Supporting Information

Stereocontrolled Synthesis of Multisubstituted 1,3-dienes via Allene-Claisen Rearrangement

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General Procedures

$^1$H NMR, $^{13}$C NMR were measured in CDCl$_3$ solution using JEOL JNM-AL-400, Varian 400-MR ($^1$H NMR at 400 MHz, $^{13}$C NMR at 100 MHz), Varian 500-MR, Bruker AVANCE III HD-500 ($^1$H NMR at 500 MHz, $^{13}$C NMR at 125 MHz), JEOL JNM-ECA-600 spectrometers ($^1$H NMR at 600 MHz, $^{13}$C NMR at 150 MHz), and as the referenced standard ($^1$H NMR at 0.00 ppm (TMS), $^{13}$C NMR at 77.0 ppm (CDCl$_3$)). Chemical shifts are reported in ppm. Peak multiplicities are used the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sext, sextet; sept, septet; m, multiplet; br, broadend. IR spectra were recorded on JAS.CO FT/IR-4200 and Shimadzu FT/IR-8300 spectrometers. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS-K9, JEOL JMS-700 and Waters SYNAPT G2-Si HDMS mass spectrometers. Elemental analyses were performed with PerkinElmer 2400 series II CHNS/O analyzer. Melting points were measured with a Yanaco MP-500D apparatus and SRS Opti Melt MPA 100 melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on precoated plates (0.25 mm, silica gel Merck 60F$_{254}$). Column chromatography was performed on silica gel (Kanto Chemical Co., Inc.). Preparative HPLC was performed on a recycling system utilizing a LC-9210 II Next (JAI Co., Inc.), and also a system utilizing a JAS.CO PU-2087 Intelligent Pump with Dynamic Mixer MX-2080-32 and UV detector UV-2075 and RI detector RI-2031. All reactions were performed under an air atmosphere unless otherwise noted, and dry dichloromethane (CH$_2$Cl$_2$), diethyl ether (Et$_2$O), and tetrahydrofuran (THF) were purchased from Kanto Chemical and Wako Chemical Co., Inc.. Unless otherwise noted, reagents were obtained from chemical sources and used without further purification.

General synthetic protocol of allenyl alcohol: 4-Ethyl-1-phenylhexa-2,3-dien-1-ol

To a solution of alkyne$^1$ (4.5 g, 23 mmol) in THF (80 ml), cooled to -78 °C under argon, was added n-BuLi (12.4 ml, 28 mmol, 2.2 M in hexane) and then stirred at 0 °C for 30 min. A solution of benzaldehyde (3.6 ml, 35 mmol) in THF (40 ml) was added. After being stirred at rt for 75 min, the resulting mixture was quenched with H$_2$O, extracted with AcOEt, washed with brine, dried over MgSO$_4$, filtered and concentrated to afford a crude product, which was purified

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by silica gel column chromatography (AcOEt/ hexane = 1: 4) to give 6.6 g of propargyl alcohol as a pale yellow oil. To a suspension of LAH (5.0 g, 132 mmol) in Et2O (190 ml), cooled to 0 °C under argon, was added a solution of propargyl alcohol (6.5 g, 22 mmol) in Et2O (30 ml) and then stirred at rt for 15 h. The reaction was carefully quenched with H2O (5 ml), 15% NaOH aq (5 ml), and H2O (15 ml) at 0 °C, and then stirred at rt for 1 h. The resulting mixture was filtered through a celite pad and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 10 to 1: 5) to give 3.5 g (75%, 2 steps) of alcohol as a colorless oil.

1H-NMR (CDCl3, 400 MHz) δ 0.99 (t, J = 7.4 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H), 1.96-2.05 (m, 4H), 2.10 (d, J = 4.4 Hz, 1H), 5.20 (dd, J = 4.4, 5.2 Hz, 1H), 5.47-5.52 (m, 1H), 7.25-7.42 (m, 5H). 13C-NMR (CDCl3, 100 MHz) δ 12.3 (q), 12.4 (q), 25.6 (t), 25.7 (t), 72.4 (d), 98.5 (d), 113.3 (s), 126.1 (d), 127.4 (d), 128.3 (d), 143.5 (s), 197.9 (s). IR (neat) 3281, 2961, 1960, 1458, 1009 cm⁻¹. MS (EI) m/z 202 (M⁺), 107 (100%). HRMS (EI) calcd for C14H18O (M⁺) 202.1358, found 202.1353.

General synthetic protocol of allenyl acetate: 4-Ethyl-1-phenylhexa-2,3-dien-1-yl acetate (4a)

To a solution of alcohol (3.5 g, 17 mmol) in CH2Cl2 (85 ml) were added acetic anhydride (3.2 ml, 34 mmol), pyridine (2.5 ml, 34 mmol), and DMAP (0.21 g, 1.7 mmol). After being stirred for 39 h, the reaction mixture was quenched with a solution of saturated NaHCO3 solution, extracted with CH2Cl2, washed with brine, dried over MgSO4, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 5) to give 4.2 g (quant) of 4a as a colorless oil.

1H-NMR (CDCl3, 400 MHz) δ 0.92 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.87-1.96 (m, 4H), 2.10 (s, 3H), 5.40-5.45 (m, 1H), 6.26 (d, J = 6.0 Hz, 1H), 7.25-7.39 (m, 5H). 13C-NMR (CDCl3, 150 MHz) δ 12.09 (q), 12.12 (q), 21.3 (q), 25.4 (t), 25.5 (t), 74.6 (d), 94.2 (d), 111.5 (s), 126.8 (d), 127.9 (d), 128.3 (d), 139.9 (s), 170.0 (s), 201.1 (s). IR (neat) 2969, 1966, 1732, 1233 cm⁻¹. MS (FAB) m/z 244 (M⁺), 202 (M⁺-C2H2O). HRMS (FAB) caled for C16H20O2 (M⁺) 244.1463, found 244.1467.
4-Ethyl-1-(3-methoxyphenyl)hexa-2,3-dien-1-ol

![Chemical Structure](image)

$^1$H-NMR (CDCl$_3$, 270 MHz) $\delta$ 1.00 (t, $J = 7.6$ Hz, 3H), 1.03 (t, $J = 7.6$ Hz, 3H), 1.96-2.08 (m, 4H), 2.11 (d, $J = 4.3$ Hz, 1H), 3.81 (s, 3H), 5.18 (dd, $J = 4.3$, 5.4 Hz, 1H), 5.45-5.52 (m, 1H), 6.79-6.85 (m, 1H), 6.95-7.00 (m, 2H), 7.22-7.30 (m, 1H). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 12.3 (q), 12.4 (q), 25.6 (t), 25.7 (t), 55.1 (q), 72.3 (d), 98.5 (d), 111.4 (d), 113.2 (d), 113.3 (s), 118.4 (d), 129.3 (d), 145.2 (s), 159.7 (s), 197.9 (s). IR (KBr) 3284, 2961, 1960, 1254 cm$^{-1}$. MS (EI) $m/z$ 232 (M$^+$), 203 (M$^+$-Et), 109 (100%). HRMS (EI) calcd for C$_{15}$H$_{20}$O$_2$ (M$^+$) 232.1463, found 232.1464.

4-Ethyl-1-(3-methoxyphenyl)hexa-2,3-dien-1-y acetate (4b)

![Chemical Structure](image)

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.94 (t, $J = 7.6$ Hz, 3H), 0.96 (t, $J = 7.6$ Hz, 3H), 1.90-1.98 (m, 4H), 2.09 (s, 3H), 3.80 (s, 3H), 5.38-5.44 (m, 1H), 6.23 (d, $J = 6.3$ Hz, 1H), 6.82 (dd, $J = 2.8$, 8.3 Hz, 1H), 6.91-6.97 (m, 2H), 7.23-7.27 (m, 1H). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 12.08 (q), 12.13 (q), 21.2 (q), 25.4 (t), 25.5 (t), 55.2 (q), 74.5 (d), 94.1 (d), 111.5 (s), 112.3 (d), 113.4 (d), 119.1 (d), 129.3 (d), 141.4 (s), 159.5 (s), 169.9 (s), 200.9 (s). IR (neat) 2967, 1967, 1736, 1233 cm$^{-1}$. MS (FAB) $m/z$ 274 (M$^+$), 215 (100%). HRMS (FAB) calcd for C$_{17}$H$_{22}$O$_3$ (M$^+$) 274.1569, found 274.1572.

4-Ethyl-1-[3-(trifluoromethyl)phenyl]hexa-2,3-dien-1-ol (6b)

![Chemical Structure](image)

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$: 0.98 (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 7.2$ Hz, 3H), 1.95-2.05 (m, 4H), 2.16 (d, $J = 4.0$ Hz, 1H), 5.27 (dd, $J = 4.0$, 4.8 Hz, 1H), 5.46-5.54 (m, 1H), 7.43-7.59 (m,
4-Ethyl-1-[3-(trifluoromethyl)phenyl]hexa-2,3-dien-1-yl acetate (4c)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{OAc} \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.88 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H), 1.84-1.93 (m, 4H), 2.12 (s, 3H), 5.42-5.48 (m, 1H), 6.30 (d, $J = 6.4$ Hz, 1H), 7.42-7.56 (m, 3H), 7.62 (brs, 1H).

$^{13}$C-NMR (CDCl$_3$, 150 MHz) $\delta$ 11.96 (q), 12.02 (q), 21.2 (q), 25.27 (t), 25.32 (t), 73.9 (d), 93.9 (d), 112.1 (s), 123.7 (d, q: $J_{C,F} = 2.9$ Hz), 124.1 (s, q: $J_{C,F} = 270$ Hz), 124.6 (d, q: $J_{C,F} = 2.9$ Hz), 128.7 (d), 130.2 (d), 130.7 (s, q: $J_{C,F} = 33$ Hz), 140.8 (s), 169.9 (s), 201.6 (s). IR (neat) 2970, 1966, 1744, 1231 cm$^{-1}$. MS (EI) $m/z$ 312 (M$^+$), 270 (M$^+$-C$_2$H$_2$O, 100%). HRMS (EI) calced for C$_{16}$H$_{18}$O$_2$F$_3$ (M$^+$) 312.1338, found 312.1337.

1-(2,4-Dichlorophenyl)-4-ethyl-4-ethylhexa-2,3-dien-1-ol

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.94 (t, $J = 7.6$ Hz, 3H), 0.97 (t, $J = 7.6$ Hz, 3H), 1.92-2.02 (m, 4H), 2.30 (d, $J = 3.9$ Hz, 1H), 5.50-5.58 (m, 2H), 7.24 (dd, $J = 2.0$, 8.8 Hz, 1H), 7.34 (d, $J = 2.0$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 1H). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 12.3 (q), 25.5 (t), 25.6 (t), 68.2 (d), 96.7 (d), 114.3 (s), 127.2 (d), 128.3 (d), 129.0 (d), 132.6 (s), 133.4 (s), 139.6 (s), 198.1 (s). IR (KBr) 3325, 2967, 1966, 1471 cm$^{-1}$. MS (FAB) $m/z$ 273 (M$^+$+2+H), 271 (M$^+$+H). HRMS (FAB) calced for C$_{14}$H$_{17}$OCl$_2$ (M$^+$+H) 271.0656, found 271.0659.

1-(2,4-Dichlorophenyl)-4-ethyl-4-ethylhexa-2,3-dien-1-yl acetate (4d)

\[
\begin{align*}
\text{Cl} & \quad \text{OAc} \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.89 (t, $J = 7.2$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H), 1.84-1.92 (m,
4-H), 2.10 (s, 3H), 5.40-5.46 (m, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H). ¹³C-NMR (CDCl₃, 150 MHz) δ 12.0 (q), 12.1 (q), 21.1 (q), 25.2 (t), 25.3 (t), 70.7 (d), 92.6 (d), 112.2 (s), 127.0 (d), 128.9 (d), 129.1 (d), 133.2 (s), 133.9 (s), 136.4 (s), 169.5 (s), 201.5 (s). IR (neat) 2969, 1964, 1744, 1229 cm⁻¹. MS (FAB) m/z 314 (M⁺+2), 312 (M⁺). HRMS (FAB) calcd for C₁₆H₁₈O₂Cl₂ (M⁺) 312.0684, found 312.0684.

4-Ethyl-1-(naphthalen-1-yl)hexa-2,3-dien-1-ol

![Structure](image)

¹H-NMR (CDCl₃, 600 MHz) δ 0.95 (t, J = 7.8 Hz, 3H), 0.97 (t, J = 7.8 Hz, 3H), 1.94-2.00 (m, 4H), 2.30 (d, J = 4.0 Hz, 1H), 5.66-5.69 (m, 1H), 5.96 (t, J = 4.0 Hz, 1H), 7.45-7.53 (m, 3H), 7.71 (d, J = 8.4 Hz, 1H), 7.79 (t, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H). ¹³C-NMR (CDCl₃, 150 MHz) δ 12.45 (q), 12.49 (q), 25.6 (t), 25.8 (t), 69.7 (d), 97.9 (d), 113.4 (d), 123.2 (d), 124.0 (d), 125.5 (d), 125.6 (d), 125.9 (d), 128.1 (d), 128.8 (d), 130.7 (d), 133.9 (d), 139.1 (s), 198.6 (s). IR (neat) 3260, 2965, 1956 cm⁻¹. MS (EI) m/z 252 (M⁺), 157 (100%). HRMS (EI) calcd for C₁₈H₂₀O (M⁺) 252.1514, found 252.1514.

4-Ethyl-1-(naphthalen-1-yl)hexa-2,3-dien-1-yl acetate (4e)

![Structure](image)

¹H-NMR (CDCl₃, 400 MHz) δ 0.83 (t, J = 7.6 Hz, 3H), 0.85 (t, J = 7.6 Hz, 3H), 1.80-1.88 (m, 4H), 2.12 (s, 3H), 5.56-5.60 (m, 1H), 7.00 (d, J = 5.9 Hz, 1H), 7.43-7.51 (m, 3H), 7.63 (d, J = 7.8 Hz, 1H), 7.77-7.87 (m, 2H), 8.14 (d, J = 7.8 Hz, 1H). ¹³C-NMR (CDCl₃, 100 MHz) δ 12.0 (q), 12.1 (q), 21.3 (q), 25.2 (t), 25.4 (t), 72.1 (d), 93.7 (d), 111.7 (s), 124.0 (d), 124.5 (d), 125.2 (d), 125.6 (d), 126.0 (d), 128.5 (d), 128.6 (d), 130.6 (s), 133.8 (s), 135.5 (s), 170.0 (s), 201.1 (s). IR (neat) 2967, 1964, 1742, 1231 cm⁻¹. MS (EI) m/z 294 (M⁺), 252 (M⁺-C₂H₂O), 181 (100%). HRMS (EI) calcd for C₂₀H₂₂O₂ (M⁺) 294.1620, found 294.1625.
3-Cyclohexylidene-1-phenylprop-2-en-1-ol (6a)

\[
\text{C}_7\text{H}_8\text{O} + \text{C}_7\text{H}_8\text{O}
\]

\[\delta 1.44-1.64 (m, 6H), 2.08-2.18 (m, 5H), 5.20 (t, J = 5.2 Hz, 1H),
5.28-5.33 (m, 1H), 7.26-7.40 (m, 5H). 1^3\text{C-NMR}(\text{CDCl}_3, 100 \text{ MHz}) \delta 25.9 (t), 27.3 (t), 31.4 (t),
31.5 (t), 72.4 (d), 94.2 (d), 107.1 (s), 126.1 (d), 127.4 (d), 128.3 (d), 143.4 (s), 196.5 (s). IR
(neat) 3333, 2928, 1966, 1447 cm\(^{-1}\). MS (EI) \(m/z\) 214 (M\(^+\)), 150 (100%). HRMS (EI) calcd for
\(\text{C}_{15}\text{H}_{18}\text{O} \ (M^+)\) 214.1357, found 214.1358.

3-Cyclohexylidene-1-phenylallyl acetate (4f)

\[
\text{C}_7\text{H}_8\text{O} + \text{C}_7\text{H}_8\text{O}
\]

\[\delta 1.22-1.58 (m, 6H), 1.94-2.08 (m, 4H), 2.05 (s, 3H), 5.22-5.28 (m,
1H), 6.23 (d, J = 5.2 Hz, 1H), 7.20-7.37 (m, 5H). 1^3\text{C-NMR}(\text{CDCl}_3, 100 \text{ MHz}) \delta 20.9 (q), 25.6
(t), 26.8 (t), 26.9 (t), 30.7 (t), 30.8 (t), 74.3 (d), 90.0 (d), 105.3 (s), 126.7 (d), 127.6 (d), 128.0 (d),
139.4 (s), 169.5 (s), 199.1 (s). IR (neat) 2930, 169, 1740, 1231 cm\(^{-1}\). MS (EI) \(m/z\) 256 (M\(^+\)),
214 (M\(^+\)-C\(_2\)H\(_2\)O), 131 (100%). HRMS (EI) calcd for \(\text{C}_{17}\text{H}_{20}\text{O}_2 \ (M^+)\) 256.1463, found 256.1463.

3-Ethyltrideca-3,4-dien-6-ol

\[
\text{C}_7\text{H}_15\text{O}_2 + \text{C}_7\text{H}_15\text{O}_2
\]

\[\delta 0.88 (t, J = 6.9 Hz, 3H), 1.00 (t, J = 6.9 Hz, 3H), 1.02 (t, J = 6.9
Hz, 3H), 1.24-1.46 (m, 10H), 1.52-1.58 (m, 3H), 1.96-2.02 (m, 4H), 4.06-4.10 (m,
2H), 5.29-5.33 (m, 1H). 1^3\text{C-NMR}(\text{CDCl}_3, 150 \text{ MHz}) \delta 12.4 (q), 14.1 (q), 22.6 (t), 25.5 (t), 25.6 (t),
25.7 (t), 29.3 (t), 29.5 (t), 31.8 (t), 37.7 (t), 70.2 (d), 98.2 (d), 112.0 (s), 198.0 (s). IR (neat) 3358,
1962, 1456 cm\(^{-1}\). MS (EI) \(m/z\) 224 (M\(^+\)), 126 (100%). HRMS (EI) calcd for \(\text{C}_{12}\text{H}_{23}\text{O} \ (M^+)\)
224.2140, found 224.2136.
3-Ethyltrideca-3, 4-dien-6-yl acetate (4g)

![Chemical structure](https://example.com/structure.png)

**1H-NMR** (CDCl$_3$, 600 MHz) δ 0.88 (t, $J = 7.2$ Hz, 3H), 0.96-1.01 (m, 6H), 1.22-1.38 (m, 10H), 1.58-1.68 (m, 2H), 1.93-2.00 (m, 2H), 2.03 (s, 3H), 5.18-5.22 (m, 2H). **13C-NMR** (CDCl$_3$, 150 MHz) δ 12.1 (q), 12.2 (q), 14.0 (q), 21.3 (q), 22.6 (t), 25.38 (t), 25.42 (t), 25.46 (t), 29.2 (t), 29.3 (t), 31.8 (t), 34.4 (t), 73.0 (d), 93.6 (d), 110.6 (s), 170.4 (s), 200.4 (s). IR (neat) 1966, 1742, 1236 cm$^{-1}$. MS (EI) $m/z$ 266 (M$^+$), 224 (M$^+$-C$_2$H$_4$O, 100%). HRMS (EI) calcd for C$_{17}$H$_{30}$O$_2$ (M$^+$) 266.2246, found 266.2245.

1-Cyclohexylidenedec-1-en-3-ol

![Chemical structure](https://example.com/structure.png)

**1H-NMR** (CDCl$_3$, 600 MHz) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.22-1.43 (m, 10H), 1.50-1.65 (m, 8H), 2.01-2.16 (m, 5H), 4.06-4.10 (m, 1H). **13C-NMR** (CDCl$_3$, 100 MHz) δ 14.1 (q), 22.6 (t), 25.4 (t), 26.0 (t), 27.4 (t), 29.3 (t), 29.5 (t), 31.8 (t), 37.5 (t), 70.3 (d), 93.6 (d), 105.9 (s), 196.4 (s). IR (neat) 3331, 2926, 1966, 1447 cm$^{-1}$. MS (EI) $m/z$ 236 (M$^+$), 127 (100%). HRMS (EI) calcd for C$_{16}$H$_{28}$O (M$^+$) 236.2140, found 236.2138.

1-Cyclohexylidenedec-1-en-3-yl acetate (4h)

![Chemical structure](https://example.com/structure.png)

**1H-NMR** (CDCl$_3$, 600 MHz) δ 0.87 (t, $J = 6.6$ Hz, 3H), 1.22-1.34 (m, 10H), 1.44-1.64 (m, 8H), 2.03 (s, 3H), 2.00-2.16 (m, 4H), 4.98-5.02 (m, 1H), 5.16 (q, $J = 6.6$ Hz, 1H). **13C-NMR** (CDCl$_3$, 150 MHz) δ 14.1 (q), 21.4 (q), 22.7 (t), 25.4 (t), 26.1 (t), 27.4 (t), 29.3 (t), 29.4 (t), 31.27 (t), 31.31 (t), 31.9 (t), 34.1 (t), 73.1 (d), 89.2 (d), 105.0 (s), 170.5 (s), 198.6 (s). IR (neat) 2928, 1969, 1740, 1236 cm$^{-1}$. MS (EI) $m/z$ 278 (M$^+$), 236 (M$^+$-C$_2$H$_4$O, 100%). HRMS (EI) calcd for C$_{18}$H$_{30}$O$_2$ (M$^+$) 278.2246, found 278.2242.

1-cyclobutylidenedec-1-en-3-ol (6c)
1H-NMR (CDCl3, 400 MHz) δ 0.88 (t, J = 6.4 Hz, 3H), 1.22-1.58 (m, 12H), 1.97 (quin, J = 8.0 Hz, 2H), 2.86-2.92 (m, 4H), 4.10 (q, J = 6.4 Hz, 1H), 5.20-5.28 (m, 1H). 13C-NMR (CDCl3, 100 MHz) δ: 14.1 (q), 17.5 (t), 22.6 (t), 25.4 (t), 29.3 (t), 29.5 (t), 29.9 (t), 31.8 (t), 37.4 (t), 70.3 (d), 98.1 (d), 104.4 (s), 193.4 (s). IR (neat) 3370, 2928, 1966, 1717 cm⁻¹. MS (FAB) m/z 207 (M⁺-H).

HRMS (FAB) calcd for C14H23O (M⁺-H) 207.1749, found 207.1754.

7-tert-Butyldimethylsiloxy-1-phenylecta-4,5-dien-3-ol (6d)

To a solution of allenoate² (850 mg, 3.5 mmol) in CH₂Cl₂ (35 ml), cooled to -78 °C under argon, was added DIBAL (1.0 M in toluene, 10.4 ml, 10.4 mmol) and then stirred at -78 °C for 30 min. The reaction mixture was quenched with H₂O, stirred at rt for 1 h, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/hexane = 1: 4 to 1: 1) to give 467 mg (66%) of diol as a pale yellow oil. The diol (102 mg, 0.50 mmol) was diluted with CH₂Cl₂ (10 ml) and then added TBSCI (83 mg, 0.55 mmol) and imidazole (60 mg, 0.88 mmol) at rt. After being stirred for 11 h, the reaction mixture was concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/hexane = 1: 10) to give 123 mg (77%) of 6d as a colorless oil.

1:1 Diastereomer mixture. 1H-NMR (CDCl₃, 500 MHz) δ 0.07 (s, 6H), 0.90 (s, 9H), 1.85-1.92 (m, 2H), 2.67-2.81 (m, 2H), 4.15-4.23 (m, 3H), 5.34-5.46 (m, 2H), 7.16-7.22 (m, 3H), 7.25-7.30 (m, 2H). 13C-NMR (CDCl₃, 125 MHz) δ -5.2 (q), 18.3 (s), 25.9 (q), 31.7 (t), 39.0 (t), 61.3 (t), 69.0 (d), 95.0 (d), 97.2 (d), 125.8 (d), 128.4 (d), 128.5 (d), 141.8 (s), 201.8 (s). IR (ATR) 3405, 1965, 1254, 1081 cm⁻¹. MS (ESI) m/z 341 (M⁺+Na, 100%). HRMS (ESI) calcd for C₁₉H₃₀O₂NaSi (M⁺+Na) 341.1913, found 341.1909.

1-(Octa-1,2-dienyl)cyclohexanol (6e)

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1H-NMR (CDCl₃, 500 MHz) δ 0.87-0.91 (m, 3H), 1.29-1.70 (m, 16H), 2.00-2.06 (m, 2H), 5.25-5.33 (m, 2H). 13C-NMR (CDCl₃, 125 MHz) δ 14.0 (q), 22.45 (t), 22.57 (t), 22.61 (t), 25.5 (t), 28.8 (t), 28.9 (t), 31.3 (t), 38.4 (t), 70.7 (s), 94.9 (d), 100.3 (d), 201.3 (s). IR (ATR) 3373, 2927, 1959 cm⁻¹. MS (EI) m/z 208 (M⁺), 99 (100%). HRMS (EI) calcd for C₁₄H₂₂O (M⁺) 208.1827, found 208.1833.

Synthesis of syn- and anti-allenyl alcohol 8

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Compound S-1

To a solution of ester (5.5 g, 16.8 mmol) and N,O-dimethylhydroxylamine hydrochloride (6.7 g, 68.7 mmol) in THF (80 ml), cooled to 0 °C under argon, was added dropwise iPrMgCl·LiCl (69 ml, 138 mmol, 2.0 M in THF) and then stirred at rt for 30 min. The reaction mixture was quenched with a saturated NaHCO₃ solution, extracted with AcOEt, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/hexane = 1: 5 to 1: 2) to give 4.1 g (71%) of S-1 as a colorless solid.

1H-NMR (CDCl₃, 500 MHz) δ 1.90-2.10 (m, 2H), 2.62-2.70 (m, 1H), 2.80-2.88 (m, 1H), 3.16 (s, 3H), 3.36 (brs, 3H), 3.82 (s, 3H), 4.13-4.19 (m, 1H), 4.27 (d, J = 11.5 Hz, 1H), 4.63 (d, J = 11.5 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 7.07-7.25 (m, 5H), 7.30 (d, J = 8.5 Hz, 2H). 13C-NMR
Compound S-2

To a solution of 1-hexyne (2.5 g, 30.6 mmol) in Et₂O (120 ml), cooled to -20 °C under argon, was added dropwise n-BuLi (10.6 ml, 24.4 mmol, 2.3 M in hexane) and then stirred at 0 °C for 20 min. The reaction mixture was cooled to -20 °C and a solution of S-1 (4.2 g, 12.2 mmol) in Et₂O (10 ml) was added. After being stirred at -20 °C for 30 min, the resulting mixture was quenched with H₂O, extracted with AcOEt, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1:10) to give 4.9 g (quant.) of S-2 as a colorless oil.

¹H-NMR (CDCl₃, 500 MHz) δ 0.92 (t, J = 7.0 Hz, 3H), 1.42 (sext, J = 7.0 Hz, 2H), 1.57 (quin, J = 7.0 Hz, 2H), 2.02-2.08 (m, 2H), 2.39 (t, J = 7.0 Hz, 2H), 2.61-2.83 (m, 2H), 3.82 (s, 3H), 3.85 (dd, J = 5.5, 7.5 Hz, 1H), 4.32 (d, J = 11.5 Hz, 1H), 4.67 (d, J = 11.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 7.11-7.28 (m, 5H), 7.30 (d, J = 8.5 Hz, 2H). ¹³C-NMR (CDCl₃, 125 MHz) δ 13.5 (q), 18.9 (t), 22.0 (t), 29.6 (t), 31.3 (t), 33.9 (t), 55.3 (q), 72.1 (t), 79.3 (s), 83.7 (d), 98.0 (s), 113.8 (d), 126.0 (d), 128.4 (d), 128.5 (d), 129.6 (s), 129.8 (d), 141.1 (s), 159.5 (s), 189.9 (s). IR (ATR) 2208, 1770, 1669, 1247 cm⁻¹. MS (EI) m/z 364 (M⁺), 121 (100%). HRMS (EI) calcd for C₂₄H₂₈O₃ (M⁺) 364.2038, found 364.2037.

Compound S-3

To a solution of S-2 (3.8 g, 10.4 mmol) in THF (80 ml), cooled to -78 °C under argon, was added K-selectride (15.6 ml, 15.6 mmol, 1.0 M in THF) and then stirred at -78 °C for 1 h. The reaction mixture was quenched with H₂O, extracted with EtOAc, washed with brine, dried over
MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 10) to give 3.7 g (quant.) of S-3 as a colorless oil. ¹H-NMR (CDCl₃, 500 MHz) δ 0.90 (t, J = 7.0 Hz, 3H), 1.37-1.53 (m, 4H), 1.95-2.01 (m, 2H), 2.23 (dt, J = 2.0, 7.0 Hz, 2H), 2.64-2.80 (m, 2H), 3.52 (ddd, J = 6.0, 7.5, 7.5 Hz, 1H), 3.81 (s, 3H), 4.34 (dt, J = 2.0, 6.0 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 7.15-7.21 (m, 3H), 7.25-7.30 (m, 4H). ¹³C-NMR (CDCl₃, 125 MHz) δ 13.6 (q), 18.4 (t), 22.0 (t), 30.6 (t), 31.4 (t), 32.8 (t), 55.3 (q), 64.9 (d), 72.9 (t), 78.7 (s), 81.5 (d), 86.9 (s), 113.9 (d), 125.8 (d), 128.4 (d), 129.6 (d), 130.3 (s), 142.0 (s), 159.4 (s). IR (ATR) 3338, 2208, 1611, 1513, 1246 cm⁻¹. MS (Cl) m/z 366 (M⁺), 365 (M⁺-H), 121 (100%). HRMS (Cl) calcd for C₂₄H₃₀O₃ (M⁺) 366.2195, found 366.2192.

**Compound S-4**

To a solution of S-3 (3.8 g, 10.7 mmol) in THF (35 ml) were added IPNBSH³ (5.5 g, 21.4 mmol) and PPh₃ (13.8 g, 52.7 mmol) and then DEAD (23.8 ml, 52.7 mmol, 40% in toluene) was added dropwise to the reaction mixture. After being stirred for 30 min, the reaction mixture was quenched with CF₃CH₂OH and H₂O (1: 1, 15 ml) and stirred for 30 min. The resulting mixture was extracted with EtOAc-hexane (1: 10), washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 10) to give 2.1 g (72%) of S-4.

¹H-NMR (CDCl₃, 500 MHz) δ 0.91 (t, J = 7.0 Hz, 3H), 1.33-1.47 (m, 4H), 1.81-2.10 (m, 4H), 2.62-2.79 (m, 2H), 3.78-3.83 (m, 1H), 3.80 (s, 3H), 4.34 (d, J = 11.5 Hz, 1H), 4.62 (d, J = 11.5 Hz, 1H), 5.02-5.08 (m, 1H), 5.18 (dd, J = 6.0, 7.0 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 7.13-7.29 (m, 7H). ¹³C-NMR (CDCl₃, 125 MHz) δ 13.9 (q), 22.2 (t), 28.7 (t), 31.4 (t), 31.8 (t), 37.7 (t), 55.3 (q), 69.7 (t), 77.3 (d), 91.9 (d), 92.1 (d), 113.7 (d), 125.7 (d), 128.3 (d), 128.5 (d), 129.4 (d), 130.8 (s), 142.1 (s), 159.1 (s), 204.6 (s). IR (ATR) 1967, 1759, 1612, 1513, 1247 cm⁻¹. MS (CI) m/z 350 (M⁺), 349 (M⁺-H), 121 (100%). HRMS (CI) calcd for C₂₄H₃₀O₂ (M⁺) 350.2246, found 350.2240.

**syn-1-Phenyldeca-4,5-dien-3-ol (syn-8)**

To a solution of S-4 (2.0 g, 5.7 mmol) in CH₂Cl₂-H₂O (10: 1, 77 ml), cooled to 0 °C under argon, was added DDQ (1.9 g, 8.6 mmol) and then stirred at 0 °C for 1 h. A saturated Na₂S₂O₃ solution was added and then the resulting mixture was extracted with CH₂Cl₂, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 20) to give 849 mg (65%) of **syn-8**.

**1H-NMR** (CDCl₃, 500 MHz) δ 0.90 (t, J = 7.0 Hz, 3H), 1.31-1.44 (m, 4H), 1.84-1.91 (m, 2H), 2.00-2.07 (m, 2H), 2.68-2.81 (m, 2H), 4.12-4.18 (m, 1H), 5.23-5.35 (m, 2H), 7.16-7.30 (m, 5H).

**13C-NMR** (CDCl₃, 125 MHz) δ 13.9 (q), 22.1 (t), 28.4 (t), 31.2 (t), 31.7 (t), 39.1 (t), 69.1 (d), 94.7 (d), 95.6 (d), 125.8 (d), 128.3 (d), 128.5 (d), 142.0 (s), 202.1 (s). IR (ATR) 3350, 1962, 1770, 1247 cm⁻¹. MS (EI) m/z 230 (M⁺), 212 (M⁺-H₂O), 91 (100%). HRMS (EI) calcd for C₁₆H₂₂O (M⁺) 230.1671, found 230.1675.

**anti-1-Phenyldeca-4,5-dien-3-ol (anti-8)**

To a solution of alcohol **syn-8** (400 mg, 1.7 mmol), 4-nitrobenzoic acid (584 mg, 3.5 mmol) and PPh₃ (544 mg, 2.0 mmol) in THF (15 ml) was added DEAD (0.88 ml, 2.0 mmol, 40% in toluene) and then stirred at 45 °C for 3 h. The reaction mixture was extracted with AcOEt, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 20) to give 574 mg of 4-nitrobenzoate. The benzoate was dissolved in DME (15 ml) and treated with 1M KOH (3 ml). After being stirred at 45 °C for 2 h, the reaction mixture was extracted with AcOEt, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 10) to give 171 mg (43%, 2 steps) of **anti-8**.

**1H-NMR** (CDCl₃, 500 MHz) δ 0.90 (t, J = 7.0 Hz, 3H), 1.31-1.44 (m, 4H), 1.84-1.91 (m, 2H), 2.00-2.06 (m, 2H), 2.68-2.80 (m, 2H), 4.12-4.18 (m, 1H), 5.22-5.34 (m, 2H), 7.16-7.30 (m, 5H).

**13C-NMR** (CDCl₃, 125 MHz) δ 13.9 (q), 22.1 (t), 28.4 (t), 31.2 (t), 31.7 (t), 39.1 (t), 69.4 (d),
Representative procedure for Ireland-Claisen rearrangement: 

\((E)-4\)-Ethyl-3-styrylhex-3-enoic acid (5a)

\[
\begin{align*}
\text{CO}_2\text{H} \\
\text{CO}_2\text{H}
\end{align*}
\]

To a solution of acetate 4a (122 mg, 0.50 mmol) in THF (5 ml), cooled to \(-78^\circ\text{C}\) under argon, were added TBSCl (151 mg, 1.0 mmol) and KHMDS (0.5 M in toluene, 2.0 ml, 1.0 mmol). After being stirred at \(-78^\circ\text{C}\) for 3 h, the reaction mixture was stirred at rt for 13 h and then concentrated in vacuo. The resulting mixture was diluted with MeOH (2 ml) and treated with K2CO3 (150 mg). After being stirred at rt for 4 h, the reaction was quenched by the addition of 3 M HCl and extracted with CH2Cl2. The combined organic layer was washed with brine, dried over MgSO4, filtered, concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1:10 to 1:2) to give 89 mg (70%) of 5a. Recrystallization from hexane afforded 5a as colorless needles (105–106 \(^\circ\text{C}\)).

\(^1\)H-NMR (CDCl3, 600 MHz) \(\delta\) 1.05 (t, \(J = 7.5\) Hz, 3H), 1.09 (t, \(J = 7.5\) Hz, 3H), 2.23 (q, \(J = 7.8\) Hz, 2H), 2.37 (q, \(J = 7.5\) Hz, 2H), 3.45 (s, 2H), 6.51 (d, \(J = 16.2\) Hz, 1H), 7.18-7.22 (m, 1H), 7.20 (d, \(J = 16.2\) Hz, 1H), 7.27-7.32 (m, 2H), 7.39-7.42 (m, 2H). \(^13\)C-NMR (CDCl3, 150 MHz) \(\delta\) 12.9 (q), 13.9 (q), 25.1 (t), 26.8 (t), 33.7 (t), 123.2 (s), 126.3 (d), 126.8 (d), 127.08 (d), 127.11 (d), 128.5 (d), 138.1 (s), 148.6 (s), 177.3 (s). IR (KBr) 2969, 1699, 1624, 1595 cm\(^{-1}\). MS (EI) \(m/z\) 244 (M\(^+\)), 215 (M\(^+\)-Et), 169 (100%). Anal. calcd for C16H20O2: C 78.65, H 8.25; found: C 78.55, H 8.22.

\((E)-4\)-Ethyl-3-(3'-methoxystyryl)hex-3-enoic acid (5b)

\[
\begin{align*}
\text{MeO} \\
\text{Et} \\
\text{Et}
\end{align*}
\]

Yield 130 mg (95%) from allenyl acetate 4b (137 mg, 0.50 mmol) according to Representative Procedure. Recrystallization from hexane afforded 5b as colorless needles (76.5–77.5 \(^\circ\text{C}\)).
\(^{1}\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.05 (t, \(J = 7.6\) Hz, 3H), 1.08 (t, \(J = 7.6\) Hz, 3H), 2.23 (q, \(J = 7.6\) Hz, 2H), 2.37 (q, \(J = 7.6\) Hz, 2H), 3.45 (s, 2H), 3.82 (s, 3H), 6.48 (d, \(J = 16.0\) Hz, 1H), 6.76 (dd, \(J = 2.0, 7.6\) Hz, 1H), 6.94 (d, \(J = 2.0\) Hz, 1H), 7.01 (d, \(J = 7.6\) Hz, 1H), 7.19 (d, \(J = 16.0\) Hz, 1H), 7.22 (t, \(J = 7.6\) Hz, 1H). \(^{13}\)C-NMR (CDCl\(_3\), 125 MHz) \(\delta\) 12.9 (q), 13.9 (q), 25.1 (t), 26.8 (t), 33.8 (t), 55.2 (q), 111.8 (d), 112.6 (d), 119.0 (d), 123.1 (s), 127.0 (d), 127.1 (d), 129.5 (d), 139.6 (s), 148.9 (s), 159.8 (s), IR (KBr) 2965, 1697, 1601, 1576 cm\(^{-1}\). MS (EI) \(m/z\) 274 (M\(^{+}\)), 245 (M\(^{+}\)-Et), 199 (100%). Anal. calcd for C\(_{17}\)H\(_{22}\)O\(_3\): C 74.42, H 8.08; found: C 74.38, H 8.10.

(E)-4-Ethyl-1-(3'-trifluoromethylstyryl)hex-3-enoic acid (5c)

Yield 81 mg (52%) from allenyl acetate 4c (156 mg, 0.50 mmol) according to Representative Procedure. Brown oil. \(^{1}\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.06 (t, \(J = 7.6\) Hz, 3H), 1.11 (t, \(J = 7.6\) Hz, 3H), 2.25 (q, \(J = 7.6\) Hz, 2H), 2.40 (q, \(J = 7.6\) Hz, 2H), 3.46 (s, 2H), 6.53 (d, \(J = 16.4\) Hz, 1H), 7.21-7.27 (m, 1H), 7.37-7.46 (m, 2H), 7.55-7.62 (m, 2H). \(^{13}\)C-NMR (CDCl\(_3\), 150 MHz) \(\delta\) 12.9 (q), 14.0 (q), 25.2 (t), 26.8 (t), 33.6 (t), 123.0 (d), 123.5 (d, q: \(J_{C,F} = 2.9\) Hz), 124.2 (s, q: \(J_{C,F} = 276\) Hz), 125.7 (d), 128.4 (d), 129.0 (d), 129.2 (d), 131.0 (s, q: \(J_{C,F} = 32\) Hz), 138.9 (s), 150.2 (s), 176.5 (s). IR (KBr) 3453, 2976, 1697, 1333 cm\(^{-1}\). MS (EI) \(m/z\) 312 (M\(^{+}\)), 173 (100%). HRMS (EI) calcd for C\(_{17}\)H\(_{19}\)F\(_3\)O\(_2\) (M\(^{+}\)) 312.1337, found 312.1338.

(E)-3-(2',4'-Dichrolostyryl)-4-ethylhex-3-enoic acid (5d)

Yield 106 mg (68%) from allenyl acetate 4d (157 mg, 0.50 mmol) according to Representative Procedure. Recrystallization from hexane afforded 5d as colorless prism (114–115 °C).

\(^{1}\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.06 (t, \(J = 7.6\) Hz, 3H) 1.09 (t, \(J = 7.6\) Hz, 3H), 2.25 (q, \(J = 7.6\) Hz, 2H), 2.37 (q, \(J = 7.6\) Hz, 2H), 3.48 (s, 2H), 6.81 (d, \(J = 16.0\) Hz, 1H), 7.13 (d, \(J = 16.0\) Hz, 1H), 7.19 (dd, \(J = 2.0, 8.4\) Hz, 1H), 7.34 (d, \(J = 2.0\) Hz, 1H), 7.48 (d, \(J = 8.4\) Hz, 1H). \(^{13}\)C-NMR (CDCl\(_3\), 150 MHz) \(\delta\) 12.9 (q), 14.0 (q), 25.2 (t), 26.9 (t), 33.6 (t), 122.3 (d), 123.5 (s), 127.0 (d),
(E)-4-Ethyl-3-[2’-(naphthalen-1’-yl)vinyl]hex-3-enoic acid (5e)

Yield 87 mg (58%) from allenyl acetate 4e (149 mg, 0.50 mmol) according to Representative Procedure. Recrystallization from hexane afforded 5e as pale brown needles (84–85 °C).

1H-NMR (CDCl3, 400 MHz) δ 1.09 (t, J = 7.8 Hz, 3H), 1.11 (t, J = 7.8 Hz, 3H), 2.28 (q, J = 7.8 Hz, 2H), 2.39 (q, J = 7.8 Hz, 2H), 3.58 (s, 2H), 7.20 (d, J = 16.0 Hz, 1H), 7.32 (d, J = 16.0 Hz, 1H), 7.41-7.50 (m, 3H), 7.61 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H). 13C-NMR (CDCl3, 100 MHz) δ 13.0 (q), 13.9 (q), 25.2 (t), 26.8 (t), 34.2 (t), 123.2 (d), 123.7 (s), 123.9 (d), 124.4 (d), 125.6 (d), 125.7 (d), 126.0 (d), 127.5 (d), 128.4 (d), 129.7 (d), 131.4 (s), 133.6 (s), 135.9 (s), 148.8 (s), 177.7 (s). IR (KBr) 2986, 1719, 1676, 1223 cm⁻¹. MS (EI) m/z 294 (M⁺), 265 (M⁺−Et), 219 (100%). Anal. calcd for C20H22O2: C 81.60, H 7.53; found: C 81.40, H 7.50.

(E)-3-Cyclohexyliden-5-phenylpent-4-enoic acid (5f)

Yield 38 mg (73%) from allenyl acetate 4f (52 mg, 0.20 mmol) according to Representative Procedure. Recrystallization from hexane afforded 5f as colorless needles (114–116 °C).

1H-NMR (CDCl3, 400 MHz) δ 1.60-1.68 (m, 6H), 2.30-2.36 (m, 2H), 2.48-2.54 (m, 2H), 3.49 (s, 2H), 6.54 (d, J = 16.0 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.26-7.32 (m, 2H), 7.32 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 7.2 Hz, 2H). 13C-NMR (CDCl3, 150 MHz) δ 26.7 (t), 28.1 (t), 28.2 (t), 30.8 (t), 32.5 (t), 33.5 (t), 120.8 (s), 126.3 (d), 126.4 (d), 127.1 (d), 127.4 (d), 128.5 (d), 138.1 (s), 145.6 (s), 175.9 (s). IR (CHCl3) 3030, 2986, 1715, 1192 cm⁻¹. MS (EI) m/z 256 (M⁺), 196 (M⁺−Et), 72 (100%). Anal. calcd for C17H20O2: C 79.65, H 7.86; found: C 79.46, H 7.91.
(E)-3-(Pentan-3’-ylidene)dodec-4-enoic acid (5g)

To a solution of acetate 4g (133 mg, 0.50 mmol) in THF (4.5 ml), cooled to -40 °C under argon, were added KHMDS (2.0 ml, 1.0 mmol, 0.5 M in toluene) and a solution of TBSCl (151 mg, 1.0 mmol) in THF (0.5 ml) and then stirred at -40 °C for 3 h. The reaction mixture was concentrated in vacuo, diluted with hexane (chilled), washed with brine (chilled), dried over Na₂SO₄, filtered and concentrated to afford a crude product of O-silyl ketene acetal. The resulting compound was dissolved in hexane (5 ml) and refluxed for 1.5 h. The reaction mixture was concentrated to afford a crude product of O-silyl ester. The resulting compound was dissolved in THF (4 ml) and treated with TBAF (1.0 ml, 1.0 mmol, 1.0 M in THF). After being stirred at rt for 10 min, the reaction was quenched with a solution of saturated NH₄Cl solution, extracted with AcOEt, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/hexane = 1:2) to give 80 mg (60%) of 5g. Recrystallization from MeCN afforded 5g as colorless powder (32.5-33.5 °C).

1H-NMR (CDCl₃, 600 MHz) δ 0.88 (t, J = 7.6 Hz, 3H), 1.00 (t, J = 7.8 Hz, 3H), 1.02 (t, J = 7.8 Hz, 3H), 1.22-1.42 (m, 10H), 2.08-2.16 (m, 4H), 2.24 (q, J = 7.8 Hz, 2H), 3.32 (s, 2H), 5.61 (dt, J = 7.6, 15.6 Hz, 1H), 6.41 (d, J = 15.6 Hz, 1H). 13C-NMR (CDCl₃, 150 MHz) δ 13.0 (q), 13.6 (q), 14.1 (q), 22.7 (t), 24.7 (t), 26.3 (t), 29.1 (t), 29.6 (t), 31.8 (t), 33.4 (t), 33.9 (t), 122.8 (s), 127.5 (d), 129.6 (d), 144.7 (s), 178.0 (s). IR (KBr) 2969, 1705, 1616, 1589, 1290 cm⁻¹. MS (EI) m/z 266 (M⁺), 237 (M⁺−Et), 93 (100%). HRMS (EI) calcd for C₁₇H₃₀O₂ (M⁺) 266.2246, found 266.2245. Anal. calcd for C₁₇H₃₀O₂: C 76.64, H 11.35; found: C 76.26, H 11.47.

(E)-3-Cyclohexylidenedodec-4-enoic acid (5h)

To a solution of acetate 4h (139 mg, 0.50 mmol) in THF (4.5 ml), cooled to -40 °C under argon, were added KHMDS (2.0 ml, 1.0 mmol, 0.5 M in toluene) and a solution of TBSCl (151 mg, 1.0 mmol) in THF (0.5 ml) and then stirred at -40 °C for 3 h. The reaction mixture was...
concentrated in vacuo, diluted with hexane (chilled), washed with brine (chilled), dried over Na₂SO₄, filtered and concentrated to afford a crude product of O-silyl ketene acetal. The resulting compound was dissolved in hexane (5 ml) and refluxed for 1.5 h. The reaction mixture was concentrated to afford a crude product of O-silyl ester. The resulting compound was dissolved in THF (4 ml) and treated with TBAF (1.0 ml, 1.0 mmol, 1.0 M in THF). After being stirred at rt for 10 min, the reaction was quenched with a solution of saturated NH₄Cl solution, extracted with AcOEt, washed with brine, dried over MgSO₄, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 2) to give 69 mg (50%) of 5h as a colorless solid (42-44 °C).

1H-NMR (CDCl₃, 600 MHz) δ 0.88 (t, J = 6.6 Hz, 3H), 1.24-1.42 (m, 10H), 1.54-1.62 (m, 6H), 2.11 (q, J = 7.2 Hz, 2H), 2.22-2.28 (m, 2H), 2.36-2.40 (m, 2H), 3.34 (s, 2H), 5.64 (dt, J = 7.2, 15.6 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H). 13C-NMR (CDCl₃, 150 MHz) δ 14.1 (q), 22.6 (t), 26.8 (t), 27.97 (t), 28.00 (t), 29.14 (t), 29.16 (t), 29.6 (t), 30.3 (t), 31.8 (t), 32.1 (t), 33.4 (t), 34.0 (t), 120.4 (s), 127.3 (d), 129.9 (d), 141.5 (s), 178.9 (s). IR (KBr) 2920, 1693, 1227, 961 cm⁻¹. MS (EI) m/z 278 (M⁺, 100%). HRMS (EI) calcd for C₁₈H₃₀O₂ (M⁺) 278.2246, found 278.2242. Anal. calcd for C₁₈H₃₀O₂: C 77.65, H 10.86; found: C 77.12, H 10.78.

Representative procedure for Eschenmoser-Claisen rearrangement:

(4E)-N,N-Dimethyl-3-cyclohexylidene-dodec-4-enamide (7a)

To a solution of 6a (214 mg, 1.0 mmol) in toluene (2 ml) was added N,N-dimethylacetamide dimethylacetal (0.81 ml, 5.0 mmol) and then stirred at 80 °C for 9 h. The reaction mixture was concentrated in vacuo to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 5 to 1: 1) to give 255 mg (90%) of 7a as a pale yellow solid (100-102 °C).

1H-NMR (CDCl₃, 500 MHz) δ 1.58-1.66 (m, 6H), 2.24-2.28 (m, 2H), 2.50-2.54 (m, 2H), 2.97 (s, 3H), 3.12 (s, 3H), 3.43 (s, 2H), 6.37 (d, J = 16.0 Hz, 1H), 7.15-7.19 (m, 1H), 7.25-7.30 (m, 1H), 7.33 (d, J = 16.0 Hz, 1H), 7.37-7.41 (m, 2H). 13C-NMR (CDCl₃, 125 MHz) δ 26.8 (t), 28.1 (t), 28.3 (t), 30.9 (t), 32.4 (t), 33.4 (t), 35.8 (q), 37.4 (q), 122.5 (s), 126.2 (d), 126.7 (d), 126.8 (d), 127.5 (d), 128.4 (d), 138.4 (s), 144.5 (s), 170.9 (s). IR (ATR) 1636, 1390, 1135 cm⁻¹. MS (EI) m/z 283 (M⁺, 100%). HRMS (EI) calcd for C₁₈H₂₅NO (M⁺) 283.1936, found 283.1940.
(3E)-N,N-Dimethyl-4-ethyl-3-(3’-trifluoromethylstyrlyl)hex-3-enamide (7b)

![Chemical structure image]

^1H-NMR (CDCl$_3$, 500 MHz) δ 1.04 (t, $J = 7.5$ Hz, 3H), 1.12 (t, $J = 7.5$ Hz, 3H), 2.17 (q, $J = 7.5$ Hz, 2H), 2.40 (q, $J = 7.5$ Hz, 2H), 2.98 (s, 3H), 3.14 (s, 3H), 3.39 (s, 2H), 6.34 (d, $J = 16.0$ Hz, 1H), 7.29 (d, $J = 16.0$ Hz, 1H), 7.35-7.43 (m, 2H), 7.55-7.59 (m, 2H). ^13C-NMR (CDCl$_3$, 125 MHz) δ 12.9 (q), 14.1 (q), 25.2 (t), 26.8 (t), 33.1 (t), 35.8 (q), 37.3 (q), 123.1 (d, q: $J_{C-F} = 3.6$ Hz), 123.2 (d, q: $J_{C-F} = 3.6$ Hz), 124.2 (s, q: $J_{C-F} = 271$ Hz), 124.7 (s), 125.0 (d), 128.8 (d), 129.0 (d), 129.4 (d), 130.8 (s, q: $J_{C-F} = 32$ Hz), 139.2 (s), 148.9 (s), 170.6 (s). IR (ATR) 1643, 1156 cm$^{-1}$. MS (EI) $m/z$ 339 (M$^+$, 100%). HRMS (EI) calcd for C$_{19}$H$_{24}$F$_3$NO (M$^+$) 339.1810, found 339.1813.

(4E)-N,N-Dimethyl-3-cyclobutylidene-dodec-4-enamide (7c)

![Chemical structure image]

^1H-NMR (CDCl$_3$, 500 MHz) δ 0.88 (t, $J = 7.5$ Hz, 3H), 1.24-1.39 (m, 10H), 1.96 (quin, $J = 7.5$ Hz, 2H), 2.07 (q, $J = 7.5$ Hz, 2H), 2.66-2.72 (m, 2H), 2.80-2.85 (m, 2H), 2.93 (s, 3H), 3.01 (s, 3H), 3.08 (s, 2H), 5.46 (dt, $J = 7.5$, 16.0 Hz, 1H), 6.03 (d, $J = 16.0$ Hz, 1H). ^13C-NMR (CDCl$_3$, 125 MHz) δ 14.1 (q), 16.1 (t), 22.6 (t), 29.2 (t), 29.7 (t), 29.82 (t), 29.84 (t), 31.8 (t), 33.1 (t), 33.5 (t), 35.6 (q), 37.4 (q), 123.3 (s), 126.5 (d), 127.6 (d), 141.7 (s), 171.3 (s). IR (ATR) 1644, 1138 cm$^{-1}$. MS (EI) $m/z$ 277 (M$^+$), 249 (100%). HRMS (EI) calcd for C$_{18}$H$_{31}$NO (M$^+$) 277.2406, found 277.2402.

(3Z,4E)-N,N-Dimethyl-3-[2’-(tert-butyldimethylsiloxy)ethylidene]-7-phenylhept-4-enamide (Z-7d)

![Chemical structure image]
1H-NMR (CDCl3, 500 MHz) δ 0.06 (s, 6H), 0.89 (s, 9H), 2.44 (q, J = 7.0 Hz, 2H), 2.72 (t, J = 7.0 Hz, 2H), 2.94 (s, 3H), 2.95 (s, 3H), 3.20 (s, 2H), 4.34 (d, J = 6.5 Hz, 2H), 5.37 (t, J = 6.5 Hz, 1H), 5.71 (dt, J = 7.0, 15.5 Hz, 1H), 6.31 (d, J = 15.5 Hz, 1H), 7.14-7.20 (m, 3H), 7.26-7.30 (m, 2H). 13C-NMR (CDCl3, 125 MHz) δ -5.2 (q), 18.3 (s), 25.9 (q), 32.5 (t), 34.6 (t), 35.7 (q), 35.8 (t), 37.4 (q), 60.2 (t), 125.8 (d), 128.3 (d), 128.4 (d), 128.5 (d), 132.2 (d), 132.6 (s), 133.4 (d), 141.8 (s), 170.0 (s). IR (ATR) 1650, 1254, 834 cm⁻¹. MS (ESI) m/z 410 (M⁺+Na, 100%). HRMS (ESI) calcd for C23H37NO2NaSi (M⁺+Na) 410.2491, found 410.2484.

(3E,4E)-N,N-Dimethyl-3-[2’-(tert-butyldimethylsiloxy)ethylidene]-7-phenylhept-4-enamide (E-7d)

(3Z)-N,N-Dimethyl-3-(cyclohexylidenemethyl)-non-3-enamide (7e)

1H-NMR (CDCl3, 400 MHz) δ 0.07 (s, 6H), 0.90 (s, 9H), 2.36-2.44 (m, 2H), 2.67-2.72 (m, 2H), 2.94 (s, 3H), 3.00 (s, 3H), 3.25 (s, 2H), 4.27 (d, J = 6.8 Hz, 2H), 5.57 (dt, J = 6.8, 16.0 Hz, 1H), 5.72 (t, J = 6.8 Hz, 1H), 6.12 (d, J = 16.0 Hz, 1H), 7.14-7.30 (m, 5H). 13C-NMR (CDCl3, 125 MHz) δ -5.2 (q), 18.3 (s), 25.9 (q), 32.5 (t), 34.6 (t), 35.7 (q), 35.8 (t), 37.4 (q), 60.2 (t), 125.8 (d), 128.3 (d), 128.4 (d), 128.5 (d), 132.2 (d), 132.6 (s), 133.4 (d), 141.8 (s), 170.0 (s). IR (ATR) 1647, 1252, 775 cm⁻¹. MS (ESI) m/z 410 (M⁺+Na, 100%). HRMS (ESI) calcd for C23H37NO2NaSi (M⁺+Na) 410.2491, found 410.2482.

1H-NMR (CDCl3, 400 MHz) δ 0.87 (t, J = 6.8 Hz, 3H), 1.21-1.34 (m, 6H), 1.42-1.58 (m, 6H), 1.90-2.03 (m, 4H), 2.10-2.15 (m, 2H), 2.94 (s, 3H), 2.99 (s, 3H), 3.07 (s, 2H), 5.28 (t, J = 6.8 Hz, 1H), 5.47 (s, 1H). 13C-NMR (CDCl3, 125 MHz) δ 14.1 (q), 22.6 (t), 26.6 (t), 27.5 (t), 28.6 (t), 29.0 (t), 29.2 (t), 30.2 (t), 31.6 (t), 35.5 (q), 36.6 (t), 37.8 (q), 43.7 (t), 119.4 (d), 129.7 (d), 130.3 (s), 142.8 (s), 171.3 (s). IR (ATR) 1645, 1393 cm⁻¹. MS (EI) m/z 277 (M⁺, 100%). HRMS (EI) calcd for C18H31NO (M⁺) 277.2406, found 277.2398.
**N,N-Dimethyl-3-(4'-phenylbut-1'-enyl)oct-3-enamide (1E,3Z)-9**

1H-NMR (CDCl3, 600 MHz) δ 0.89 (t, J = 7.2 Hz, 3H), 1.27-1.38 (m, 4H), 2.17 (q, J = 7.2 Hz, 2H), 2.45 (q, J = 7.2 Hz, 2H), 2.72 (t, J = 7.2 Hz, 2H), 2.93 (s, 3H), 2.95 (s, 3H), 3.18 (s, 2H), 5.24 (t, J = 7.2 Hz, 1H), 5.65 (dt, J = 7.2, 15.0 Hz, 1H), 6.42 (d, J = 15.0 Hz, 1H), 7.15-7.19 (m, 3H), 7.25-7.29 (m, 2H). 13C-NMR (CDCl3, 125 MHz) δ 13.9 (q), 22.3 (t), 27.2 (t), 31.8 (t), 35.0 (t), 35.5 (q), 35.9 (t), 37.6 (q), 39.5 (t), 125.8 (d), 126.7 (d), 128.3 (d), 128.5 (d), 129.3 (d), 129.7 (s), 130.7 (d), 141.8 (s), 171.6 (s). IR (ATR) 1644, 1393, 1135 cm⁻¹. MS (EI) m/z 299 (M⁺), 208 (M⁺-Bn, 100%). HRMS (EI) calcd for C20H29NO (M⁺) 299.2249, found 299.2252.

**N,N-Dimethyl-3-(4'-phenylbut-1'-enyl)oct-3-enamide (1E,3E)-9**

1H-NMR (CDCl3, 600 MHz) δ 0.89 (t, J = 7.2 Hz, 3H), 1.28-1.40 (m, 4H), 2.09 (q, J = 7.2 Hz, 2H), 2.39 (q, J = 7.2 Hz, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.94 (s, 3H), 3.00 (s, 3H), 3.22 (s, 2H), 5.49 (dt, J = 7.2, 15.6 Hz, 1H), 5.60 (t, J = 7.2 Hz, 1H), 6.01 (d, J = 15.6 Hz, 1H), 7.15-7.19 (m, 3H), 7.25-7.29 (m, 2H). 13C-NMR (CDCl3, 125 MHz) δ 13.9 (q), 22.4 (t), 28.1 (t), 31.6 (t), 32.3 (t), 34.7 (t), 35.7 (q), 36.0 (t), 37.3 (q), 125.7 (d), 126.6 (d), 128.2 (d), 128.5 (d), 131.7 (s), 133.88 (d), 133.92 (d), 142.0 (s), 170.5 (s). IR (ATR) 1645, 1391, 1135 cm⁻¹. MS (EI) m/z 299 (M⁺), 208 (M⁺-Bn), 72 (100%). HRMS (EI) calcd for C20H29NO (M⁺) 299.2249, found 299.2258.

**N,N-Dimethyl-3-(4'-phenylbut-1'-enyl)oct-3-enamide (1Z,3Z)-9**
$^1$H-NMR (CDCl$_3$, 600 MHz) $\delta$ 0.86 (t, $J = 7.2$ Hz, 3H), 1.25-1.34 (m, 4H), 1.96 (q, $J = 7.2$ Hz, 2H), 2.26-2.32 (m, 2H), 2.66 (t, $J = 7.2$ Hz, 2H), 2.92 (s, 6H), 3.01 (s, 2H), 5.29 (t, $J = 7.2$ Hz, 1H), 5.54 (dt, $J = 7.2$, 10.8 Hz, 1H), 5.83 (d, $J = 10.8$ Hz, 1H), 7.15-7.19 (m, 3H), 7.25-7.29 (m, 2H).

(3Z,4E)-N,N-Dimethyl-3-(2-hydroxyethylidene)-7-phenylhept-4-enamide (10)

To a solution of TBS ether Z-7d (40 mg, 0.10 mmol) in THF (3 ml) was added TBAF (0.30 ml, 0.30 mmol, 1.0 M in THF) at rt and then stirred for 1 h. The reaction mixture was extracted with CH$_2$Cl$_2$, washed with brine, dried over MgSO$_4$, filtered and concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 1 to 1: 0) to give 30 mg (quant.) of 10 as a colorless oil.

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 2.43 (q, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 7.2$ Hz, 2H), 2.95 (s, 3H), 2.96 (s, 3H), 3.20 (s, 2H), 4.27 (d, $J = 6.8$ Hz, 2H), 5.46 (t, $J = 6.8$ Hz, 1H), 5.66 (dt, $J = 7.2$, 16 Hz, 1H), 6.39 (d, $J = 16$ Hz, 1H), 7.12-7.30 (m, 5H). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 34.8 (t), 35.57 (q), 35.61 (t), 37.6 (q), 39.0 (t), 58.2 (t), 125.8 (d), 126.0 (d), 128.2 (d), 128.4 (d), 129.1 (d), 131.4 (d), 132.4 (s), 141.5 (s), 171.1 (s). IR (ATR) 3377, 1627, 1396 cm$^{-1}$. MS (EI) m/z 273 (M$^+$), 72 (100%). HRMS (EI) calcd for C$_{17}$H$_{23}$NO$_2$ (M$^+$) 273.1729, found 273.1730.

(2Z,4E)-3-[2-(N,N-Dimethylamino)-2-oxoethyl]-7-phenylepta,2,4-dienoic acid (11)

To a solution of alcohol 10 (150 mg, 0.55 mmol) in CH$_2$Cl$_2$ (20 ml) was added MnO$_2$ (1.5 g, 17.3 mmol) at rt and then stirred for 1 h. The reaction mixture was filtered and concentrated to afford a crude product, which was used to the next reaction without purification. The resulting aldehyde was dissolved in tert-BuOH: THF: 2-methyl-2-buten (10 ml, 3: 1: 1) and treated with a solution of NaClO$_2$ (373 mg, 3.3 mmol) and NaH$_2$PO$_4$-2H$_2$O (429 mg, 2.8 mmol) in H$_2$O (2 ml) at rt. After being stirred for 3 h, the reaction mixture was extracted with CHCl$_3$, washed with brine, dried over MgSO$_4$, filtered and concentrated to afford a crude product, which was
purified by silica gel column chromatography (MeOH/CHCl₃ = 1: 20) to give 111 mg (70%, 2 steps) of 11 as a pale yellow oil.

1H-NMR (CDCl₃, 500 MHz) δ 2.54 (q, J = 7.0 Hz, 2H), 2.76 (t, J = 7.0 Hz, 2H), 2.95 (s, 3H), 2.97 (s, 3H), 3.39 (s, 2H), 5.62 (s, 1H), 6.12 (dt, J = 7.0, 16 Hz, 1H), 7.15-7.30 (m, 5H), 7.60 (d, J = 16 Hz, 1H). 13C-NMR (CDCl₃, 125 MHz) δ 35.0 (t), 35.2 (t), 35.7 (q), 37.7 (q), 39.4 (t), 116.7 (d), 125.9 (d), 127.1 (d), 128.3 (d), 128.4 (d), 137.7 (q), 138.4 (d), 141.2 (s), 149.6 (s), 169.7 (s), 169.8 (s). MS (EI) m/z 287 (M⁺), 91 (100%). HRMS (EI) calcd for C₁₇H₂₁NO₃ (M⁺) 287.1521, found 287.1522.

**Compound 12**

![Compound 12](image)

To a solution of 1,3-diene 7c (70 mg, 0.25 mmol) in toluene (5 ml) was added N-methyl-maleimide (173 mg, 1.0 mmol) and refluxed for 2 h. The reaction mixture was concentrated to afford a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1: 3 to 1: 1) to give 112 mg (99%) of adduct as a yellow oil.

1H-NMR (CDCl₃, 600 MHz) δ 0.88 (t, J = 7.2 Hz, 3H), 1.22-1.62 (m, 11H), 1.82-2.09 (m, 3H), 2.20-2.26 (m, 1H), 2.32-2.48 (m, 3H), 2.77-2.84 (m, 1H), 2.87 (s, 3H), 2.95 (s, 3H), 3.17 (d, J = 16.2 Hz, 1H), 3.27 (d, J = 16.2 Hz, 1H), 3.33 (t, J = 7.8 Hz, 1H), 3.51 (d, J = 7.8 Hz, 1H), 5.32 (d, J = 2.4 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H). 13C-NMR (CDCl₃, 150 MHz) δ 14.0 (q), 16.3 (t), 16.3 (t), 22.5 (t), 27.5 (t), 28.0 (t), 29.1 (t), 29.4 (t), 31.4 (t), 31.7 (t), 33.9 (t), 35.2 (q), 35.8 (d), 37.4 (q), 39.2 (t), 43.0 (d), 45.2 (s), 50.4 (d), 126.2 (d), 127.4 (d), 128.1 (d), 128.7 (d), 131.8 (s), 141.2 (s), 170.5 (s), 176.2 (s), 177.3 (s). IR (ATR) 1704, 1645, 1381 cm⁻¹. MS (EI) m/z 450 (M⁺, 100%). HRMS (EI) calcd for C₂₈H₃₈N₂O₃ (M⁺) 450.2882, found 450.2884.