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C–C bond formation *via* 1,2-addition of a *tert*-butylzinc reagent and carbonyls across conjugated dienes†

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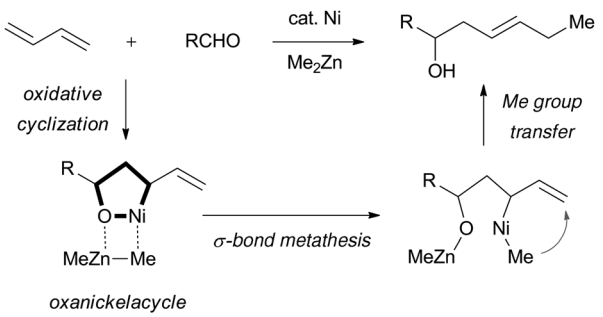
A mixture of *t*-butylzinc halide and an aldehyde reacts with conjugated dienes to provide 2-neopentyl homoallyl alcohols in high yields by 1,2-addition. Without the aldehyde, under carbon dioxide atmospheric pressure, the three components of *t*-butylzinc halide, butadiene, and carbon dioxide combine in a 1:1:1 ratio to give 2-neopentyl-3-butenoic acid in excellent yield.

Introduction

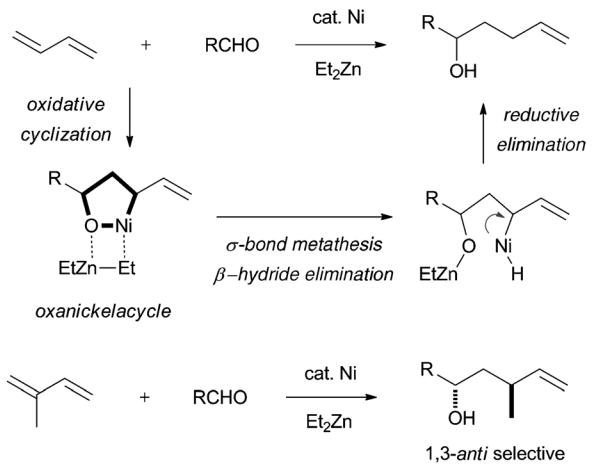
Multi-component coupling reactions involving conjugated dienes are among the most efficient and useful synthetic strategies for natural products and complex molecules.[1] We have developed a Ni catalyst that accelerates the three-component coupling reaction of aldehydes, conjugated dienes, and dimethylzinc in a 1:1:1 ratio to provide homoallyl alcohols (Scheme 1).[2] In this case, oxidative cyclization of 1,3-butadiene and an aldehyde proceeds smoothly to form an oxanickelacycle intermediate followed by σ-bond metathesis with dimethylzinc leading to the allylmethylnickel species. Methyl group transfer from the Ni metal center to the allylic terminus then leads to the homoallyl alcohol *via* 1,4-addition.

When diethylzinc was employed in place of dimethylzinc, the reaction features changed, and the homoallylation of the aldehyde with the conjugated diene proceeded *via* the key oxanickelacycle intermediate (Scheme 2).[3] Ethyl group transfer from diethylzinc to the oxanickelacycle provided the allylethylnickel which underwent β-hydride elimination to give rise to the allylnickel hydride species. Reductive elimination of Ni(0) metal from the allylnickel hydride species formed the homoallylation product, a bis-homoallyl alcohol, predominantly with retention of configuration. When isoprene was used as the diene, the reductive coupling reaction proceeded with high regio- and stereoselectivities to provide 1,3-*anti* bis-homoallyl alcohols exclusively. Thus, diethylzinc serves as a reducing agent as well as a promoter of stereocontrolled homoallylation reactions.

Based on the results of Schemes 1 and 2, we studied the reaction further using various kinds of organozinc reagents. Herein, we report that *t*-butylzinc halides react with a mixture of conjugated dienes and aldehydes to provide 2-neopentyl homoallyl alcohols **1** (Scheme 3). It is notable that the coupling



Scheme 1 Ni-catalyzed three-component coupling reaction of RCHO, conjugated diene, and Me_2Zn.



Scheme 2 Ni-catalyzed homoallylation of RCHO with conjugated dienes promoted by Et_2Zn.

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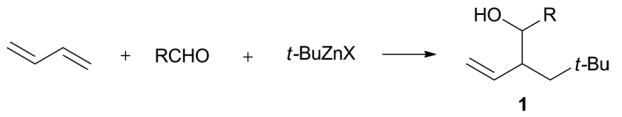


Scheme 3 Three-component coupling of RCHO with conjugated dienes and *t*-BuZnX.

reaction proceeds in the absence of Ni catalyst, and the *t*-butyl group and aldehyde add to the C–C double bond of 1,3-butadiene *via* 1,2-addition to give branched type homoallyl alcohols in contrast to the regioselectivities of the Ni-catalyzed reaction systems. A similar coupling reaction proceeds under the atmospheric pressure of carbon dioxide to give the 2-neopentyl-3-butenoic acids exclusively with high regio- and stereoselectivities.

Results and discussions

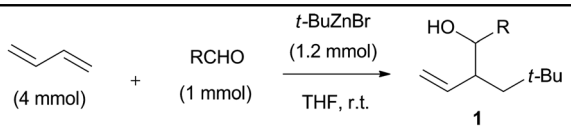
Reaction with *t*-BuZnBr

The three-component coupling reaction was conducted in the presence of a wide variety of aldehydes, 1,3-butadiene, and commercially available *t*-BuZnBr THF solution. *t*-BuZnBr was introduced into a mixture of 1,3-butadiene and aldehyde, and the reaction mixture was stirred at room temperature under a nitrogen atmosphere. The results of the coupling reactions with various carbonyl compounds are shown in Table 1.

Irrespective of the kinds of aromatic and aliphatic aldehydes, *t*-BuZnBr reacted with 1,3-butadiene at the C1 position and the aldehydes reacted at the C2 position to provide 2-neopentyl homoallyl alcohols **1** in excellent yields (entries 1–4). The reaction proceeded with high regio- and stereoselectivities and *anti* isomers were formed predominantly. Although *n*-hexanal could participate in the coupling reaction, non-selective formation of *syn* and *anti* diastereoisomers was observed (entry 5).

Besides aromatic and aliphatic aldehydes, ketones also took part in the coupling reaction. When acetone was used as the carbonyl electrophile, the desired homoallyl alcohol was obtained in reasonable yield (entry 6, Table 1). As there was no change in reactivities and selectivities regardless of the presence or absence of an Ni catalyst,[4] the coupling reactions did not involve nickelacycles, but an alternative multi-component coupling mechanism might be active.

Table 1 Three-component coupling reaction of various aldehydes, 1,3-butadiene, and ^{t}BuZnBr[a]



Entry	Electrophile	Time (h)	Yield (%) [*anti* : *syn*]
1	PhCHO	6	**1a** (98) [10 : 1]
2	(*p*-OMe)PhCHO	24	**1b** (91) [6 : 1]
3	(*p*-Cl)PhCHO	24	**1c** (93) [9 : 1]
4	*c*-C_6H_{11}CHO	24	**1d** (91) [12 : 1]
5	*n*-C_5H_{11}CHO	24	**1e** (42) [1 : 1]
6	Acetone	24	**1f** (70)

[a] The reaction was undertaken in the presence of butadiene (4 mmol), aldehyde (1 mmol), and *t*-BuZnBr (1.2 mmol) at room temperature in THF (5 mL) under nitrogen atmosphere.

Reaction with *t*-BuZnI prepared from *t*-BuI and Zn dust

The *t*-BuZnI reagent, which was prepared from Zn dust and *t*-BuI *in situ*, was useful for a similar coupling reaction providing homoallyl alcohols **1** efficiently (Table 2). *t*-BuI, butadiene, and various kinds of aldehydes were introduced to the Zn dust suspension, and the reaction mixture was stirred at room temperature. As a result of many investigations in various kinds of solvents, such as DMSO (dimethyl sulfoxide), DMF (*N*,*N*-dimethylformamide), DMA (*N*,*N*-dimethylacetamide), nitromethane, toluene, and dichloromethane, it was found that a combination of 3 : 1 v/v THF and DMA was the most effective solvent for producing good yields and stereoselectivities, compared to the reaction in THF alone (entries 1 and 2, Table 2).[5]

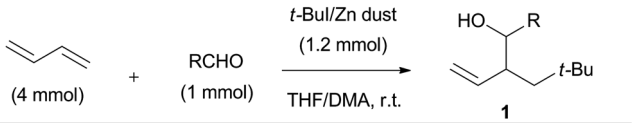
In comparison with the result of *t*-BuZnBr in Table 1, the reactions using *t*-BuI and zinc dust showed similar reactivities; however, the stereoselectivities were slightly lower than that with *t*-BuZnBr (entries 1–5, Table 2). Although the isolated yield of the reaction with *n*-hexanal was improved, the stereoselectivity did not change (entry 6, Table 2). Acetone provided the desired product in modest yield, although by-products, such as direct coupling products derived from alkylzinc reagent and carbonyls were not produced at all (entry 7, Table 2).

Reaction with various dienes

These coupling reactions utilizing *t*-BuZnBr and *t*-BuZnI prepared from Zn dust and *t*-BuI were capable of the efficient and straightforward stereodefined construction of homoallyl alcohols. The results using various substituted dienes are shown in Table 3.

The reactions with a wide variety of conjugated dienes were conducted with both commercially available *t*-BuZnBr (condition A) and *t*-BuZnI reagent prepared from Zn dust and *t*-BuI (condition B). In the case of isoprene, the *t*-Bu group added to the diene at the C1 position and benzaldehyde reacted at the C2

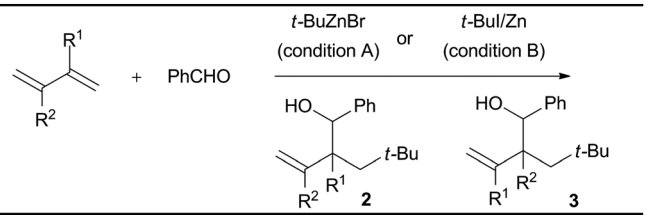
Table 2 Three-component coupling reaction of various aldehydes, 1,3-butadiene, and ^{t}BuZnI reagent prepared from ^{t}BuI and Zn dust[a]



Entry	Electrophile	Yield (%) [*anti* : *syn*]
1	PhCHO	**1a** (77) [7 : 1]
2	PhCHO	**1a** (75) [4 : 1][b]
3	(*p*-OMe)PhCHO	**1b** (87) [5 : 1]
4	(*p*-Cl)PhCHO	**1c** (84) [5 : 1]
5	*c*-C_6H_{11}CHO	**1d** (84) [10 : 1]
6	*n*-C_5H_{11}CHO	**1e** (57) [1 : 1]
7	Acetone	**1f** (10)

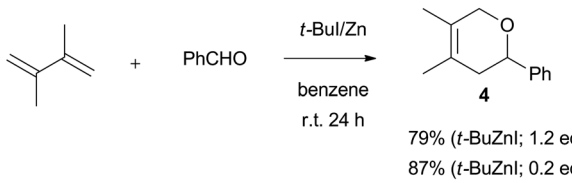
[a] The reaction was undertaken in the presence of Zn dust (1.2 mmol) in THF–DMA solution (3 mL/1 mL) by employment of butadiene (4 mmol), aldehyde (1 mmol), and *t*-BuI (1.2 mmol) at room temperature for 24 hours under nitrogen atmosphere. [b] THF (5 mL) was used as solvent.

Table 3 Three-component coupling reaction of various dienes, PhCHO, and ^{t}BuZnX[a]



Entry	Diene	Isolated yield (%) [*anti* : *syn*] Condition A	Condition B
1	Isoprene (R^1 = Me, R^2 = H)	**2a** (63) [10 : 1] **3a** (20) [9 : 1]	**2a** (55) [6 : 1] **3a** (12) [8 : 1]
2	2,3-Dimethyl-1,3-butadiene (R^1, R^2 = Me)	**2b** (62) [3 : 1]	**2b** (79) [2 : 1]
3	Myrcene (R^1 = C_6H_{11}, R^2 = H)	**2c** (60) [1 : 1] **3c** (36) [1 : 1]	**2c** (58) [1 : 1] **3c** (18) [single]
4	Cyclohexadiene	No reaction	No reaction
5	Methyl sorbate	No reaction	No reaction

[a] Condition A: diene (4 mmol), benzaldehyde (1 mmol), and *t*-BuZnBr (1.2 mmol) in THF (5 mL) at r.t. for 24 h; condition B: Zn dust (1.2 mmol) in THF–DMA (3 mL/1 mL), diene (4 mmol), benzaldehyde (1 mmol), *t*-BuI (1.2 mmol) at r.t. for 24 h.



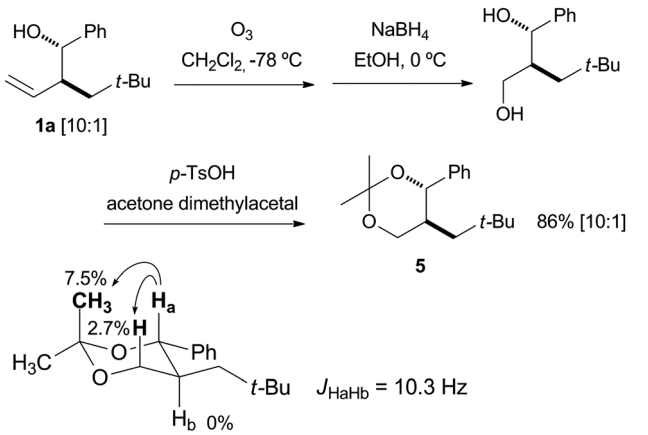
Scheme 4 Hetero Diels–Alder reaction of PhCHO and 2,3-dimethyl-1,3-butadiene promoted by Zn dust and *t*-BuI.

position to construct the sterically congested quaternary carbon center giving rise to the homoallyl alcohol **2a** along with the regioisomer **3a** as a minor product (entry 1, Table 3). Irrespective of the conditions, *anti* stereoselectivities were predominantly observed in 6 : 1 to 10 : 1 ratios.

2,3-Dimethyl-1,3-butadiene provided the desired product in modest to good yields, but with lower *anti* stereoselectivities than that of 1,3-butadiene and isoprene (entry 2, Table 3). In benzene solvent, the hetero Diels–Alder reaction adduct from 2,3-dimethyl-1,3-butadiene and benzaldehyde was obtained exclusively, instead of the homoallyl alcohol (Scheme 4). While the combination of benzaldehyde and conjugated dienes is generally reluctant to undergo the hetero Diels–Alder reaction,[6] 3,6-dihydro-2*H*-pyran is afforded smoothly under benzene. Myrcene could participate in the coupling reaction as well as isoprene, but the diastereoselectivities were by no means satisfactory (entry 3, Table 3). No reaction took place at all with cyclohexadiene and electron deficient dienes such as methyl sorbate (entries 4 and 5, Table 3).

Structure determination

The structure of product **1a** was determined unequivocally by conversion to the six-membered ring acetonide by ozonolysis, reduction with $NaBH_4$, and acetonization with acetone



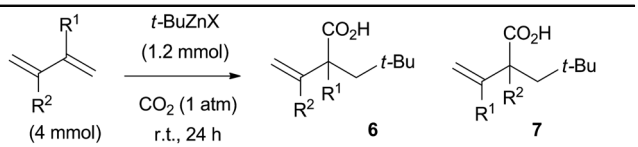
Scheme 5 Structure determination and % NOE enhancement upon irradiation of H_a and the coupling constant.

dimethylacetal. NOE enhancement of the boldface protons by irradiation at H_a and the coupling constant between the vicinal diaxial H_a and H_b protons of the acetonide **5** are illustrated in Scheme 5. These results confirmed the relative configuration of **5** as the *anti* form. Thus, the stereochemistry of the major homoallyl alcohol product was unambiguously determined as the *anti* form by means of chemical derivatization and spectral analysis.[7]

Coupling reaction under CO_2

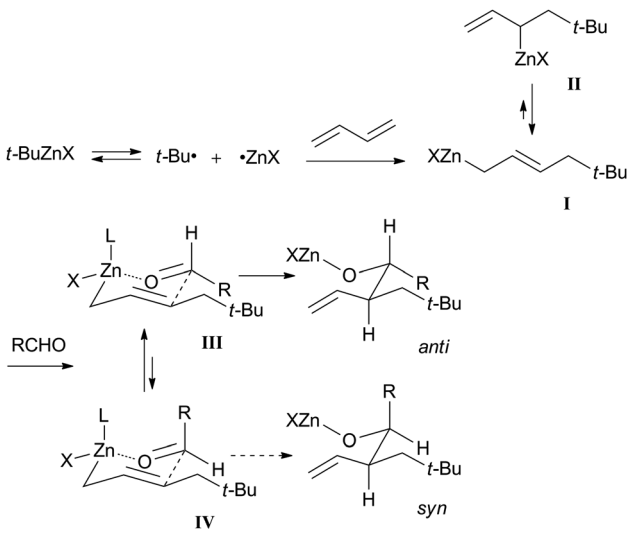
A series of these coupling reactions in the absence of aldehydes was conducted under a carbon dioxide atmosphere (1 atm). In the presence of *t*-BuZnBr or *t*-BuZnI, 1,3-butadiene underwent the three-component coupling reaction to provide 2-neopentyl-3-butenoic acid **6a** as a single isomer by addition of the *t*-Bu group and carbon dioxide in a 1,2-addition manner (entry 1, Table 4). When using 2,3-dimethyl-1,3-butadiene, *t*-BuZnBr reacted with the diene at the C1 position and carbon dioxide reacted at the C2 position to provide the desired product **6b** in excellent yield with high regioselectivity, whereas *t*-BuZnI provided the same product **6b** in modest yields (entry 2, Table 4).

Table 4 Three-component coupling reaction of various dienes, CO_2, and ^{t}BuZnX[a]



Entry	Diene	Isolated yield (%) Condition A	Condition B
1	Butadiene (R^1, R^2 = H)	**6a** (86)	**6a** (61)
2	2,3-Dimethyl-1,3-butadiene (R^1, R^2 = Me)	**6b** (86)	**6b** (41)
3	Isoprene (R^1 = Me, R^2 = H)	**6c** (60), **7c** (28)	**6c** (12), **7c** (5)
4	Myrcene (R^1 = C_6H_{11}, R^2 = H)	**6d** (54), **7d** (23)	**6d** (0), **7d** (11)

[a] Condition A: diene (4 mmol), and *t*-BuZnBr (1.2 mmol) in THF (2 mL) at r.t. under CO_2 (1 atm); condition B: diene (4 mmol), Zn dust (1.2 mmol), *t*-BuI (1.2 mmol) in THF (2 mL) at r.t. under CO_2 (1 atm).



Scheme 6 A plausible reaction mechanism for three-component coupling reaction of *t*-Bu group, butadiene, and aldehyde.

Isoprene and myrcene also underwent 1,2-addition to afford more congested carboxylic acids **6c** and **6d** along with the less substituted regioisomers of **7c** and **7d** as minor products (entries 3 and 4, Table 4). It is noteworthy that *t*-BuZn remains intact under carbon dioxide atmospheric pressure and does not undergo direct coupling with carbon dioxide to give the corresponding carboxylic acids in comparison to the reaction with Grignard reagents.[8] Instead, the three-component coupling reaction of conjugated dienes, *t*-Bu groups, and carbon dioxide predominates over the direct coupling reaction of *t*-Bu and carbon dioxide.

Plausible reaction mechanism

A plausible reaction mechanism for the three-component coupling reaction is shown in Scheme 6. The C–Zn bonds of *t*-BuZnX are readily cleaved by homolysis to form *t*-Bu and ZnX radicals, which then add to the 1,3-butadiene in 1,4-addition fashion forming allylzinc species **I** and **II** in equilibrium with each other. The carbonyl species add to the γ-position of the allylzinc species to form the six-membered transition states **III** and **IV**. The more stable allylzinc species **I** with an aldehyde would undergo the coupling reaction *via* six-membered transition state **III** predominating over **IV** to avoid steric repulsion between the neopentyl group and the substituents on the aldehyde, and result in the formation of homoallyl alcohols with *anti* stereoselectivity.[9]

Conclusions

In summary, the addition of *t*-butylzinc halide to the reaction mixture of butadiene and an aldehyde provides 2-neopentyl homoallyl alcohols in high yields by 1,2-addition of the aldehyde and the *t*-butyl group to butadiene. Furthermore, *t*-BuZnI prepared from Zn dust and *t*-BuI was also useful for the coupling reaction to provide homoallyl alcohols with high regio- and stereoselectivities. Without the aldehyde, under carbon dioxide atmospheric pressure, the three components of *t*-butylzinc halide, butadiene, and carbon dioxide combine to give 2-neopentyl-3-butenoic acids in excellent yields.

Experimental

General procedures

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). Microanalyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ±0.4%. High resolution mass spectra (HRMS) were measured with JEOL JMSDX303. Infrared spectra were recorded with a JASCO A-100 or SHIMAZU FTIR-8700 infrared spectrophotometer. ^{1}H and ^{13}C magnetic resonance spectra were measured on JEOL-GX400 instrument with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard.

Tetrahydrofuran was dried and distilled from benzophenone-sodium immediately prior to use under nitrogen atmosphere. DMA were distilled over calcium hydride. Benzaldehyde, *p*-anisaldehyde, cyclohexanecarbaldehyde, *n*-hexanal, isoprene, 2,3-dimethyl-1,3-butadiene, myrcene, cyclohexadiene, methyl sorbate were distilled *via* Kugelrohr apparatus under reduced pressure prior to use. *t*-BuZnBr (0.5 M THF, Aldrich), *t*-BuI (Aldrich), Zinc dust (Aldrich), $Ni(cod)_2$ (KANTO Kagaku) were used without further purification. 1,3-Butadiene (Tokyo Kasei Kogyo Co., Ltd) was purchased, and was liquefied by cooling at −78 °C (dry ice/isopropanol) prior to use under argon atmosphere. 1,3-Butadiene could be measured by syringe kept cool in the freezer as well beforehand, and then was introduced into the reaction mixture at room temperature.

Typical procedure for the three-component coupling reaction of aldehydes, 1,3-butadiene, and *t*-BuZnBr (entry 1, Table 1). Into a nitrogen-purged flask were introduced successively THF (5 mL), 1,3-butadiene (0.4 mL, 4 mmol), benzaldehyde (106 mg, 1 mmol), and *t*-BuZnBr (2.4 mL, 0.5 M in THF) *via* syringe. The homogeneous mixture was stirred at room temperature for 6 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 = 32/1, v/v) to give an analytically pure sample of **1a** (213 mg, 98%).

Three-component coupling reaction of aldehydes, 1,3-butadiene, and *t*-BuZnI reagent prepared from *t*-BuI and Zn dust (entry 1, Table 2). Into a nitrogen-purged flask containing zinc dust (78 mg, 1.2 mmol) were introduced successively THF (3 mL), and DMA (1 mL), *t*-BuI (220 mg, 1.2 mmol), 1,3-butadiene (0.4 mL, 4 mmol), and benzaldehyde (106 mg, 1 mmol) *via* syringes. The reaction 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 = 32/1, v/v) to give **1a** (167 mg, 77%).

4,4-Dimethyl-1-phenyl-2-vinylpentan-1-ol (1a) (a mixture of 1,2-*anti*:*syn* = 7:1 ratio). IR (neat) 3423 (s), 2866 (s), 1495 (s), 1001 (s), 910 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) d 0.75 (s, 9H), 1.18 (dd, J = 2.8, 13.9 Hz, 1H), 1.24 (dd, J = 8.8, 13.9 Hz, 1H), 2.34 (d, J = 2.1 Hz, 1H), 2.45 (br dq, J = 2.8, 8.8 Hz, 1H),

4.28 (br dd, J = 2.1, 8.1 Hz, 1H), 5.20 (br dd, J = 1.8, 17.2 Hz, 1H), 5.23 (br dd, J = 1.8, 10.3 Hz, 1H), 5.72 (ddd, J = 9.5, 10.3, 17.2 Hz, 1H), 7.13–7.53 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, *anti*-isomer) d 30.0, 31.0, 44.1, 49.4, 77.4, 118.2, 127.4, 127.6, 128.2, 141.9, 142.3; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) d 0.81 (s, 9H), 1.16 (dd, J = 9.5, 13.9 Hz, 1H), 1.47 (dd, J = 2.2, 13.9 Hz, 1H), 2.14 (br d, J = 5.3 Hz, 1H), 2.54 (br dq, J = 2.2, 9.5 Hz, 1H), 4.58 (br t, J = 5.3 Hz, 1H), 5.08 (br d, J = 10.8, 1H), 5.09 (br dd, J = 16.9 Hz, 1H), 5.62 (ddd, J = 9.0, 10.8, 16.9 Hz, 1H), 7.13–7.53 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, *syn*-isomer) d 30.1, 31.0, 42.9, 47.8, 77.4, 116.6, 126.8, 127.2, 127.9, 141.4, 142.4; high-resolution MS, calcd for $C_{15}H_{22}O$: 218.1671. Found m/z (relative intensity) 218.1692 (M^+, 100), 201 (88), 147 (34), 146 (32).

1-(4-Methoxyphenyl)-4,4-dimethyl-2-vinylpentan-1-ol (1b) (a mixture of 1,2-*anti*:*syn* = 6:1 ratio). IR (neat) 3452 (m), 2866 (m), 1612 (m), 1514 (s), 1248 (s), 1038 (s), 833 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.76 (s, 9H), 1.17 (dd, J = 3.0, 14.0 Hz, 1H), 1.23 (dd, J = 8.6, 14.0 Hz, 1H), 2.27 (d, J = 1.7 Hz, 1H), 2.42 (ddm, J = 3.0, 8.6 Hz, 1H), 3.80 (s, 3H), 4.22 (dd, J = 1.7, 8.1 Hz, 1H), 5.20 (dd, J = 1.8, 17.1 Hz, 1H), 5.23 (dd, J = 1.8, 10.2 Hz, 1H), 5.72 (ddd, J = 9.3, 10.2, 17.1 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 30.0, 31.0, 44.1, 49.5, 55.2, 76.4, 113.4, 118.0, 128.3, 134.2, 142.1, 158.9; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.83 (s, 9H), 2.51–2.53 (m, 1H), 3.80 (s, 3H), 4.53 (t, J = 5.1 Hz, 1H), 5.05 (dd, J = 1.9, 9.1 Hz, 1H), 5.07 (dd, J = 1.9, 16.8 Hz, 1H), 5.62 (ddd, J = 9.1, 10.5, 16.8 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 30.1, 43.2, 47.8, 113.2, 116.5, 127.8, 134.4, 141.2; high-resolution MS, calcd for $C_{15}H_{21}ClO$: 248.1776, found m/z (relative intensity): 248.1767 (M^+, 75), 215 (100).

1-(4-Chlorophenyl)-4,4-dimethyl-2-vinylpentan-1-ol (1c) (a mixture of 1,2-*anti*:*syn* = 9:1 ratio). IR (neat) 3433 (m), 2909 (s), 1638 (w), 1090 (s), 831 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.76 (s, 9H), 1.16 (dd, J = 2.4, 13.9 Hz, 1H), 1.25 (dd, J = 9.0, 13.9 Hz, 1H), 2.32 (br s, 1H), 2.39 (dddd, J = 2.4, 7.8, 9.0, 9.3 Hz, 1H), 4.57 (d, J = 7.8 Hz, 1H), 5.17 (dd, J = 1.3, 17.2 Hz, 1H), 5.18 (dd, J = 1.3, 10.2 Hz, 1H), 5.70 (ddd, J = 9.3, 10.2, 17.2 Hz, 1H), 7.25 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 30.0, 31.0, 44.0, 49.4, 76.2, 118.5, 128.1, 128.6, 133.1, 140.6, 141.3; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.81 (s, 9H), 2.50–2.52 (m, 1H), 4.27 (t, J = 4.6 Hz, 1H), 5.08 (dm, J = 17.2 Hz, 1H), 5.10 (dm, J = 10.4 Hz, 1H), 5.60 (ddd, J = 9.3, 10.4, 17.2 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 30.1, 42.8, 47.7, 116.9, 140.7, 140.8; high-resolution MS, calcd for $C_{15}H_{21}ClO$: 252.1281, found m/z (relative intensity): 252.1295 (M^+, 68), 219 (100).

1-Cyclohexyl-4,4-dimethyl-2-vinylpentan-1-ol (1d) (a mixture of 1,2-*anti*:*syn* = 9:1 ratio). IR (neat) 3368 (br m), 3071 (s), 2853 (s), 1636 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.90 (s, 9H), 0.96–1.30 (m, 5H), 1.32–1.42 (m, 3H), 1.64–1.76 (m, 4H), 1.81–1.86 (m, 1H), 2.37 (dq, J = 5.2, 9.2 Hz, 1H), 3.07 (t, J = 5.2 Hz, 1H), 5.08 (ddd, J = 0.7, 1.9, 17.3 Hz, 1H), 5.14 (dd, J = 1.9, 10.4 Hz, 1H), 5.73 (ddd, J = 9.2, 10.4, 17.3 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 26.1, 26.3, 26.5, 27.8, 30.0, 30.1, 31.3, 40.3, 42.9, 45.5, 79.1, 116.7, 140.8; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.86 (s, 9H), 3.13 (m, 1H), 5.02 (dm, J = 1.0 Hz, 1H), 5.07 (dm, J = 1.0 Hz, 1H), 5.75 (dd, J = 8.5, 17.6 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 27.2, 29.2, 30.3, 30.4, 39.9, 42.7, 43.8, 80.2, 115.0, 143.1; high-resolution MS, calcd for $C_{15}H_{28}O$: 224.2140, found m/z (relative intensity): 224.2079 (M^+, 24), 223 (100).

2,2-Dimethyl-4-vinyldecan-5-ol (1e) (a mixture of 1,2-*anti*:*syn* = 1:1 ratio). IR (neat) 3362 (w), 2934 (s), 2862 (s), 1638 (w) cm^{-1}; (one isomer): ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.87 (t, J = 5.6 Hz, 3H), 0.89 (s, 9H), 1.21–1.39 (ddm, J = 4.6, 7.8 Hz, 10H), 2.28 (dq, J = 4.1, 8.3 Hz, 1H), 3.33–3.40 (m, 1H), 5.08 (dd, J = 1.7, 18.5 Hz, 1H), 5.13 (dd, J = 1.7, 10.0, Hz, 1H), 5.69 (ddd, J = 8.3, 10.0, 18.5 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, one isomer) δ 14.0, 22.6, 26.0, 30.1, 31.1, 33.2, 44.1, 75.7, 116.4, 141.5; (minor isomer): ^{1}H NMR (400 MHz, $CDCl_3$, other isomer) δ 0.90 (s, 9H), 0.94 (t, J = 7.2 Hz, 3H), 2.12–2.18 (dddm, J = 0.7, 4.6, 8.8 Hz, 1H), 5.09 (dd, J = 0.7, 15.9 Hz, 1H), 5.09 (d, J = 11.5 Hz, 1H), 5.68 (ddd, J = 8.8, 11.5, 15.9 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, other isomer) δ 25.6, 30.2, 31.2, 31.9, 34.4, 44.9, 46.8, 74.9, 116.9, 141.2; high-resolution MS, calcd for $C_{12}H_{24}O$: 212.214, found m/z (relative intensity): 212.2099 (M^+, 46), 197 (100).

2,5,5-Trimethyl-3-vinylhexan-2-ol (1f). IR (neat) 3435 (w), 2959 (m), 2868 (w), 2345 (w), 1720 (w), 1466 (w), 1020 (m), 802 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H), 1.10 (s, 3H), 1.18 (s, 3H), 1.24 (dd, J = 9.5, 13.9 Hz, 1H), 1.45 (dd, J = 1.6, 13.9 Hz, 1H), 1.75 (s, 1H), 2.12 (br td, J = 1.0, 9.5 Hz, 1H), 5.12 (ddd, J = 1.0, 2.0, 17.3 Hz, 1H), 5.15 (dd, J = 2.0, 10.2 Hz, 1H), 5.67 (ddd, J = 9.5, 10.2, 17.3 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 26.4, 26.9, 30.2, 31.1, 43.6, 52.3, 71.9, 117.9, 141.9; high-resolution MS, calcd for $C_{11}H_{22}O$: 170.1671, found m/z (relative intensity): 171 (M^+ + 1, 76), 170.1578 (M^+, 59), 169 (89).

2,4,4-Trimethyl-1-phenyl-2-vinylpentan-1-ol (2a) (a mixture of 1,2-*anti*:*syn* = 10:1 ratio). IR (neat) 3462 (br m), 3030 (m), 2953 (s), 1634 (w), 1454 (s), 1022 (s), 910 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.90 (s, 9H), 1.10 (s, 3H), 1.24 (d, J = 13.8 Hz, 1H), 1.55 (d, J = 13.8 Hz, 1H), 2.14 (d, J = 1.7 Hz, 1H), 4.24 (d, J = 1.7 Hz, 1H), 5.12 (dd, J = 1.2, 17.6 Hz, 1H), 5.26 (dd, J = 1.2, 10.9 Hz, 1H), 5.98 (dd, J = 10.9, 17.6 Hz, 1H), 7.20–7.34 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 17.2, 29.7, 31.9, 46.9, 50.7, 80.7, 114.8, 126.2, 127.2, 128.3, 139.9, 145.9; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 0.76 (s, 9H), 1.23 (s, 3H), 1.23 (d, J = 4.3 Hz, 1H), 1.41 (d, J = 4.3 Hz, 1H), 2.04 (d, J = 6.0 Hz, 1H), 4.27 (d, J = 6.0 Hz, 1H), 5.01 (dd, J = 1.3, 17.6 Hz, 1H), 5.15 (dd, J = 1.3, 11.8 Hz, 1H), 5.97 (dd, J = 11.8, 17.6 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 19.9, 30.7, 32.2, 46.1, 50.1, 82.3, 113.9, 126.9, 127.3, 127.9, 141.3, 144.7; high-resolution MS, calcd for $C_{16}H_{24}O$: 232.1827, found m/z (relative intensity): 232.1823 (M^+, 2), 199 (100).

4,4-Dimethyl-1-phenyl-2-(prop-1-en-2-yl)pentan-1-ol (3a) (a mixture of 1,2-*anti*:*syn* = 9:1 ratio). IR (neat) 3470 (m), 3030 (w), 2866 (m), 1641 (w), 1196 (m), 1022 (m), 889 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.71 (s, 9H), 0.97 (dd, J = 2.0, 14.1 Hz, 1H), 1.39 (dd, J = 9.6, 14.1 Hz, 1H), 1.78 (dd, J = 0.7, 1.5 Hz, 3H), 2.35 (br s, 1H), 2.52 (dt, J = 2.0, 9.6 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 5.04 (dd, J = 0.7, 1.8 Hz, 1H), 5.07 (dd, J = 1.5, 1.8, Hz, 1H), 7.33 (d, J = 4.4 Hz, 5H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 18.9, 29.5, 31.0, 41.2, 52.6, 75.5, 116.1, 127.4, 127.5, 128.0, 142.5, 146.9; ^{1}H NMR (400 MHz, $CDCl_3$, *syn*-

isomer) δ 0.90 (s, 9H), 0.97 (dm, J = 10.0 Hz, 1H), 1.39 (dm, J = 10.0 Hz, 1H), 1.69 (dd, J = 0.7, 1.5 Hz, 3H), 4.99 (d, J = 0.7 Hz, 1H), 5.03 (d, J = 1.5 Hz, 1H); high-resolution MS, calcd for $C_{16}H_{24}O$: 232.1827, found m/z (relative intensity): 232.1823 (M^+, 13), 199 (100).

2,4,4-Trimethyl-1-phenyl-2-(prop-1-en-2-yl)pentan-1-ol (2b) (a mixture of 1,2-*anti*:*syn* = 3:1 ratio). IR (neat) 3462 (w), 2953 (s), 2872 (s), 1630 (w), 1452 (m), 1364 (m), 1242 (m), 1190 (m), 1043 (m), 1022 (m), 894 (m), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.87 (s, 9H), 1.05 (d, J = 14.5 Hz, 1H), 1.10 (s, 3H), 1.72 (d, J = 14.5 Hz, 1H), 1.95 (br s, 3H), 4.45 (br s, 1H), 5.10 (br s, 1H), 5.18 (br s, 1H), 7.24–7.35 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 18.5, 21.9, 26.5, 32.2, 48.5, 49.0, 80.4, 114.0, 127.2, 128.1, 141.0, 148.9; (1,2-*syn* isomer): ^{13}C NMR (400 MHz, $CDCl_3$, *syn*-isomer) δ 17.9, 20.3, 26.4, 31.6, 45.8, 47.4, 78.2, 115.9, 127.4, 128.9, 140.3, 149.7; high-resolution MS, calcd for $C_{17}H_{26}O$: 246.1984, found m/z (relative intensity): 246.1992 (M^+, 1), 245 (4), 244 (6), 229 (100).

6-Methyl-2-neopentyl-1-phenyl-2-vinylhept-5-en-1-ol (2c) (a mixture of 1,2-*anti*:*syn* = 1:1 ratio). IR (neat) 3470 (m), 3030 (m), 2934 (s), 1634 (w), 1196 (m), 899 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 1.02 (s, 9H), 1.42 (ddd, J = 2.4, 8.4, 19.8, Hz, 1H), 1.43 (dd, J = 8.4, 19.8, Hz, 1H), 1.57 (s, 3H), 1.64 (d, J = 1.2 Hz, 3H), 1.75 (s, 2H), 1.89 (d, J = 4.1 Hz, 1H), 2.04 (ddm, J = 7.1, 8.4, Hz, 2H), 4.64 (d, J = 4.1 Hz, 1H), 4.96 (dt, J = 1.2, 7.1 Hz, 1H), 4.96 (dd, J = 18.1, 1.3 Hz, 1H), 5.20 (dd, J = 11.2, 1.3 Hz, 1H), 5.94 (dd, J = 18.1, 11.2 Hz, 1H), 7.25–7.31 (dm, J = 6.1 Hz, 5H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 23.0, 25.7, 32.1, 32.1, 33.0, 44.1, 48.6, 79.1, 114.6, 124.6, 127.3, 128.2, 141.2, 143.3; high-resolution MS, calcd for $C_{21}H_{32}O$: 300.2453, found m/z (relative intensity): 300.2461 (M^+, 11), 282 (100).

7-Methyl-3-methylene-2-neopentyl-1-phenyloct-6-en-1-ol (3c) (a mixture of 1,2-*anti*:*syn* = 1:1 ratio). IR (neat) 3470 (br m), 3030 (m), 2866 (m), 1634 (w), 1196 (m), 899 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 0.71 (s, 9H), 1.03 (dd, J = 2.0, 14.1 Hz, 1H), 1.44 (dd, J = 9.8, 14.1 Hz, 1H), 1.63 (s, 3H), 1.70 (d, J = 1.2 Hz, 3H), 2.04 (dt, J = 6.8, 8.2 Hz, 2H), 2.16–2.24 (m, 2H), 2.34 (d, J = 2.4 Hz, 1H), 2.51 (ddd, J = 2.0, 9.0, 9.8 Hz, 1H), 4.32 (dd, J = 2.4, 9.0 Hz, 1H), 5.11 (d, J = 1.7 Hz, 1H), 5.12 (d, J = 1.2 Hz, 1H), 5.14 (tq, J = 1.2, 6.8 Hz, 1H), 7.31 (d, J = 4.4 Hz, 5H); ^{13}C NMR (400 MHz, $CDCl_3$, *anti*-isomer) δ 17.7, 25.6, 26.1, 29.6, 31.0, 32.3, 41.9, 52.9, 75.9, 113.9, 123.9, 127.3, 127.5, 128.0, 132.0, 142.6, 150.7; high-resolution MS, calcd for $C_{21}H_{32}O$: 300.2453, found m/z (relative intensity): 300.2461 (M^+, 11), 282 (100).

Hetero Diels–Alder reaction of PhCHO and 2,3-dimethyl-1,3-butadiene (Scheme 4). Into a nitrogen-purged flask containing Zinc dust (13 mg, 0.2 mmol) were introduced benzene (3 mL), 2,3-dimethyl-1,3-butadiene (0.45 mL, 4 mmol), benzaldehyde (106 mg, 1 mmol), and *t*-BuI (37 mg, 0.2 mmol) *via* syringes. The reaction mixture was stirred at room temperature for 24 h, during which the reaction was monitored by TLC. After dilution with ethyl acetate (20 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 = 32/1, v/v) to give **4** (164 mg, 87%).

3,6-Dihydro-4,5-dimethyl-2-phenyl-2*H*-pyran (4). IR (neat) 2916 (s), 2812 (m), 1495 (m), 1103 (s), 758 (s), 698 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 3H), 1.69 (s, 3H), 2.09 (dm, J = 16.3 Hz, 1H), 2.30 (m, 1H), 4.15 (m, 2H), 4.54 (dd, J = 3.5, 10.6 Hz, 1H), 7.20–7.38 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 13.8, 18.3, 38.5, 70.2, 123.7, 124.4, 125.7, 127.2, 128.2, 139.0. High-resolution MS, calcd for $C_{13}H_{16}O$: 188.1201, found m/z (relative intensity): 188.1169 (M^+, 100), 187 (6).

Structure determination of 2,2-dimethyl-5-neopentyl-4-phenyl-1,3-dioxane (5). A solution of 4,4-dimethyl-1-phenyl-2-vinylpentan-1-ol (**1a**) (218 mg, 1 mmol) in dichloromethane (10 mL) was cooled to −78 °C, and ozone was bubbled through for 20 min until a blue color appeared. The excess of ozone was removed by a flow of nitrogen and the solvent was removed by a rotary evaporator. The residue was dissolved in EtOH (3 mL) and treated with $NaBH_4$ (152 mg, 4 mmol) at 0 °C and then at room temperature for 6 h. The reaction mixture was concentrated *in vacuo* and the residue was diluted with ethyl acetate (30 mL) and washed with 2 M HCl, sat. $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. Into a solution of the residue dissolved in 2,2-dimethoxypropane (10 mL, 80 mmol) was added *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol), and the reaction mixture was stirred at room temperature for 12 h. After dilution with ethyl acetate (10 mL), the mixture was washed with sat. $NaHCO_3$ and brine. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by means of column chromatography over silica gel (hexane/ethyl acetate = 24/1, v/v) to provide 1,3-dioxane **5** in 86% yield.

2,2-Dimethyl-5-neopentyl-4-phenyl-1,3-dioxane (5) (a mixture of *anti* and *syn* = 10:1, major isomer was assigned). mp = 79.5–80.1 °C. IR (KBr) 2995 (s), 2955 (s), 1059 (s), 1026 (s) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.58 (s, 9H), 0.78 (dd, J = 7.5, 14.5 Hz, 1H), 0.99 (dd, J = 1.5, 14.5 Hz, 1H), 1.48 (s, 3H), 1.56 (s, 3H), 1.86–1.95 (m, 1H, coalescing to ddm, J = 1.5, 5.3, 7.5 Hz by irradiation at 4.41), 3.70 (t, J = 11.6 Hz, 1H), 4.00 (dd, J = 5.3, 11.6 Hz, 1H), 4.41 (d, J = 10.3 Hz, 1H), 7.20–7.43 (m, 5H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 29.5, 29.9, 30.4, 37.8, 40.6, 66.8, 78.0, 98.5, 128.1, 128.2, 128.3, 140.3; high-resolution MS, calcd for $C_{17}H_{26}O_2$: 262.1933. Found m/z (relative intensity) 262.1934 (M^+, 25), 247 (79), 165 (94), 163 (100).

Typical procedure for the three-component coupling reaction of diene, carbon dioxide, and *t*-BuZnBr (entry 1, Table 4, condition A). Into a carbon dioxide-purged flask were introduced successively THF (2 mL), 1,3-butadiene (0.4 mL, 4 mmol), and *t*-BuZnBr (2.4 mL, 0.5 M in THF, 1.2 mmol) *via* syringes. The homogeneous mixture was stirred at room temperature for 24 h under carbon dioxide atmospheric pressure, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, 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 = 16/1, v/v) to give an analytically pure sample of **6a** (161 mg, 86%).

Typical procedure for the three-component coupling reaction of diene, carbon dioxide, and *t*-BuZnI reagent prepared from *t*-BuI and Zn dust (entry 1, Table 4, condition B): into a carbon dioxide-purged flask containing zinc dust (78 mg, 1.2 mmol) were introduced successively THF (2 mL), *t*-BuI (220 mg, 1.2 mmol), 1,3-butadiene (0.4 mL, 4 mmol) *via* syringes. The reaction mixture was stirred at room temperature for 24 h under carbon dioxide atmospheric pressure, during which the reaction was monitored by TLC. After dilution with ethyl acetate (30 mL), the mixture was washed successively with 2 N-HCl, 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 = 16/1, v/v) to give an analytically pure sample of **6a** (114 mg, 61%).

4,4-Dimethyl-2-vinylpentanoic acid (6a). IR (neat) 2957 (s), 2870 (s), 1709 (s), 1638 (m), 922 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.92 (s, 9H), 1.37 (dd, J = 4.3, 13.9 Hz, 1H), 1.87 (dd, J = 8.5, 13.9 Hz, 1H), 3.09 (ddt, J = 0.7, 4.3, 8.5 Hz, 1H), 5.04 (ddd, J = 0.7, 1.3, 10.1 Hz, 1H), 5.13 (dd, J = 1.3, 17.2 Hz, 1H), 5.81 (ddd, J = 8.5, 10.1, 17.2 Hz, 1H); ^{13}C NMR (400 MHz, CD_3OD) δ 30.0, 31.8, 47.2, 48.6, 116.1, 139.6, 178.5; high-resolution MS, calcd for $C_9H_{16}O_2$: 156.1150, found m/z (relative intensity): 156.1129 (M^+, 24), 141 (100).

2,4,4-Trimethyl-2-(prop-1-en-2-yl)pentanoic acid (6b). IR (neat) 2955 (s), 2876 (s), 1701 (s), 1638 (w), 897 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.99 (s, 9H), 1.39 (s, 3H), 1.67 (d, J = 14.4 Hz, 1H), 1.76 (d, J = 1.2 Hz, 3H), 2.04 (d, J = 14.4 Hz, 1H), 4.85 (q, J = 1.2 Hz, 1H), 4.94 (s, 1H); ^{13}C NMR (400 MHz, CD_3OD) δ 20.5, 23.0, 31.8, 32.5, 49.5, 52.4, 111.4, 150.0, 180.1; high-resolution MS, calcd for $C_{11}H_{20}O_2$: 184.1463, found m/z (relative intensity): 184.1437 (M^+, 25), 169 (100).

2,4,4-Trimethyl-2-vinylpentanoic acid (6c). IR (neat) 2955 (br s), 2874 (s), 1703 (s), 1643 (w), 918 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.96 (s, 9H), 1.34 (s, 3H), 1.65 (d, J = 14.4 Hz, 1H), 1.84 (d, J = 14.4 Hz, 1H), 5.01 (dd, J = 1.0, 10.7 Hz, 1H), 5.07 (dd, J = 1.0, 17.6, Hz, 1H), 6.17 (dd, J = 10.7, 17.6 Hz, 1H); ^{13}C NMR (400 MHz, CD_3OD) δ 23.4, 31.6, 32.7, 49.5, 54.0, 112.5, 145.2, 180.2; high-resolution MS, calcd for $C_{10}H_{18}O_2$: 170.1307, found m/z (relative intensity): 170.1303 (M^+, 100), 155 (60).

4,4-Dimethyl-2-(prop-1-en-2-yl)pentanoic acid (7c). IR (neat) 2955 (br s), 2874 (s), 1703 (s), 1643 (w), 918 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.91 (s, 9H), 1.35 (dd, J = 3.3, 14.0 Hz, 1H), 1.77 (dd, J = 0.9, 1.5 Hz, 3H), 1.98 (dd, J = 9.0, 14.0 Hz, 1H), 3.08 (dd, J = 3.3, 9.0 Hz, 1H), 4.81 (q, J = 1.5 Hz, 1H), 4.88 (q, J = 0.9 Hz, 1H); ^{13}C NMR (400 MHz, CD_3OD) δ 20.8, 29.7, 31.4, 45.5, 50.8, 112.9, 146.0, 177.8; high-resolution MS, calcd for $C_{10}H_{18}O_2$: 170.1307, found m/z (relative intensity): 170.1303 (M^+, 100), 155 (60).

6-Methyl-2-neopentyl-2-vinylhept-5-enoic acid (6d). IR (neat) 2955 (s), 2876 (s), 2608 (w), 1699 (s), 1638 (m), 914 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.92 (s, 9H), 1.55 (s, 3H), 1.62 (d, J = 14.1 Hz, 1H), 1.65 (d, J = 1.2 Hz, 3H), 1.67 (dd, J = 4.9, 12.2 Hz, 1H), 1.71–1.81 (m, 1H), 1.85 (dd, J = 3.9, 12.2 Hz, 1H), 1.94–2.01 (m, 1H), 1.99 (d, J = 14.1 Hz, 1H), 2.16 (s, 1H), 5.05 (dq, J = 1.2, 7.0 Hz, 1H), 5.17 (dd, J = 1.0, 17.8 Hz, 1H), 5.22 (dd, J = 1.0, 11.2 Hz, 1H), 6.31 (dd, J = 11.2, 17.8 Hz, 1H); ^{13}C NMR (400 MHz, CD_3OD) δ 17.6, 22.9, 25.6, 31.3, 31.9, 40.2, 51.2, 53.9, 114.1, 123.6, 131.8, 139.4, 181.0; high-resolution MS, calcd for $C_{15}H_{26}O_2$: 238.1933, found m/z (relative intensity): 238.1915 (M^+, 30), 195 (100).

7-Methyl-3-methylene-2-neopentyloct-6-enoic acid (7d). IR (neat) 2955 (s), 2874 (s), 2608 (w), 1699 (s), 1638 (m), 916 (m) cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.90 (s, 9H), 1.38 (dd, J = 2.8, 14.1 Hz, 1H), 1.61 (s, 3H), 1.68 (s, 3H), 2.02 (dd, J = 9.5, 14.1 Hz, 1H), 2.08–2.17 (m, 4H), 3.07 (dd, J = 2.8, 9.5 Hz, 1H), 4.89 (s, 1H), 5.01 (s, 1H), 5.09–5.14 (m, 1H); ^{13}C NMR (400 MHz, CD_3OD) δ 17.7, 25.6, 26.3, 29.2, 30.8, 44.9, 47.9, 111.4, 123.6, 131.8, 147.8, 179.7; high-resolution MS, calcd for $C_{15}H_{26}O_2$: 238.1933, found m/z (relative intensity): 238.1915 (M^+, 30), 195 (100).

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