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# Catalytic asymmetric synthesis of Japonilure and its enantiomer

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ABSTRACT

A mild, concise, and highly enantioselective (93% ee) synthesis of Japonilure and its enantiomer, *Anomala osakana* pheromone, is described. The key steps involve the asymmetric addition of methyl propionate to undec-2-ynal with a Zn-ProPhenol catalyst and the selective and partial reduction of the diynol ester to the *cis*-enol ester with Brown's P2-Ni catalyst, providing the first synthesis of the enol ester via semi-hydrogenating diynol ester.



## 1. Introduction

Japonilure (*R*)-**1** is the sex pheromone produced by the female Japanese beetle, *Popillia japonica*, a devastating pest of a variety of trees, grasses, ornamentals, and cultivated crops. The pheromone was isolated and identified as (*R*,*Z*)-5-(1-decenyl) dihydro-2(3*H*)-furanone (Fig. 1) by Tumlinson in 1977.[1] Field bioassay showed that the presence of small amounts of its enantiomer (*S*)-**1** to Japonilure significantly reduced the attraction of male beetles.[2] On the other hand, (*S*)-**1** is the sex pheromone of Osaka beetle, *Anomala osakana*, a species which shares the same native habitat with the Japanese beetle (Fig. 1).[3] Although the (*S*)-isomer attracts males, its enantiomer exhibits a strong inhibitory affect.[4] Therefore, it is essential for the practical use to synthesize Japonilure and its enantiomer with high enantiomeric purity.

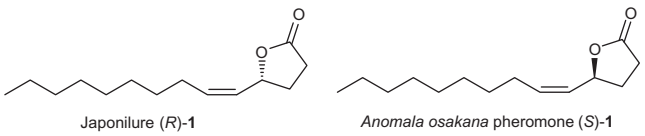


**Figure 1.** Japonilure and *Anomala osakana* pheromone.

The original synthesis of Japonilure and its enantiomer, *Anomala osakana* pheromone, was carried out by Tumlinson from (*R*)- and (*S*)-glutamic acid.[1,2] Shortly thereafter, there were a number of synthetic approaches reported.[5–19] One of the most impressive previous syntheses involved the asymmetric reduction of prochiral carbonyl substrates with chiral reducing agents, such as B-3-pinanyl-9-borabicyclo[3.3.1]nonane,[5] binaphthol-modified lithium aluminum hydride reagent,[6] and the complex of lithium aluminum hydride and (2*S*,3*R*)-4-dimethylamino-l,2-diphenyl-3-methyl-2-butanol.[7] Other syntheses were devised from optically active starting materials D-arabinoses,[8] (*S*)-glycerol 2,3-acetonide,[9] protected D-ribose,[10] (*R*,*R*)-1,2-dicyclohexyl-1,2-ethanediol,[11] and (*R*)-4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane;[12] from resolutions by chemical[13] and enzymatic[14] means; or from asymmetric catalytic Sharpless epoxidation of allylic alcohol[15] and the enantioselective deprotonation of achiral alkyl carbamates.[16]

The requirements for the practical use of pheromones and some disadvantages in previous synthetic strategies prompted us to search for a more efficient and convenient asymmetric synthesis. The enantioselective addition of terminal alkynes to aldehydes is the most convenient protocol to obtain optically active propargyl alcohols.[17] In 2006, this strategy was first introduced in the synthesis of Japonilure and its enantiomer with 87% ee and 86% ee, respectively, by Dos Santos.[18] Three years later, Wang reported on the asymmetric synthesis of the target compound (*S*)-**1** with 84% ee via the asymmetric alkynylation of the aldehyde.[19] However, the enantiomeric excess of these syntheses was not sufficient due to the unique feature of Japonilure and its enantiomer. Herein, Japonilure and its enantiomer, *Anomala osakana* pheromone, were synthesized with high enantiomeric purity (93% ee) by using the catalytic asymmetric alkynylation of aldehyde and selective and partial reduction of diynol ester.

## 2. Results and discussion

As depicted by our retrosynthetic analysis of Japonilure (Fig. 2), the chiral butyrolactone (*R*)-**1** could be formed by the intramolecular lactonization of enol ester (*R*)-**6** with *p*-toluenesulfonic acid.[20] Furthermore, semi-hydrogenating the alkyne bond of diynol ester

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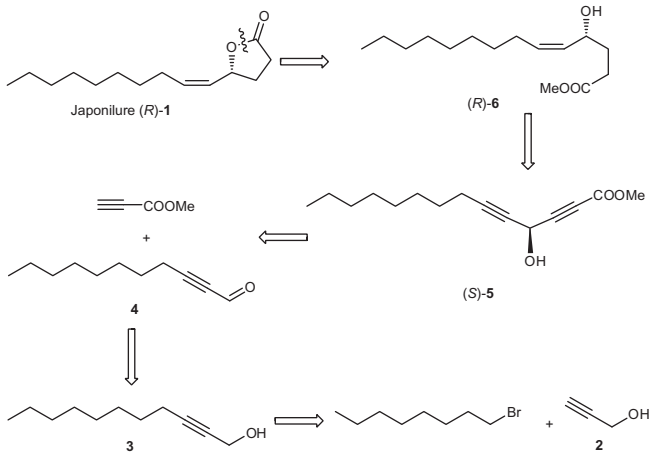
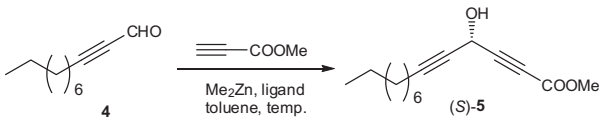



**Figure 2.** Retrosynthetic analysis of Japonilure.

(*S*)-**5** was expected to give enol ester (*R*)-**6** with Brown's P2-Ni catalyst.[21] Most importantly, the asymmetric addition of methyl propionate to propargylic aldehyde **4** was envisioned to generate the key intermediate (*S*)-**5**.[17a]

Although the asymmetric alkynylation of α,β-unsaturated aldehydes with methyl propionate catalyzed by Zn-ProPhenol led to the requisite chiral alcohols with high enantioselectivity and excellent yield,[17a] it was unclear whether propargylic aldehyde **4** would be compatible with the catalyst. We therefore tested the asymmetric alkynylation of **4** and optimized the reaction conditions (Table 1). Initially, three chiral amino alcohols (Chart 1) were examined, and the results indicated that (*R*,*R*)-ProPhenol **L3** was the optimal ligand, providing diynol ester (*S*)-**5** with 75% yield and 95% ee (entry 3). The yield increased to 80% without a decrease in the enantioselectivity when the temperature was increased from 0 to 4 °C (entry 4 vs 3). However, a further increase of the temperature to 10 and 25 °C had a detrimental effect on the enantioselectivity (entries 5 and 6 vs 3). Previous studies[22] demonstrated that the addition of triphenylphosphine oxide to Zn-ProPhenol catalyzed alkynylation of aldehyde can improve the enantioselectivity. In our case, the addition of triphenylphosphine oxide only reduced the yield (entry 7 vs 4). Moreover, decreasing the amount of ligand from 20 to 10 mol %, resulted in decrease in both the yield and enantioselectivity (entry 8 vs 4). As expected, employing (*S*,*S*)-ProPhenol **L4** afforded diynol ester (*R*)-**5** with 93% ee and 81% yield (entry 9). Consequently, the optimized reaction conditions involved 20 mol % of ligand **L3** in toluene at 4 °C (entry 4).

**Table 1**
Reaction optimization for the addition of methyl propionate into undec-2-ynal[a]




| Entry | Ligand | Ligand (%) | Additive | Temp (°C) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|---|
| 1 | **L1** | 20 | No | 0 | 52 | 20 |
| 2 | **L2** | 20 | No | 0 | 5 | 0 |
| 3 | **L3** | 20 | No | 0 | 75 | 95 |
| 4 | **L3** | 20 | No | 4 | 80 | 95 |
| 5 | **L3** | 20 | No | 10 | 77 | 89 |
| 6 | **L3** | 20 | No | 25 | 77 | 88 |
| 7 | **L3** | 20 | $Ph_3PO$ | 4 | 75 | 95 |
| 8 | **L3** | 10 | No | 4 | 70 | 85 |
| 9 | **L4** | 20 | No | 4 | 81 | −93 |

[a] Reaction performed with 1 equiv of undec-2-ynal and 3 equiv of methyl propionate and dimethylzinc.
[b] Isolated yield.
[c] Determined by chiral HPLC with an OD-H column.

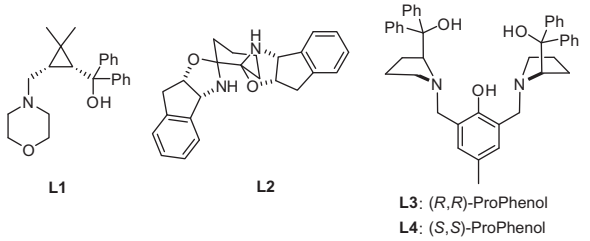
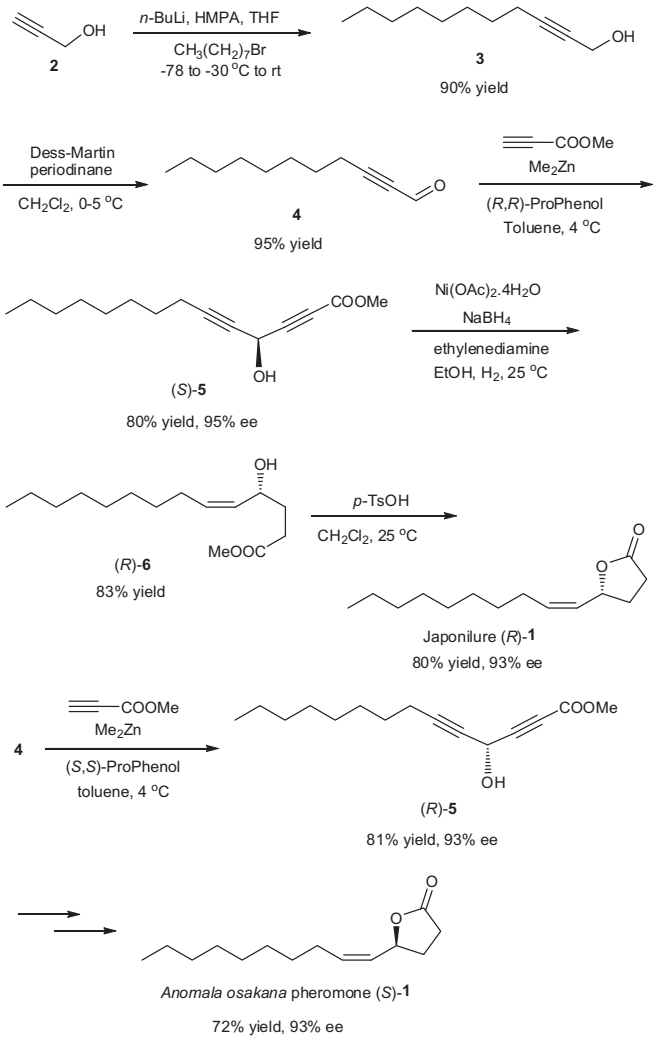



**Chart 1.** Ligands examined in the alkynylation of undec-2-ynal.

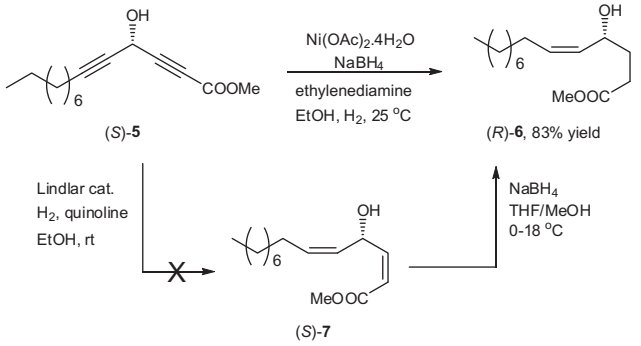
With the success of the asymmetric addition of methyl propionate to propargylic aldehyde **4**, the enantioselective synthesis of Japonilure and its enantiomer, *Anomala osakana* pheromone, was achieved (Scheme 1). In the presence of *n*-BuLi, the coupling of propargyl alcohol **2** with 1-bromooctane gave undec-2-yn-1-ol **3** in 90% yield.[23] Subsequent oxidation of **3** with Dess–Martin periodinane offered undec-2-ynal **4** in 95% yield.[24] The key intermediate (*S*)-**5** was obtained with 80% yield and 95% ee under the optimized reaction conditions (Table 1, entry 4). The selective and partial reduction of diynol ester (*S*)-**5** yielded *cis*-enol ester (*R*)-**6** in 83% yield with 3.5 equiv of Brown's P2-Ni catalyst.[21] Finally, treating **6** with 10% *p*-toluenesulfonic acid in DCM resulted in the formation




**Scheme 1.** Synthesis of Japonilure and its enantiomer.

of Japonilure in 90% yield with 93% ee.[20] Similarly, the synthesis of the Osaka Beetle pheromone (*S*)-**1** with 93% ee was accomplished via asymmetric alkynylation of **4** with (*S*,*S*)-ProPhenol. The racemic **1** was obtained by repeating the similar approach from (±)-**5**, which was prepared from the direct alkynylation of propargylic aldehyde **4** without any chiral ligand.[17a]

The selective reduction of two alkyne bonds of (*S*)-**5** (Scheme 2) is particularly noteworthy. Initially, we intended to convert (*S*)-**5** into (*R*)-**6** in two steps; the partial reduction of the carbon–carbon triple bonds to two *cis*-double bonds[25] followed by selective reduction of the conjugate double bond.[26] However, treatment of diynol ester (*S*)-**5** with hydrogen gas in the presence of Lindlar's catalyst did not give the desired dienol ester (*S*)-**7**.[25b] Fortunately, semi-hydrogenating (*S*)-**5**, catalyzed by Brown's P2-Ni catalyst, directly afforded enol ester (*R*)-**6** in 83% yield.[21] To the best of our knowledge, this is the first synthesis of enol ester via selective and partial reduction from diynol ester.




**Scheme 2.** The reduction of (*S*)-**5**.

## 3. Conclusion

Herein, Japonilure and its enantiomer, *Anomala osakana* pheromone, were prepared in five steps with 93% ee. The synthetic procedure is mild, concise, and highly enantioselective, involving the asymmetric addition of methyl propionate to undec-2-ynal with Zn-ProPhenol catalyst. This is the first synthesis of an enol ester via a semi-hydrogenating diynol ester.

## 4. Experimental

### 4.1. General

All reactions were performed under an argon atmosphere. Solvents were dried according to standard procedures and distilled before use. All reagents were purchased commercially and used without further purification, unless stated otherwise. $^{1}$H and $^{13}$C NMR spectra were recorded at 300 and 75 MHz, respectively. High-resolution Mass spectra were recorded on an Agilent instrument by the TOF MS technique. Enantiomeric excesses (ee) were determined on an Agilent 1200 HPLC system using Chiralcel OD-H column, and elution with *n*-hexanes and isopropanol; or determined on an Agilent GC 7890B with FID using Astec Chiraldex G-TA column. The optical rotations were mensured on a PERKIN ELMER 341 Polarimeter.

### 4.2. Synthesis of the Japonilure and its enantiomer (*Anomala osakana* pheromone)

#### 4.2.1. Synthesis of undec-2-yn-1-ol 3

A solution of propargyl alcohol **2** (21.3 mL, 180 mmol), HMPA (187.9 mL, 180 mmol), and THF (200 mL) was cooled to −78 °C, and *n*-BuLi (288 mL, 2.5 M in hexanes, 720 mmol) was added slowly. The mixture was stirred for 3 h at −30 °C, and then 1-bromooctane (31.2 mL, 180 mmol) was added dropwise via syringe. The resulting mixture was stirred for another 30 min and warmed to room temperature. After stirring for 24 h at room temperature, the reaction mixture was quenched with water (50 mL) at 0 °C. The aqueous phase was extracted with ether, and the combined organic phases were washed with saturated brine solution, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexanes/ethyl acetate 10:1) to give **3** (27.26 g, 90% yield) as a colorless oil. $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$: 0.88 (t, $J$ = 6.9 Hz, 3H), 1.28–1.39 (m, 10H), 1.46–1.55 (m, 2H), 2.17–2.24 (m, 2H), 2.28 (t, $J$ = 5.9 Hz, 1H), 4.23–4.26 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 13.95, 18.64, 22.55, 28.55, 28.80, 29.02, 29.09, 31.75, 51.12, 78.27, 86.35; HRMS (ESI-TOF) calcd for $C_{11}H_{21}O$ $[M+H]^+$ 169.1592, found 169.1589.

#### 4.2.2. Synthesis of undec-2-ynal 4

A solution of **3** (24.352 g, 144.95 mmol) in DCM (200 mL) was cooled to 0 °C, and Dess–Martin reagent (79.90 g, 188.44 mmol) was added slowly at 0–5 °C. The reaction mixture was maintained for 3 h at 5 °C and quenched with $Na_2S_2O_3$ (950 mL, 5% in saturated aqueous $NaHCO_3$, 191.9 mmol) at 0 °C. The resulting mixture was stirred for another 1 h, and filtered through a Celite pad. The aqueous phase was extracted with ether. The combined organic phases were washed with saturated brine solution, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexanes/ethyl acetate 30:1) to furnish **4** (22.89 g, 95% yield) as a colorless oil. $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$: 0.89 (t, $J$ = 7.0 Hz, 3H), 1.28–1.45 (m, 10H), 1.55–1.65 (m, 2H), 2.39–2.44 (m, 2H), 9.18 (t, $J$ = 0.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 14.04, 19.11, 22.60, 27.54, 28.82, 28.95, 29.05, 31.76, 81.70, 99.38, 177.20; HRMS (ESI-TOF) calcd for $C_{11}H_{17}O$ $[M-H]^-$ 165.1279, found 165.1281.

#### 4.2.3. Synthesis of (*S*)-methyl 4-hydroxytetradeca-2,5-diynoate (*S*)-5

To a stirred solution of methyl propionate (10.089 g, 120 mmol) in toluene (60 mL), dimethylzinc (100 mL, 1.2 M in toluene, 120 mmol) was added slowly at 25 °C. After stirring for 1.5 h at room temperature, a solution of (*R*,*R*)-ProPhenol (5.344 g, 8 mmol) in toluene (10 mL) was added slowly at 0–5 °C. The resulting mixture was stirred at 4 °C for 1 h and aldehyde **4** (6.651 g, 40 mmol) was added via syringe at a slow rate. The reaction solution was stirred for another 24 h at 4 °C, and then quenched with water (20 mL) at 0 °C. The mixture was stirred for 1 h and filtered through a Celite pad. The aqueous phase was extracted with ether. The combined organic phases were washed with a saturated brine solution, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexanes/ethyl acetate 10:1) to give (*S*)-**5** (8.01 g, 80% yield, 95% ee) as a colorless oil. $[\alpha]_D^{25}$ = +4.5 (*c* 1.0, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$: 0.88 (t, $J$ = 6.9 Hz, 3H), 1.26–1.38 (m, 10H), 1.50–1.55 (m, 2H), 2.20–2.25 (m, 2H), 2.36 (d, $J$ = 7.9 Hz, 1H), 3.80 (s, 3H), 5.20 (sextet, $J$ = 7.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 14.05, 18.65, 22.62, 28.13, 28.83, 29.01, 29.11, 31.79, 52.18, 52.88, 74.76, 75.29, 84.02, 87.67, 153.52; HRMS (ESI-TOF) calcd for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1647, found 251.1642. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 *n*-hexanes: isopropanol, 1.0 mL/min, 220 nm); minor (*R*)-enantiomer $t_r$ = 9.64 min, major (*S*)-enantiomer $t_r$ = 10.36 min.

#### 4.2.4. Synthesis of (*R*)-methyl 4-hydroxytetradeca-2,5-diynoate (*R*)-5

According to the similar procedure described above, aldehyde **4** (6.651 g, 40 mmol) was converted into (*R*)-**5** (8.09 g, 81% yield, 93%

ee) as a colorless oil with (*S*,*S*)-ProPhenol. $[\alpha]_D^{25} = -3.9$ (*c* 1.0, $CHCl_3$), lit.[8] $[\alpha]_D^{25} = -4.0$ (*c* 1.31, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 0.88 (t, *J* = 6.5 Hz, 3H), 1.27–1.39 (m, 10H), 1.47–1.55 (m, 2H), 2.20–2.25 (m, 2H), 2.38 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 5.21 (sextet, *J* = 7.9 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 14.04, 18.65, 22.62, 28.13, 28.83, 29.01, 29.11, 31.79, 52.18, 52.88, 74.77, 75.29, 84.01, 87.67, 153.52; HRMS (ESI-TOF) calcd for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1647, found 251.1636. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 *n*-hexanes: isopropanol, 1.0 mL/min, 220 nm); major (*R*)-enantiomer $t_r$ = 9.58 min, minor (*S*)-enantiomer $t_r$ = 10.40 min.

#### 4.2.5. Synthesis of (*R*,*Z*)-methyl 4-hydroxytetradec-5-enoate (*R*)-6

To a stirred solution of nickel acetate tetrahydrate (3.712 g, 21 mmol) in ethanol (20 mL), a solution of sodium borohydride (0.794 g, 21 mmol) in ethanol (40 mL) was added slowly at 0 °C. After stirring for 1 h at room temperature, (*S*)-**5** (1.5 g, 6 mmol) and ethylenediamine (0.60 mL, 11 mmol) were added consecutively. The reaction mixture was maintained for 3–5 h at 25 °C under hydrogen (monitored by TLC), and filtered through a Celite pad. The combined organic phases were concentrated and the residue was purified by silica gel chromatography (*n*-hexanes/ethyl acetate 5:1) to give (*R*)-**6** (1.276 g, 83% yield). $^1H$ NMR (300 MHz, $CD_3SOCD_3$) $\delta$: 0.86 (t, *J* = 6.9 Hz, 3H), 1.25 (m, 12H), 1.54–1.69 (m, 2H), 1.97–2.01 (m, 2H), 2.29–2.33 (m, 2H), 3.57 (s, 3H), 4.22–4.26 (m, 1H), 4.67 (d, *J* = 4.8 Hz, 1H), 5.23–5.37 (m, 2H); $^{13}C$ NMR (75 MHz, $CD_3SOCD_3$) $\delta$: 14.05, 22.22, 27.18, 28.81, 28.99, 29.29, 29.64, 31.41, 32.75, 51.26, 65.21, 129.86, 133.83, 173.50; one resonance was not observed due to overlapping resonances. HRMS (ESI-TOF) calcd for $C_{15}H_{28}NaO_3$ $[M+Na]^+$ 279.1936, found 279.1926.

#### 4.2.6. Synthesis of (*R*,*Z*)-5-(dec-1-en-1-yl)dihydrofuran-(3*H*)-one (*R*)-1

To a solution of (*R*)-**6** (0.512 g, 2 mmol) in DCM (20 mL), *p*-toluenesulfonic acid (34.4 mg, 0.2 mmol) was added slowly at 0 °C. The reaction mixture was maintained for 3–5 h at 25 °C, and then quenched with water (2 mL) at 0 °C. The resulting mixture was stirred for another 0.5 h, and the aqueous phase was extracted with DCM. The combined organic phases were washed with saturated brine solution, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexanes/ethyl acetate 20:1) to give Japonilure (*R*)-**1** (0.323 g, 80% yield, 93% ee) as a colorless oil. $[\alpha]_D^{25} = -69.3$ (*c* 1.01, $CHCl_3$); lit.[1] $[\alpha]_D^{26} = -69.6$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 0.87 (t, *J* = 6.9 Hz, 3H), 1.26–1.39 (m, 12H), 1.90–2.00 (m, 1H), 2.05–2.15 (m, 2H), 2.33–2.42 (m, 1H), 2.52–2.58 (m, 2H), 5.20–5.28 (m, 1H), 5.41–5.48 (m, 1H), 5.61–5.68 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 14.02, 22.59, 27.78, 28.94, 29.14, 29.17, 29.26, 29.35, 29.38, 31.80, 76.37, 127.22, 135.78, 177.01; HRMS (ESI-TOF) calcd for $C_{14}H_{25}O_2$ $[M+H]^+$ 225.1855, found 225.1848. Enantiomeric excess was determined by GLC with Astec Chiraldex G-TA column (30 m × 0.25 mm × 0.12 μm) and operated at a constant 150 °C using $H_2$ as the carrier gas at 50 cm/s; major (*R*)-enantiomer $t_r$ = 63.69 min, minor (*S*)-enantiomer $t_r$ = 68.24 min.

#### 4.2.7. Synthesis of (*S*,*Z*)-5-(dec-1-en-1-yl)dihydrofuran-2(3*H*)-one (*S*)-1

According to the similar procedure described above, (*R*)-**5** (1.5 g, 6 mmol) was converted into crude (*S*)-**6** (1.256 g), and subsequent direct lactonization of (*S*)-**6** (0.512 g, 2 mmol) gave (*S*)-**1** (0.323 g, 72% yield, 93% ee) as colorless oil. $[\alpha]_D^{25} = +69.1$ (*c* 1.0, $CHCl_3$); lit.[1] $[\alpha]_D^{26} = +70.5$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 0.88 (t, *J* = 6.9 Hz, 3H), 1.27–1.40 (m, 12H), 1.91–1.98 (m, 1H), 2.06–2.16 (m, 2H), 2.35–2.43 (m, 1H), 2.53–2.59 (m, 2H), 5.21–5.29 (m, 1H), 5.42–5.49 (m, 1H), 5.63–5.72 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$: 14.02, 22.59, 27.77, 28.93, 29.14, 29.16, 29.26, 29.35, 29.37, 31.80, 76.36, 127.22, 135.77, 177.00; HRMS (ESI-TOF) calcd for $C_{14}H_{25}O_2$ $[M+H]^+$ 225.1855, found 225.1866. Enantiomeric excess was determined by GLC with Astec Chiraldex G-TA column (30 m × 0.25 mm × 0.12 μm) and operated at a constant 150 °C using $H_2$ as the carrier gas at 50 cm/s; minor (*R*)-enantiomer $t_r$ = 63.89 min, major (*S*)-enantiomer $t_r$ = 67.86 min.

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