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A New Asymmetric Synthesis of (*S*)-14-Methyloctadec-1-ene, the Sex Pheromone of the Peach Leafminer Moth

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Abstract—An asymmetric synthesis of 14-methyl-1-octadecene, the sex pheromone of the peach leafminer moth has been achieved. Based on the asymmetric methylation of chiral (*S*)-4-benzyloxazolidin-2-one, the carbon chain of the target molecule was assembled through a $C_1+C_{10}+C_4+C_3$ procedure. The γ-lactone was transformed into 4-(benzyloxy)butanoic acid and then, with the induction of Evan's template, a chiral methyl group was introduced to the position of the carboxylic group in 97% *de*. After reduction and a couple of chemical operations, the designed key intermediate **A1** was obtained. The synthesis of another moiety was started from decane-1,10-diol which was selectively protected and oxidized. The long carbon chain was installed according to a Wittig protocol. After deprotection, oxidization, and methylenation, the target molecule was synthesized in 7 linear steps with an overall yield of 30.3%.

Keywords: 14-methyloctadec-1-ene, pheromone synthesis, peach leafminer moth

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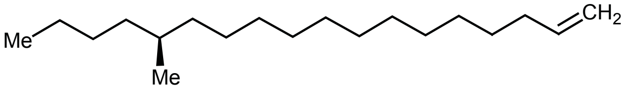
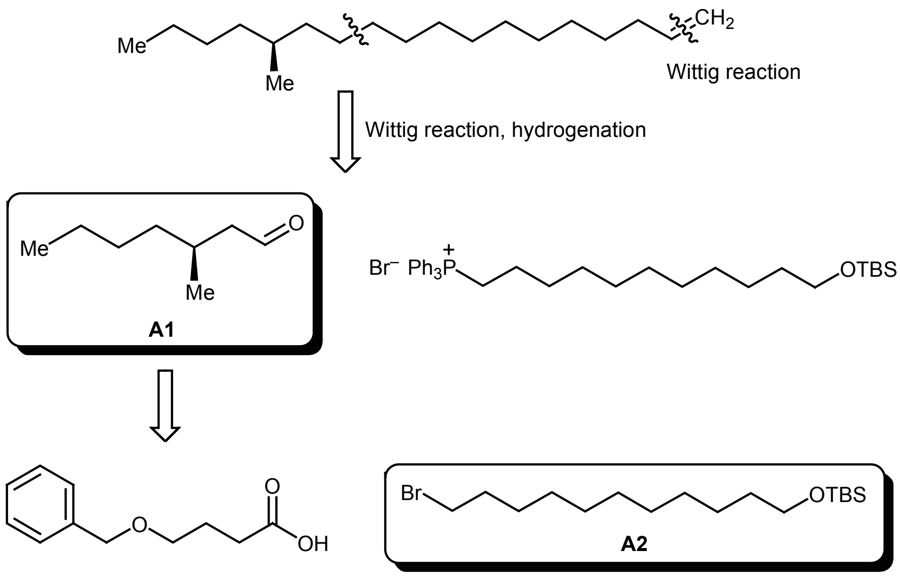
Pheromones are substances produced as messengers that affect the behaviour of other insects [1]. Insect pheromones can be mainly divided into the following groups by function: trace pheromones (to locate a food source or to share something), aggregation pheromones (to find individuals of the same species), alarm pheromones (to warn of any sort of danger), and sex pheromones (to attract adults of the opposite sex for mating). Among them, sex pheromones have been studied most thoroughly and used to control the overall population. The peach leafminer moth *Lyonetia clerkella* [2] is one of the most destructive pests in the peach orchards of East Asia. It causes defoliation when the leaves are infested by only a few larvae of this insect. Traditionally, highly toxic pesticides have been adopted by Chinese farmers to prevent it. In the context of integrated pest management (IPM)), a promising method is to kill them physically, e.g., by using a high-voltage electrical shock, drowning in water, or collecting them into a designated container after using its sex pheromone to seduce them and disrupt their mating process.

Sugie et al. [2] were the first to identify the sex pheromone of the moth as (*S*)-14-methyloctadec-1-ene (**1**). Some early syntheses of **1** in the racemic form have been reported by several teams [3, 4]. The asymmetric synthesis of **1** has been reported by Mori [5], Kharisov [6], and Tai [7] who used expensive chiral starting materials through a chiral pool strategy. Sonnet [8] and Sankaranarayanan [9] described a synthesis through resolution methodology. Recently, a carbon coupling strategy has been developed by us, but if the carbon chain is long (more than 10 carbon atoms), the coupling reaction was generally sluggish. Therefore, the existing synthetic pathways have some drawbacks



(*S*)-14-Methyloctadec-1-ene (**1**)

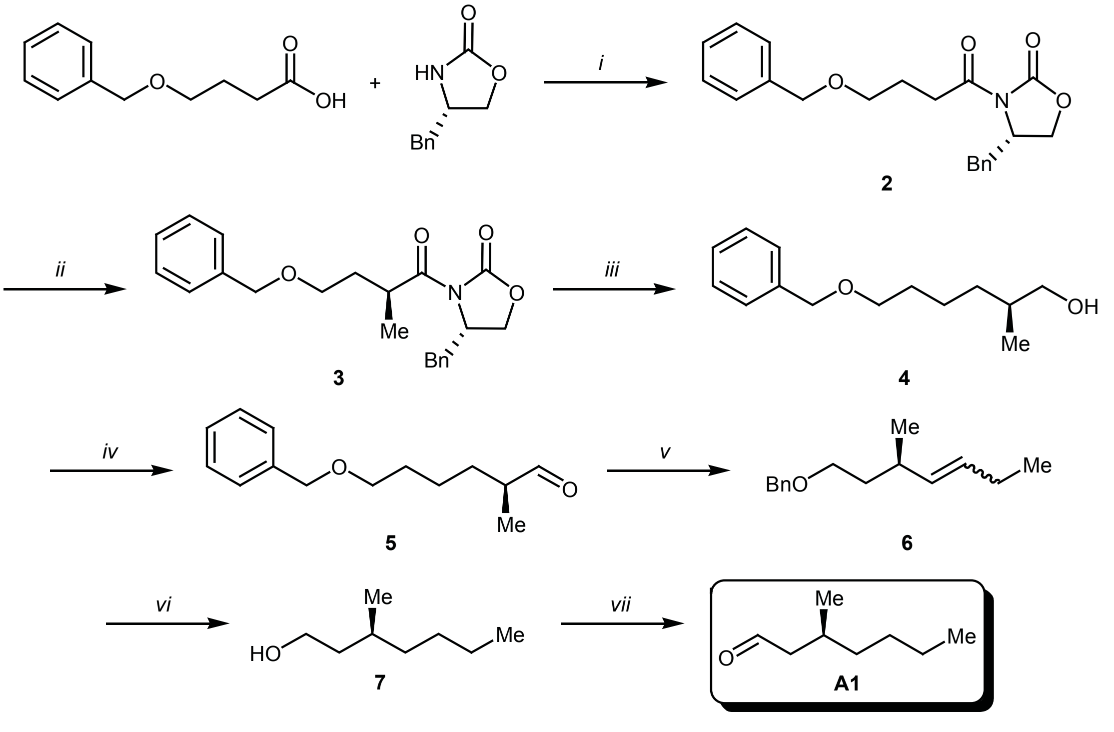
Scheme 1.



such as too many chemical operations or lack of cost-effectiveness. So, there is high demand to develop an economical synthesis of the natural stereoisomer of **1**. As a continuation of our research in new agrichemicals and "green" pesticides [10–15], we are interested in utilizing chiral methylation and the Wittig reaction in efficient and convenient formation of these kinds of sex pheromones. Herein, we report a new synthesis of (*S*)-**1** by chiral template induction and Wittig reactions.

The retrosynthetic analysis of compound **1** is shown in Scheme 1. The molecule was disconnected into chiral synthon **A1** and C_{10} moiety. The chiral synthon

Scheme 2.



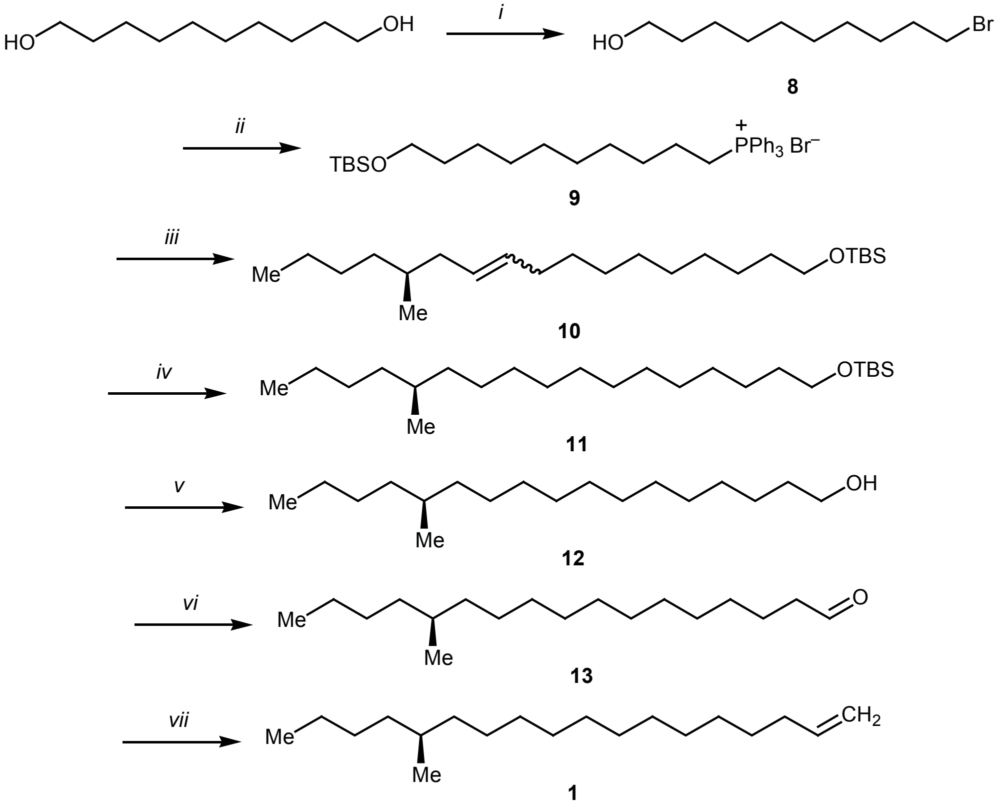
Reagents and conditions: *i*: Et_3N, Trimethylacetyl chloride, LiCl, THF, –78°C, 87%; *ii*: NaHMDS, THF, –78°C, MeI, 50%, 98% *de*; *iii*: $LiAlH_4$, –10°C, 86%; *iv*: PCC, CH_2Cl_2, 0°C to room temp., 88%; *v*: triphenyl(propyl)phosphonium bromide, *n*-BuLi, THF, –30°C to room temp., 98%; *vi*: H_2, Pt/C, Pd/C, MeOH, 45°C, 84%; *vii*: PCC, CH_2Cl_2, 0°C to room temp., 65%.

A1 could be furnished from 4-(benzyloxy)butanoic acid, while the C_{10} moiety **A2** can be obtained from decane-1,10-diol.

With the basic synthetic plan in hand, as shown in Scheme 2, our synthesis commenced with (*S*)-4-benzyloxazolidin-2-one and 4-(benzyloxy)butanoic acid which could be prepared through literature procedures [16, 17]. After activation with a mixed anhydride, 4-(benzyloxy)butanoic acid was connected to (*S*)-4-benzyloxazolidin-2-one to give **2** in 87% yield [18]. Compound **2** was deprotonated in the presence of NaHMDS at –78°C and then methylated to afford **3**. Because of the induction by the chiral benzyl group in the oxazolidine ring, the methyl group was directed to the *d*-face with 98% *de* and 50% yield. Then the Wittig reaction with phosphorus ylide produced the key intermediate **A1** in 65% yield in two steps. The chiral oxazolidine was removed by reduction with $LiAlH_4$ at –10°C to give alcohol **4**. Alcohol **4** was treated with PCC in methylene chloride, and aldehyde **5** was thus obtained in 88% yield. The Wittig reaction with propyl(triphenyl)phosphonium bromide gave the C_8 moiety **6** in 98% yield with an *E*/*Z* ratio of 8:1. It should be noted that the geometry of the double bond did not matter in the subsequent transformations. In order to prevent palladium-catalyzed allylic racemization, the hydrogenation was carried out over Pt/C in one-pot fashion, and alcohol **7** was obtained in 84% yield. Alcohol **7** was then subjected to oxidation with PCC, and subunit **A1** was smoothly prepared.

Then, as shown in Scheme 3, decane-1,10-diol was selectively brominated in a way similar to a literature method [19]. The remaining hydroxyl group was effectively protected as *tert*-butyl(dimethyl)silyl ether which was converted to triphenylphosphonium bromide and then coupled with **A1** under the Wittig reaction protocol to form **10** in 78% yield. Thus, the main carbon chain of the target molecule was constructed successfully. Afterwards, the TBS protecting group was removed by the action of tetrabutylammonium fluoride in tetrahydrofuran. The subsequent conventional oxidation and another Wittig reaction with

Scheme 3.



Reagents and conditions: *i*: 48% HBr, benzene, reflux, 89%; *ii*:(1) TBSCl, imidazole, CH_2Cl_2, 0°C to room temp., 94%; (2) PPh_3, MeCN, reflux, 91%; *iii*: **A1**, *n*-BuLi, THF, –10°C to room temp., 78%; *iv*: H_2, Pt/C, MeOH, 45°C, 84%; *v*: TBAF, CH_2Cl_2, 0°C to room temp., 86%; *vi*: PCC, CH_2Cl_2, 0°C to room temp., 65%; *vii*: (1) PCC, CH_2Cl_2, 0° to room temp., 88%; (2) methyl(triphenyl)-phosphonium bromide, NaHMDS, THF, –30°C to room temp., 85%.

methyl(triphenyl)phosphonium bromide afforded the target (*S*)-**1** in 50% yield. Thus, the asymmetric total synthesis of (*S*)-**1** was achieved in 6 linear steps with an overall yield of 30.3%.

In summary, we have completed the asymmetric total synthesis of the sex pheromone of the peach leafminer moth, (*S*)-14-methyloctadec-1-ene, through Evan's template induction and Wittig reaction. Compared with other methods, this process has several advantages such as high yield, easy operation, and cost-effectiveness. Further biological study is in progress, and this may be a promising way for orchardists to produce "green" fruits in the future. Further applications in modern agriculture will be reported elsewhere.

EXPERIMENTAL

Tetrahydrofuran (THF) was dried by sodium and distilled before use. Methylene chloride was dried by calcium hydride and distilled before use. 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 eluent. The NMR spectra were recorded on a Bruker AC-500 instrument (Madison, WI, USA) at 500 MHz for ^{1}H. The chemical shifts were referenced to tetramethylsilane as internal standard for ^{1}H or $CDCl_3$ (δ_C 77.16 ppm) for ^{13}C. The high-resolution mass spectra were measured on a Thermo Fisher Scientific (LTQ-Orbitrap-XL, ESI, GER) instrument. The optical rotations were measured on a Digipol-P910 polarimeter (Shanghai JIAHANG) with a sodium lamp.

(*S*)-4-Benzyl-3-[4-(Benzyloxy)butanoyl]oxazolidin-2-one (2). Triethylamine (31.58 mL, 0.22 mol) was added dropwise to a solution of 4-benzyloxybutyric acid (22 g, 0.11 mol) in THF (440 mL) under argon at –78°C, and trimethylacetyl chloride (16.64 mL, 0.14 mol) was then added. The mixture was stirred at –78°C for 20 min and allowed to warm up to room temperature over a period of 1 h. The mixture was cooled again to –78°C, lithium chloride (14.40 g, 0.33 mol) was added, and a solution of (*S*)-4-benzyloxazolidin-2-one (22.08 g, 0.12 mol) in anhydrous THF was slowly added dropwise. The mixture was stirred for 1 h at –78°C, allowed to spontaneously warm up to room temperature, and left overnight. A yellow oily liquid was obtained. Yield 35.45 g (87.43%). ^{1}H NMR spectrum, δ, ppm: 7.42–7.34 m (5H, H_{arom}), 7.34–7.29 m (2H, CH_2), 7.23 d (2H, CH_2, J = 7.0 Hz), 4.65 d.d.t (1H, H_{arom}, J = 10.3, 7.0, 3.4 Hz), 4.56 s (1H, CH), 4.29–3.99 m (1H, CH), 3.63 t (1H, CH, J = 6.2 Hz), 3.32 d.d (1H, CH, J = 13.4, 3.2 Hz), 3.11 d (1H, CH, J = 7.5 Hz), 2.75 d.d (1H, CH, J = 13.4, 9.7 Hz), 2.09 d.q (1H, CH, J = 13.5, 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 173.10, 153.50, 138.49, 135.41, 129.43, 128.96, 128.39, 127.73, 127.59, 127.33, 72.93 (CH_2), 69.28 (CH_2), 66.17 (CH_2), 55.20 (CH_2), 37.93 (CH_2), 24.54 (CH_2).

(*S*)-4-Benzyl-3-[(*S*)-4-(benzyloxy)-2-methylbutanoyl]oxazolidin-2-one (3). A three-necked flask was charged under argon with compound **2** (23 g, 65.08 mmol) and anhydrous THF (300 mL), the mixture was cooled to –78°C and kept for 15 min at that temperature, NaHMDS (65.08 mL, 130.16 mmol) was added dropwise, and the mixture was stirred at –78°C for 30 min. Methyl iodide (32.07 mL, 325.39 mmol) was slowly recondensed to the mixture, and the mixture was stirred for 2 h at –78°C, adjusted to –50°C, and left overnight. The mixture was then quenched with NH_4Cl at –50°C, and the product was isolated as a colorless oily liquid. Yield 12.12 g (50.18%), $[\alpha]_D^{20}$ = +73.81° (c = 0.22, *n*-hexane). ^{1}H NMR spectrum, δ, ppm: 7.41–7.35 m (5H, H_{arom}), 7.34–7.29 m (2H, CH_2), 7.23 d (2H, CH_2, J = 7.0 Hz), 4.65 d.d.t (1H, CH, J = 10.3, 7.0, 3.4 Hz), 4.56 s (2H, CH_2), 4.20–4.09 m (2H, CH_2), 3.63 t (2H, CH_2, J = 6.0 Hz), 3.32 d.d (1H, CH, J = 13.5, 3.0 Hz), 3.12 t (2H, CH_2, J = 7.3 Hz), 2.75 d.d (1H, CH, J = 13.4, 9.7 Hz), 2.09 d.q (2H, CH_2, J = 13.5, 7.0 Hz), 1.31 d (3H, CH_3, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 173.10, 153.50, 138.49, 135.41, 130.25–125.56, 72.93 (CH_2), 69.28 (CH_2), 66.17 (CH_2), 55.20 (CH_2), 37.93 (CH_2), 32.52 (CH_2), 24.54(CH_3).

(*S*)-4-(Benzyloxy)-2-methylbutan-1-ol (4). A flask was charged under argon with $LiAlH_4$ (4.54 g, 0.12 mol) in anhydrous THF, and a solution of **3** (11 g, 29.94 mmol) in anhydrous THF was slowly added dropwise from a dropping funnel at –10°C. The temperature was naturally raised to 0°C and stirred overnight. The mixture was quenched in succession with water and 10% aqueous sodium hydroxide. The product was a colorless oily liquid. Yield 5.14 g (84.58%), $[\alpha]_D^{20}$ = +7.85° (c = 0.2, *n*-hexane). ^{1}H NMR spectrum, δ, ppm: 7.39 d (4H, H_{arom}, J = 4.2 Hz), 7.37–7.29 m (1H, H_{arom}), 5.38 d.t (1H, CH, J = 10.6, 7.3 Hz), 5.16 d.t (1H, CH, J = 20.5, 10.3 Hz), 4.67–4.41 m (1H, CH), 3.60–3.41 m (1H, CH), 2.79–2.64 m (1H, CH), 2.09 t.t (1H, CH, J = 14.5, 7.2 Hz), 1.73 t.d (1H, J = 12.9, 7.2 Hz), 1.52 d.d.d (1H, CH, J = 14.0, 9.1, 6.1 Hz), 1.06–0.96 m (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 138.74, 130.81, 128.36, 127.67, 127.48, 73.03 (CH_2), 68.85 (CH_2), 37.30, 28.56 (CH_2), 21.57 (CH_2), 20.75 (CH_3). HRMS (ESI): *m*/*z* 195.13756 $[M + H]^+$. Calculated for $C_{12}H_{19}O_2^+$: 195.13796.

(*S*)-4-(Benzyloxy)-2-methylbutanal (5). Compound **4** (9 g, 46.33 mmol) was dissolved in methylene chloride under argon, the solution was cooled in an ice bath, 9 g of silica gel was added, pyridinium chlorochromate (11.98 g, 55.59 mmol) was then added, and the mixture was allowed to warm up to room temperature. A colorless oily liquid was obtained. Yield 5.14 g (87.58%), $[\alpha]_D^{20}$ = +8.65° (*c* = 0.2, *n*-hexane). ^1H NMR spectrum, δ, ppm: 9.69 d (1H, CH, *J* = 1.7 Hz), 7.46–7.28 m (5H, H_{arom}), 4.58–4.47 m (2H, CH_2), 3.66–3.48 m (2H, CH_2), 2.59 d.d.d (1H, CH, *J* = 13.7, 7.0, 1.6 Hz), 2.10 d.t.d (2H, CH_2, *J* = 12.6, 7.0, 5.6 Hz), 1.86–1.62 m (2H, CH_2), 1.21 d (6H, CH_3, *J* = 7.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 204.74 (C=O), 138.22, 128.43, 127.68, 73.09 (CH_2), 67.42 (CH_2), 43.78 (CH_2), 30.86 (CH_2), 13.29 (CH_3). HRMS (ESI): *m*/*z* 193.12201 $[M + H]^+$. Calculated for $C_{12}H_{17}O_2^+$: 193.12231.

(*S*,*E*)-{[(3-Methylhept-4-en-1-yl)oxy]methyl}benzene (6). A three-necked flask was charged under argon with triphenyl(propyl)phosphonium bromide (7.86 g, 25.75 mmol) in anhydrous THF, and the mixture was flushed with argon. *n*-Butyllithium (9.83 mL, 23.58 mmol) was added on cooling with an ice bath, the mixture was stirred for 30 min at room temperature and cooled again with an ice bath, a solution of **5** (4.50 g, 23.41 mmol) in THF was slowly added dropwise, and the mixture was stirred at room temperature overnight. A colorless oily liquid was obtained. Yield 5.02 g (97.84%), $[\alpha]_D^{20}$ = +9.57° (*c* = 0.14, *n*-hexane). ^1H NMR spectrum, δ, ppm: 7.44–7.28 m (5H, H_{arom}), 5.41–5.30 m (1H, CH), 5.14 t (1H, CH, *J* = 10.3 Hz), 4.59–4.48 m (2H, CH_2), 3.63–3.42 m (2H, CH_2), 2.78–2.61 m (1H, CH), 2.17–2.00 m (2H, CH_2), 1.73 m (2H, *J* = 12.9, 7.2 Hz), 1.07–0.95 m (6H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 138.74 (C=C), 134.92, 130.81 (C=C), 128.36, 127.67, 127.48, 73.03 (CH_2), 68.85 (CH_2), 37.30, 28.56 (CH_2), 21.57 (CH_2), 20.75 (CH_2), 14.58 (CH_3). HRMS (ESI): *m*/*z* 219.17393 $[M + H]^+$. Calculated for $C_{15}H_{23}O^+$: 219.17434.

(*S*)-3-Methylheptan-1-ol (7). Compound **6** (3 g, 13.74 mmol) was dissolved in 50 mL of methanol, Pt/C (10 mol % of the substrate) was added, and the mixture was stirred in a hydrogen atmosphere at room temperature for 24 h. To continue the reaction, Pd/C (10 mol % of the substrate) was added, the reaction vessel was refilled with hydrogen, and the mixture was stirred at room temperature for 24 h. After completion of the reaction (TLC), the mixture was filtered with suction, and the filtrate was concentrated under reduced pressure. A colorless oily liquid was obtained. Yield 1.51 g (83.83%), $[\alpha]_D^{20}$ = +1.5° (*c* = 0.16, *n*-hexane). ^1H NMR spectrum, δ, ppm: 3.82–3.62 m (2H, CH_2), 1.74–1.51 m (1H, CH), 1.42 d.t (4H, CH_2, *J* = 13.0, 6.5 Hz), 1.36–1.26 m (4H, CH_2), 1.21–1.10 m (2H, CH_2), 0.93 d.d (3H, CH_3, *J* = 6.5, 4.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 61.52 (CH_2), 40.27 (CH_2), 37.10 (CH_2), 29.62, 22.98 (CH_2), 20.15 (CH_2), 19.92 (CH_3), 14.38 (CH_3).

(*S*)-3-Methylheptanal (A1). Compound **7** (1.5 g, 11.52 mmol) was dissolved in methylene chloride under argon, the solution was cooled in an ice bath, an equal amount of silica gel was added, pyridinium chlorochromate (2.98 g, 13.82 mmol) was then added, and the mixture was allowed to return to room temperature. A colorless oily liquid was obtained. Yield 0.95 g (64.94%). $[\alpha]_D^{20}$ = +7.58° (*c* = 0.12, *n*-hexane). ^1H NMR spectrum, δ, ppm: 9.80 t (1H, CHO, *J* = 2.0 Hz), 2.48–2.34 m (2H, CH_2), 2.31–1.94 m (4H, CH_2), 1.64–1.14 m (6H, CH_2), 1.19–0.67 m (6H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 203.25 (CH), 51.11 (CH_2), 36.62 (CH_2), 29.16 (CH_2), 28.18 (CH), 22.78 (CH_2), 20.01 (CH_3), 14.05 (CH_3).

Bromodecan-1-ol (8). Decane-1,10-diol (5 g, 28.69 mmol) was dissolved in toluene, 48% aqueous HBr (3.73 mL, 32.99 mmol) was added, and the mixture was refluxed for 24 h. A yellow oily liquid was obtained. Yield 6.12 g (88.93%). ^1H NMR spectrum, δ, ppm: 3.80–3.59 m (1H, CH), 1.71–1.54 m (1H, CH), 1.50–1.12 m (4H, CH_2), 0.93 d.d (3H, CH_2, *J* = 6.5, 4.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 61.25 (CH_2), 40.01 (CH_2), 36.83 (CH_2), 29.51 (CH_2), 29.20 (CH_2), 22.97 (CH_2), 19.66 (CH_2), 14.11 (CH_2).

10-{[(*tert*-Butyl)dimethylsilyl]oxy}decyl(triphenyl)phosphonium bromide (9). A solution of compound **8** (5 g, 21.08 mmol) in methylene chloride was cooled in an ice bath, imidazole (2.87 g, 41.26 mmol) was added, a solution of TBSCl (3.81 g, 25.30 mmol) in methylene chloride was then added, and the mixture was stirred overnight. A colorless oily liquid, [(10-bromodecyl)oxy](*tert*-butyl)dimethylsilane, was obtained. Yield 7.02 g (94.21%). ^1H NMR spectrum, δ, ppm: 3.64 t (2H, CH_2, *J* = 6.5 Hz), 3.45 t (2H, CH_2, *J* = 7.0 Hz), 2.00–1.84 m (2H, CH_2), 1.54 d.d (2H, CH_2, *J* = 13.5, 6.5 Hz), 1.46 d.d (2H, CH_2, *J* = 14.0, 7.0 Hz), 1.33 s (10H, CH_2), 0.94 s (9H, CH_3), 0.09 s (6H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 34.00 (CH_2), 32.90, 32.87 (CH_2), 29.52 (CH_2), 29.40 (CH_2), 28.77 (CH_2), 28.20 (CH_2), 26.01 (CH_2), 25.81 (CH_2), 25.72 (CH_2), 18.40 (CH_3), –5.23 (CH_3). HRMS (ESI): *m*/*z* 351.17099 $[M + H]^+$. Calculated for $C_{16}H_{36}BrOSi^+$: 351.17133.

[(10-Bromodecyl)oxy](*tert*-butyl)dimethylsilane (5 g, 14.82 mmol), was dissolved in toluene, and triphenylphosphine (4.66 g, 17.17 mmol) was added. The mixture was refluxed for 24 h, cooled, and filtered with suction, and the filtrate was evaporated. Yield of **9** 7 g (90.88%), white solid.

(*S*,*E*)-*tert*-Butyl(dimethyl)[(13-methylheptadec-10-en-1-yl)oxy]silane (10). A solution of compound **9** (8.11 g, 15.6 mmol) in THF was cooled in an ice bath, *n*-butyllithium (3.90 mL, 9.75 mmol) was added under argon, and the mixture was allowed to warm up to room temperature and stirred for 2 h. (*S*)-3-Methylheptanal (**A1**, 1 g, 7.80 mmol) was added with cooling in an ice bath, and the mixture was stirred at room temperature overnight. It was then quenched with NH_4Cl. Yield 2.15 g (77.65%), colorless oily liquid, $[\alpha]_D^{20}$ = +1.25° (*c* = 0.12, *n*-hexane). ^{1}H NMR spectrum, δ, ppm: 5.42 q.d (2H, CH_2, *J* = 11.0, 5.6 Hz), 3.64 t (2H, CH_2, *J* = 6.5 Hz), 2.11–1.99 m (2H, CH_2), 1.90 d.d (1H, CH, *J* = 13.9, 7.2 Hz), 1.72–1.10 m (22H, CH_2), 0.97–0.80 m (15H, CH_3), 0.09 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 130.64 (C=C), 128.47 (C=C), 63.35 (CH_2), 36.43 (CH_2), 34.55 (CH), 33.46 (CH_2), 32.92 (CH_2), 29.76 (CH_2), 29.63 (CH_2), 29.52 (CH_2), 29.46 (CH_2), 29.45 (CH_2), 29.35 (CH_2), 27.35 (CH_2), 26.00 (CH_2), 25.83 (CH_2), 23.01 (CH_3), 19.64 (CH_2), 18.39 (CH_3), 14.15 (CH_3), –5.24 (CH_3).

(*S*)-*tert*-Butyl(dimethyl)[(13-methylheptadecyl)-oxy]silane (11). Compound **10** (3 g, 13.74 mmol) was dissolved in methanol (50 mL), Pt/C (10 mol % of the substrate) was added, and the mixture was stirred in a hydrogen atmosphere at room temperature for 24 h. A colorless oily liquid was obtained. Yield 2.75 g (83.56%), $[\alpha]_D^{20}$ = +1.57° (*c* 0.14, *n*-hexane). ^{1}H NMR spectrum, δ, ppm: 3.64 t (2H, CH_2, *J* = 6.5 Hz), 1.68–1.48 m (1H, CH), 1.38–1.03 m (28H, CH_2), 1.02–0.83 m (15H, CH_3), 0.10 s (6H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 63.37 (CH_2), 37.13 (CH_2), 36.81 (CH_2), 32.93, 32.77, 30.06 (CH_2), 29.75 (CH_2), 29.71 (CH_2), 29.69 (CH_2), 29.67 (CH_2), 29.64 (CH_2), 29.47 (CH_2), 29.37 (CH_2), 27.12 (CH_2), 26.01 (CH_2), 25.84 (CH_2), 23.07 (CH_3), 19.74 (CH_2), 18.39 (CH_3), 14.17 (CH_3), –5.24 (CH_3).

(*S*)-13-Methylheptadecan-1-ol (12). Compound **11** (1 g, 2.6 mmol) was dissolved in THF, the solution was cooled in an ice bath, a 1 M solution of tetrabutylammonium fluoride (3.12 mL, 3.12 mmol) was added dropwise with cooling, and the mixture was allowed to slowly warm up to room temperature. A colorless oily liquid was obtained. Yield 0.65 g (85.72%), $[\alpha]_D^{20}$ = +0.75° (*c* = 0.08, *n*-hexane). ^{1}H NMR spectrum, δ, ppm: 3.68 t (2H, CH_2, *J* = 6.5 Hz), 1.67–1.55 m (1H, CH), 1.45–1.17 m (26H, CH_2), 1.18–1.05 m (2H, CH_2), 0.98–0.84 m (6H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 63.12 (CH_2), 37.13 (CH_2), 36.80 (CH_2), 32.85 (CH), 32.76 (CH_2), 30.05 (CH_2), 29.74 (CH_2), 29.70 (CH_2), 29.68 (CH_2), 29.63 (CH_2), 29.62 (CH_2), 29.46 (CH_2), 29.36 (CH_2), 27.11 (CH_2), 25.77 (CH_2), 25.72 (CH_2), 25.66 (CH_2), 23.06 (CH_2), 19.74 (CH_3), 14.16 (CH_3).

(*S*)-14-Methyloctadec-1-ene (1). Compound **12** (0.4 g, 1.48 mmol) was treated under argon with a solution of pyridinium chlorochromate (0.38 g, 1.77 mmol) in methylene chloride with cooling in an ice bath. The corresponding aldehyde (**13**) was isolated by column chromatography. Hexamethyldisilazane sodium salt (2.1 mL, 4.19 mmol) was added dropwise under argon to a solution of methyl(triphenyl)phosphonium bromide (1.8 g, 5.03 mmol) in THF, and the mixture was stirred at room temperature for 2 h. A solution of aldehyde **13** (0.9 g, 3.35 mmol) in THF was added dropwise on cooling with ice, and the mixture was stirred overnight. After a conventional workup, (*S*)-14-methyloctadec-1-ene (**1**) was isolated as an oily material. Yield 0.76 g (85.07%), $[\alpha]_D^{20}$ = +1.82° (*c* = 0.2, *n*-hexane). ^{1}H NMR spectrum, δ, ppm: 5.86 d.d.t (1H, CH, *J* = 17.0, 10.0, 7.0 Hz), 5.01 d.d.d (2H, CH_2, *J* = 13.5, 11.0, 1.2 Hz), 2.09 q (2H, CH_2, *J* = 7.0 Hz), 1.49–1.07 m (27H, CH_2), 0.97–0.83 m (3H, CH_3), 0.89 d (3H, CH_3, *J* = 6.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 139.28 (C=C), 114.08 (C=C), 37.14 (CH_2), 36.82 (CH_2), 33.85 (CH_2), 32.77 (CH), 30.06 (CH_2), 29.75 (CH_2), 29.71 (CH_2), 29.70 (CH_2), 29.65 (CH_2), 29.54 (CH_2), 29.37 (CH_2), 29.19 (CH_2), 28.99 (CH_2), 27.12 (CH_2), 23.07 (CH_2), 19.74 (CH_3), 14.17 (CH_3).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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