Supporting Information

Remarkably Selective Formation of Allenyl and Dienyl Alcohols via Ni-Catalyzed Coupling Reaction of Conjugated Enyne, Aldehyde, and Organozinc Reagents

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General procedures

Reaction employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silicagel plates with UV indicator (Merck Silica gel 60F254). Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL JNM-AL400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with JEOL JMS-700N. Distillation were carried out in a Kugelrohr apparatus (SIBATA glass tube oven GTO-350RG). Boiling points are meant to refer to the oven temperature (±1 °C).

Solvents and Reagents

Tetrahydrofuran, N,N-dimethylacetamide (DMA), toluene, and n-hexane were dried and distilled from benzophenone-sodium immediately prior to use under nitrogen atmosphere. Dichloromethane was dried and distilled from CaH2 immediately prior to
use under nitrogen atmosphere. Dimethylzinc, diethylzinc (1 M hexane, KANTO Kagaku), Ni(cod)$_2$ (KANTO Kagaku), P(n-Bu)$_3$, PPh$_3$, PPh$_2$Cy, IPr, SIMes·HCl, IMes, IrBu, and ICy·HCl (Tokyo Kasei Kogyo Co., Ltd), t-BuOK (99.99%), PCy$_3$, P(t-Bu)$_3$·HBF$_4$, SIPr, and AuCl (Aldrich) were used without further purification. IPr·HCl was furnished by the known procedures.$^{[1]}$ Dibenzylzinc and diphenylzinc were prepared from ZnCl$_2$ with 2-equivalents of benzylmagnesium chloride and phenylmagnesium bromide, respectively. t-BuZnBr (Aldrich) were used without further purification. Benzaldehyde, p-anisaldehyde, mesitylaldehyde, hexanal, cyclohexane-carbaldehyde, and pivalaldehyde (Tokyo Kasei Kogyo Co., Ltd) were purchased and distilled via Kugelrohl apparatus under reduced pressure prior to use. p-Chlorobenzaldehyde (Tokyo Kasei Kogyo Co., Ltd) was purchased and used without further purification. N,N-Diisopropylethylamine (Tokyo Kasei Kogyo Co., Ltd) and 2-Methyl-1-hexen-3-yne (Aldrich) were purchased and distilled via Kugelrohl apparatus under reduced pressure prior to use. Other conjugated enynes were prepared by Sonogashira cross-coupling of terminal alkyne and alkenylbromide. Spectral data of the enynes were consistent with literature data.$^{[2,3]}$ The NHCs employed in this paper are as follows: IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; SIPr, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene; IPr·HCl, 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazolium Chloride; IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; SIMes·HCl, 1,3-bis(2,4,6-trimethylphenyl)imidazolinium Chloride; ICy·HCl, 1,3-dicyclohexylimidazolium Chloride; IrBu, 1,3-di-t-butylimidazol-2-ylidene.

**Preparation of diphenylzinc and dibenzylzinc reagents**

A 50 mL Schlenk flask equipped with a rubber septum was charged with ZnCl$_2$ solution (2 mL of 1 M ethyl ether, 2 mmol) under nitrogen atmosphere. A solution of phenyl magnesium bromide (4 mL of 1 M THF, 4 mmol) or benzyl magnesium chloride (4.5 mL of 0.9 M THF, 4 mmol) was added to the ZnCl$_2$ solution via syringe at 0 °C, and then was diluted with THF solvent to 0.25 M solution. The reaction mixture was
stirred at room temperature for 12 hours. Thus, diphenylzinc and dibenzylzinc reagents were freshly prepared prior to use.

**Typical procedure for the three-component coupling reaction of aldehydes, en-yne, and Me$_2$Zn to give allenyl alcohol** (entry 3, Table 1): The reaction was undertaken as follows: Into a nitrogen-purged flask with Ni(cod)$_2$ (13.8 mg, 0.05 mmol) was introduced successively THF (1.5 mL), benzaldehyde (53.1 mg, 0.5 mmol), 2-methyl-1-hexen-3-yne (113 mg, 1.2 mmol), and dimethylzinc (1.2 mL of 1 M hexanes, 1.2 mmol) via syringe. The homogeneous mixture was stirred at room temperature for 24 h, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, sat. NaHCO$_3$, and brine, and then dried (MgSO$_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 20/1, v/v) to give 1a (71.4 mg, 66%) in 83:17 ratio.

**3,5-dimethyl-1-phenylhepta-3,4-dien-1-ol** (1a): a mixture of diastereomers in a ratio of 83:17  
$\text{R}_f$ = 0.50 (hexane-EtOAc, 4:1)  
IR (neat): 3356 (m), 3065 (w), 3030 (w), 2964 (s), 2897 (s), 1750 (w) cm$^{-1}$.  
$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 0.96 (t, $J$ = 7.3 Hz, 3 H), 1.66 (s, 3 H), 1.70 (s, 3 H), 1.92 (q, $J$ = 7.3 Hz, 2 H), 2.33-2.38 (m, 3 H), 4.77-4.81 (m, 1 H), 7.22-7.38 (m, 5 H).  
$^{13}$C NMR (100 MHz, CDCl$_3$, major isomer): $\delta$ 12.3, 19.5, 19.9, 27.4, 44.9, 72.1, 95.9, 101.5, 125.7, 127.2, 128.1, 143.8, 198.6.  
$^1$H NMR (400 MHz, CDCl$_3$, minor isomer): $\delta$ 0.98 (t, $J$ = 7.3 Hz, 3 H), 1.65 (s, 3 H), 1.70 (s, 3 H), 1.94 (q, $J$ = 7.3 Hz, 2 H), 2.33-2.41 (m, 3 H), 4.77-4.83 (m, 1 H), 7.22-7.38 (m, 5 H).  
$^{13}$C NMR (100 MHz, CDCl$_3$, minor isomer): $\delta$ 12.4, 19.2, 19.9, 27.5, 44.8, 72.1, 96.0, 101.5, 125.8, 127.2, 128.1, 143.8, 198.6.  
HRMS: $m/z$ (M$^+$) calcd for C$_{15}$H$_{20}$O: 216.1514; found 216.1496.

**1-(4-methoxyphenyl)-3,5-dimethylhepta-3,4-dien-1-ol** (1b): a mixture of
diastereomers in a ratio of 75:25

R_f = 0.35 (hexane-EtOAc, 4:1)

IR (neat): 3452 (m), 3040 (w), 2976 (s), 2939 (s), 2837 (s), 1751 (w), 1612 (s), 1514 (s), 1456 (s), 1248 (s), 1038 (s), 831 (m) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\) 0.96 (t, \(J = 7.3\) Hz, 3 H), 1.65 (s, 3 H), 1.69 (s, 3 H), 1.92 (q, \(J = 7.3\) Hz, 2 H), 2.28-2.40 (m, 3 H), 3.80 (s, 3 H), 4.72-4.77 (m, 1 H), 6.85-7.30 (m, 4 H).

\(^1\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta\) 12.3, 19.5, 19.9, 27.4, 44.8, 55.2, 71.8, 95.9, 101.4, 113.6, 127.0, 136.1, 158.8, 198.6.

\(^1\)H NMR (400 MHz, CDCl\(_3\), minor isomer): \(\delta\) 0.98 (t, \(J = 7.6\) Hz, 3 H), 1.65 (s, 3 H), 1.69 (s, 3 H), 1.93 (q, \(J = 7.6\) Hz, 2 H), 2.28-2.40 (m, 3 H), 3.80 (s, 3 H), 4.72-4.77 (m, 1 H), 6.85-7.30 (m, 4 H).

\(^1\)C NMR (100 MHz, CDCl\(_3\), minor isomer): \(\delta\) 12.4, 19.2, 19.9, 27.5, 44.7, 55.2, 71.8, 96.1, 101.7, 113.6, 127.0, 136.1, 158.8, 198.4.

HRMS: \(m/z\) (M\(^+\)) calcd for C\(_{16}\)H\(_{22}\)O\(_2\): 246.1620; found 246.1606.

1-(4-chlorophenyl)-3,5-dimethylhepta-3,4-dien-1-ol (1c): a mixture of diastereomers in a ratio of 83:17

R_f = 0.45 (hexane-EtOAc, 4:1)

IR (neat): 3435 (m), 3065 (w), 3030 (w), 2964 (s), 2930 (s), 2901 (s), 1718 (m) 1493 (s), 1445 (w), 1092 (s), 1015 (s), 829 (m), 779 (w) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\) 0.96 (t, \(J = 7.3\) Hz, 3 H), 1.66 (s, 3 H), 1.70 (s, 3 H), 1.93 (q, \(J = 7.3\) Hz, 2 H), 2.28-2.41 (m, 3 H), 4.75-4.79 (m, 1 H), 7.28-7.33 (m, 4 H).

\(^1\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta\) 12.3, 19.5, 19.9, 27.4, 44.9, 71.5, 95.7, 101.8, 127.1, 128.3, 132.8, 142.3, 198.6.

\(^1\)H NMR (400 MHz, CDCl\(_3\), minor isomer): \(\delta\) 0.98 (t, \(J = 7.6\) Hz, 3 H), 1.65 (s, 3 H), 1.69 (s, 3 H), 1.94 (q, \(J = 7.6\) Hz, 2 H), 2.28-2.41 (m, 3 H), 4.75-4.79 (m, 1 H), 7.28-7.33 (m, 4 H).

\(^1\)C NMR (100 MHz, CDCl\(_3\), minor isomer): \(\delta\) 12.4, 19.2, 19.9, 27.5, 44.8, 71.5, 95.8, 102.0, 127.1, 128.2, 132.8, 142.3, 198.6.

HRMS: \(m/z\) (M\(^+\)) calcd for C\(_{16}\)H\(_{22}\)ClO: 250.1124; found 250.1111.
1-mesityl-3,5-dimethylhepta-3,4-dien-1-ol (1d): a mixture of diastereomers in a ratio of >96:4

R_f = 0.60 (hexane-EtOAc, 4:1)

IR (neat): 3445 (m), 3005 (w), 3030 (w), 2964 (s), 2932 (s), 2874 (s), 1722 (w) 1612 (w), 1445 (s), 1373 (m), 1038 (m), 1016 (m), 851 (s), 785 (w) cm⁻¹.

¹H NMR (400 MHz, CDCl₃, major isomer): δ 0.99 (t, J = 7.3 Hz, 3 H), 1.71 (s, 3 H), 1.73 (s, 3 H), 1.96 (q, J = 7.3 Hz, 2 H), 2.08 (d, J = 2.4 Hz, 1 H), 2.20 (dd, J = 3.4, 15.1 Hz, 1 H), 2.23 (s, 3 H), 2.39 (s, 6 H), 2.59 (dd, J = 10.2, 15.1 Hz, 1 H), 5.24 (ddd, J = 2.4, 3.4, 10.2 Hz, 1 H), 6.79 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃, major isomer): δ 12.4, 19.5, 19.7, 20.7, 20.7, 27.5, 41.3, 69.6, 96.4, 101.4, 129.9, 135.8, 136.1, 198.5.

1H NMR (400 MHz, CDCl₃, minor isomer): δ 1.01 (t, J = 7.3 Hz, 3 H), 1.70 (s, 3 H), 1.73 (s, 3 H), 1.95 (q, J = 7.3 Hz, 2 H), 2.08 (d, J = 2.4 Hz, 1 H), 2.20 (dd, J = 3.4, 15.1 Hz, 1 H), 2.23 (s, 3 H), 2.38 (s, 6 H), 2.59 (dd, J = 10.2, 15.1 Hz, 1 H), 5.24 (ddd, J = 2.4, 3.4, 10.2 Hz, 1 H), 6.79 (s, 2 H).

¹²C NMR (100 MHz, CDCl₃, minor isomer): δ 12.4, 19.3, 19.7, 20.7, 20.7, 27.5, 41.0, 69.6, 96.4, 101.4, 129.8, 135.8, 136.1, 198.5.

HRMS: m/z (M⁺) calcd for C₁₈H₂₆O: 258.1984; found 258.1996.

8,10-dimethyldodeca-8,9-dien-6-ol (1e): a mixture of diastereomers in a ratio of 83:17

R_f = 0.70 (hexane-EtOAc, 4:1)

IR (neat): 3441 (m), 2959 (s), 2932 (s), 2860 (s), 1715 (m) 1456 (m), 1373 (m), 1086 (w), 1016 (w) cm⁻¹.

¹H NMR (400 MHz, CDCl₃, major isomer): δ 0.89 (t, J = 7.3 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.26-1.50 (m, 8 H), 1.68 (s, 3 H), 1.68 (s, 3 H), 1.94 (q, J = 7.3 Hz, 2 H), 1.99-2.11 (m, 3 H), 3.67-3.73 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, major isomer): δ 12.3, 14.0, 19.6, 20.0, 22.6, 25.5, 27.4, 32.0, 36.8, 42.8, 69.7, 96.2, 101.1 198.3.

¹H NMR (400 MHz, CDCl₃, minor isomer): δ 0.89 (t, J = 7.3 Hz, 3 H), 0.99 (t, J = 7.3 Hz, 3 H), 1.26-1.50 (m, 8 H), 1.68 (s, 3 H), 1.68 (s, 3 H), 1.94 (q, J = 7.3 Hz, 2 H), 1.99-2.11 (m, 3 H), 3.67-3.73 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, minor isomer): δ 12.4, 14.0, 19.3, 20.0, 22.6, 25.5, 27.5, 32.0, 36.8, 42.6, 69.7, 96.3, 101.1 198.2.
**1-cyclohexyl-3,5-dimethylhepta-3,4-dien-1-ol (1f):** a mixture of diastereomers in a ratio of 88:12

\[ R_f = 0.70 \text{ (hexane-EtOAc, 4:1)} \]

IR (neat): 3474 (m), 2964 (m), 2928 (s), 2853 (s), 1726 (w) 1450 (m), 1371 (m), 1101 (w), 1086 (w), 893 (w) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \( \delta 0.98 \text{ (t, } J = 7.3 \text{ Hz, 3 H)}, 1.02-1.30 \text{ (m, 5 H)}, 1.38 \text{ (dm, } J = 5.4 \text{ Hz, 1 H)}, 1.64-1.79 \text{ (m, 5 H)}, 1.68 \text{ (s, 3 H)}, 1.68 \text{ (s, 3 H)}, 1.84 \text{ (br s, 1 H)}, 1.94 \text{ (q, } J = 7.3 \text{ Hz, 2 H)}, 2.00 \text{ (dd, } J = 9.5, 14.6 \text{ Hz, 1 H)}, 2.13 \text{ (dd, } J = 3.2, 14.6 \text{ Hz, 1 H}), 3.47 \text{ (ddd, } J = 3.2, 5.4, 9.5 \text{ Hz, 1 H})

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), major isomer): \( \delta 12.4, 19.6, 19.9, 26.3, 26.4, 26.6, 27.4, 28.2, 29.3, 39.8, 43.1, 73.5, 96.4, 101.0, 198.3 \)

\(^1\)H NMR (400 MHz, CDCl\(_3\), minor isomer): \( \delta 0.98 \text{ (t, } J = 7.3 \text{ Hz, 3 H)}, 1.02-1.30 \text{ (m, 5 H)}, 1.34-1.43 \text{ (m, 1 H)}, 1.64-1.79 \text{ (m, 5 H)}, 1.68 \text{ (s, 3 H)}, 1.68 \text{ (s, 3 H)}, 1.87 \text{ (br s, 1 H)}, 1.94 \text{ (q, } J = 7.3 \text{ Hz, 2 H)}, 2.00 \text{ (dd, } J = 9.8, 14.9 \text{ Hz, 1 H)}, 2.15 \text{ (dd, } J = 2.9, 14.9 \text{ Hz, 1 H}), 3.49 \text{ (ddm, } J = 2.9, 9.8 \text{ Hz, 1 H})

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), minor isomer): \( \delta 12.5, 19.3, 19.9, 26.3, 26.4, 26.6, 27.5, 28.1, 29.3, 39.6, 43.1, 73.5, 96.5, 101.3, 198.3 \)

HRMS: \( m/z \) (M\(^+\)) calcd for C\(_{15}\)H\(_{26}\)O: 222.1984; found 222.1971.

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**2,2,5,7-tetramethylnona-5,6-dien-3-ol (1g):** a mixture of diastereomers in a ratio of 91:9

\[ R_f = 0.70 \text{ (hexane-EtOAc, 4:1)} \]

IR (neat): 3558 (m), 2963 (m), 2910 (s), 2872 (s), 1718 (w) 1460 (m), 1364 (m), 1072 (w), 1009 (w), 897 (w) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), major isomer): \( \delta 0.99 \text{ (t, } J = 7.3 \text{ Hz, 3 H)}, 1.00 \text{ (s, 9 H)}, 1.59 \text{ (s, 3 H)}, 1.66 \text{ (s, 3 H)}, 1.83 \text{ (q, } J = 7.3 \text{ Hz, 2 H)}, 2.01 \text{ (dd, } J = 10.5, 14.4 \text{ Hz, 1 H)}, 2.02 \text{ (m, 1 H)}, 2.10 \text{ (dd, } J = 2.0, 14.4 \text{ Hz, 1 H}), 3.45 \text{ (ddm, } J = 2.0, 10.5 \text{ Hz, 1 H})

\(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\), major isomer): \( \delta 12.3, 19.7, 19.7, 25.8, 25.9, 27.4, 34.3, 37.7, 96.8, 101.1, 198.3 \)

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), minor isomer): \( \delta 0.95 \text{ (s, 9 H)}, 0.99 \text{ (t, } J = 7.3 \text{ Hz, 3 H)}, 1.60 \text{ (s, 3 H)}, 1.66 \text{ (s, 3 H)}, 1.83 \text{ (q, } J = 7.3 \text{ Hz, 2 H)}, 1.95-2.12 \text{ (m, 3H)}, 3.46-3.49 \text{ (m, 1H)} \)
$^{13}$C NMR (100 MHz, CDCl$_3$, minor isomer): $\delta$ 12.5, 19.7, 19.7, 25.7, 25.8, 27.5, 34.4, 
37.4, 96.8, 101.1, 198.3.
HRMS: $m/z$ (M$^+$) calcd for C$_{13}$H$_{24}$O: 196.1827; found 196.1826.

3,5-dimethyl-1-phenylnona-3,4-dien-1-ol (1h): a mixture of diastereomers in a ratio of 83:17
$R_f = 0.55$ (hexane-EtOAc, 4:1)
IR (neat): 3410 (m), 3074 (w), 3032 (w), 2953 (s), 2930 (s), 2860 (s), 1718 (w) 1452
(m), 1369 (m), 1043 (m), 1026 (m), 756 (m), 700 (m) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 0.89 (t, $J = 7.3$ Hz, 3 H), 1.28-1.38 (dm, $J$
= 7.3 Hz, 4 H), 1.65 (s, 3 H), 1.69 (s, 3 H), 1.91 (t, $J = 7.3$ Hz, 2 H), 2.34-2.36 (dm, $J$
= 7.8 Hz, 2 H), 4.77-4.81 (dm, $J = 7.8$ Hz, 1 H), 7.22-7.38 (m, 5 H).
$^{13}$C NMR (100 MHz, CDCl$_3$, major isomer): $\delta$ 13.9, 19.5, 19.8, 22.3, 29.8, 34.1, 44.9,
72.1, 95.0, 99.7, 125.8, 127.2, 128.1, 143.8, 199.1.

$^1$H NMR (400 MHz, CDCl$_3$, minor isomer): $\delta$ 0.90 (t, $J = 7.3$ Hz, 3 H), 1.28-1.38 (dm, $J$
= 7.6 Hz, 4 H), 1.62 (s, 3 H), 1.68 (s, 3 H), 1.90 (t, $J = 7.6$ Hz, 2 H), 2.34-2.36 (dm, $J$
= 7.8 Hz, 2 H), 4.77-4.81 (dm, $J = 7.8$ Hz, 1 H), 7.22-7.38 (m, 5 H).

$^{13}$C NMR (100 MHz, CDCl$_3$, minor isomer): $\delta$ 14.0, 19.6, 19.8, 22.3, 29.9, 34.2, 44.7,
72.2, 95.1, 99.9, 125.8, 127.2, 128.1, 143.8, 199.1.
HRMS: $m/z$ (M$^+$) calcd for C$_{17}$H$_{24}$O: 244.1827; found 244.1830.

3-methyl-1,5-diphenylhexa-3,4-dien-1-ol (1i): a mixture of diastereomers in a ratio of 67:33
$R_f = 0.60$ (hexane-EtOAc, 4:1)
IR (neat): 3395 (m), 3090 (m), 3028 (m), 2980 (m), 2903 (m), 2864 (m), 1950 (w),
1597 (m) 1493 (s), 1445 (s), 1047 (m), 1026 (m), 760 (s), 696 (s) cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 1.82 (s, 3 H), 2.02 (s, 3 H), 2.13 (br s, 1
H), 2.49 (dd, $J = 5.1$, 15.1 Hz, 1 H), 2.53 (dd, $J = 8.1$, 15.1 Hz, 1 H), 4.83 (dd, $J = 5.1$
8.1 Hz, 1 H), 7.12-7.36 (m, 10 H).
$^{13}$C NMR (100 MHz, CDCl$_3$, major isomer): $\delta$ 17.3, 19.3, 44.3, 72.4, 98.3, 100.4, 125.5,
125.8, 126.3, 127.4, 128.2, 128.3, 137.5, 143.7, 202.0.
$^1$H NMR (400 MHz, CDCl$_3$, minor isomer): $\delta$ 1.82 (s, 3 H), 1.98 (s, 3 H), 2.16 (br s, 1
H), 2.55 (dd, $J = 6.8$, 14.4 Hz, 2 H), 4.84 (t, $J = 6.8$ Hz, 1 H), 7.12-7.36 (m, 10 H).
$^{13}$C NMR (100 MHz, CDCl$_3$, minor isomer): $\delta$ 17.1, 19.3, 44.3, 72.4, 98.0, 100.4, 125.5, 125.8, 126.3, 127.3, 128.2, 128.2, 137.8, 143.7, 202.0.
HRMS: $m/z$ (M$^+$) calced for C$_{19}$H$_{20}$O: 264.1514; found 264.1517.

3-methyl-5-(trimethylsilyl)-1-phenylhexa-3,4-dien-1-ol (1j): a mixture of diastereomers in a ratio of 50:50
$R_f = 0.60$ (hexane-EtOAc, 4:1)
IR (neat): 3447 (m), 3065 (w), 2957 (m), 2899 (m), 2860 (w), 1940 (m) 1713 (m), 1450 (m), 1248 (s), 1047 (m), 839 (m), 754 (m), 700 (m) cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$, one isomer): $\delta$ 0.07 (s, 9 H), 1.66 (s, 3 H), 1.70 (s, 3 H), 2.29-2.39 (m, 2 H), 2.31 (dm, $J = 4.4$ Hz, 1 H), 4.75 (dm, $J = 4.4$ Hz, 1 H), 7.24-7.40 (m, 5 H).
$^{13}$C NMR (100 MHz, CDCl$_3$, one isomer): $\delta$ -1.8, 16.1, 18.7, 44.8, 71.8, 89.2, 91.8, 125.9, 127.4, 128.3, 144.0, 204.6.
$^1$H NMR (400 MHz, CDCl$_3$, the other isomer): $\delta$ 0.09 (s, 9 H), 1.64 (s, 3 H), 1.67 (s, 3 H), 2.29-2.39 (m, 2 H), 2.31 (dm, $J = 4.6$ Hz, 1 H), 4.75 (dm, $J = 4.6$ Hz, 1 H), 7.24-7.40 (m, 5 H).
$^{13}$C NMR (100 MHz, CDCl$_3$, the other isomer): $\delta$ -1.7, 15.8, 19.0, 44.1, 72.4, 89.4, 92.2, 125.8, 127.3, 128.3, 144.0, 204.3.
HRMS: $m/z$ (M$^+$) calced for C$_{16}$H$_{24}$OSi: 260.1596; found 260.1591.

5-ethyl-3-methyl-1-phenylhepta-3,4-dien-1-ol (1k)
$R_f = 0.50$ (hexane-EtOAc, 4:1)
IR (neat): 3379 (m), 3063 (w), 3030 (w), 2964 (s), 2932 (s), 2876 (s), 1717 (w) 1493 (w), 1454 (s), 1373 (m), 1028 (m), 756 (m), 700 (m) cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.98 (t, $J = 7.6$ Hz, 6 H), 1.72 (s, 3 H), 1.95 (q, $J = 7.6$ Hz, 4 H), 2.37-2.40 (br s, 1 H), 2.38 (d, $J = 6.6$ Hz, 2 H) 4.82 (t, $J = 6.6$ Hz, 1 H), 7.24-7.39 (m, 5 H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 12.4, 12.5, 20.0, 26.0, 26.0, 45.0, 72.2, 98.2, 108.5, 125.7, 127.1, 128.1, 143.9, 197.8.
HRMS: $m/z$ (M$^+$) calced for C$_{16}$H$_{22}$O: 230.1671; found 230.1671.

3-methyl-1,5-diphenylhepta-3,4-dien-1-ol (1l): a mixture of diastereomers in a ratio of
IR (neat): 3410 (m), 3028 (m), 2964 (m), 2910 (m), 2874 (m), 1950 (w), 1597 (m), 1493 (s), 1454 (s), 1367 (m), 1055 (m), 1030 (m), 754 (s), 696 (s) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$, one isomer): $\delta$ 1.08 (t, $J = 7.3$ Hz, 3 H), 1.85 (s, 3 H), 2.37 (br s, 1 H), 2.39 (q, $J = 7.3$ Hz, 2 H), 2.53 (d, $J = 6.1$ Hz, 2 H), 4.86 (t, $J = 6.1$ Hz, 1 H), 7.14-7.37 (m, 10 H).

$^{13}$C NMR (100 MHz, CDCl$_3$, one isomer): $\delta$ 11.5, 18.4, 22.3, 43.6, 71.4, 99.4, 106.4, 124.7, 124.8, 125.3, 126.3, 127.2, 136.7, 142.7, 200.5.

$^1$H NMR (400 MHz, CDCl$_3$, the other isomer): $\delta$ 1.09 (t, $J = 7.3$ Hz, 3 H), 1.85 (s, 3 H), 2.37 (br s, 1 H), 2.41 (q, $J = 7.3$ Hz, 2 H), 2.53 (d, $J = 6.1$ Hz, 2 H), 4.86 (t, $J = 6.1$ Hz, 1 H), 7.14-7.37 (m, 10 H).

$^{13}$C NMR (100 MHz, CDCl$_3$, the other isomer): $\delta$ 11.7, 18.4, 22.3, 43.4, 71.4, 99.1, 106.6, 124.7, 124.8, 125.3, 126.3, 127.2, 136.3, 142.7, 200.3.

HRMS: $m/z$ (M$^+$) calcd for C$_{20}$H$_{22}$O: 278.1671; found 278.1668.

**Typical procedure for the three-component coupling reaction of aldehydes, en-yne, and Me$_2$Zn to give dienyl alcohol** (entry 1, Table 6): The reaction was undertaken as follows: Into a nitrogen-purged flask with Ni(cod)$_2$ (13.8 mg, 0.05 mmol) and IPr (19.5 mg, 0.05 mmol) was introduced successively n-hexane (1.5 mL), benzaldehyde (127.3 mg, 1.2 mmol), 2-methyl-1-hexen-3-yne (47.1 mg, 0.5 mmol), and dimethylzinc (1.2 mL of 1M hexanes, 1.2 mmol) via syringe. The homogeneous mixture was stirred at 50 °C for 24 h, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, sat. NaHCO$_3$, and brine, and then dried (MgSO$_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 20/1, v/v) to give 2a (88.7 mg, 82%) in 97:3 ratio.

*(E)-2-ethyl-3,4-dimethyl-1-phenylpenta-2,4-dien-1-ol (2a):* a mixture of regioisomers in a ratio of 97:3

IR (neat): 3409 (br), 2964 (s), 2932 (s), 2873 (s), 1691 (w), 1630 (w), 1448 (s) 1371 (w), 1028 (s), 1003 (m), 895 (m), 748 (m), 700 (m) cm$^{-1}$.
\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\ 0.81\ (t, J = 7.3\ Hz, 3\ H), 1.78\ (s, 1H), 1.85\ (t, J = 1.5\ Hz, 3\ H), 1.87\ (s, 3\ H), 1.94\ (dq, J = 7.3, 14.0\ Hz, 1\ H), 2.13\ (dq, J = 7.3, 14.0\ Hz, 1\ H), 4.71\ (dq, J = 0.98, 1.5\ Hz, 1\ H), 4.88\ (dq, J = 0.98, 1.5\ Hz, 1\ H), 5.77\ (s, 1H), 7.21-7.39\ (m, 5\ H).

\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta\ 15.8, 18.4, 22.1, 22.2, 72.7, 111.8, 125.7, 126.8, 128.2, 136.2, 137.1, 143.3, 147.7.

HRMS: \(m/z\ (M^+)\) calcd for C\(_{15}\)H\(_{20}\)O: 216.1514; found: 216.1512.

NOE experimental data of product 2a (major isomer)

\((E)-2\text{-ethyl-1-(4-methoxyphenyl)-3,4-dimethylpenta-2,4-dien-1-ol (2b)\:}\) a mixture of regioisomers in a ratio of 95:5
\(R_f = 0.35\) (hexane-EtOAc, 4:1)
IR (neat): 3422 (br), 2936 (s), 2914 (s), 2874 (w), 1612 (m), 1510 (s), 1443 (w), 1248 (w), 1171 (m), 1038 (m), 895 (w), 833 (w) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\ 0.83\ (t, J = 7.3\ Hz, 3\ H), 1.84\ (t, 1.5\ Hz, 3\ H), 1.84\ (s, 3H), 1.96\ (dq, J = 7.3, 14.0\ Hz, 1\ H), 2.01\ (s, 1H), 2.12\ (dq, J = 7.3, 14.0\ Hz, 1\ H), 3.79\ (s, 3 H), 4.70\ (dq, J = 0.98, 1.5 Hz, 1 H), 4.88\ (dq, J = 0.98, 1.5 Hz, 1 H), 5.71\ (s, 1 H), 6.83-6.89\ (m, 2 H), 7.26-7.32\ (m, 2 H).

\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta = 15.8, 18.2, 22.0, 22.1, 55.1, 72.2, 111.6, 113.5, 126.8, 135.3, 136.1, 136.5, 147.7, 158.4.

HRMS: \(m/z\ (M^+)\) calcd for C\(_{16}\)H\(_{22}\)O\(_2\): 246.1620; found: 246.1621.

\((E)-1-(4-chlorophenyl)-2\text{-ethyl-3,4-dimethylpenta-2,4-dien-1-ol (2c)\:}\) a mixture of regioisomers in a ratio of 95:5
\(R_f = 0.45\) (hexane-EtOAc, 4:1)
IR (neat): 3402 (br), 3074 (w), 2966 (s), 2934 (s), 2973 (s), 1631 (m) 1489 (s), 1448 (m), 1091 (s), 1014 (s), 897 (m), 783 (m) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\ 0.81\ (t, J = 7.3\ Hz, 3\ H), 1.85\ (t, J = 1.5\ Hz, 3\ H), 1.87\ (s, 3\ H), 1.94\ (dq, J = 7.3, 14.0\ Hz, 1\ H), 2.13\ (dq, J = 7.3, 14.0\ Hz, 1\ H), 4.71\ (dq, J = 0.98, 1.5\ Hz, 1\ H), 4.88\ (dq, J = 0.98, 1.5\ Hz, 1\ H), 5.77\ (s, 1H), 7.21-7.39\ (m, 5\ H).

\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta\ 15.8, 18.4, 22.1, 22.2, 72.7, 111.8, 125.7, 126.8, 128.2, 136.2, 137.1, 143.3, 147.7.

HRMS: \(m/z\ (M^+)\) calcd for C\(_{15}\)H\(_{20}\)O: 216.1514; found: 216.1512.
(E)-2-ethyl-1-mesityl-3,4-dimethylpenta-2,4-dien-1-ol (2d): a mixture of regioisomers in a ratio of >99:1
R_f = 0.60 (hexane-EtOAc, 4:1)
IR (neat): 3418 (br), 3074 (w), 2968 (s), 2934 (s), 2871 (s), 1610 (m), 1447 (s), 1036 (s), 853 (m), 799 (m) cm\(^{-1}\).
\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\) 0.86 (t, \(J = 7.3\) Hz, 3 H), 1.60 (s, 3 H), 1.81 (s, 3 H), 2.21 (dq, \(J = 7.3, 14.6\) Hz, 1 H), 2.23 (dq, \(J = 7.3, 14.6\) Hz, 1 H), 2.24 (s, 1H), 2.25 (s, 3 H), 2.37 (s, 6 H), 4.65 (m, 1 H), 4.84 (m, 1 H), 5.88 (s, 1 H), 6.81 (s, 2 H).
\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta\) 16.0, 18.3, 20.7, 21.0, 22.2, 33.4, 71.4, 111.2, 130.1, 135.1, 136.2, 136.4, 136.4, 136.7, 148.5.
HRMS: \(m/z\) (M\(^+\)) calcd for C\(_{18}\)H\(_{26}\)O: 258.1984; found: 250.1988.

(E)-4-ethyl-2,3-dimethyldeca-1,3-dien-5-ol (2e): a mixture of regioisomers in a ratio of 97:3
R_f = 0.70 (hexane-EtOAc, 4:1)
IR (neat): 3368 (br), 2961 (s), 2934 (s), 2873 (s), 2860 (s) 1629 (m), 1456 (m), 1371 (m), 895 (s), 735 (s) cm\(^{-1}\).
\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \(\delta\) 0.89 (m, 3 H), 1.02 (t, \(J = 7.3\) Hz, 3 H), 1.21-1.72 (m, 8 H), 1.57 (s, 1 H) 1.75 (s, 3 H), 1.80 (t, \(J = 1.5\) Hz, 3 H), 2.04 (dq, \(J = 7.3, 14.0\) Hz, 1 H), 2.15 (dq, \(J = 7.3, 14.0\) Hz, 1 H), 4.56 (dd, \(J =5.9, 8.3, 1\) H ), 4.64 (dq, \(J = 0.98, 1.5\) Hz, 1 H), 4.84 (dq, \(J = 0.98, 1.5\) Hz, 1 H).
\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer): \(\delta\) 13.9, 16.1, 17.7, 21.2, 22.1, 22.6, 25.8, 31.8, 35.8, 71.7, 111.3, 135.3, 136.5, 148.0.
HRMS: \(m/z\) (M\(^+\)) calcd for C\(_{14}\)H\(_{26}\)O: 210.1984; found: 210.1983.
(E)-1-cyclohexyl-2-ethyl-3,4-dimethylpenta-2,4-dien-1-ol (2f): a mixture of regioisomers in a ratio of 93:7

R$_f$ = 0.70 (hexane-EtOAc, 4:1)

IR (neat): 3443 (br), 2928 (s), 2853 (s), 1703 (m), 1631 (s) 1371 (w), 1450 (s) 1371 (w), 1001 (m), 893 (m), 790 (w) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 0.78-1.04 (m, 2 H), 1.03 (t, $J$ = 7.3 Hz, 3 H), 1.10-1.32 (m, 3 H), 1.35-1.75 (m, 6 H), 1.76 (s, 3 H), 1.82 (t, $J$ = 1.5 Hz, 3 H), 2.02 (dq, $J$ = 7.3, 14.0 Hz, 1 H), 2.12 (s, 1H), 2.14 (dq, $J$ = 7.3, 14.0 Hz, 1 H), 4.21 (d, $J$ = 9.8, 1 H), 4.65 (dq, $J$ = 0.98, 1.5 Hz), 4.85 (dq, $J$ = 0.98, 1.5 Hz, 1 H).

$^{13}$C NMR (100 MHz, CDCl$_3$, major isomer): $\delta$ 16.2, 18.2, 21.6, 22.2, 26.0, 26.1, 26.5, 29.1, 30.2, 42.2, 76.4, 111.4, 135.1, 136.9, 148.2.

HRMS: m/z (M$^+$) calcd for C$_{15}$H$_{26}$O: 222.1984; found: 222.1985.

(E)-4-ethyl-2,2,5,6-tetramethylhepta-4,6-dien-3-ol (2g): a mixture of regioisomers in a ratio of 97:3

R$_f$ = 0.70 (hexane-EtOAc, 4:1)

IR (neat): 3504 (br), 2966 (s), 2874 (s), 2249 (w), 1732 (m), 1697 (w), 1464 (m) 1364 (m), 1259 (m), 1047 (m), 1002 (m), 910 (s), 732 (s) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 0.95 (s, 9 H), 1.01 (t, $J$ = 1.5 Hz, 3 H) 1.41 (d, $J$ = 4.4 Hz, 1 H), 1.76 (s, 3 H), 1.85 (t, $J$ = 1.5 Hz, 3 H), 2.09 (dq, $J$ = 7.3, 14.0 Hz, 1 H), 2.18 (dq, $J$ = 7.3, 14.0 Hz, 1 H), 4.36 (d, $J$ = 4.4 Hz, 1 H), 4.69 (dq, $J$ = 0.98, 1.5 Hz, 1 H), 4.86 (dq, $J$ = 0.98, 1.5 Hz, 1 H).

$^{13}$C NMR (100 MHz, CDCl$_3$, major isomer): $\delta$ 16.5, 19.8, 22.3, 22.5, 26.9, 37.6, 78.5, 111.6, 135.4, 137.2, 148.4.

HRMS: m/z (M$^+$) calcd for C$_{13}$H$_{24}$O: 196.1827; found: 196.1827.

(E)-2-(3-methylbut-3-en-2-ylidene)-1-phenylhexan-1-ol (2h): a mixture of regioisomers in a ratio of 98:2

R$_f$ = 0.55 (hexane-EtOAc, 4:1)

IR (neat): 3410 (br), 3069 (w), 2959 (s), 2932 (s), 2872 (s), 2860 (s), 1691 (m) 1450 (s), 1375 (w), 1007 (m), 895 (m), 700 (s) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 0.75 (t, $J$ = 7.3 Hz, 3 H), 0.98-1.39 (m, 4 H), 1.84 (s, 3 H), 1.87 (s, 3 H), 1.87 (dt, $J$ = 4.4, 12.0 Hz, 1 H), 1.88 (s, 1 H) 2.07 (dt,
4.4, 12.0 Hz, 1 H), 4.69 (d, \( J = 0.98 \) Hz, 1 H), 4.88 (d, \( J = 0.98 \) Hz, 1 H), 5.75 (s, 1 H), 7.18-7.43 (m, 5 H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), major isomer): \( \delta \) 13.7, 18.4, 22.1, 23.3, 29.2, 33.2, 72.6, 111.7, 125.7, 126.7, 128.1, 135.1, 137.1, 142.6, 147.6.

HRMS: \( m/z \) (M\(^+\)) calcd for C\(_{17}\)H\(_{24}\)O: 244.1827; found: 244.1831.

**(E)-3,4-dimethyl-1,2-diphenylpenta-2,4-dien-1-ol (2i):** a mixture of regioisomers in a ratio of >99:1

R\(_f\) = 0.60 (hexane-EtOAc, 4:1)

IR (neat): 3417 (br), 3059 (m), 3028 (m), 2914 (m), 1633 (m), 1601 (m), 1493 (s), 1448 (s), 1011 (m), 894 (m), 700 (s) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \( \delta \) 1.62 (s, 3 H), 1.85 (d, \( J = 7.3 \) Hz, 1 H), 2.10 (s, 3 H), 4.54 (s, 1 H), 4.67 (s, 1 H), 5.96 (d, \( J = 7.3 \) Hz, 1 H), 6.80-6.93 (m, 2 H), 7.06-7.37 (m, 8 H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), major isomer): \( \delta \) 18.8, 22.3, 72.1, 114.2, 125.8, 126.6, 126.9, 127.4, 128.1, 130.4, 136.8, 138.1, 138.3, 142.8, 147.0.

HRMS: \( m/z \) (M\(^+\)) calcd for C\(_{19}\)H\(_{20}\)O: 264.1514; found: 264.1518.

**(Z)-3,4-dimethyl-2-(trimethylsilyl)-1-phenylpenta-2,4-dien-1-ol (2j):** a mixture of regioisomers in a ratio of >99:1

R\(_f\) = 0.60 (hexane-EtOAc, 4:1)

IR (neat): 3458 (br), 3069 (w), 2952 (m), 2897 (m), 1638 (m), 1597 (m) 1492 (m), 1448 (m), 1245 (s), 1020 (m), 840 (s), 760 (m), 701 (s) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer): \( \delta \) 0.00 (s, 9 H), 1.83 (s, 3 H), 1.92 (s, 3 H), 1.92 (d, \( J = 3.4 \) Hz, 1 H), 4.83 (s, 1 H), 4.86 (s, 1 H), 5.76 (d, \( J = 3.4 \) Hz, 1 H), 7.19-7.38 (m, 5 H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), major isomer): \( \delta \) 2.4, 19.9, 22.4, 74.0, 113.5, 125.8, 126.6, 128.1, 136.8, 143.5, 149.7, 153.4.

HRMS: \( m/z \) (M\(^+\)) calcd for C\(_{16}\)H\(_{24}\)OSi: 260.1596; found: 260.1597.
(E)-2-(but-3-en-2-ylidene)-1-phenylhexan-1-ol (2k): a mixture of regioisomers in a ratio of >99:1

\[ R_f = 0.55 \text{ (hexane-EtOAc, 4:1)} \]

IR (neat): 3369 (br), 2957 (s), 2933 (s), 2871 (m), 1602 (w), 1492 (w) 1450 (m), 1153 (w), 1018 (s), 734 (m), 700 (s) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer):

\[ \delta \]

- 0.80 (t, \( J = 7.3 \text{ Hz, 3 H} \)),
- 0.81-1.43 (m, 4 H),
- 1.79 (d, \( J = 3.4 \text{ Hz, 1 H} \)),
- 1.97 (s, 3 H),
- 2.05 (dt, \( J = 4.9, 12.8 \text{ Hz, 1 H} \)),
- 2.20 (dt, 4.9, 12.8 Hz, 1 H),
- 5.16 (d, \( J = 10.7 \text{ Hz, 1 H} \)),
- 5.32 (d, \( J = 17.1 \text{ Hz, 1 H} \)),
- 5.95 (d, \( J = 3.4 \text{ Hz, 1 H} \)),
- 6.80 (dd, \( J = 10.7, 17.1 \text{ Hz, 1H} \)),

\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer):

\[ \delta \]

- 13.6,
- 13.7,
- 23.3,
- 27.4,
- 33.6,
- 72.9,
- 114.1,
- 125.7,
- 127.0,
- 128.2,
- 129.5,
- 136.0,
- 140.7,
- 141.1.

HRMS: \( m/z \) (M\(^+\)) calcd for C\(_{16}\)H\(_{22}\)O: 230.1671; found: 230.1662.

NOE experimental data of product 2\( k \) (major isomer)

\[(E)-3\text{-methyl-1,2-diphenylpent-2,4-dien-1-ol (2l): a mixture of regioisomers in a ratio of } >99:1\]

\[ R_f = 0.60 \text{ (hexane-EtOAc, 4:1)} \]

IR (neat): 3416 (br), 3059 (m), 3026 (m), 2928 (m), 1811 (w), 1684 (m), 1601 (m), 1493 (s), 1448 (s), 997 (s), 905 (m), 752 (m), 700 (s) cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\), major isomer):

\[ \delta \]

- 1.88 (m, 1 H),
- 2.12 (s, 3 H),
- 4.98 (d, \( J = 10.7 \text{ Hz, 1 H} \)),
- 5.30 (d, \( J = 16.9 \text{ Hz, 1 H} \)),
- 6.08 (m, 1 H),
- 6.22 (dd, \( J = 10.7, 16.9 \text{ Hz, 1 H} \)),
- 6.83 (m, 2 H),

\(^13\)C NMR (100 MHz, CDCl\(_3\), major isomer):

\[ \delta \]

- 13.8,
- 72.5,
- 114.3,
- 125.9,
- 127.0,
- 127.1,
- 127.8,
- 128.1,
- 130.6,
- 131.7,
- 137.2,
- 137.7,
- 141.7,
- 142.5.

HRMS: \( m/z \) (M\(^+\)) calcd for C\(_{18}\)H\(_{18}\)O: 250.1358; found: 250.1364.

\[(Z)-2\text{-ethyl-4-methyl-1,3-diphenylpent-2,4-dien-1-ol (2m): a mixture of}\]
regioisomers in a ratio of >99 : 1

$R_f = 0.60$ (hexane-EtOAc, 4:1)

IR (neat) 3398 (m), 3074 (m), 3024 (m), 2966 (s), 2933 (m), 2874 (m), 1601 (w), 1491 (m) 1448 (s), 1024 (m), 764 (m), 702 (s) cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 0.89 (t, $J = 7.3$ Hz, 3 H), 1.71 (br s, 1 H), 1.75 (s, 3 H), 2.02 (dq, $J = 15.1$, 7.3 Hz, 1 H), 2.33 (dq, $J = 15.1$, 7.3 Hz, 1 H), 4.99 (m, 2 H), 5.47 (s, 1 H), 7.19-7.38 (m, 10 H).

$^{13}$C NMR (100 MHz, CDCl$_3$, major isomer): $\delta$ 15.9, 21.4, 21.4, 73.5, 113.4, 125.6, 126.7, 126.9, 128.1, 128.3, 128.8, 139.0, 140.5, 143.1, 144.2, 145.8.

HRMS: $m/z$ (M$^+$) calcd for C$_{20}$H$_{22}$O: 278.1671; found 278.1674.

**Procedure for Au-Catalyzed cyclization of allenyl alcohol** (equation 1): The reaction was undertaken as follows: Into a nitrogen-purged flask with AuCl (11.6 mg, 0.05 mmol) was introduced successively dichloromethane (10 mL) and allenyl alcohol 1a (216 mg, 1 mmol) via syringe. The homogeneous mixture was stirred at room temperature for 4 days, during which the reaction was monitored by TLC. The reaction mixture was concentrated in vacuo, then the residual oil was subjected to column chromatography over silica gel (hexane/ethyl acetate = 50/1, v/v) to give 3a (169 mg, 78%) in 83:7 diastereomeric ratio.

**2-ethyl-5,6-dihydro-2,4-dimethyl-6-phenyl-2H-pyran** (3a, 3b): a mixture of diastereomers 3a, 3b in a ratio of 83:17

$R_f = 0.70$ (hexane-EtOAc, 4:1)

IR (neat): 3089 (w), 3053 (w), 2968 (s), 2928 (s), 2887 (m), 1680 (w) 1495 (w), 1450 (s), 1377 (m), 1200 (m), 1096 (m), 752 (s), 698 (s) cm$^{-1}$.

$^1$H NMR (400 MHz, C$_6$D$_6$, 3a): $\delta$ 1.02 (t, $J = 7.3$ Hz, 3 H), 1.22 (s, 3 H), 1.55 (s, 3 H), 1.72 (q, $J = 7.3$ Hz, 2 H), 1.79 (dd, $J = 3.2$, 16.6 Hz, 1 H), 2.04 (dd, $J = 10.7$, 16.6 Hz, 1 H), 4.66 (dd, $J = 3.2$, 10.7 Hz, 1 H), 5.16 (s, 1 H), 7.10-7.45 (m, 5 H).

$^{13}$C NMR (100 MHz, C$_6$D$_6$, 3a): $\delta$ 8.4, 23.0, 24.9, 35.7, 38.4, 70.7, 75.6, 126.1, 127.8, 128.0, 128.2, 131.4, 144.1.

$^1$H NMR (400 MHz, C$_6$D$_6$, 3b): $\delta$ 0.90 (t, $J = 7.3$ Hz, 3 H), 1.30 (s, 3 H), 1.53 (s, 3 H), 1.75 (q, $J = 7.3$ Hz, 2 H), 1.81 (dd, $J = 3.4$, 16.8 Hz, 1 H), 2.08 (dd, $J = 10.7$, 16.8 Hz, 1 H), 4.64 (dd, $J = 3.4$, 10.7 Hz, 1 H), 5.34 (s, 1 H), 7.10-7.45 (m, 5 H).
$^{13}$C NMR (100 MHz, C$_6$D$_6$, 3b): $\delta$ 8.4, 23.0, 26.2, 31.3, 38.0, 70.4, 75.3, 127.1, 128.0, 128.4, 128.8, 130.2, 143.9.
HRMS: $m/z$ (M$^+$) calcd for C$_{13}$H$_{20}$O: 216.1514; found 216.1522.

References