding γ-allylated product was not accessed directly under the optimized reaction conditions, nor with most of the alternate strategies investigated,[5] it can be accessed via Cope rearrangement of the α-allylated product (Scheme 3). Examination of this rearrangement (Table SI-5),[5] although not exhaustive, revealed that temperatures of at least 110 °C were required for rearrangement.

Scheme 3. γ-Allylated Product via Cope Rearrangement.



In conclusion, we have developed an enantioselective allylation of enals via a dienamine intermediate, by combining organo- and Pd-catalysis. These conditions strongly favor deconjugative allylation, and a variety of enals underwent this transformation in high yields and ee's. This deconjugative allylation was the key step in a short formal synthesis of (*S*)-bakuchiol,[6c] installing its divinyl quaternary stereocenter, thereby demonstrating the synthetic utility of this new transformation. Additionally, α-allyl products can be readily transformed into γ-allyl products via Cope rearrangement, without significant loss of ee. Investigations into direct γ-allylation of enals are ongoing.

EXPERIMENTAL SECTION

General Information. NMR data were acquired on Bruker 500 MHz NMR spectrometers and use the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, broad s = broad singlet. HRMS spectra were acquired using an MS spectrometer with Q-TOF mass analyzer. $[\alpha]_D^{22}$ were acquired using Jasco P-2000 Polarimeter. HPLC data were acquired on PerkinElmer Flexar HPLC set. Flash chromatography was carried out with 40−60 µm, 60 Å silica gel and EMD silica 60 F254 glass TLC plates. Solvents were dried and kept air-free in a solvent purification unit, and were evaporated using a standard rotavapor and high vacuum. All reactions were carried out in oven-dried glassware, under an Ar atmosphere.

Preparation of Aldehyde Substrates (1). Aldehyde substrates **1a**,[7] **1b**,[8] **1c-d**,[7] **1g**,[9] **1i**,[7] **1l**[7] were prepared using established literature protocol, which were adapted to produce other aldehyde substrates as described next. To a stirred solution of aldehyde ($ArCH_2CHO$, 20 mmol, 1.0 equiv) in anhydrous toluene (0.25 M) was added ethyl 2-(triphenylphosphoranylidene)propionate (24 mmol, 1.2 equiv) in one portion at rt. The reaction was heated in an oil bath to reflux, and was stirred at reflux overnight. Reaction completion was confirmed by TLC. The solvent was removed by rotavapor, and the residue was purified by silica gel flash chromatography to afford the corresponding α,β-unsaturated ester.

A reaction flask was oven-dried and cooled to rt under vacuum, then backfilled with Ar. $LiAlH_4$ (36 mmol, 2.0 equiv) and dry Et_2O (0.2 M) were added under Ar. The reaction flask was cooled to 0 °C, and α,β-unsaturated ester (18 mmol, 1.0 equiv) was added, dropwise. The reaction was warmed to rt and stirred overnight. Reaction completion was confirmed by TLC. The reaction was quenched by 2N HCl, and thrice extracted with DCM. The combined organic layer was dried over Na_2SO_4 anhydrous. The solvent was removed by rotavapor. The crude alcohol product was used without further purification.

To a stirred solution of the crude alcohol (10 mmol, 1.0 equiv) in DCM (0.2 M) was added DMP (11 mmol, 1.1 equiv), and the solution was stirred for 3 h at rt. Reaction completion was confirmed by TLC. Sat. $Na_2S_2O_3$ and sat. $NaHCO_3$ were added to the reaction, which was then thrice extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by rotavapor, and the residue was purified by silica gel flash chromatography to afford the α,β-unsaturated aldehydes (**1**).

(*E*)-2-methyl-4-(4-(trifluoromethyl)phenyl)but-2-enal (1e). TLC petroleum ether/EtOAc=90:10, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a pale yellow oil (261 mg, 49% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.60 (t, *J* = 7.5 Hz, 1H), 3.76 (d, *J* = 7.3 Hz, 2H), 1.88 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.8, 150.3, 142.3, 140.3, 129.2 (q, *J* = 32.6 Hz), 128.8, 125.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271.8 Hz), 34.9, 9.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.50 (s, 3F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{12}H_{11}F_3O$ 228.0762; Found 228.0766.

(*E*)-4-(3-methyl-4-oxobut-2-en-1-yl)benzonitrile (1f). In lieu of the $LiAlH_4$ reduction/DMP reoxidation following the initial Wittig reaction as described above, a DIBAL reduction was instead performed according to the following procedure. The mixture of ethyl (*E*)-4-(4-cyanophenyl)-2-methylbut-2- and 3-enoate (1:1, 1.11 g, 4.84 mmol) generated in the initial Wittig reaction was dissolved in toluene (55 mL), and cooled to -78 °C. DIBAL-H (5.57 mL, 5.57 mmol, 1 M in hexane) was added via syringe pump over 40 min. The mixture was then stirred at -78 °C for 1 h. The reaction mixture was quenched with 2N HCl (50 mL), and warmed to rt. The organic layer was separated, and the aqueous layer was extracted with DCM (2 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. TLC petroleum ether/EtOAc=80:20, R_f=0.31. Purified by column chromatography using petroleum ether/EtOAc=80:20. Further purification by column chromatography using CH_2Cl_2 provided a pure orange oil (82 mg, 9% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.61 – 6.54 (m, 1H), 3.76 (d, *J* = 7.4 Hz, 2H), 1.87 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.6, 149.3, 143.7, 140.7, 132.7, 129.3, 118.6, 110.9, 35.1, 9.5; HRMS (ESI) m/z: $[M-H]^+$ Calcd for $C_{12}H_{10}NO$ 184.0762; Found 184.0770.

(*E*)-2-methyl-4-(2-(trifluoromethyl)phenyl)but-2-enal (1h). TLC petroleum ether/EtOAc=90:10, R_f=0.5. Purified by column chromatography using petroleum ether/EtOAc=99:1 to 95:5 and isolated as a pale yellow oil (674 mg, 69% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 6.55 (t, *J* = 7.0 Hz, 1H), 3.87 (d, *J* = 7.1 Hz, 2H), 1.88 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.9, 150.9, 139.9, 136.9 (q, *J* = 1.7 Hz), 132.3, 131.1, 128.7 (q, *J* = 30.2 Hz), 127.0, 126.3 (q, *J* = 5.8 Hz), 124.4 (q, *J* = 273.4 Hz), 32.0 (q, *J* = 2.1 Hz), 9.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.85 (s, 3F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{12}H_{11}F_3O$ 228.0762; Found 228.0762.

2-(3,4-dihydronaphthalen-2-yl)propanal (1j). In lieu of the initial Wittig reaction as described above, a Horner-Wadsworth-Emmons was instead performed according to the following procedure. To an oven-dried reaction flask that was

cooled to rt under vacuum, then backfilled with Ar, were added ethyl 2-(diethoxyphosphoryl)propanoate (476 mg, 2.0 mmol) and dry hexane (5 mL) under Ar. The reaction flask was cooled to 0 °C, and *n*-BuLi (1.25 mL, 2.0 mmol, 1.6 M in hexane) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min. Then, β-tetralone (146 mg, 1.0 mmol) was added dropwise at 0 °C. The reaction was then heated to reflux, and stirred at reflux overnight. After cooling to rt, the reaction was quenched and diluted with sat. aq. Na_2CO_3 (30 mL), then extracted with DCM (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (212 mg, 92% yield). Subsequently, the $LiAlH_4$ reduction/DMP reoxidation protocol described above provided **1j** as a β,γ- (not α,β-) unsaturated aldehyde substrate: TLC petroleum ether/EtOAc=90:10, R_f=0.67. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a yellow oil (43 mg, 74% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (d, *J* = 1.7 Hz, 1H), 7.20 – 7.09 (m, 3H), 7.07 – 7.02 (m, 1H), 6.38 (s, 1H), 3.22 (q, *J* = 6.9 Hz, 1H), 2.83 (t, *J* = 8.1 Hz, 2H), 2.36 – 2.14 (m, 2H), 1.31 (d, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.1, 136.9, 134.6, 133.9, 127.3, 127.2, 126.6, 126.2, 126.1, 54.2, 27.9, 25.9, 12.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}O$ 187.1123; Found 187.1126.

***tert*-butyl (E)-2-(3-methyl-4-oxobut-2-en-1-yl)-1H-pyrrole-1-carboxylate (1k)**. TLC petroleum ether/EtOAc=95:5, R_f=0.5. Purified by column chromatography using petroleum ether/EtOAc=95:5 and isolated as a colorless oil (125 mg, 80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.23 – 7.20 (m, 1H), 6.70 – 6.64 (m, 1H), 6.09 (t, *J* = 3.3 Hz, 1H), 6.00 – 5.97 (m, 1H), 3.92 (d, *J* = 7.0 Hz, 2H), 1.81 (s, 3H), 1.59 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 195.2, 150.9, 149.3, 139.9, 131.2, 121.5, 112.1, 110.2, 83.9, 28.7, 28.0, 9.2; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{19}NO_3$ 249.1365; Found 249.1369.

Preparation of Allyl Substrates (4). Known allyl and cinnamyl substrates were prepared according to the literature procedure,[4a] which was also used to prepare the β-methallyl substrate (**4a**).

N-benzhydryl-2-methylprop-2-en-1-amine (4a). TLC petroleum ether/EtOAc=90:10, R_f=0.7. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (1.25 g, 66% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 2H), 4.94 – 4.86 (m, 3H), 3.16 (s, 2H), 1.80 (s, 3H), 1.69 (broad s, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.2, 144.1, 128.5, 127.4, 127.0, 110.8, 66.3, 53.7, 20.9; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{17}H_{19}N$ 237.1517; Found 237.1513.

General Procedure for Deconjugative Allylation Reaction. To an oven-dried Schlenk tube charged with activated 5Å molecular sieves (pellet, 250 mg) and a magnetic stirring bar, was added (*R*)-TRIP (4 mg, 0.005 mmol), O_2 and H_2O-free toluene (1 mL), α,β-unsaturated aldehyde **1** (0.34 mmol), and allyl amine **4** (0.34 mmol) under a positive Ar pressure. The reaction was stirred for 15 min at rt, and then $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) was added under Ar. The reaction was stirred in an oil bath heated to 60 °C for 48 h or longer. The reaction mixture was diluted with Et_2O (4 mL), 2N HCl (5 mL) was then added and the mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers, after drying over anhydrous Na_2SO_4, were concentrated in vacuo to obtain the crude product. Purification by column chromatography afforded the pure α-allylated aldehyde products. Select aldehyde products necessitated reduction under standard $NaBH_4$ conditions for ee determination.

***(S,E)*-2-methyl-2-styrylpent-4-enal (2a).** TLC petroleum ether/EtOAc=95:5, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a light yellow liquid (55 mg, 81% yield), 96% ee: $[\alpha]_D^{22}$= +47.3 (c= 0.9 in CH_2Cl_2); HPLC with an OD-H column (*n*-hexane/*i*-PrOH= 99:1 at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 9.20 min, minor enantiomer t_R= 8.29 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 16.4 Hz, 1H), 6.16 (d, *J* = 16.4 Hz, 1H), 5.79 – 5.68 (m, 1H), 5.15 – 5.07 (m, 2H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.29 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.9, 136.7, 132.9, 132.0, 129.7, 128.7, 127.9, 126.4, 118.8, 52.0, 40.4, 18.5; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{16}ONa$ 223.1093; Found 223.1078.

(*S,E*)-2-(4-methoxystyryl)-2-methylpent-4-enal (2b). TLC petroleum ether/EtOAc=95:5, R_f=0.5. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (63 mg, 80% yield): $[\alpha]_D^{22}$= +23.6 (c= 0.8 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 16.4 Hz, 1H), 6.00 (d, *J* = 16.4 Hz, 1H), 5.74 (d, *J* = 7.2 Hz, 1H), 5.15 – 5.09 (m, 3H), 3.81 (s, 3H), 2.45 (d, *J* = 7.3 Hz, 2H), 1.27 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.9, 159.5, 133.0, 131.4, 129.5, 127.6, 127.3, 118.7, 114.1, 55.3, 51.9, 40.4, 18.5; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}O_2Na$ 253.1199; Found 253.1192.

(*S,E*)-2-(4-methoxystyryl)-2-methylpent-4-en-1-ol (corresponding alcohol of **2b).** TLC petroleum ether/EtOAc=95:5, R_f=0.2. Colorless oil (quantitative yield from **2b**), 96% ee: $[\alpha]_D^{22}$= +71.0 (c= 0.4 in CH_2Cl_2); HPLC with an AS-H column (*n*-*h*exane/i-PrOH= 95:5 at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 23.75 min, minor enantiomer t_R= 16.26 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.36 (d, *J* = 16.3 Hz, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 5.82 (ddt, *J* = 17.0, 9.2, 7.3 Hz, 1H), 5.12 – 5.04 (m, 2H), 3.81 (s, 3H), 3.47 (q, *J* = 10.7 Hz, 2H), 2.22 (qd, *J* = 13.7, 7.3 Hz, 2H), 1.26 (-OH, s, 1H), 1.11 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.0, 134.6, 133.2, 130.1, 129.0, 127.3, 117.6, 114.0, 70.2, 55.3, 42.3, 41.7, 20.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2$ 233.1536; Found 233.1525.

(*S,E*)-2-(4-chlorostyryl)-2-methylpent-4-enal (2c). TLC petroleum ether/EtOAc=95:5, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a light yellow liquid (68 mg, 85% yield), 92% ee: $[\alpha]_D^{22}$= +39.3 (c= 0.8 in CH_2Cl_2); HPLC with an AD-H column (pure *n*-hexane at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 19.54 min, minor enantiomer t_R= 22.31 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.31-7.27 (m, 4H), 6.39 (d, *J* = 16.4 Hz, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 5.77 – 5.68 (m, 1H), 5.16 – 5.10 (m, 2H), 2.46 (d, *J* = 7.3 Hz, 2H), 1.29 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.7, 135.2, 133.5, 132.7, 130.7, 130.4, 128.8, 127.6, 119.0, 52.0, 40.4, 18.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}ClO$ 236.0918; Found 236.0899.

(*S,E*)-2-(4-fluorostyryl)-2-methylpent-4-enal (2d). TLC petroleum ether/EtOAc=95:5, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a pale yellow oil (61 mg, 82% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 16.4 Hz, 2H), 6.08 (d, *J* = 16.4 Hz, 2H), 5.73 (dq, *J* = 16.0, 7.7 Hz, 1H), 5.16 – 5.08 (m, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.28 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.8, 162.5 (d, *J* = 248.2 Hz), 132.9 (d, *J* = 3.4 Hz), 132.8, 130.7, 129.5 (d, *J* = 2.1 Hz), 127.9 (d, *J* = 8.0 Hz), 118.9, 115.6 (d, *J* = 21.7 Hz), 51.9, 40.4, 18.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.0 (m, 1F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}FO$ 218.1107; Found 218.1109.

(*S,E*)-2-(4-fluorostyryl)-2-methylpent-4-en-1-ol (corresponding alcohol of **2d).** TLC petroleum ether/EtOAc=90:10, R_f=0.2. Colorless oil (quantitative yield from **2d**), 95% ee: $[\alpha]_D^{22}$= +24.3 (c= 1 in CH_2Cl_2); HPLC with an AS-H column (*n*-hexane/*i*-PrOH= 99:1 at 1 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 20.05 min, minor enantiomer t_R= 17.59 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.37 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 5.81 (dq, *J* = 16.1, 8.1 Hz, 1H), 5.13 – 5.04 (m, 2H), 3.48 (q, *J* = 10.7 Hz, 2H), 2.23 (qd, *J* = 13.7, 7.5 Hz, 2H), 1.72 (broad s, 1H), 1.11 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.3 Hz), 135.3 (d, *J* = 2.0 Hz), 134.4, 133.5 (d, *J* = 3.3 Hz), 128.3, 127.6 (d, *J* = 7.9 Hz), 117.7, 115.4 (d, *J* = 21.5 Hz), 70.1, 42.1, 41.7, 20.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.1 (m, 1F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{17}FO$ 220.1263; Found 220.1260.

(*S,E*)-2-methyl-2-(4-(trifluoromethyl)styryl)pent-4-enal (2e). TLC petroleum ether/EtOAc=95:5, R_f=0.7. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a pale yellow oil (70 mg, 77% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 16.4 Hz, 1H), 6.29 (d, *J* = 16.4 Hz, 1H), 5.78 – 5.67 (m, 1H), 5.17 – 5.10 (m, 2H), 2.50 – 2.46 (m, 2H), 1.31 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.6, 140.1, 132.6, 132.5, 130.5, 129.7 (q, *J* = 32.4 Hz), 126.5, 125.6 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 271.7 Hz), 119.1, 52.1, 40.4, 18.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.53 (s, 3F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{15}F_3O$ 268.1075; Found 268.1072.

(*S,E*)-2-methyl-2-(4-(trifluoromethyl)styryl)pent-4-en-1-ol (corresponding alcohol of **2e).** TLC petroleum ether/EtOAc=95:5, R_f=0.2. Pale yellow oil (quantitative yield from **2e**), 89% ee: $[\alpha]_D^{22}$= +27.2 (c= 1.0 in CH_2Cl_2); HPLC with an AS-H column (*n*-hexane/*i*-PrOH= 99.5:0.5 at 1 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 22.63 min, minor enantiomer t_R= 20.64 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.43 (d, *J* = 16.4 Hz, 1H), 6.30 (d, *J* = 16.4 Hz, 1H), 5.85 – 5.75 (m, 1H), 5.14 – 5.06 (m, 2H), 3.51 (q, *J* = 10.8 Hz, 2H), 2.31 – 2.18 (m, 2H), 1.13 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.9, 138.4, 134.2, 129.1 (q, *J* = 32.3 Hz), 128.1, 126.3, 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.8 Hz), 117.9, 70.0, 42.0, 42.0, 20.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.42 (s, 3F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{17}F_3O$ 270.1232; Found 270.1237.

(*E*)-2-methyl-4-(4-(trifluoromethyl)phenyl)hepta-2,6-dienal (2e-γ). TLC petroleum ether/EtOAc=95:5, R_f=0.5. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a pale yellow oil (7 mg, 8% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 9.8 Hz, 1H), 5.72 – 5.61 (m, 1H), 5.11 – 5.02 (m, 2H), 3.99 – 3.91 (m, 1H), 2.67 – 2.50 (m, 2H), 1.78 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.8, 154.4, 146.0, 139.5, 134.4, 129.3 (q, *J* = 32.5 Hz), 127.8, 125.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.0 Hz), 117.9, 44.7, 40.1, 9.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.51 (s, 3F); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{15}F_3O$ 268.1075; Found 268.1076.

(*R,E*)-4-(3-formyl-3-methylhexa-1,5-dien-1-yl)benzonitrile (2f). TLC petroleum ether/EtOAc=90:10, R_f=0.35. Purified by column chromatography using petroleum ether/EtOAc=90:10. Further purified via column chromatography using DCM/petroleum ether=2:1 and isolated as a colorless oil (50 mg, 65% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 16.4 Hz, 1H), 6.33 (d, *J* = 16.4 Hz, 1H), 5.71 (ddt, *J* = 17.1, 9.6, 7.3 Hz, 1H), 5.17 – 5.09 (m, 2H), 2.52 – 2.42 (m, 2H), 1.31 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.4, 141.1, 133.9, 132.5, 132.3, 130.2, 126.9, 119.3, 124.1, 118.8, 111.1, 52.2, 40.4, 18.6; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{15}NO$ 225.1154; Found 225.1162.

(*R,E*)-4-(3-(hydroxymethyl)-3-methylhexa-1,5-dien-1-yl)benzonitrile (corresponding alcohol of **2f).** TLC in DCM, R_f=0.26. Colorless oil (quantitative yield from **2f**), 77% ee: $[\alpha]_D^{22}$= -31.8 (c= 0.75 in CH_2Cl_2); HPLC with an AD-H column (*n*-hexane/*i*-PrOH= 90:10 at 1 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 17.15 min, minor enantiomer t_R= 18.55 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.35 (d, *J* = 16.4 Hz, 1H), 5.79 (ddt, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.14 – 5.07 (m, 2H), 3.57 – 3.47 (m, 2H), 2.31 – 2.19 (m, 2H), 1.13 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9, 139.9, 134.0, 132.4, 127.9, 126.7, 119.0, 118.1, 110.5, 69.9, 42.1, 42.0, 20.7; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{17}NO$ 227.1310; Found 227.1317.

(*E*)-4-(6-methyl-7-oxohepta-3-1,5-dien-4-yl)benzonitrile (2f-γ). TLC petroleum ether/EtOAc=90:10, R_f=0.23. Purified by column chromatography using petroleum ether/EtOAc=90:10. Further purified via column chromatography using DCM/petroleum ether=2:1 and isolated as a colorless oil (8 mg, 11% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 9.6 Hz, 1H), 5.65 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.11 – 5.02 (m, 2H), 3.94 (dt, *J* = 9.7, 7.3 Hz, 1H), 2.58 (qt, *J* = 14.2, 7.1 Hz, 2H), 1.77 (d, *J* = 1.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.7, 153.5, 147.4, 139.9, 134.1, 132.7, 128.3, 118.6, 118.2, 111.0, 44.9, 40.0, 9.8; HRMS (ESI-TOF) m/z: $[M-H]^-$ Calcd for $C_{15}H_{14}NO$ 224.1075; Found 224.1080.

(*E*)-2-methyl-2-(4-nitrostyryl)pent-4-enal (2g). TLC petroleum ether/EtOAc=90:10, R_f=0.4: Purified by column chromatography using petroleum ether/EtOAc=99:1 to 90:10 and isolated as an orange oil (28 mg, 33% yield), 96% ee: $[\alpha]_D^{22}$= +44.7 (c= 1.0 in CH_2Cl_2); HPLC with an AS-H column (*n*-hexane/*i*-PrOH=90:10 at 1 mL/min, UV detector λ=254 nm); major enantiomer t_R= 33.25 min, minor enantiomer t_R= 56.07 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 16.4 Hz, 1H), 6.40 (d, *J* = 16.3 Hz, 1H), 5.72 (ddt, *J* = 17.1, 9.7, 7.3 Hz, 1H), 5.22 – 5.09 (m, 2H), 2.49 (dd, *J* = 7.6, 3.5 Hz, 2H), 1.33 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.4, 147.1, 143.0, 134.9,

132.2, 129.8, 126.9, 124.1, 119.4, 52.3, 40.4, 18.6; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}NO_3$ 245.1052; Found 245.1050.

(*E*)-2-methyl-4-(4-nitrophenyl)hepta-2,6-dienal (2g-γ). TLC petroleum ether/EtOAc=90:10, R_f=0.2. Purified by column chromatography using petroleum ether/EtOAc=99:1 to 90:10 and isolated as an orange oil (19 mg, 23% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 9.6 Hz, 1H), 5.72 – 5.59 (m, 1H), 5.12 – 5.01 (m, 2H), 4.00 (dt, *J* = 9.6, 7.3 Hz, 1H), 2.68 – 2.53 (m, 2H), 1.78 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.6, 153.3, 149.5, 146.9, 140.0, 134.0, 128.4, 124.2, 118.3, 44.7, 40.1, 9.8; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}NO_3$ 245.1052; Found 245.1055.

(*S,E*)-2-methyl-2-(2-(trifluoromethyl)styryl)pent-4-enal (2h). TLC petroleum ether/EtOAc=90:10, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (73 mg, 80% yield), 91% ee: $[\alpha]_D^{22}$= +49.1 (c= 0.6 in CH_2Cl_2); HPLC with an OD-H column (pure *n*-hexane at 1 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 33.96 min, minor enantiomer t_R= 24.74 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 16.2, 2.4 Hz, 1H), 6.13 (d, *J* = 16.1 Hz, 1H), 5.78 – 5.67 (m, 1H), 5.17 – 5.11 (m, 2H), 2.53 – 2.41 (m, 1H), 1.31 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.7, 136.1 (q, *J* = 1.7 Hz), 134.2, 132.5, 131.9, 128.2 (q, *J* = 1.8 Hz), 127.5, 127.5, 127.5 (q, *J* = 30.2 Hz), 125.8 (q, *J* = 5.8 Hz), 124.3 (q, *J* = 273.4 Hz), 119.1, 52.3, 40.3, 18.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.58 (s, 3F); HRMS m/z: (ESI) $[M]^+$ Calcd for $C_{15}H_{15}F_3O$ 268.1075; Found 268.1080.

(*S,E*)-2-methyl-2-(2-(naphthalen-1-yl)vinyl)pent-4-enal (2i). TLC petroleum ether/EtOAc=95:5, R_f=0.7. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (61 mg, 72% yield), 97% ee: $[\alpha]_D^{22}$= +34.6 (c= 0.4 in CH_2Cl_2); HPLC with an OD-H column (*n*-hexane/*i*-PrOH= 99:1 at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 20.99 min, minor enantiomer t_R= 17.11 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.49 – 7.45 (m, 1H), 7.23 (d, *J* = 16.1 Hz, 1H), 6.21 (d, *J* = 16.1 Hz, 1H), 5.84 (ddt, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.23 – 5.17 (m, 2H), 2.62 – 2.53 (m, 2H), 1.42 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.9, 134.7, 133.6, 133.1, 132.9, 131.1, 129.5, 128.6, 128.3, 126.2, 125.9, 125.6, 124.0, 123.7, 119.0, 52.5, 40.5, 18.7; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}O$ 274.1284; Found 274.1298.

(*R*)-2-(3,4-dihydronaphthalen-2-yl)-2-methylpent-4-enal (2j). TLC petroleum ether/EtOAc=95:5, R_f=0.59. Purified by column chromatography using petroleum ether/EtOAc=97:3 and isolated as a colorless oil (63 mg, 82% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.20 – 7.05 (m, 4H), 6.41 (s, 1H), 5.66 (ddt, *J* = 17.3, 10.2, 7.3 Hz, 1H), 5.15 – 5.04 (m, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.60 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.43 (dd, *J* = 14.2, 7.6 Hz, 1H), 2.27 – 2.12 (m, 2H), 1.29 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.0, 138.4, 134.8, 133.9, 133.3, 127.3, 127.2, 126.6, 126.4, 126.1, 118.4, 55.1, 37.4, 28.1, 24.2, 17.4; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{16}H_{18}O$ 226.1358; Found 226.1360.

(*R*)-2-(3,4-(dihydronaphthalen-2-yl)-2-methylpent-4-en-1-ol (corresponding alcohol of **2j).** TLC petroleum ether/EtOAc=95:5, R_f=0.13. Colorless oil (quantitative yield from **2j**), 92% ee: $[\alpha]_D^{22}$= -35.2 (c= 1.0 in CH_2Cl_2); HPLC with an OD-H column (*n*-hexane/*i*-PrOH= 99:1 at 1 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 51.91 min, minor enantiomer t_R= 57.91 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 3H), 7.05 (d, *J* = 6.7 Hz, 1H), 6.35 (s, 1H), 5.73 (ddt, *J* = 17.2, 10.2, 7.3 Hz, 1H), 5.11 – 5.00 (m, 2H), 3.64 (d, *J* = 10.8 Hz, 1H), 3.46 (d, *J* = 10.8 Hz, 1H), 2.78 (td, *J* = 7.6, 2.9 Hz, 2H), 2.34 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.28 (t, *J* = 7.7 Hz, 2H), 2.15 (dd, *J* = 13.9, 7.6 Hz, 1H), 1.18 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.5, 134.7, 134.5, 134.3, 127.0, 126.7, 126.5, 126.2, 124.5, 117.5, 68.8, 44.6, 40.2, 28.4, 23.5, 20.5; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{16}H_{20}O$ 228.1514; Found 228.1517.

tert-butyl (*S,E*)-2-(3-formyl-3-methylhexa-1,5-dien-1-yl)-1H-pyrrole-1-carboxylate (2k). TLC petroleum ether/EtOAc=95:5, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (59mg, 81%), 75% ee: $[\alpha]_D^{22}$= +21.4 (c= 1 in *i*PrOH), HPLC with an AD-H column (pure *n*-hexane at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 17.51 min, minor enantiomer t_R= 23.19 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.24 (dd, *J* = 3.3, 1.7 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.41 – 6.35 (m, 1H), 6.13 (t, *J* = 3.4 Hz, 1H), 5.92 (d, *J* = 16.3 Hz, 1H), 5.74 (ddt, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.14 – 5.07 (m, 2H), 2.44 (d, *J* = 7.3 Hz, 2H), 1.60 (s, 9H), 1.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.8, 149.3, 133.3, 133.0, 129.0, 123.5, 122.2, 118.7, 111.0, 110.8, 84.0, 52.1, 40.3, 28.1, 18.4; HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{17}H_{23}NO_3K$ 328.1310; Found 328.1308.

(*S,E*)-2-ethyl-2-styrylpent-4-enal (2l). TLC petroleum ether/EtOAc=95:5, R_f=0.7. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a pale yellow oil (29 mg, 40% yield, 40% of starting material recovered): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 6.45 (d, *J* = 16.6 Hz, 1H), 6.11 (d, *J* = 16.6 Hz, 1H), 5.73 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.12 (m, 2H), 2.52 (qd, *J* = 14.4, 7.3 Hz, 2H), 1.80 (hept, *J* = 7.0 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.4, 136.8, 133.0, 132.6, 128.8, 128.7, 127.9, 126.3, 118.5, 55.5, 36.9, 25.7, 8.1; HRMS (ESI) $[M]^+$ calcd. for $[C_{15}H_{18}O]$ 214.1358, found 214.1355.

(*S,E*)-2-ethyl-2-styrylpent-4-en-1-ol (corresponding alcohol of **2l):** TLC petroleum ether/EtOAc=95:5, R_f=0.3. Pale yellow oil (quantitative yield from **2l**), 80% ee: $[\alpha]_D^{22}$= -1.1 (c= 0.7 in CH_2Cl_2); HPLC with an OD-H column (*n*-hexane/*i*-PrOH= 99:1 at 0.9 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 23.03 min, minor enantiomer t_R= 24.61 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 16.6 Hz, 1H), 6.09 (d, *J* = 16.6 Hz, 1H), 5.84 (ddt, *J* = 17.3, 10.1, 7.4 Hz, 1H), 5.18 – 5.07 (m, 2H), 3.55 (s, 2H), 2.37 – 2.22 (m, 2H), 1.52 (ddt, *J* = 21.5, 13.9, 7.1 Hz, 2H), 1.26 (-OH, s, 1H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.4, 134.9, 134.5, 129.9, 128.6, 127.3, 126.1, 117.7, 67.1, 44.6, 38.1, 26.8, 7.9; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{20}O$ 216.1514; Found 216.1512.

(*S,E*)-2-methyl-5-phenyl-2-((E)-styryl)pent-4-enal (3b). TLC petroleum ether/EtOAc=95:5, R_f=0.6. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a light yellow solid (70 mg, 75% yield), m.p. 45-47 °C, 93% ee. $[\alpha]_D^{22}$= +70.8 (c= 1.0 in CH_2Cl_2), HPLC with an OD-H column (n-hexane/i-PrOH= 99:1 at 1.0 mL/min for 30

minutes, UV detector λ = 254 nm); major enantiomer t_R= 21.20 min, minor enantiomer t_R= 19.07 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.23 (m, 8H), 6.56 – 6.48 (m, 2H), 6.25 (d, *J* = 16.4 Hz, 1H), 6.22 – 6.13 (m, 1H), 2.66 (d, *J* = 7.6 Hz, 2H), 1.37 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.9, 137.2, 136.7, 133.9, 132.2, 129.7, 128.7, 128.6, 128.0, 127.4, 126.5, 126.2, 124.6, 52.6, 39.7, 18.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}ONa$ 299.1406; Found 299.1403.

(*S,E*)-2,4-dimethyl-2-styrylpent-4-enal (3a). TLC petroleum ether/EtOAc=95:5, R_f=0.5. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (42 mg, 57% yield), 87% ee: $[\alpha]_D^{22}$= +20.0 (c= 1.0 in CH_2Cl_2); HPLC with an OD-H column (*n*-hexane/i-PrOH= 99:1 at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 8.67 min, minor enantiomer t_R= 7.18 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 16.4 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H), 4.88 (s, 1H), 4.74 (s, 1H), 2.53 (d, *J* = 13.9 Hz, 1H), 2.45 (d, *J* = 13.9 Hz, 1H), 1.70 (s, 3H), 1.30 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.9, 141.2, 136.8, 131.5, 130.4, 128.7, 127.8, 126.3, 115.4, 52.0, 44.4, 24.3, 18.7; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{18}O$ 214.1358; Found 214.1358.

(*E*)-2,6-dimethyl-4-phenylhepta-2,6-dienal (3a-γ). TLC petroleum ether/EtOAc=95:5, R_f=0.4. Purified by column chromatography using petroleum ether/EtOAc=99:1 and isolated as a colorless oil (8 mg, 11% yield), 28% ee: HPLC with an AD-H column (pure *n*-hexane at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 19.56 min, minor enantiomer t_R= 20.49 min; $[\alpha]_D^{22}$= -10.1 (c= 0.4 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 3H), 6.56 (d, *J* = 9.7 Hz, 1H), 4.75 (s, 1H), 4.67 (s, 1H), 4.01 (q, *J* = 9.1 Hz, 1H), 2.62 – 2.46 (m, 2H), 1.79 (s, 3H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 195.2, 156.6, 142.3, 142.3, 138.6, 128.9, 127.4, 126.9, 113.0, 44.5, 43.3, 22.4, 9.5; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{15}H_{18}O$ 214.1358; Found 214.1359.

Preparation of (*E*)-1-methoxy-4-(3-methyl-3-vinylhexa-1,5-dien-1-yl)benzene (6). To an oven-dried reaction flask, cooled under vacuum and backfilled with Ar, methyltriphenylphosphonium bromide (206 mg, 0.58 mmol) and dry THF (1 mL) were added under Ar. The reaction flask was cooled to 0 °C, and *n*-Buli (0.36mL, 0.58 mmol, 1.6 M in hexane) was added, dropwise. The reaction mixture was then stirred at 0 °C for 30 min. A solution of ***ent*-2b** (102 mg, 0.44 mmol) in dry THF (1 mL) was added at 0 °C. The reaction was warmed to rt and stirred at rt for 24 h. Reaction completion was confirmed by TLC (petroleum ether/EtOAc=95:5, R_f=0.6). Solvent was removed by rotavapor, and the residue was purified by column chromatography using petroleum ether/EtOAc=99:1. The desired product was isolated as a light yellow oil (128 mg, 97% yield): $[\alpha]_D^{22}$= +22.0 (c= 1.0 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.29 (d, *J* = 16.2 Hz, 1H), 6.10 (d, *J* = 16.2 Hz, 1H), 5.91 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.86 – 5.74 (m, 1H), 5.09 – 5.00 (m, 4H), 3.81 (s, 3H), 2.27 (d, *J* = 7.3 Hz, 2H), 1.20 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 145.6, 135.3, 135.0, 130.6, 127.2, 126.8, 117.3, 113.9, 112.2, 55.3, 45.7, 42.4, 23.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O$ 229.1592; Found 229.1583.

Preparation of (*S,E*)-6-(4-methoxyphenyl)-4-methyl-4-vinylhex-5-enal (7). To an oven-dried reaction flask, cooled under vacuum and backfilled with Ar, **6** (133 mg, 0.58 mmol) and dry THF (2 mL) were added under Ar. The reaction flask was cooled to 0 °C, and 9-BBN (1.16 mL, 0.58 mmol, 0.5 M in THF) was added via syringe pump over 24 min (0.05 mL/min) at 0 °C. The reaction was warmed to rt, stirred at rt for 3 h, and then cooled to 0 °C again. Aqueous NaOH (1 mL, 3M) and H_2O_2 (1 mL, 35% in H_2O) were slowly added to the reaction mixture, which was then stirred at rt for 10 min. The reaction was diluted with H_2O (20 mL), and extracted with DCM (3 x 20 mL). The combined organic layers, after drying over anh. Na_2SO_4, were concentrated in vacuo to obtain the crude alcohol product (TLC petroleum ether/EtOAc=8:2, R_f=0.2.) The crude alcohol product was purified by column chromatography using petroleum ether/EtOAc=8:2, and the desired pure alcohol product was isolated as a light yellow oil (114 mg, 80% yield): $[\alpha]_D^{22}$= +25.6 (c= 1.0 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 16.2 Hz, 1H), 6.05 (d, *J* = 16.2 Hz, 1H), 5.88 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.08 – 4.99 (m, 2H), 3.80 (s, 3H), 3.64 (t, *J* = 5.9 Hz, 2H), 1.62 – 1.50 (m, 4H), 1.20 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 145.8, 135.5, 130.5, 127.2, 126.8, 113.9, 112.1, 63.6, 55.3, 42.2, 37.2, 27.9, 23.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}O_2$ 247.1698; Found 247.1687.

To a stirred solution of the pure alcohol product (44 mg, 0.18 mmol) in DCM (2 mL) was added DMP (114 mg, 0.27 mmol), and the solution was stirred for 2 h at rt. Reaction completion was confirmed by TLC (petroleum ether/EtOAc=8:2, R_f=0.6). Sat. aq. $Na_2S_2O_3$ (10 mL) and sat. aq. $NaHCO_3$ (10 mL) were added to the reaction, which was then extracted with DCM (3 x 20 mL). The combined organic layers were dried over anh. Na_2SO_4. The solvent was removed by rotavapor, and the crude product was purified by column chromatography using petroleum ether/EtOAc=95:5. Pure **6** was isolated as a light yellow oil (36 mg, 81% yield): $[\alpha]_D^{22}$= +22.1 (c= 0.7 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.28 (d, *J* = 16.3 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 5.84 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.11 – 5.01 (m, 2H), 3.80 (s, 3H), 2.45 (td, *J* = 7.9, 1.6 Hz, 2H), 1.84 (dd, *J* = 8.6, 7.1 Hz, 2H), 1.20 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.5, 159.0, 144.9, 134.4, 130.2, 127.5, 127.3, 114.0, 112.9, 55.3, 41.9, 39.7, 32.5, 23.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_2$ 245.1542; Found 245.1534.

Preparation of (*S,E*)-1-(3,7-dimethyl-3-vinylocta-1,6-dien-1-yl)-4-methoxybenzene (8). To an oven-dried reaction flask, cooled under vacuum and backfilled with Ar, isopropyltriphenylphosphonium iodide (48 mg, 0.11 mmol) and dry THF (0.5 mL) were added under Ar. The reaction flask was cooled to 0 °C, and *n*-Buli (0.069mL, 0.11 mmol, 1.6 M in hexane) was added, dropwise. The reaction mixture was stirred at 0 °C for 30 min. A solution of **7** (21 mg, 0.09 mmol) in dry THF (0.5 mL) was added at 0 °C. The reaction was warmed to rt and stirred at rt for 24 h. Reaction completion was confirmed by TLC (petroleum ether/EtOAc=95:5, R_f=0.55). The solvent was then removed by rotavapor, and the residue was purified by column chromatography using petroleum ether/EtOAc=99:1. Pure **8** was isolated as a colorless oil (22 mg, 92% yield): $[\alpha]_D^{22}$= +21.5 (c= 1.0 in CH_2Cl_2) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 16.2 Hz, 1H), 6.06 (d, *J* = 16.2 Hz, 1H), 5.88 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.11 (t, *J* = 7.0 Hz, 1H), 5.06 – 4.98 (m, 2H), 3.80 (s,

3H), 1.95 (dd, J = 10.8, 6.2 Hz, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.52 – 1.47 (m, 2H), 1.20 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.7, 146.0, 135.8, 131.3, 130.7, 127.2, 126.5, 124.8, 113.9, 111.9, 55.3, 42.5, 41.3, 25.7, 23.4, 23.2, 17.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O$ 271.2062; Found 271.2061.

General Procedure for Cope Rearrangement: *ent*-2a (50 mg, 0.25 mmol) was dissolved in 1,2-dichlorobenzene (0.5 mL) and stirred in an oil bath heated to 150 °C for 24 h. The reaction mixture was directly loaded onto a silica column (petroleum ether/EtOAc=99:1 to 97:3). Product **2a-γ** was isolated as a light yellow oil (23 mg, 45% yield), 93% ee: TLC petroleum ether/EtOAc=95:5, R_f=0.4. HPLC with an OD-H column (*n*-hexane/*i*-PrOH= 99:1 at 1.0 mL/min, UV detector λ = 254 nm); major enantiomer t_R= 9.95 min, minor enantiomer t_R= 10.95 min; $[\alpha]_D^{22}$= +97.3 (c= 0.2 in CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 – 7.21 (m, 3H), 6.59 (d, J = 9.9 Hz, 1H), 5.75 – 5.62 (m, 1H), 5.05 (m, 2H), 3.89 (q, J = 8.3 Hz, 1H), 2.68 – 2.48 (m, 2H), 1.79 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 195.2, 156.1, 142.0, 138.8, 135.1, 128.9, 127.4, 127.0, 117.3, 44.9, 40.3, 9.6; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{14}H_{16}O$ 200.1201; Found 200.1203.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of reaction optimizations, structural assignments, and ^1H, ^{13}C, and HPLC spectra (PDF)

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