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A Novel Synthesis of Sex Pheromone from the Longicorn Beetle (*Psacothea hilaris*)

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Abstract—An asymmetric synthesis of (8*Z*,21*R*)-21-methylpentatriacont-8-ene, the sex pheromone of the yellow-spotted longicorn beetle *Psacothea hilaris*, has been achieved using Evan's induction as the key step. Based on the asymmetric methylation product of chiral (*R*)-4-benzyl-1,3-oxazolidin-2-one, the carbon chain of the target molecule was assembled through a C_5+C_{12}+C_{11}+C_8 sequence. (2*R*)-4-(Benzyloxy)-2-methylbutan-1-ol, which can be obtained from γ-lactone following Evan's protocol, was connected to a C_{12} alkyl group. The chiral methyl group remained the key moiety (97% *ee*). After another Wittig reaction and catalytic hydrogenation step, the designed key intermediate (13*R*)-13-methylheptacosan-1-ol was obtained. Finally, after oxidation and Wittig reaction, the synthesis of the target molecule was completed in 10 linear steps with an ultra-high overall yield of 36.2%.

Keywords: 21-methylpentatriacont-8-ene, sex pheromone, synthesis, yellow-spotted longicorn beetle

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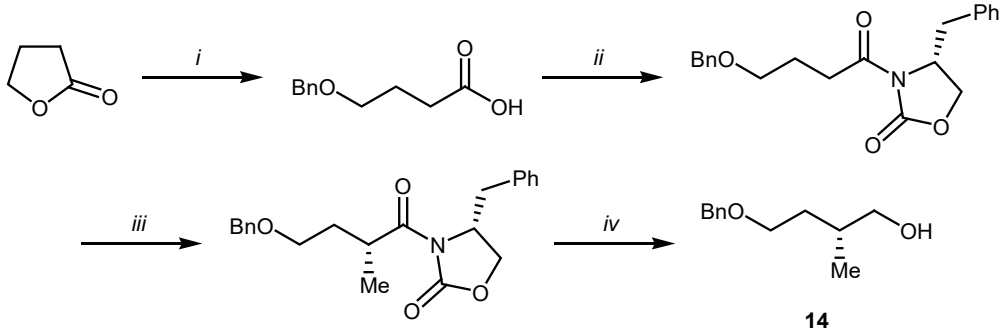
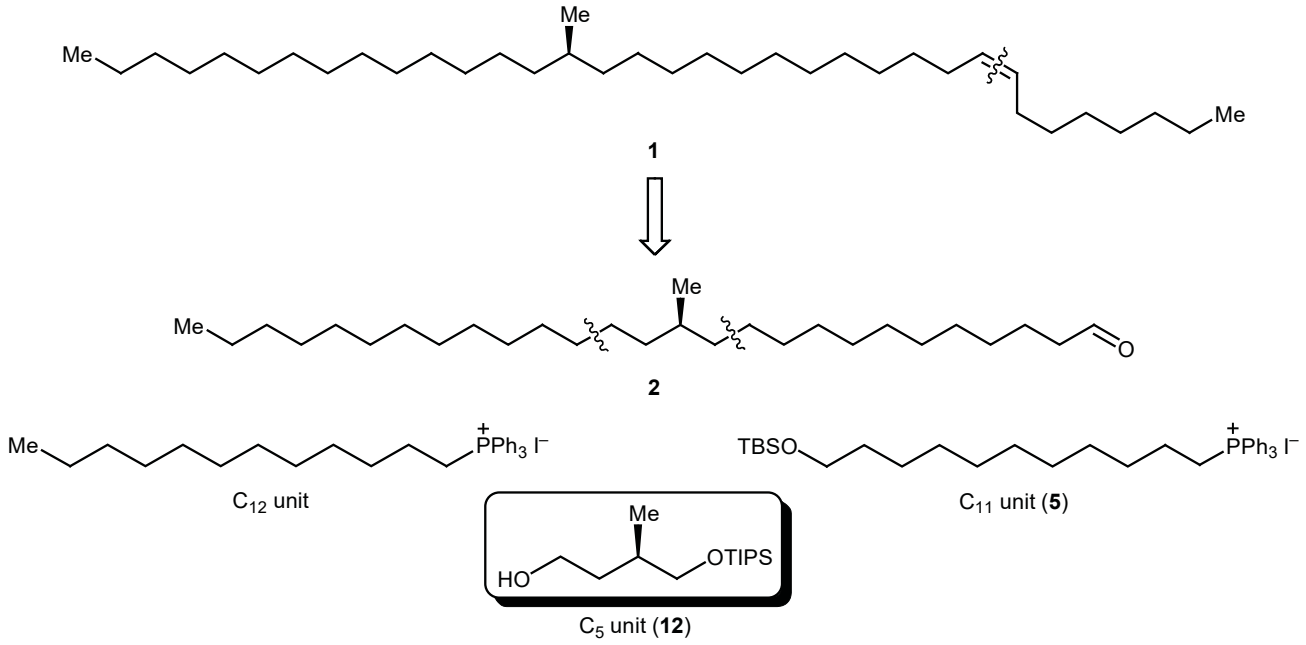
It is well known that traditional pesticides are putting more and more pressure on the environment or ecology in agricultural production. Indeed, there has been a trend toward using some "green" pesticides to suppress and control the pest population in agricultural production when coupled with physical approaches such as mass trapping, attracticides, and mating disruption [1]. In this context, the use of low-dose substances such as insect pheromones would be favorable [2]. The yellow-spotted longicorn beetle *Psacothea hilaris* from the order *Coleoptera* and family *Cerambycidae* is distributed throughout China. The beetle larvae eat tree branches until they reach maturity. This herbivory of the insect accounts for the massive destruction of fig trees and mountain mulberry. The sex pheromone from the yellow-spotted longicorn beetle is composed of long-chain aliphatic compounds with methylated branches. With regard to the methyl position in the pheromone, it is expected that the mass spectrum will not produce reliable fragment ions that specify the branch position, so that determination of the detailed structure is very difficult [3]. Fukaya and co-workers reported the isolation and identification of the *P. hilaris* contact sex pheromone as (8*Z*)-21-methylpentatriacont-8-ene in 1996 [4–6], although the chirality of the methyl had yet to be determined (Scheme 1). Mori's group had been interested in the absolute chirality of the methyl group, and they synthesized the two enantiomers and asserted that the chirality of the methyl group is uncertain [7]. However, Fukaya demonstrated that the *R* enantiomer attracted more male insects, although their number was less than that attracted by female elytra extracts [5]. At this time, only those groups have reported the synthesis of 21-methylpentatriacont-8-ene only, although they obtained different enantiomers. As a continuation of our research on new agrichemicals and "green" pesticides from resource materials [8–13], we were interested in utilizing chiral methylation and the Wittig reaction for the efficient, inexpensive, and convenient preparation of 21-methyl-

Scheme 1.



Reagents and conditions: *i*: (1) BnCl, NaOH, toluene, 130°C, reflux; (2) H^+ (91% yield); *ii*: Et_3N, Me_3CCOCl, LiCl, THF, (*R*)-4-benzyl-1,3-oxazolidin-2-one, –78°C to room temperature (91%); *iii*: NaHMDS, THF, –78 to –50°C, MeI (65% yield, 97% *ee*); *iv*: $LiAlH_4$, –10 to 0°C (92% yield).

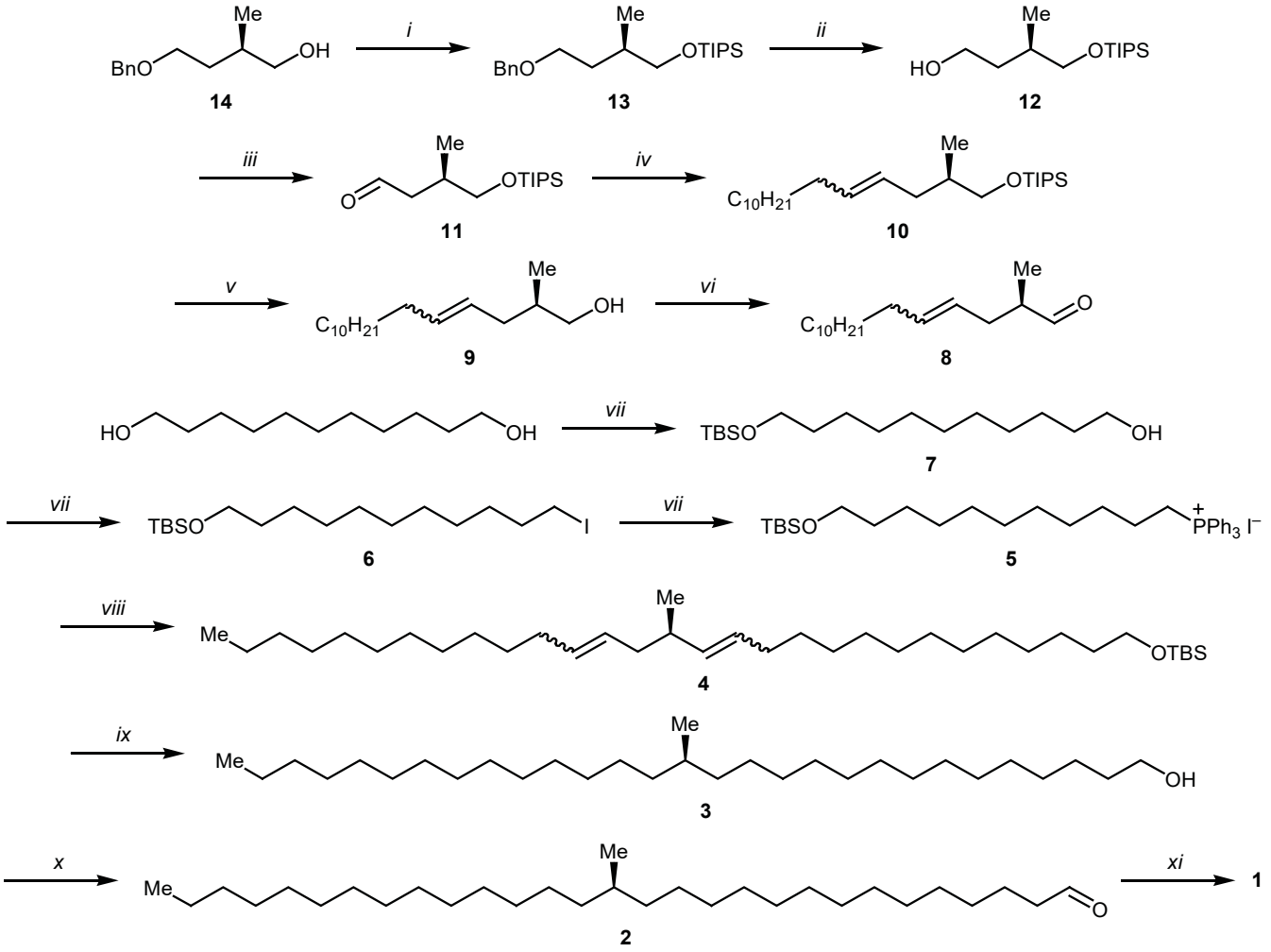


pentatriacont-8-ene. Herein, we report this novel synthesis of (*R*)-**1** by means of the manipulation of template induction and the Wittig reaction as the key steps.

The starting material was (2*R*)-4-(benzyloxy)-2-methylbutan-1-ol (**14**) which could be provided in large quantity according to the previous procedure [9, 14, 15]; $[\alpha]_D^{25} = +12.43°$ ($c = 0.267$, $CHCl_3$); HRMS (ESI): m/z 195.13815 $[M + H]^+$, calculated for $C_{12}H_{19}O_2$:195.13796. The retrosynthesis of 21-methylpentatriacont-8-ene (**1**) is summarized in Scheme 1. The *cis*-double bond can be obtained through an alkyl ylide and aldehyde. Aldehyde **2** can be assembled from three subunits, namely C_{12}, C_5, and C_{11} units.

The synthesis commenced from (2*R*)-4-(benzyloxy)-2-methylbutan-1-ol (**14**) (Scheme 2). It was protected with triisopropylsilyl (TIPS) chloride in the presence of imidazole to give **13** with a 95% yield. After a conventional hydrogenolysis procedure, the benzyl protection was smoothly removed (with a 93% yield) to give compound **12**. It was subjected to Dess–Martin periodinane to give aldehyde **11** with an excellent yield. After the Wittig reaction, aldehyde **11** was transformed into carbon chain elongation product **10** with an 86% yield [16]. Removal of the TIPS protection yielded alcohol **9** [17, 18] which was oxidized with pyridinium chlorochromate (PCC) to afford aldehyde **8** with an 84% yield. In comparison, one of the undecane-1,11-diol hydroxyl groups was selectively masked using *tert*-butyldimethylsilyl (TBS) chloride to deliver 11-[(*tert*-butyldimethylsilyl)oxy]undecan-1-ol (**7**) with a 58% yield. Compound **7** was converted to *tert*-butyl[(11-iodoundecyl)oxy]dimethylsilane (**6**) with

Scheme 2.



Reagents and conditions: *i*: *t*-$BuMe_2SiCl$, imidazole, 4-dimethylaminopyridine (DMAP), CH_2Cl_2, 0°C to room temperature (95% yield); *ii*: H_2, Pd/C, MeOH, 45°C (93% yield); *iii*: Dess–Martin periodinane (DMP), CH_2Cl_2, 0°C to room temperature (93% yield); *iv*: $C_{12}H_{25}Ph_3PI$, *n*-BuLi, THF, –78°C to room temperature (87% yield); *v*: Bu_4NF, CH_2Cl_2, 0°C to room temperature (93% yield); *vi*: PCC, CH_2Cl_2, 0°C to room temperature (84% yield); *vii*: TBSCl, imidazole, DMAP, CH_2Cl_2, 0°C to room temperature (58% yield); *viii*: PPh_3, imidazole, I_2 (92% yield); *ix*: PPh_3, toluene, 130°C, reflux (100% yield); *x*: *n*-BuLi, THF, **8**, –78°C to room temperature (85% yield); *xi*: H_2, Pt/C, MeOH, 45°C (93% yield); *xii*: DMP, CH_2Cl_2, 0°C to room temperature (86% yield); *xiii*: $C_8H_{17}Ph_3PBr$, NaHMDS, THF, –78 to 0°C (95% yield).

a 91% yield by employing a protocol with triphenyl phosphine, iodine, and imidazole [19]. Iodide **6** was reacted with triphenyl phosphine to furnish phosphonium salt **5** with an outstanding yield. With these two key intermediates secured, after a standard Wittig protocol, compound **4** was obtained with an 85% yield. If the chiral carbon bearing methyl group is located in the allylic position, palladium on carbon (Pd/C) and Raney nickel catalysis will cause isomerization and racemization [20]. In order to avoid that outcome, we chose platinum on carbon (10% Pt/C) to reduce the carbon–carbon double bond [13], and the expected carbon–carbon double bond reduction occurred during the conventional hydrogenation process. To our surprise, the TBS protecting group was also removed with good efficiency. In this way, compound **3** was provided with a total yield of 93%. After oxidation, the yield of aldehyde **2** was 86%. The chemical selectivity of the Wittig coupling reaction is related to the base and solvent. Finally, the coupling of aldehyde **2** and ylide generated by protonation of (octyl)triphenylphosphonium bromide in tetrahydrofuran (THF) solution under the action of sodium bis(trimethylsilyl)azanide (NaHMDS) was characterized by high *Z* selectivity (*Z*/*E* > 49:1) [21] to afford (8*Z*,21*R*)-21-methylpentatriacont-8-ene (**1**) with a 95% yield.

In summary, we have solved the problems of complicated steps, difficult optical resolution, and low yield in the synthesis of chiral raw materials. Under the premise of preserving the chiral carbon configuration of the raw material, we successfully completed the asymmetric total synthesis of the contact pheromone of the yellow-spotted longhorn beetle, (8*Z*,21*R*)-21-methylpentatriacont-8-ene, through three Wittig reactions. Compared with other methods, this process has several advantages such as high yield, easy chemical operation, and a competitive cost. Further applications in modern agriculture will be reported in due time.

EXPERIMENTAL

Tetrahydrofuran was dried over metallic sodium and distilled before use. Methylene chloride was dried over calcium hydride and distilled before use. All reactions were performed in flame-dried glassware under a dry argon atmosphere. The reactions were monitored by thin-layer chromatography (TLC) on glass plates coated with silica gel containing a fluorescent indicator. Flash chromatography was performed on silica gel (200–300 mesh) with petroleum ether–ethyl acetate as an eluent. The NMR spectra were recorded on a Bruker AC-500 instrument (Madison, WI, USA) at 500 MHz for ^{1}H and 126 MHz for ^{13}C; the chemical shifts were referenced to tetramethylsilane as an internal standard for ^{1}H or deuterated chloroform used as solvent ($CDCl_3$, δ_C 77.16 ppm) for ^{13}C. The high-resolution mass spectra (electrospray ionization) were measured on a Thermo Fisher Scientific LTQ-Orbitrap-XL instrument (Germany). The optical rotations were measured on a JiaHang Instruments Digipol-P910 polarimeter (Shanghai, China) using a sodium lamp.

[(2*R*)-4-(Benzyloxy)-2-methylbutyl]tri(propan-2-yl)silane (13). Compound **14** (3.00 g, 16.64 mmol) was added to a single-necked flask charged with dichloromethane (50 mL). The flask was cooled to 0°C, imidazole (2.23 g, 33.34 mmol) and 4-(dimethylamino)-pyridine (0.20 g, 1.66 mmol) were added, and TIPS chloride was then added dropwise. The mixture was allowed to slowly warm up to room temperature and kept for 16 h. It was quenched by adding H_2O, the organic phase was collected and concentrated under reduced pressure, and the crude product was purified by column chromatography (petroleum ether–ethyl acetate, 30:1). Yield 5.55 g (15.83 mmol, 95%), colorless oil, $[\alpha]_D^{25}$ = –2.67° (*c* = 0.200, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 7.38 d (5H, *J* = 4.4 Hz), 4.87–4.21 m (2H), 3.57 d.t.d (4H, *J* = 15.3, 9.5, 5.6 Hz), 1.87–1.82 m (1H), 1.5–1.11 m (5H), 1.10 d (18H, *J* = 4.7 Hz), 0.97 d (3H, *J* = 6.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 138.75, 128.35, 127.64, 127.47, 72.86, 68.81, 68.54, 33.26, 18.07, 17.73, 16.92, 12.32, 12.03. Mass spectrum: *m*/*z* 351.27148 [*M* + H]$^+$; calculated for $C_{21}H_{39}O_2Si$: 351.27138.

(3*R*)-3-Methyl-4-{[tri(propan-2-yl)silyl]oxy}-butan-1-ol (12). A single-necked flask was charged with methanol (100 mL), compound **13** (5.20 g, 14.83 mmol) and Pd/C (10% of the substrate) were added, and hydrogen was used to ventilate the system three times. The reaction progress was monitored by TLC. After completion of the reaction (4 h), the product was purified by column chromatography (petroleum ether–ethyl acetate, 5:1). Yield 3.75 g (14.20 mmol, 95%), colorless oil, $[\alpha]_D^{25}$ = +7.44° (*c* = 0.200, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 3.76 s (1H), 3.68 d.d.d (2H, *J* = 14.4, 12.8, 6.9 Hz), 3.56 d.d (1H, *J* = 9.8, 7.3 Hz), 1.98–1.79 m (1H), 1.77–1.56 m (3H), 1.17 d.d.d (3H, *J* = 14.0, 9.8, 5.2 Hz), 1.11 d (18H, *J* = 5.7 Hz), 0.96 d (3H, *J* = 6.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 69.15, 61.29, 38.14, 34.23, 17.99, 17.72, 17.48, 11.96, Mass spectrum: *m*/*z* 261.22461 [*M* + H]$^+$; calculated for $C_{14}H_{33}O_2Si$: 261.22443.

(3*R*)-3-Methyl-4-{[tri(propan-2-yl)silyl]oxy}-butanal (11). Dess–Martin periodinane (5.73 g, 13.51 mmol) and sodium hydrogen carbonate (4.13 g, 49.14 mmol) were added to a three-necked flask, CH_2Cl_2 (10 mL) was added, and the mixture was stirred rapidly at 0°C. A solution of compound **12** (3.20 g, 12.28 mmol) in CH_2Cl_2 was slowly added dropwise, and the mixture was stirred at room temperature for 6 h and was then quenched with a saturated aqueous solution of $Na_2S_2O_3$. The organic phase was separated and washed with a saturated solution of $NaHCO_3$ (3×10 mL). The organic phase was dried and concentrated under reduced pressure, and the crude product was purified by column chromatography (petroleum ether–ethyl acetate, 30:1). Yield 2.96 g (11.45 mmol, 93%), $[\alpha]_D^{25}$ = +7.22° (*c* = 0.200, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 9.84 s (1H), 3.84–3.40 m (2H), 2.60–2.63 m (1H), 2.37–2.19 m (2H), 1.37–1.17 m (3H), 1.10 s (18H), 1.01 d (3H, *J* = 6.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 202.83, 68.08, 48.22, 31.69, 18.01, 17.72, 11.95. Mass spectrum: *m*/*z* 257.19348 [*M* + H]$^+$; calculated for $C_{14}H_{29}O_2Si$: 257.19313.

{[(2*R*)-2-Methylhexadec-4-en-1-yl]oxy}tri(propan-2-yl)silane (10). A mixture of (dodecyl)triphenylphosphonium bromide (5.66 g, 11.07 mmol) and THF (30 mL) was cooled to –78°C, a 2.5 M solution of

n-butyllithium in hexane (3.92 mL, 9.79 mmol) was slowly added dropwise, and the mixture was stirred for 1 h. A solution of compound **11** (2.20 g, 8.51 mmol) in anhydrous THF was then added dropwise, and the mixture was stirred for 4 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride, the mixture was washed with brine, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×15 mL). The combined organic phases were dried over anhydrous magnesium sulfate and evaporated, and the residue was purified by column chromatography (petroleum ether). Yield 3.04 g (7.40 mmol, 87%), colorless liquid, $[\alpha]_D^{25}$ = +4.90° (*c* = 0.200, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 5.75–5.15 m (2H), 3.63–3.49 m (2H), 2.28–2.18 m (1H), 2.11–2.00 m (2H), 1.94–1.87 m (1H), 1.76–1.66 m (1H), 1.41–1.22 m (21H), 1.12–1.07 m (18H), 0.96–0.92 m (6H). ^{13}C NMR spectrum, δ_C, ppm: 130.99, 128.01, 68.31, 36.78, 34.05, 32.88, 31.95, 30.83, 29.78, 29.68, 29.60, 29.47, 29.38, 28.80, 28.21, 27.33, 22.71, 18.07, 16.59, 14.13, 12.06. Mass spectrum: *m*/*z* 411.40204 $[M + H]^+$; calculated for $C_{26}H_{55}OSi$: 411.40167.

(2*R*)-2-Methylhexadec-4-en-1-ol (9). A single-necked flask was charged with THF (20 mL) and compound **10** (1.86 g, 4.53 mmol), the mixture was cooled to 0°C, tetrabutylammonium fluoride (1.42 g, 5.43 mmol) was added, and the mixture was stirred for 4 h (TLC) and quenched with a saturated aqueous solution of NH_4Cl. The product was isolated by column chromatography (petroleum ether–ethyl acetate, 10:1). Yield 1.08 g (4.24 mmol, 93%), colorless oil, $[\alpha]_D^{25}$ = –0.92° (*c* = 0.200, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 5.63–5.15 m (2H), 3.68–3.18 m (2H), 2.22–1.90 m (4H), 1.80–1.70 m (1H), 1.44–1.25 m (18H), 1.10 s (1H), 0.98–0.91 m (6H). ^{13}C NMR spectrum, δ_C, ppm: 131.54, 127.47, 68.21, 36.33, 31.94, 31.05, 29.72, 29.66, 29.58, 29.37, 27.34, 22.71, 16.57, 14.13. Mass spectrum: *m*/*z* 255.26811 $[M + H]^+$; calculated for $C_{17}H_{35}O$: 255.26824.

(2*R*)-2-Methylhexadec-4-enal (8). Compound **9** (0.42 g, 1.65 mmol) was dispersed in CH_2Cl_2 (2 mL), an equal amount of silica gel (0.42 g) was added, and pyridinium chlorochromate (0.45 g, 2.10 mmol) was then added at 0°C. The mixture was heated for 4 h and concentrated under reduced pressure, and the resulting crude product was purified by column chromatography (petroleum ether). Yield 0.35 g (1.39 mmol, 84%), oily material, $[\alpha]_D^{25}$ = –0.95° (*c* = 0.200, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 9.69 d (1H, *J* = 7.9 Hz), 5.65–5.09 m (2H), 2.51–2.37 m (2H), 2.27–2.16 m (1H), 2.10–1.99 m (2H), 1.40–1.29 m (18H), 1.18–1.13 m (3H), 0.92 t (3H, *J* = 6.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 204.88, 133.72, 132.68, 125.98, 125.42, 46.55, 31.92, 29.64, 29.56, 29.54, 29.35, 29.34, 28.23, 27.34, 22.69, 22.61, 17.75, 14.11, 13.07. Mass spectrum: *m*/*z* 253.25238 $[M + H]^+$; calculated for $C_{17}H_{33}O$: 253.25259.

11-{[*tert*-Butyl(dimethyl)silyl]oxy}undecan-1-ol (7). A three-necked flask was charged with undecane-1,11-diol (40.00 g, 212.42 mmol) and THF (800 mL), the mixture was cooled to 0°C, imidazole (28.92 g, 424.84 mmol) was added, and a solution of *tert*-butyl(dimethyl)silyl chloride (38.42 g, 254.90 mmol) in THF (80 mL) was added dropwise. The mixture was stirred at room temperature for 16 h and quenched with water. The aqueous phase was extracted with ethyl acetate (3×100 mL), the organic phases were combined and evaporated, and the product was purified by column chromatography (petroleum ether–ethyl acetate, 10:1). Yield 37.32 g (123.34 mmol, 58%). ^{1}H NMR spectrum, δ, ppm: 3.68 t (2H, *J* = 6.6 Hz), 3.64 t (2H, *J* = 6.6 Hz), 1.59 d.d.d (4H, *J* = 21.8, 12.8, 6.4 Hz), 1.32 s (15H), 0.95 d (9H, *J* = 10.1 Hz), 0.07 d (6H, *J* = 22.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 63.36, 63.11, 32.91, 32.84, 29.62, 29.60, 29.54, 29.44, 26.01, 25.82, 25.76, 18.40, –5.24. Mass spectrum: *m*/*z* 303.27078 $[M + H]^+$; calculated for $C_{17}H_{39}O_2Si$: 303.27138.

***tert*-Butyl[(11-iodoundecyl)oxy]dimethylsilane (6).** A mixture of triphenylphosphine (5.63 g, 21.48 mmol) and imidazole (2.25 g, 33.05 mmol) in CH_2Cl_2 (50 mL) was cooled to 0°C, iodine was added, and the mixture was stirred for 0.5 h. Compound **7** (5.00 g, 16.53 mmol) was then added, and the mixture was stirred at room temperature for 4 h. The product was purified by column chromatography (petroleum ether). Yield 6.22 g (15.10 mmol, 92%), colorless oily liquid. ^{1}H NMR spectrum, δ, ppm: 3.64 t (2H, *J* = 6.6 Hz), 3.23 t (2H, *J* = 7.0 Hz), 1.92–1.76 m (2H), 1.55 d.d (2H, *J* = 13.2, 6.6 Hz), 1.48–1.28 m (14H), 0.94 s (9H), 0.07 s (6H). ^{13}C NMR spectrum, δ_C, ppm: 63.34, 33.61, 32.91, 30.53, 29.59, 29.50, 29.43, 29.42, 28.56, 26.02, 25.82, 18.40, 7.25, –5.22. Mass spectrum: *m*/*z* 413.17316 $[M + H]^+$; calculated for $C_{17}H_{38}IOSi$: 413.17311.

(11-{[*tert*-Butyl(dimethyl)silyl]oxy}undecyl)triphenylphosphonium iodide (5). A single-necked flask was charged with toluene (20 mL) as solvent, compound **6** (4.20 g, 16.00 mmol) and triphenylphosphine (4.20 g, 16.00 mmol) were added, and the mixture was heated to 130°C and refluxed for 24 h. After cooling to room

temperature, the solvent was removed under reduced pressure to obtain a yellow colloid. The product was treated with diethyl ether (50 mL), the mixture was cooled in a refrigerator for 24 h, and the white solid was filtered off. Yield 10.80 g (16.00 mmol, 100%).

***tert*-Butyl(dimethyl)[(13-methylheptacosa-11,15-dien-1-yl)oxy]silane (4).** A solution of compound **5** (1.21 g, 1.83 mmol) in THF (30 mL) was cooled to –78°C, and a 2.5 M solution of *n*-BuLi in hexane (0.66 mL, 1.64 mmol) was added. The mixture was stirred for 1 h, compound **8** (0.33 g, 1.31 mmol) was added, and the mixture was kept at room temperature for 6 h. The mixture was quenched with a saturated aqueous solution of NH_4Cl, washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated on a rotary evaporator under reduced pressure. The product was purified by column chromatography (petroleum ether). Yield 0.58 g (1.11 mmol, 85%), colorless liquid, $[\alpha]_D^{25}$ = +9.25° (*c* = 0.267, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 5.56–5.04 m (4H), 3.65 q (2H, *J* = 6.5 Hz), 2.53 t.t (1H, *J* = 13.6, 6.8 Hz), 2.13–1.92 m (6H), 1.55 d.d (2H, *J* = 13.5, 6.7 Hz), 1.34 d (32H, *J* = 24.9 Hz), 1.02–0.97 m (3H), 0.97–0.89 m (12H), 0.10 d (6H, *J* = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 135.76, 130.78, 128.63, 127.93, 63.37, 34.95, 32.92, 32.19, 31.95, 29.95, 29.76, 29.67, 29.60, 29.58, 29.48, 29.38, 27.53, 27.40, 26.01, 25.83, 22.71, 20.88, 18.40, 14.13, –5.23. Mass spectrum: *m*/*z* 521.51172 $[M + H]^+$; calculated for $C_{34}H_{69}OSi$: 521.51122.

(13*R*)-13-Methylheptacosan-1-ol (3). A dry single-neck burner was charged with compound **4** (0.32 g, 0.61 mmol) and methanol (30 mL), and Pt/C (20% of the substrate) was then added as a catalyst. The flask was filled with hydrogen, and the mixture was stirred at 45°C for 16 h. The mixture was concentrated under reduced pressure, and the crude product was subjected to column chromatography (petroleum ether–ethyl acetate, 10:1). Yield 0.24 g (0.58 mmol, 95%), white solid, $[\alpha]_D^{25}$ = +1.72° (*c* = 0.267, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 3.68 t (2H, *J* = 6.6 Hz), 1.64–1.58 m (2H), 1.46–1.08 m (48H), 0.93 t (3H, *J* = 6.9 Hz), 0.88 d (3H, *J* = 6.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 63.13, 37.13, 32.85, 32.79, 31.96, 30.07, 29.76, 29.73, 29.70, 29.63, 29.47, 29.39, 27.12, 25.77, 22.72, 19.75, 14.14. Mass spectrum: *m*/*z* 433.43924 $[M + Na]^+$; calculated for $C_{28}H_{58}ONa$: 433.43799.

(13*R*)-13-Methylheptacosanal (2). Dess–Martin periodinane (0.17 g, 0.40 mmol) and $NaHCO_3$ (0.12 g, 1.46 mmol) were placed in a three-necked flask, CH_2Cl_2 (0.5 mL) was added, and the mixture was stirred to obtain a white suspension. A solution of compound **3** (0.15 g, 0.37 mmol) in CH_2Cl_2 (0.5 mL) was slowly added, and the mixture was stirred continuously at room temperature for 6 h. The reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$, the organic phase was washed with a solution of $NaHCO_3$ (3× 10 mL) and concentrated, and the crude product was subjected to column chromatography (petroleum ether–ethyl acetate, 30:1). Yield 0.13 g (0.32 mmol, 86%), white solid, $[\alpha]_D^{25}$ = +1.67° (*c* = 0.233, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 9.81 d (1H, *J* = 1.7 Hz), 2.46 t.d (2H, *J* = 7.4, 1.7 Hz), 1.72–1.64 m (2H), 1.32 d (45H, *J* = 21.2 Hz), 0.93 t (3H, *J* = 6.9 Hz), 0.88 d (3H, *J* = 6.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 202.98, 43.95, 37.13, 32.78, 31.95, 30.06, 29.73, 29.68, 29.61, 29.45, 29.38, 29.20, 27.11, 22.71, 22.13, 19.75, 14.13. Mass spectrum: *m*/*z* 409.44064 $[M + H]^+$; calculated for $C_{28}H_{57}O$: 409.44039.

(8*Z*,21*R*)-21-Methylpentatriacont-8-ene (1). A mixture of THF (15 mL) and (octyl)triphenylphosphonium bromide (0.87 g, 1.92 mmol) in a three-neck flask was stirred at –78°C for 5 min. Sodium hexamethyldisilazide (a 2.5 M solution in hexane, 0.49 mL, 1.24 mmol) was added, and the mixture was stirred continuously for 1 h. Compound **2** (0.11 g, 0.27 mmol) was then added, and the mixture spontaneously warmed up to 0°C. It was stirred for 6 h, quenched with a saturated solution of NH_4Cl, washed with brine, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether). Yield 0.13 g (0.26 mmol), colorless liquid with a distinctive odor, $[\alpha]_D^{25}$ = –2.60° (*c* = 0.200, $CHCl_3$). ^{1}H NMR, δ, ppm: 5.44–5.36 m (2H), 2.11–1.96 m (4H), 1.49–1.04 m (57H), 0.92 t (6H, *J* = 7.0 Hz), 0.88 d (3H, *J* = 6.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 129.93, 37.13, 32.79, 31.96, 31.91, 30.07, 29.81, 29.76, 29.73, 29.69, 29.60, 29.39, 29.35, 29.31, 29.26, 27.24, 27.12, 22.70, 19.75, 14.13 (several carbon signals were overlapped).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

SUPPLEMENTARY INFORMATION

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