Supporting Information

Ni-Catalyzed Formal Carbonyl-Ene Reaction of Terminal Alkenes via Carbon Dioxide Insertion

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Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel 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 a 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**

1,4-Dioxane (Wako Chemicals) was purchased as an anhydrous solvent and used without further purification. Ni(cod)$_2$ (KANTO Kagaku), PPh$_3$, P(n-Bu)$_3$, PCyp$_3$, IDM·HCl, ICy·HCl, IMes·HCl (Tokyo Kasei Kogyo Co., Ltd), PCy$_3$, P(t-Bu)$_3$·HBF$_4$, Xphos, dCype (Sigma-Aldrich) were purchased and used without further purification. Trimethylaluminum (1 M solution in $n$-hexane, KANTO Kagaku) was purchased and used without further purification. Benzyltriethylaluminium and Allyltriethylaluminium were prepared from diethylaluminium chloride (1 M solution in $n$-hexane, KANTO Kagaku) with benzylmagnesium bromide (0.9 M solution in THF, Tokyo Kasei Kogyo Co., Ltd) and allylmagnesium bromide (1 M solution in diethyl ether, Sigma-Aldrich), respectively. Allylbenzene, 1-allylnaphthalene, 1-octene, 4-phenyl-1-butene, 5-hexen-1-ol, methyl 5-hexenoate (Tokyo Kasei Kogyo Co., Ltd), 1-allyl-2-methylbenzene, 4-allyltoluene, 4-allylanisole, and 1-allyl-4-fluorobenzene (Sigma-Aldrich) were purchased and distilled via Kugelrohr apparatus under reduced pressure prior to use. 3-Allylindole$^1$ and 3,3-diphenyl-1-propene$^2$ were prepared by the literature methods and the spectral data of alkenes were consistent with the literature data. 4-(4-tert-Butylphenyl)-3-methyl-1-butene was prepared by the literature method.$^3$ Acetone (Tokyo Kasei Kogyo Co., Ltd) was purchased and distilled via Kugelrohr apparatus under reduced pressure prior to use. trans-4-Phenyl-3-butenoic acid (Sigma-Aldrich) was purchased and used without further purification.
Preparation of 4-(4-tert-butylphenyl)-3-methyl-1-butene (1m)³

The reaction was undertaken as follows: To a stirred suspension of methyltriphenylphosphine bromide (2.14 g, 6.0 mmol) in dry Et₂O (30 mL) under nitrogen was added n-BuLi (1.6 M solution in hexanes, 3.8 mL, 6.0 mmol) at room temperature. After 1 h, 3-(4-tert-Butylphenyl)isobutyraldehyde (1.02 g, 5.0 mmol) was added and the homogeneous mixture was stirred at room temperature for 24 h. Then, the mixture was poured into water (20 mL) and extracted with CH₂Cl₂ three times. The combined organic extracts were washed with brine, and then dried (MgSO₄) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel.

4-(4-tert-Butylphenyl)-3-methyl-1-butene (1m): The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 100/1, v/v) to give the title compound 1m (507.9 mg, 2.51 mmol, 50%) as a pale yellow oil. TLC: R_f = 0.85 (hexane/ethyl acetate = 4/1, v/v); IR (neat) 3074 (m), 2964 (s), 2925 (s), 2868 (s), 1458 (m), 1363 (s), 910 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.98 (d, J = 5.9 Hz, 3 H), 1.31 (s, 9 H), 2.41-2.52 (m , 2 H), 2.63-2.70 (m , 1 H), 4.92 (d, J = 10.8 Hz, 1 H), 4.96 (d, J = 17.6 Hz, 1 H), 5.82 (ddd, J = 6.4, 10.8, 17.6 Hz, 1 H), 7.08 (d, J = 8.0 Hz, 2 H), 7.29, (d, J = 8.0 Hz, 2 H) ; ¹³C NMR (100 MHz, CDCl₃) δ 19.3, 31.4, 34.3, 39.1, 42.7, 112.5, 125.0, 128.8, 137.6, 144.2, 148.5; High-resolution MS, calcd for C₁₅H₂₂: 202.1722. Found m/z (relative intensity): 202.1725 (M⁺, 78), 187 (100).

Preparation of benzyldiethylaluminium and allyldiethylaluminium solution

A 100 mL Schlenk flask equipped with a rubber septum was charged with Et₂AlCl (4.5
mL of 1 M solution in n-hexane, 4.5 mmol) under nitrogen atmosphere. A solution of PhCH₂MgBr (5 mL of 0.9 M solution in THF, 4.5 mmol) was added to the Et₂AlCl via syringe at 0 °C. The reaction mixture was stirred at room temperature for 12 hours. Thus, (PhCH₂)Et₂Al (0.47 M solution) was prepared prior to use. (CH₂CHCH₂)Et₂Al (0.5 M solution) was prepared following the above procedure from (CH₂CHCH₂)MgBr (4.5 mL of 1 M solution in diethyl ether, 4.5 mmol).

**Typical procedure for the Ni-catalyzed three-component coupling reaction of alkene, CO₂, organoaluminum reagent** (entry 4, Table 1)

The reaction was undertaken as follows: Into a carbon dioxide-purged flask with Ni(cod)₂ (13.8 mg, 0.05 mmol) and PCy₃ (28.1 mg, 0.1 mmol) were introduced successively 1,4-dioxane (4 mL), allylbenzene (59.1 mg, 0.5 mmol), and Me₃Al (1.5 mL of 1 M solution in n-hexane, 1.5 mmol) via syringe. The homogeneous mixture was stirred at 40 °C for 24 h, during which the reaction was monitored by TLC. Then the mixture was quenched by adding 2 N HCl (10 ml) and extracted with ethyl acetate three times. The combined organic extracts were washed with brine, and then dried (MgSO₄) and concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel.

***(E)-2-Methyl-5-phenylpent-4-en-2-ol (3aa).*** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3aa (64.3 mg, 0.36 mmol, 73%) as a pale yellow oil.

TLC: Rₜ = 0.25 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3387 (m), 3059 (m), 2970 (s), 1599 (s), 1497 (m), 1377 (s), 1140 (s), 968 (s), 692 (s) cm⁻¹; ¹H NMR (400 MHz,
CDCl₃): δ 1.27 (s, 6 H), 1.54 (br, 1 H), 2.39 (d, J = 7.6 Hz, 2 H), 6.28 (dt, J = 15.9, 7.6 Hz, 1 H), 6.46 (d, J = 15.9 Hz, 1 H), 7.21 (t, J = 7.3 Hz, 1 H), 7.30 (t, J = 7.3 Hz, 2 H), 7.34 (d, J = 7.3 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 29.3, 47.4, 70.9, 125.7, 126.1, 127.2, 128.5, 133.6, 137.3; High-resolution MS, calcd for C₁₂H₁₆O: 176.1201. Found m/z (relative intensity): 176.1203 (M⁺, 9), 118 (100).

(E)-2-Methyl-5-o-tolylpent-4-en-2-ol (3ba). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3ba (60.9 mg, 0.32 mmol, 64%) as a pale yellow oil.
TLC: Rᵥ = 0.30 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3364 (m), 3020 (w), 2970 (s), 2923 (s), 1602 (w), 1489 (s), 1142 (s), 968 (s), 741 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.28 (s, 6 H), 1.55 (br, 1 H), 2.34 (s, 3 H), 2.41 (d, J = 7.6 Hz, 2 H), 6.15 (dt, J = 15.6, 7.6 Hz, 1 H), 6.66 (d, J = 15.6 Hz, 1 H), 7.12-7.18 (m, 3 H), 7.42-7.44 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 19.8, 29.2, 47.6, 70.8, 125.6, 126.1, 127.2, 130.2, 131.7, 135.1, 136.6; High-resolution MS, calcd for C₁₃H₁₈O: 190.1358. Found m/z (relative intensity): 190.1353 (M⁺, 59), 157 (100).

(E)-2-Methyl-5-p-tolylpent-4-en-2-ol (3ca). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3ca (64.7 mg, 0.34 mmol, 68%) as a pale yellow oil.
TLC: Rᵥ = 0.26 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3379 (br), 3021 (m), 2970 (s), 1514 (m), 1377 (m), 1138 (m), 800 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.27 (s, 6 H), 1.53 (br, 1 H), 2.33 (s, 3 H), 2.37 (d, J = 7.6 Hz, 2 H), 6.23 (dt, J = 15.6, 7.6 Hz, 1 H), 6.43 (d, J = 15.6 Hz, 1 H), 7.11 (d, J = 7.6 Hz, 2 H), 7.27 (d, J = 7.6 Hz, 2 H); ¹³C
NMR (100 MHz, CDCl$_3$): $\delta$ 21.1, 29.2, 47.4, 70.9, 124.7, 126.1, 129.2, 133.6, 134.6, 137.0; High-resolution MS, calcd for C$_{13}$H$_{18}$O: 190.1358. Found m/z (relative intensity): 190.1367 (M$^+$, 6), 132 (100).

(E)-5-(4-Methoxyphenyl)-2-methylpent-4-en-2-ol (3da). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 1/1, v/v) to give the title compound 3da (72.2 mg, 0.35 mmol, 70%) as a pale yellow oil.

TLC: $R_f$ = 0.17 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3386 (br), 3030 (m), 2968 (s), 2931 (m), 1608 (s), 1510 (s), 1249 (s), 1174 (s), 1035 (m), 970 (m) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.26 (s, 6 H), 1.59 (br, 1 H), 2.35 (d, $J$ = 7.8 Hz, 2 H), 3.80 (s, 3 H), 6.13 (dt, $J$ = 15.6, 7.8 Hz, 1 H), 6.40 (d, $J$ = 15.6 Hz, 1 H), 6.84 (d, $J$ = 8.8 Hz, 2 H), 7.30 (d, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 29.2, 47.3, 55.3, 70.8, 114.0, 123.5, 127.2, 130.2, 133.1, 159.0; High-resolution MS, calcd for C$_{13}$H$_{18}$O$_2$: 206.1307. Found m/z (relative intensity): 206.1311 (M$^+$, 100), 191 (28).

(E)-5-(4-Fluorophenyl)-2-methylpent-4-en-2-ol (3ea). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3ea (74.8 mg, 0.39 mmol, 77%) as a pale yellow oil.

TLC: $R_f$ = 0.23 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3394 (br), 3031 (w), 2972 (m), 2929 (w), 2893 (w), 1600 (m), 1508 (s), 1228 (s), 970 (m) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.27 (s, 6 H), 1.63 (br, 1 H), 2.37 (d, $J$ = 7.6 Hz, 2 H), 6.20 (dt, $J$ = 15.6, 7.6 Hz, 1 H), 6.42 (d, $J$ = 15.6 Hz, 1 H), 6.96-7.02 (m, 2 H), 7.30-7.35 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 29.3, 47.3, 70.9, 115.4 (d, $J$ = 21.5 Hz), 125.6 (d, $J$ = 1.6 Hz), 127.6 (d, $J$ = 7.4 Hz), 132.4, 133.6 (d, $J$ = 3.3 Hz), 162.1 (d, $J$ = 244.5 Hz);
High-resolution MS, calcd for C₁₂H₁₅FO: 190.1107. Found m/z (relative intensity): 194.1103 (M⁺, 76), 179 (100).

(E)-2-Methyl-5-(naphthalen-5-yl)pent-4-en-2-ol (3fa). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3fa (61.1 mg, 0.27 mmol, 54%) as a pale yellow oil.

TLC: Rₙ = 0.30 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3361 (br), 3045 (w), 2970 (m), 2927 (w), 1589 (w), 1508 (w), 1377 (m), 1143 (m), 970 (s), 796 (s), 777 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.33 (s, 6 H), 2.51 (d, J = 7.6 Hz, 2 H), 6.30 (dt, J = 15.2, 7.6 Hz, 1 H), 7.20 (d, J = 15.2 Hz, 1 H), 7.42-7.53 (m, 3 H), 7.58 (d, J = 6.8 Hz, 1 H), 7.76 (d, J = 8.3 Hz, 1 H), 7.83-7.85 (m, 1 H), 8.12 (d, J = 8.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 29.3, 47.8, 70.9, 123.7, 123.8, 125.6, 125.7, 125.9, 127.7, 128.5, 129.2, 131.0, 131.1, 133.6, 135.2; High-resolution MS, calcd for C₁₆H₁₈O: 226.1358. Found m/z (relative intensity): 226.1358 (M⁺, 100).

Typical procedure for the Ni-catalyzed three-component coupling reaction of 3-allylindole, CO₂, organoaluminum reagent (entry 6, Table 2): The reaction was undertaken as follows: Into a carbon dioxide-purged flask with Ni(cod)₂ (13.8 mg, 0.05 mmol) and PCy₃ (28.1 mg, 0.1 mmol) were introduced successively 1,4-dioxane (4 mL), 3-allylindole (78.6 mg, 0.5 mmol), and Me₃Al (2.0 mL of 1 M solution in n-hexanes, 2.0 mmol) via syringe. The homogeneous mixture was stirred at 40 °C for 24 h, during which the reaction was monitored by TLC. Then the mixture was quenched by adding sat. NaHCO₃ (10 ml) and extracted with ethyl acetate three times. The combined organic extracts were washed with brine, and then dried (MgSO₄) and...
concentrated in vacuo. The residual oil was subjected to column chromatography over silica gel.

**(E)-5-(1H-Indol-3-yl)-2-methylpent-4-en-2-ol (3ga).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 1/1, v/v) to give the title compound 3ga (92.6 mg, 0.43 mmol, 86%) as a yellow oil.

TLC: R<sub>f</sub> = 0.46 (hexane/ethyl acetate = 2/1, v/v); IR (neat): 3402 (br), 3269 (br), 3045 (w), 2970 (m), 2927 (w), 1531 (w), 1412 (m), 740 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.30 (s, 6 H), 1.68 (br, 1 H), 2.41 (d, <i>J</i> = 15.6 Hz, 2 H), 6.24 (dt, <i>J</i> = 15.6, 7.8 Hz, 1 H), 6.64 (d, <i>J</i> = 15.6 Hz, 1 H), 7.15-7.24 (m, 3 H), 7.35 (d, <i>J</i> = 7.6 Hz, 1 H), 7.85 (d, <i>J</i> = 8.0 Hz, 1 H), 8.19 (br, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 29.2, 48.0, 70.9, 111.3, 115.3, 120.0, 120.2, 122.4, 122.5, 122.8, 125.5, 126.5, 136.8; High-resolution MS, calcd for C<sub>14</sub>H<sub>17</sub>NO: 215.1310. Found <i>m/z</i> (relative intensity): 215.1309 (M<sup>+</sup>, 100), 200 (25).

**(E)-2-Methyldec-4-en-2-ol (3ha).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3ha (46.0 mg, 0.27 mmol, 54%) as a pale yellow oil.

TLC: R<sub>f</sub> = 0.50 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3361 (br), 2962 (s), 2927 (s), 2856 (m), 1497 (w), 1377 (w), 1151 (w), 972 (w) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.89 (t, <i>J</i> = 6.8 Hz, 3 H), 1.20 (s, 6 H), 1.26-1.41 (m, 6 H), 1.50 (br, 1 H), 2.03 (q, <i>J</i> = 7.3 Hz, 2 H), 2.16 (d, <i>J</i> = 6.8 Hz, 2 H), 5.46 (dt, <i>J</i> = 15.1, 7.3 Hz, 1 H), 5.53 (dt, <i>J</i> = 15.1, 6.8 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.0, 22.5, 29.0, 29.2, 31.4, 32.7, 47.0, 70.4, 125.2, 135.4; High-resolution MS, calcd for C<sub>11</sub>H<sub>22</sub>O: 170.1671. Found <i>m/z</i>
(E)-2-Methyl-6-phenylhex-4-en-2-ol (3ia). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3ia (40.0 mg, 0.21 mmol, 42%) as a pale yellow oil.

TLC: Rf = 0.27 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3367 (br), 3028 (w), 2972 (s), 2927 (m), 1494 (m), 1454 (m), 1377 (m), 1153 (m), 972 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.21 (s, 6 H), 1.57 (br, 1 H), 2.20 (d, J = 7.6 Hz, 2 H), 3.38 (d, J = 6.4 Hz, 2 H), 5.58 (dt, J = 15.6, 7.6 Hz, 1 H), 5.69 (dt, J = 15.6, 6.4 Hz, 1 H), 7.17-7.30 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃): δ 29.1, 39.2, 46.9, 70.5, 126.0, 127.0, 128.4, 133.3, 140.6; High-resolution MS, calcd for C₁₃H₁₈O: 190.1358. Found m/z (relative intensity): 190.1353 (M⁺, 26), 175 (100).

(E)-7-Methyloct-4-ene-1,7-diol (3ja). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 1/1, v/v) to give the title compound 3ja (23.5 mg, 0.15 mmol, 30%) as a pale yellow oil.

TLC: Rf = 0.43 (hexane/ethyl acetate = 2/1, v/v); IR (neat): 3357 (br), 2968 (s), 2933 (s), 2875 (m), 1456 (w), 1377 (m), 1265 (s), 1058 (m), 740 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.20 (s, 6 H), 1.66 (tt, J = 6.8, 6.3 Hz, 2 H), 1.71 (br, 2 H), 2.15 (dt, J = 6.8, 6.3 Hz, 2 H), 2.17 (d, J = 5.9 Hz, 2 H), 3.67 (t, J = 6.3 Hz, 2 H), 5.52 (dt, J = 15.6, 6.3 Hz, 1 H), 5.56 (dt, J = 15.6, 5.9 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 29.0, 29.3, 32.2, 46.8, 62.4, 70.5, 125.9, 134.3; High-resolution MS, calcd for C₉H₁₈O₂: 158.1307. Found m/z (relative intensity): 158.1322 (M⁺, 5), 143 (100).
(E)-Methyl 7-hydroxy-7-methyloct-4-enoate (3ka). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 1/1, v/v) to give the title compound 3ka (22.3 mg, 0.12 mmol, 24%) as a pale yellow oil.

TLC: R_f = 0.40 (hexane/ethyl acetate = 2/1, v/v); IR (neat): 3423 (br), 2970 (s), 1737 (s), 1676 (m), 1438 (m), 1170 (m), 974 (m) cm^{-1}; ^1H NMR (400 MHz, CDCl_3): δ 1.20 (s, 6 H), 1.72 (br, 1 H), 2.16 (d, J = 5.9 Hz, 2 H), 2.38 (t, J = 5.9 Hz, 2 H), 2.39 (dt, J = 6.8, 5.9 Hz, 2 H), 3.67 (s, 3 H), 5.51 (dt, J = 15.6, 5.9 Hz, 1 H), 5.56 (dt, J = 15.6, 6.8 Hz, 1 H); ^13C NMR (100 MHz, CDCl_3): δ 28.0, 29.0, 33.9, 46.7, 51.6, 70.3, 126.9, 132.6, 173.5; High-resolution MS, calcd for C_{10}H_{18}O_{3}: 186.1256. Found m/z (relative intensity): 186.1329 (M^+, 10), 139 (100).

2-Methyl-5,5-diphenylpent-4-en-2-ol (3la). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 3/1, v/v) to give the title compound 3la (31.5 mg, 0.12 mmol, 25%) as a pale yellow oil.

TLC: R_f = 0.53 (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3373 (br), 3052 (s), 3024 (s), 2970 (s), 2891 (s), 1599 (s), 1495 (m), 1142 (m), 754 (m) cm^{-1}; ^1H NMR (400 MHz, CDCl_3): δ 1.23 (s, 6 H), 1.64 (br, 1 H), 2.32 (d, J = 7.8 Hz, 2 H), 6.23 (t, J = 7.8 Hz, 1 H), 7.17-7.39 (m, 10 H); ^13C NMR (100 MHz, CDCl_3): δ 29.4, 43.5, 71.4, 124.9, 127.0, 127.2, 128.1, 128.2, 129.9, 140.0, 142.6, 144.0; High-resolution MS, calcd for C_{18}H_{20}O: 252.1514. Found m/z (relative intensity): 252.1512 (M^+, 0.3), 194 (100).

(E)-6-(4-tert-Butylphenyl)-2,5-dimethylhex-4-en-2-ol (3ma). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 3ma (63.8 mg, 0.24 mmol, 49%, E/Z = 4/1) as a pale yellow oil.
TLC: $R_f = 0.28$ (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3362 (br), 3024 (w), 2959 (s), 1514 (m), 1464 (s), 1047 (s), 908 (w), 735 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, major isomer): $\delta$ 1.24 (s, 6 H), 1.31 (s, 9 H), 1.56 (br, 1 H), 1.58 (s, 3 H), 2.23 (d, $J = 8.0$ Hz, 2 H), 3.31 (s, 2 H), 5.40 (t, $J = 8.0$ Hz, 1 H), 7.10 (d, $J = 8.4$ Hz, 2 H), 7.30 (d, $J = 8.4$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$, major isomer) $\delta$ 16.1, 29.1, 31.4, 34.3, 42.1, 46.1, 71.5, 121.4, 125.2, 128.4, 137.0, 133.4, 148.8; $^1$H NMR (400 MHz, CDCl$_3$, minor isomer): $\delta$ 1.26 (s, 6 H), 1.31 (s, 9 H), 1.56 (br, 1 H), 1.69 (s, 3 H), 2.34 (d, $J = 7.2$ Hz, 2 H), 3.37 (s, 2 H), 5.43 (t, $J = 7.2$ Hz, 1 H), 7.10 (d, $J = 8.4$ Hz, 2 H), 7.30 (d, $J = 8.4$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$, minor isomer) $\delta$ 23.8, 29.2, 34.3, 37.3, 38.1, 43.1, 71.1, 121.3, 125.2, 128.1, 136.7, 137.6, 148.7; High-resolution MS, calcd for C$_{18}$H$_{28}$O: 260.2140. Found $m/z$ (relative intensity): 260.2133 (M$^+$, 43), 202 (100).

![Diagram of NOE experimental data of product 3ma (major isomer and minor isomer)]

**4-Allylhepta-1,6-dien-4-ol (5b).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 5b (38.8 mg, 0.25 mmol, 51%) as a pale yellow oil.

TLC: $R_f = 0.47$ (hexane/ethyl acetate = 4/1, v/v); IR (neat): 3431 (br), 3076 (m), 2979 (m), 2931 (m), 1639 (s), 1440 (m), 997 (s), 914 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.73 (br, 1 H), 2.24 (d, $J = 7.6$ Hz, 6 H), 5.12 (d, $J = 17.6$ Hz, 3 H), 5.16 (d, $J = 10.4$ Hz, 3 H), 5.87 (ddt, $J = 7.6$, 10.4, 17.6 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 43.6, 73.0, 118.7, 133.6; High-resolution MS, calcd for C$_{10}$H$_{16}$O: 152.1201. Found $m/z$ (relative...
intensity): 152.1199 (M⁺, 1), 120 (100).

2-Benzyl-1,3-diphenylpropan-2-ol (5c). The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to give the title compound 5c (51.4 mg, 0.17 mmol, 34%) as a pale yellow oil.

TLC: Rf = 0.51 (hexane/ethyl acetate = 4/1, v/v); IR (neat) 3090 (br), 2926 (s), 1600 (m), 1495 (m), 1265 (m), 1030 (w), 739 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.92 (s, 6 H), 4.16 (s, 1 H), 7.18-7.30 (m, 15 H); ¹³C NMR (100 MHz, CDCl₃): δ 37.9, 67.9, 125.9, 128.3, 128.4, 141.8; High-resolution MS, calcd for C₂₂H₂₂O: 302.1671. Found m/z (relative intensity): 302.1878 (M⁺, 3), 255 (100).

References