Regio- and Stereoselective Multicomponent Coupling Reaction of Alkynes and Dimethylzinc Involving Allylnickelacycles

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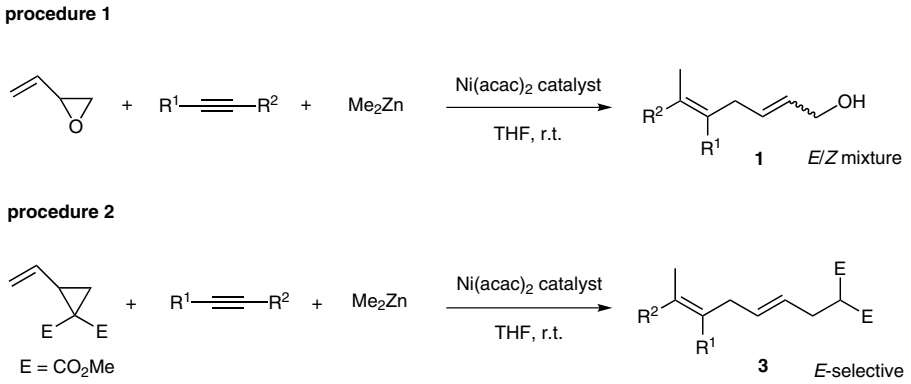
Received: 10.02.2012; Accepted: 17.02.2012

PSP No 227

Abstract: Nickel catalyzes the multicomponent coupling reaction of vinyl epoxides, alkynes, and dimethylzinc to provide hepta-2,5-dienyl alcohols as a mixture of *E*- and *Z*-isomers in high yields. Vinylcyclopropane participates in a similar multicomponent coupling reaction to afford dimethyl α-(hepta-2,5-dienyl)malonates with excellent *E*-stereoselectivity.

Key words: nickel, multicomponent coupling, alkyne, dimethylzinc, vinyl epoxide, cyclopropane



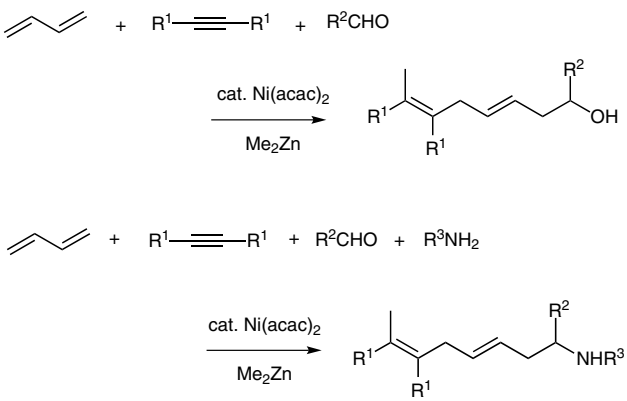
Scheme 1 Typical procedure for the three-component coupling reaction of alkyne, dimethylzinc, and vinyl epoxide/vinylcyclopropane

Introduction

Multicomponent coupling reactions are among the most efficient and straightforward synthetic strategies for C–C bond transformation.[1] In particular, nickel-catalyzed coupling reaction involving unsaturated hydrocarbons are widely utilized for the synthesis of physiologically active compounds and complicated molecules.[2]

We have previously developed nickel-catalyzed C–C bond formations by four-component coupling of buta-1,3-diene, alkynes, aldehydes, and dimethylzinc to provide octa-3,6-dienyl alcohols with excellent regio- and stereoselectivities (Scheme 2).[3]

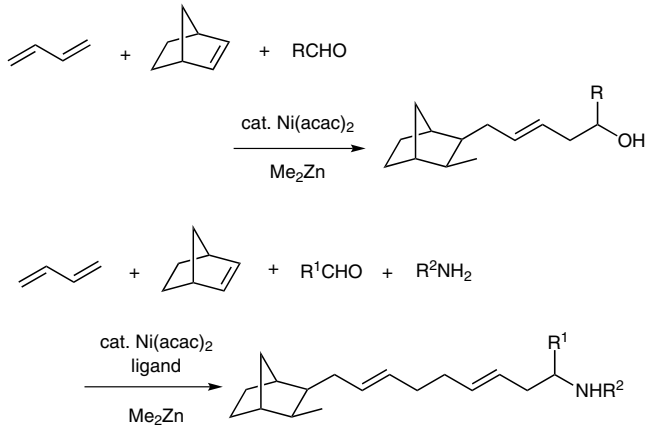
Under similar conditions, aldimines also participated in a similar multicomponent coupling reaction to afford octa-3,6-dienylamines and dodeca-3,7,10-trienylamines in reasonable yields.[4] Recently, we have shown that norbornene served as an active unsaturated hydrocarbon in place of alkynes and underwent the nickel-catalyzed coupling reaction with dimethylzinc, butadiene, and carbonyls to provide homoallylic alcohols and homoallylamines in high regio- and stereoselectivities (Scheme 3).[5]



Scheme 2 Multicomponent coupling of diene, alkyne, carbonyls, and dimethylzinc

The above-mentioned reactions seem to proceed through the oxidative cyclization of conjugated dienes and carbon-

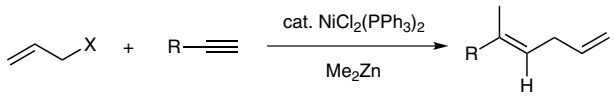
SYNTHESIS 2012, 44, 2333–2339
Advanced online publication: 12.04.2012
DOI: 10.1055/s-0031-1290764; Art ID: SS-2012-Z0141-PSP



Scheme 3 Multicomponent coupling of diene, norbornene, carbonyls, and dimethylzinc

yls to form a π-allylnickel intermediate that governs the high regio- and stereoselectivity.

Furthermore, the three-component coupling reaction of allyl halides, alkynes, and dimethylzinc in the presence of nickel catalyst via *syn*-stereoselective addition of π-allylnickel species followed by methyl group transfer to the alkyne carbon atom to construct the penta-1,4-diene skeleton has been previously reported (Scheme 4).[6] Nickel-catalyzed multicomponent coupling reactions of alkyne-tethered vinylcyclopropanes with allylic halides through the addition of π-allylnickel species to the C–C triple bonds giving (*E*)-1,3-diene analogues were also demonstrated.[7]



Scheme 4 Nickel-catalyzed coupling of allyl halides, alkyne, and dimethylzinc

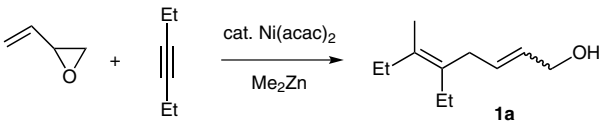
Encouraged by these studies, we report here the highly regio- and stereocontrolled three-component coupling reactions of alkynes, dimethylzinc, and vinyl epoxides/vinylcyclopropanes involving the addition of π-allylnickel species to the alkynes to provide hepta-2,5-dienyl alcohols and dimethyl α-(hepta-2,5-dienyl)malonates (Scheme 1, procedures 1 and 2).

Scope and Limitations

The reaction was conducted by exposing dimethylzinc to a mixture of vinyl epoxide and hex-3-yne in the presence of bis(acetylacetonato)nickel [Ni(acac)$_2$] catalyst under a nitrogen atmosphere. The results using various kinds of ligands and solvents are shown in Table 1.[8]

The initial investigation using vinyl epoxide and hex-3-yne made it clear that tetrahydrofuran was the most effective solvent (Table 1, entries 1–6). In all cases, hex-3-yne

Table 1 Initial Investigation for the Optimized Catalytic System[a]



Entry	Ligand	Solvent	Conditions	Product **1a** Yield (%)	Ratio *E*/*Z*
1	none	THF	r.t., 24 h	92	3:1
2	none	THF	50 °C, 24 h	89	3:1
3	none	Et_2O	r.t., 24 h	84	3:1
4	none	toluene	r.t., 24 h	81	3:1
5	none	CH_2Cl_2	r.t., 24 h	59	3:1
6	none	dioxane	r.t., 24 h	20	3:1
7	Ph_3P	THF	r.t., 48 h	71	3:1
8	Bu_3P	THF	r.t., 48 h	–[b]	–
9	dppf	THF	r.t., 48 h	–[b]	–
10	NHC	THF	r.t., 24 h	81	1:1

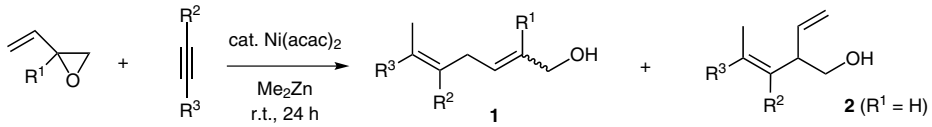
[a] Reaction conditions: vinyl epoxide (1 mmol), Ni(acac)$_2$ (0.1 mmol), ligand (0.2 mmol), hex-3-yne (1 mmol), 1 M Me_2Zn in hexane (1.2 mmol), solvent (3 mL), under N_2.
[b] No reaction.

attacked on the terminal carbon atom of the vinylic position via methyl group transfer from dimethylzinc in 1:1 to 3:1 ratio of *E*- and *Z*-isomers with respect to the C2 olefin geometry of hepta-2,5-dienyl alcohol **1a**. Among these results with various kinds of ligands using monodentate, bidentate phosphine ligands, and NHC ligands, their use at room temperature did not provide improved results in the formation of the desired product **1a**.

Based on this optimized catalytic systems, we examined the multicomponent coupling reaction of vinyl epoxide and substituted alkynes, and dimethylzinc on a multigram scale to give the corresponding dienyl alcohols **1** in good to reasonable yields (Table 2).

Hex-3-yne and diphenylacetylene participated in the coupling reaction with butadiene monoxide to afford **1a** and **1b**, respectively, in quantitative yields as a mixture of *E*- and *Z*-stereoisomers (Table 2, entries 1 and 2). Bis(trimethylsilyl)acetylene provided the marginal success in the coupling reaction (entry 3). The reaction using electron-deficient alkynes, such as bis(methoxycarbonyl)ethyne did not proceed at all (not shown in Table 2). Unsymmetrical alkynes took part in the coupling reaction in excellent yields to give **1d** as four inseparable regio- and stereoisomers and **1e** as two stereoisomers (entries 4 and 5). Two equivalents of terminal alkynes were required to afford the products **1f** and **1g** in modest yields along with the branched regioisomers **2f** and **2g**, which were produced by attack of the terminal alkynes on the internal allylic position of the vinyl epoxide.

Table 2 Coupling Reaction of Various Alkynes, Vinyl Epoxides, and Dimethylzinc on a 15-mmol Scale (Scheme 1, Procedure 1)[a]



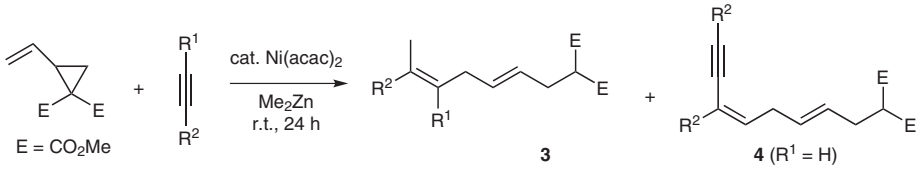
Entry	R^1	R^2	R^3	Products		
				1		**2**
				Yield (%)	Ratio *E*/*Z*	Yield (%)
1	H	Et	Et	**1a**: 99	3:1	
2	H	Ph	Ph	**1b**: 99	2:1	
3	H	TMS	TMS	**1c**: 41	2:1	
4	H	Et	Ph	**1d**: 95	8:4:2:1	
5	H	Me	TMS	**1e**: 97	2:1	
6[b]	H	H	Ph	**1f**: 37	2:1	**2f**: 18
7[b]	H	H	TMS	**1g**: 27	2:1	**2g**: 10
8	Me	Et	Et	**1h**: 93	1:2	
9	Me	Ph	Ph	**1i**: 84	1:3	
10	Me	TMS	TMS	**1j**: 41	1:1	

[a] Reaction conditions: vinyl epoxide (18 mmol), $Ni(acac)_2$ (0.15 mmol), alkyne (15 mmol), 1.0 M Me_2Zn in hexane (15 mmol), THF (30 mL), r.t., 24 h, under N_2.
[b] Using vinyl epoxide (15 mmol), $Ni(acac)_2$ (0.15 mmol), alkyne (30 mmol), 1.0 M Me_2Zn in hexane (15 mmol).

Isoprene monoxide underwent a similar coupling reaction in good to excellent yields, and employment of hex-3-yne and diphenylacetylene led to the formation of the desired product **1h** and **1i** in high yields in a 1:2 to 1:3 ratios of *E*- and *Z*-stereoisomers (entries 8 and 9). Bis(trimethylsilyl)acetylene showed modest yield and selectivity as well as the result of butadiene monoxide (entry 10).

The coupling reaction with various alkynes, dimethylzinc, and vinylcyclopropane, which is prepared from dimethyl malonate with 1,4-dichlorobut-2-ene, are summarized in Table 3. In most cases, the three-component coupling reaction proceeded at room temperature to provide the coupling products **3** in good yields with excellent *E*-stereoselectivity (entries 1 and 2). Bis(trimethylsilyl)acet-

Table 3 Coupling Reaction of Alkynes, Vinylcyclopropane, and Dimethylzinc on a 15-mmol Scale (Scheme 1, Procedure 2)[a]



Entry	R^1	R^2	Yield (%)	Ratio *E*/*Z*
1	Et	Et	**3a**: 80	7:1
2	Ph	Ph	**3b**: 68	*E* only
3	TMS	TMS	**3c**: 59	*E* only
4	Et	Ph	**3d**: 83	*E* only (3:1)[b]
5	Me	TMS	**3e**: 91	*E* only
6[c]	H	Ph	**4f**: 65	*E* only

[a] Reaction conditions: vinylcyclopropane (15 mmol), $Ni(acac)_2$ (0.15 mmol), alkyne (15 mmol), 1.0 M Me_2Zn in hexane (15 mmol), THF (30 mL), r.t., 24 h, under N_2.
[b] Product **3d** was obtained as a mixture of regioisomer in 3:1.
[c] Using vinylcyclopropane (15 mmol), $Ni(acac)_2$ (0.15 mmol), phenylacetylene (45 mmol), 1.0 M Me_2Zn in hexane (15 mmol).

ylene took part in the efficient coupling reaction to afford the desired product **3c** with exclusive *E*-selectivity in reasonable yield (entry 3). Unsymmetrical internal alkynes also participated in the coupling reaction. 1-Phenylbut-1-yne provided **3d** as regioisomers in a 3:1 ratio with excellent *E*-stereoselectivity, whereas 1-(trimethylsilyl)prop-1-yne gave **3e** as a single isomer with excellent *E*-stereoselectivity. In all cases, the stereochemistry with respect to the methyl group and the olefin main chain is the *Z*-form, as in the reaction of vinylcyclopropane. The reaction using a terminal alkyne, such as phenylacetylene, changed dramatically and the desired product **3f** was not obtained. Instead, dienyne **4f** was produced exclusively via dimerization of terminal alkyne followed by stereoselective coupling reaction with vinylcyclopropane.

Conclusions

In summary, we have demonstrated that the nickel-catalyzed multicomponent coupling reaction of vinyl epoxides, alkynes, and dimethylzinc provides hepta-2,5-dienyl alcohols as mixtures of *E*- and *Z*-isomers in high yields. Furthermore, vinylcyclopropane participated in a highly regio- and stereoselective multicomponent coupling reaction to afford dimethyl α-(hepta-2,5-dienyl)malonates with excellent *E*-stereoselectivity. We have succeeded in extending these reactions to the multigram scale for the efficient synthesis of dienyl alcohols and stereodefined dienyl esters. These reactions could be performed with standard laboratory glassware and equipment and did not require expensive and specialized chemicals and catalysts.

All reactions were carried out under an N_2 atmosphere in dried glassware. $Ni(acac)_2$ (Aldrich), and 1.0 M Me_2Zn in hexane (Kanto Kagaku) were purchased and used without further purification. Hex-3-yne, diphenylacetylene, bis(trimethylsilyl)acetylene, bis(methoxycarbonyl)ethyne, phenylacetylene, trimethylsilylacetylene, 1-phenylbut-1-yne, and 1-(trimethylsilyl)prop-1-yne (Tokyo Kasei Kogyo Co., Ltd) were purchased and distilled prior to use. Butadiene monoxide and isoprene oxide (Aldrich) were purchased and distilled prior to use. Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate was prepared according to the literature.[9] THF was dried and distilled from benzophenone and Na immediately prior to use under N_2. 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. Unless otherwise specified, short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus, in these cases, boiling points refer to the oven temperature. ^1H and ^{13}C NMR data were obtained with a Jeol-GX400 with TMS as internal standard. Infrared spectra were recorded with a Jasco A-100 FT-IR spectrophotometer. HRMS were measured with a Jeol JMS-DX303.

(2*E*/*Z*,5*E*)-5-Ethyl-6-methylocta-2,5-dien-1-ol (1a); Typical Procedure 1

An oven-dried, 100-mL, 4-necked round-bottomed flask equipped with a dropping funnel, thermometer, rubber septum cap, air condenser (fitted with a 3-way stopcock connected into an N_2 balloon), and Teflon-coated magnetic stir bar was charged with $Ni(acac)_2$ (38.5 mg, 0.15 mmol). The apparatus was purged with N_2 and the flask was charged successively via syringe with fresh anhyd THF (30 mL), butadiene monoxide (1.26 g, 18 mmol), and hex-3-yne (1.23 g, 15 mmol). 1.0 M Me_2Zn in hexane was added slowly at r.t. via the dropping funnel over a period of 10 min (the reaction temperature should not exceed 50 °C). The mixture was stirred at r.t. for 24 h (TLC monitoring). After the reaction was complete, the mixture was cooled to 0 °C, and then poured into ice-water. The resulting soln was diluted with EtOAc (30 mL) and carefully washed with 2 M HCl (20 mL) and separated, and the aqueous layer was extracted with EtOAc (50 mL). The combined organic phases were washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography (silica gel, hexane–EtOAc, 16:1) to afford **1a** (2.51 g, 99%) as a colorless oil; ratio *E*/*Z* 3:1; R_f = 0.45 (hexane–EtOAc, 4:1); bp 100 °C/0.13 mbar.

IR (neat): 3319 (m), 2962 (s), 2931 (s), 2872 (s), 1655 (w), 1373 (m), 1070 (m), 1004 (m), 970 (m), 792 cm^{-1} (w).

^1H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 0.94 (t, *J* = 7.6 Hz, 3 H), 0.97 (t, *J* = 7.6 Hz, 3 H), 1.62 (s, 3 H), 2.03 (q, *J* = 7.6 Hz, 2 H), 2.04 (q, *J* = 7.6 Hz, 2 H), 2.75 (m, 2 H), 4.09 (m, 2 H), 5.62 (m, 2 H).

^1H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.94 (t, *J* = 7.6 Hz, 3 H), 0.97 (t, *J* = 7.6 Hz, 3 H), 1.58 (s, 3 H), 2.03 (q, *J* = 7.6 Hz, 2 H), 2.04 (q, *J* = 7.6 Hz, 2 H), 2.80 (d, *J* = 7.3 Hz, 2 H), 4.26 (m, 2 H), 5.45 (dt, *J* = 11.0, 7.3 Hz, 1 H), 5.58 (dm, *J* = 11.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 13.3, 13.6, 17.5, 24.9, 27.0, 34.7, 63.8, 127.9, 128.8, 131.2, 131.6.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 13.2, 13.6, 17.5, 24.8, 27.1, 30.2, 58.7, 127.9, 128.8, 131.0, 131.4.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{11}H_{20}O$: 168.1514; found (%): 169 ($[M + 1]^+$, 1), 168.1497 (M^+, 8), 167 (20), 151 (27), 150 (31), 139 (100).

(2*E*/*Z*,5*Z*)-5,6-Diphenylhepta-2,5-dien-1-ol (1b)

Following typical procedure 1. Purification by flash chromatography (hexane–EtOAc, 8:1) afforded **1b** (3.93 g, 99%) as a colorless oil; ratio *E*/*Z* 2:1; bp 180 °C/0.13 mbar.

IR (neat): 3350 (s), 3055 (s), 3020 (s), 2993 (s), 2928 (s), 2870 (m), 1717 (s), 1682 (s), 1599 (m), 1489 (s), 1443 (s), 1026 (m), 970 (m), 912 (m), 764 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 2.17 (s, 3 H), 3.31 (m, 2 H), 4.10 (m, 2 H), 5.72 (m, 2 H), 7.00 (m, 10 H).

^1H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 2.20 (s, 3 H), 3.34 (d, *J* = 6.6 Hz, 2 H), 4.00 (d, *J* = 6.3 Hz, 2 H), 5.57 (dt, *J* = 10.2, 6.6 Hz, 1 H), 5.72 (dt, *J* = 10.2, 6.3 Hz, 1 H), 6.90–7.10 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 21.1, 37.9, 63.6, 125.6, 127.4, 127.5, 128.9, 129.0, 129.4, 129.5, 129.6, 134.7, 142.8, 143.1, 144.1.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 20.9, 33.5, 58.4, 125.8, 127.4, 127.5, 128.9, 129.3, 129.4, 129.5, 129.6, 135.4, 142.8, 143.1, 144.0.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}O$: 264.1514; found (%): 264.1440 (M^+, 42), 263 (100), 262 (51), 246 (57).

(2*E*/*Z*,5*Z*)-5,6-Bis(trimethylsilyl)hepta-2,5-dien-1-ol (1c)

Following typical procedure 1. Purification by flash chromatography (hexane–EtOAc, 12:1) afforded **1c** (1.58 g, 41%) as a colorless oil; ratio *E*/*Z* 2:1; bp 110 °C/0.13 mbar.

IR (neat): 3329 (m), 2955 (s), 2899 (m), 2864 (m), 1456 (w), 1248 (s), 1001 (m), 968 (m), 837 (s), 756 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 18 H), 1.26 (br, 1 H), 1.78 (s, 3 H), 2.89 (d, *J* = 7.6 Hz, 2 H), 4.26 (d, *J* = 6.3 Hz, 2 H), 5.60–5.68 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 0.4, 17.6, 33.4, 63.8, 128.6, 130.3, 142.9.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.4, 17.6, 31.6, 60.3, 128.6, 130.3, 143.3.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{13}H_{28}OSi_2$: 256.1679; found (%): 257 ($[M + 1]^+$, 24), 256.1679 (M^+, 100), 225 (9).

(2*E*,5*E*)-5-Ethyl-6-phenylhepta-2,5-dien-1-ol (1d)
Following typical procedure 1. Purification by flash chromatography (hexane–EtOAc, 8:1) afforded **1d** (3.09 g, 95%) as a colorless oil; a mixture of 4 isomers in the ratio 8:4:2:1, minor regioisomers were not assigned; bp 150 °C/0.13 mbar.

IR (neat): 3350 (s), 3057 (m), 3020 (m), 2968 (s), 2933 (s), 2873 (s), 1717 (s), 1682 (s), 1599 (m), 1491 (s), 1441 (s), 1026 (s), 972 (m), 766 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ (2*E*-isomer) = 0.89 (t, *J* = 7.6 Hz, 3 H), 1.58 (br s, 1 H), 1.89 (q, *J* = 7.6 Hz, 2 H), 1.93 (s, 3 H), 2.94 (m, 2 H), 4.14 (m, 2 H), 5.73 (m, 2 H), 7.10 (t, *J* = 7.6 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 7.30 (t, *J* = 7.6 Hz, 1 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (2*Z*-isomer) = 0.90 (t, *J* = 7.6 Hz, 3 H), 1.31 (br s, 1 H), 1.89 (q, *J* = 7.6 Hz, 2 H), 1.95 (s, 3 H), 2.98 (d, *J* = 7.3 Hz, 2 H), 4.31 (d, *J* = 6.6 Hz, 2 H), 5.56 (dt, *J* = 10.7, 7.3 Hz, 1 H), 5.67 (dt, *J* = 10.7, 6.6 Hz, 1 H), 7.10 (t, *J* = 7.6 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 7.29 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (2*E*-isomer) = 13.4, 21.0, 26.2, 33.8, 63.7, 125.8, 127.8, 127.9, 128.5, 129.3, 130.4, 130.9, 144.9.

^{13}C NMR (100 MHz, $CDCl_3$): δ (2*Z*-isomer) = 13.3, 20.9, 26.1, 29.4, 58.7, 125.8, 127.9, 127.9, 128.6, 129.2, 130.4, 130.9, 144.9.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{15}H_{20}O$: 216.1514; found (%): 217 ($[M + 1]^+$, 16), 216.1496 (M^+, 100), 214 (15), 199 (36).

(2*E*/*Z*,5*E*)-5-Methyl-6-(trimethylsilyl)hepta-2,5-dien-1-ol (1e)
Following typical procedure 1. Purification by flash chromatography (hexane–EtOAc, 16:1) afforded **1e** (2.89 g, 97%) as a colorless oil; ratio *E*/*Z* 2:1; bp 115 °C/0.13 mbar.

IR (neat): 3312 (s), 2953 (s), 2912 (s), 2860 (m), 1612 (m), 1445 (m), 1247 (s), 1001 (m), 835 (s), 756 (s), 687 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 0.12 (s, 9 H), 1.26 (br s, 1 H), 1.70 (s, 3 H), 1.78 (s, 3 H), 2.84 (d, *J* = 7.4 Hz, 2 H), 4.09 (d, *J* = 6.3 Hz, 2 H), 5.45–5.65 (m, 2 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.13 (s, 9 H), 1.35 (br s, 1 H), 1.71 (s, 3 H), 1.85 (s, 3 H), 2.89 (d, *J* = 7.4 Hz, 2 H), 4.25 (d, *J* = 6.3 Hz, 2 H), 5.45–5.65 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 0.4, 17.6, 21.1, 37.9, 63.7, 128.4, 129.2, 131.9, 142.9.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.7, 17.6, 22.9, 34.3, 58.6, 128.6, 129.8, 130.3, 144.7.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{11}H_{22}OSi$: 198.1440; found (%): 199 ($[M + 1]^+$, 10), 198.1431 (M^+, 60), 183 (20), 169 (16), 127 (100).

(2*E*/*Z*,5*E*)-6-Phenylhepta-2,5-dien-1-ol (1f) and (*E*)-4-Phenyl-2-vinylpent-3-en-1-ol (2f)
Following typical procedure 1 using $Ni(acac)_2$ (38.5 mg, 0.15 mmol), butadiene monoxide (1.05 g, 15 mmol), phenylacetylene (3.06 g, 30 mmol), and 1 M Me_2Zn in hexane (15 mmol) in anhyd THF (30 mL). Purification by flash column chromatography (hexane–EtOAc, 6:1) afforded **1f** and **2f** both as colorless oils with bp 160 °C/0.13 mbar.

(2*E*/*Z*,5*E*)-6-Phenylhepta-2,5-dien-1-ol (1f)
Yield: 1.05 g (37%); ratio *E*/*Z* 2:1; R_f = 0.50 (hexane–EtOAc, 4:1).

IR (neat): 3371 (br), 3024 (s), 2926 (s), 2872 (s), 1719 (m), 1647 (m), 1495 (s), 1447 (s), 1028 (s), 927 (s), 760 (s), 698 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 1.55 (br, 1 H), 2.05 (t, *J* = 1.0 Hz, 3 H), 2.99 (t, *J* = 7.0 Hz, 2 H), 4.12 (d, *J* = 5.3 Hz, 1 H), 4.27 (d, *J* = 5.3 Hz, 1 H), 5.60–5.80 (m, 3 H), 7.21 (tt, *J* = 7.0, 2.0 Hz, 1 H), 7.30 (td, *J* = 7.0, 1.5 Hz, 2 H), 7.36 (dt, *J* = 7.0, 1.3 Hz, 2 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 1.55 (br, 1 H), 2.05 (t, *J* = 1.0 Hz, 3 H), 2.95 (t *J* = 7.0 Hz, 2 H), 4.12 (d, *J* = 5.3 Hz, 1 H), 4.27 (d, *J* = 5.3 Hz, 1 H), 5.60–5.80 (m, 3 H), 7.21 (tt, *J* = 7.0, 2.0 Hz, 1 H), 7.30 (td, *J* = 7.0, 1.5 Hz, 2 H), 7.36 (dt, *J* = 7.0, 1.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 15.8, 31.4, 63.6, 125.5, 126.6, 128.0, 128.2, 129.4, 130.7, 135.9, 143.5.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 15.8, 27.3, 58.6, 125.5, 126.6, 128.0, 128.2, 128.8, 130.7, 135.6, 143.4.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O$: 188.1183; found (%): 189 ($[M + 1]^+$, 8), 188.1183 (M^+, 54), 171 (13), 157 (48).

(*E*)-4-Phenyl-2-vinylpent-3-en-1-ol (2f)
Yield: 508 mg (18%); R_f = 0.53 (hexane–EtOAc, 4:1).

IR (neat): 3362 (br), 3080 (s), 2928 (s), 2872 (s), 1726 (s), 1636 (m), 1597 (m), 1493 (m), 914 (m), 758 (s), 696 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54 (s, 1 H), 2.09 (d, *J* = 1.5 Hz, 3 H), 3.38 (ddt, *J* = 10.3, 9.0, 7.4 Hz, 1 H), 3.62 (d, *J* = 7.4 Hz, 2 H), 5.17 (dd, *J* = 7.6, 1.5 Hz, 1 H), 5.20 (dd, *J* = 17.3, 1.5 Hz, 1 H), 5.63 (dq, *J* = 9.0, 1.5 Hz, 1 H), 5.78 (ddd, *J* = 17.3, 10.3, 7.6 Hz, 1 H), 7.24 (tt, *J* = 7.9, 2.3 Hz, 1 H), 7.31 (td, *J* = 7.9, 1.5 Hz, 2 H), 7.39 (dt, *J* = 7.9, 1.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.4, 46.3, 65.5, 116.5, 125.6, 125.9, 126.9, 128.1, 137.4, 138.0, 143.3.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O$: 188.1183; found (%): 189 ($[M + 1]^+$, 7), 188.1183 (M^+, 46), 157 (100), 142 (76).

(2*E*/*Z*,5*E*)-6-(Trimethylsilyl)hepta-2,5-dien-1-ol (1g) and (*E*)-4-(Trimethylsilyl)-2-vinylpent-3-en-1-ol (2g)
Following typical procedure 1 using $Ni(acac)_2$ (38.5 mg, 0.15 mmol), butadiene monoxide (1.05 g, 15 mmol), trimethylsilylacetylene (2.95 g, 30 mmol), and 1.0 M Me_2Zn in hexane (15 mmol) in anhyd THF (30 mL). Purification by flash column chromatography (hexane–EtOAc, 10:1) afforded **1g** and **2g** both as colorless oils with bp 110 °C/0.13 mbar.

(2*E*/*Z*,5*E*)-6-(Trimethylsilyl)hepta-2,5-dien-1-ol (1g)
Yield: 756 mg (27%); ratio *E*/*Z* 2:1 R_f = 0.46 (hexane–EtOAc, 4:1).

IR (neat): 3317 (br), 3009 (s), 2955 (s), 2899 (s), 1614 (m), 1248 (s), 1013 (s), 970 (s), 837 (s), 750 (s), 689 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 0.01 (s, 9 H), 1.28 (s, 1 H), 1.63 (d, *J* = 0.9 Hz, 3 H), 2.84 (t, *J* = 6.9 Hz, 2 H), 4.06 (d, *J* = 5.6 Hz, 2 H), 5.62 (m, 3 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.01 (s, 9 H), 1.28 (s, 1 H), 1.65 (d, *J* = 0.9 Hz, 3 H), 2.81 (t, *J* = 6.9 Hz, 2 H), 4.19 (d, *J* = 5.6 Hz, 2 H), 5.62 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = –2.1, 14.4, 31.2, 63.7, 128.5, 129.1, 131.0, 135.9.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = –2.1, 14.4, 27.0, 58.6, 128.5, 129.1, 131.0, 135.9.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{10}H_{20}OSi$: 184.1283; found (%): 185 ($[M + 1]^+$, 16), 184.1261 (M^+, 100), 170 (12), 169 (82), 166 (34).

(*E*)-4-(Trimethylsilyl)-2-vinylpent-3-en-1-ol (2g)
Yield: 276 mg (10%), R_f = 0.50 (hexane–EtOAc, 4:1).

IR (neat): 3313 (br), 3080 (m), 2955 (s), 2874 (m), 1618 (m), 1248 (s), 1028 (s), 991 (m), 835 (s), 750 (s), 689 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 1.43 (s, 1 H), 1.73 (d, *J* = 1.7 Hz, 3 H), 3.38 (tdd, *J* = 8.5, 7.8, 6.7 Hz, 1 H), 3.52 (d, *J* = 7.8 Hz, 2 H), 5.11 (dd, *J* = 17.6, 1.7 Hz, 1 H), 5.12 (dd, *J* = 9.8, 1.7 Hz, 1 H), 5.53 (dq, *J* = 8.5, 1.7 Hz, 1 H), 5.72 (ddd, *J* = 17.6, 9.8, 6.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.6, 15.4, 46.3, 65.6, 116.7, 136.5, 137.9, 140.9.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{10}H_{20}OSi$: 184.1283; found (%): 185 ($[M + 1]^+$, 16), 184.1261 (M^+, 100), 170 (12), 169 (82), 166 (34).

(2*Z*/*E*,5*E*)-5-Ethyl-2,6-dimethylocta-2,5-dien-1-ol (1h)
Following typical procedure 1 using isoprene monoxide instead of butadiene monoxide. Purification by flash chromatography (hexane–EtOAc, 16:1) afforded **1h** (2.54 g, 93%) as a colorless oil; ratio *E*/*Z* 1:2; bp 105 °C/0.13 mbar.

IR (neat): 3336 (m), 2964 (s), 2934 (s), 2872 (s), 1653 (m), 1456 (s), 1375 (s), 1005 (s), 951 (w), 785 cm^{-1} (w).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.94 (t, *J* = 7.6 Hz, 3 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 1.64 (s, 3 H), 1.80 (q, *J* = 1.2 Hz, 3 H), 1.99 (q, *J* = 7.6 Hz, 2 H), 2.02 (q, *J* = 7.6 Hz, 2 H), 2.77 (d, *J* = 7.1 Hz, 2 H), 4.19 (s, 2 H), 5.31 (tq, *J* = 7.1, 1.2 Hz, 1 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 0.94 (t, *J* = 7.6 Hz, 3 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 1.64 (s, 3 H), 1.72 (s, 3 H), 1.99 (q, *J* = 7.6 Hz, 2 H), 2.02 (q, *J* = 7.6 Hz, 2 H), 2.75 (d, *J* = 6.6 Hz, 2 H), 4.00 (s, 2 H), 5.21 (t, *J* = 6.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 13.2, 13.6, 17.5, 21.3, 24.6, 27.1, 30.2, 61.7, 127.2, 130.5, 132.2, 133.7.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 13.2, 13.6, 13.8, 17.6, 24.9, 27.1, 30.4, 69.1, 125.4, 130.5, 132.3, 134.2.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{12}H_{22}O$: 182.1671; found (%): 183 ($[M + 1]^+$, 10), 182.1669 (M^+, 69), 164 (100).

(2*Z*/*E*,5*Z*)-2-Methyl-5,6-diphenylhepta-2,5-dien-1-ol (1i)
Following typical procedure 1 using isoprene monoxide instead of butadiene monoxide. Purification by flash chromatography (hexane–EtOAc, 12:1) afforded **1i** (3.51 g, 84%) as a colorless oil; ratio *E*/*Z* 1:3; bp 170 °C /0.13 mbar.

IR (neat): 3350 (s), 3057 (m), 3024 (s), 2968 (s), 2933 (s), 2876 (s), 1719 (s), 1701 (s), 1670 (m), 1599 (m), 1491 (s), 1437 (s), 1026 (m), 912 (m), 760 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 1.55 (br s, 1 H), 1.74 (d, *J* = 1.2 Hz, 3 H), 2.20 (s, 3 H), 3.30 (d, *J* = 7.6 Hz, 2 H), 3.91 (s, 2 H), 5.31 (tq, *J* = 7.6, 1.2 Hz, 1 H), 6.92–7.08 (m, 10 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 1.55 (br s, 1 H), 1.63 (d, *J* = 1.2 Hz, 3 H), 2.18 (s, 3 H), 3.30 (d, *J* = 7.6 Hz, 2 H), 3.97 (s, 2 H), 5.41 (tq, *J* = 6.8, 1.2 Hz, 1 H), 6.92–7.08 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 20.9, 21.3, 33.8, 61.5, 124.6, 125.7, 127.4, 127.5, 128.9, 129.6, 135.2, 136.0, 143.0, 144.1.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 13.8, 21.1, 33.8, 68.8, 123.5, 125.5, 127.4, 127.5, 129.0, 129.4, 135.2, 136.0, 143.0, 144.1.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{20}H_{22}O$: 278.1671; found (%): 279 ($[M + 1]^+$, 17), 278.1658 (M^+, 73), 260 (100).

(2*Z*/*E*,5*Z*)-2-Methyl-5,6-bis(trimethylsilyl)hepta-2,5-dien-1-ol (1j)
Following typical procedure 1 using isoprene monoxide instead of butadiene monoxide. Purification by flash chromatography (hexane–EtOAc, 16:1) afforded **1j** (1.65 g, 41%) as a colorless oil; ratio *E*/*Z* 1:1; bp 170 °C/0.13 mbar.

IR (neat): 3396 (br), 2955 (s), 2899 (s), 1717 (s), 1699 (s), 1248 (s), 1047 (s), 1009 (s), 839 (s), 756 (s), 689 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.14 (s, 9 H), 0.18 (s, 9 H), 1.72 (s, 3 H), 1.80 (br s, 1 H), 1.83 (s, 3 H), 2.85 (d, *J* = 6.7 Hz, 2 H), 4.19 (d, *J* = 4.2 Hz, 2 H), 5.04 (t, *J* = 6.7 Hz, 1 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 0.13 (s, 9 H), 0.17 (s, 9 H), 1.72 (s, 3 H), 1.80 (br s, 1 H), 1.83 (s, 3 H), 2.83 (d, *J* = 6.8 Hz, 2 H), 4.19 (d, *J* = 4.2 Hz, 2 H), 5.02 (t, *J* = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 0.81, 1.46, 13.9, 18.7, 25.4, 69.1, 124.3, 133.4, 143.9, 149.8.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 0.81, 1.93, 18.7, 20.2, 25.4, 61.9, 125.9, 133.5, 143.9, 151.2.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{14}H_{30}OSi_2$: 270.1835; found (%): 270.1812 (M^+, 100), 269 (72), 254 (94).

Dimethyl 2-[(2*E*/*Z*,5*E*)-5-Ethyl-6-methylocta-2,5-dienyl]malonate (3a); Typical Procedure 2
An oven-dried, 100-mL, 4-necked round-bottomed flask equipped with a dropping funnel, a thermometer, a rubber septum cap, an air condenser (fitted with a 3-way stopcock connected into N_2 balloon), and a Teflon-coated magnetic stir bar was charged with $Ni(acac)_2$ (38.5 mg, 0.15 mmol). The apparatus was purged with N_2 and the flask was charged successively via syringe with fresh anhyd THF (30 mL), vinylcyclopropane (2.76 g, 15 mmol), and hex-3-yne (1.23 g, 15 mmol). 1.0 M Me_2Zn in hexane (15 mmol) was added slowly via the dropping funnel over a period of 10 min (the reaction temperature should not exceed 50 °C). The mixture was stirred at r.t. for 24 h (TLC monitoring). After the reaction was completed, the mixture was cooled to 0 °C, and then poured into ice-water. The resulting soln was diluted with EtOAc (30 mL) and carefully washed with 2 M HCl (20 mL) and separated, and the aqueous layer was extracted with EtOAc (50 mL). The combined organic phases were washed with sat. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated in vacuo. The residual oil was subjected to column chromatography (silica gel, hexane–EtOAc, 25:1) to afford **3a** (3.38 g, 80%) as a colorless oil; ratio *E*/*Z* 7:1; R_f = 0.60 (hexane–EtOAc, 4:1); bp 130 /0.13 mbar.

IR (neat): 2959 (s), 2882 (m), 1738 (s), 1655 (w), 1437 (s), 1340 (m), 1269 (m), 1161 (m), 974 (m), 698 cm^{-1} (w).

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*-isomer) = 0.91 (t, *J* = 7.6 Hz, 3 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 1.54 (s, 3 H), 1.97 (q, *J* = 7.6 Hz, 2 H), 2.02 (q, *J* = 7.6 Hz, 2 H), 2.58 (ddd, *J* = 7.8, 6.8, 1.2 Hz, 2 H), 2.67 (d, *J* = 6.1 Hz, 2 H), 3.40 (t, *J* = 7.8 Hz, 1 H), 3.71 (s, 6 H), 5.32 (dt, *J* = 15.1, 6.8 Hz, 1 H), 5.46 (dtt, *J* = 15.1, 6.1, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E*-isomer) = 13.3, 13.6, 17.5, 24.7, 27.0, 31.9, 35.0, 52.1, 52.3, 52.7, 124.9, 127.7, 131.1, 131.8, 169.2, 172.4.

^{13}C NMR (100 MHz, $CDCl_3$): δ (*Z*-isomer) = 13.2, 13.7, 17.6, 24.9, 26.9, 27.1, 30.0, 51.7, 52.4, 52.4, 124.9, 127.7, 131.1, 132.0, 169.3, 172.4.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{26}O_4$: 282.1831; found (%): 282.1829 (M^+, 100), 253 (64), 251 (25).

Dimethyl 2-[(2*E*,5*Z*)-5,6-Diphenylhepta-2,5-dienyl]malonate (3b)
Following typical procedure 2. Purification by flash chromatography (hexane–EtOAc, 16:1) afforded **3b** (3.86 g, 68%) as a colorless oil; bp 190 °C/0.13 mbar.

IR (neat): 3078 (w), 3020 (s), 2999 (m), 2953 (s), 1732 (s), 1599 (w), 1435 (s), 1198 (m), 1155 (s), 764 (s), 700 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 2.60 (ddd, *J* = 7.6, 6.8, 1.0 Hz, 2 H), 3.23 (d, *J* = 5.9 Hz, 2 H), 3.38 (t, *J* = 7.6 Hz, 1 H), 3.69 (s, 6 H), 5.46 (dt, *J* = 15.1, 6.8 Hz, 1 H), 5.58 (dtt, *J* = 15.1, 5.9, 1.0 Hz, 1 H), 6.90–7.06 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 31.9, 38.2, 52.0, 52.3, 52.4, 125.5, 125.6, 127.3, 127.4, 128.6, 128.9, 129.4, 134.5, 134.9, 138.9, 143.3, 144.2, 169.1.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{24}H_{26}O_4$: 378.1831; found (%): 379 ($[M + 1]^+$, 27), 378.1835 (M^+, 100), 360 (3).

Dimethyl 2-[(2*E*,5*Z*)-5,6-Bis(trimethylsilyl)hepta-2,5-dienyl]malonate (3c)
Following typical procedure 2. Purification by flash chromatography (hexane–EtOAc, 20:1) afforded **3c** (3.28 g, 59%) as a colorless oil; bp 120 °C/0.13 mbar.

IR (neat): 2957 (s), 1736 (s), 1456 (m), 1437 (m), 1340 (m), 1248 (s), 1198 (s), 1155 (s), 972 (m), 839 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 18 H), 1.76 (s, 3 H), 2.62 (d, *J* = 6.4 Hz, 2 H), 2.62 (t, *J* = 7.5 Hz, 2 H), 3.42 (t, *J* = 7.5 Hz, 1 H), 3.75 (s, 6 H), 5.64–5.46 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.1, 22.8, 32.1, 52.3, 125.5, 130.1, 143.2, 150.5, 169.3.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{34}O_4Si_2$: 370.1996; found (%): 371 ($[M + 1]^+$, 22), 370.2006 (M^+, 78), 355 (100), 339 (6).

Dimethyl 2-[(2*E*,5*E*)-5-Ethyl-6-phenylhepta-2,5-dienyl]malonate (3d)
Following typical procedure 2. Purification by flash chromatography (hexane–EtOAc, 16:1) afforded **3d** (4.11 g, 83%) as a colorless oil; ratio of regioisomers 3:1; bp 140 °C/0.13 mbar.

IR (neat): 3020 (m), 2959 (s), 2934 (s), 1738 (s), 1437 (s), 1232 (s), 1153 (s), 1026 (m), 970 (m), 768 (s), 704 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ (major) = 0.86 (t, *J* = 7.4 Hz, 3 H), 1.85 (q, *J* = 7.4 Hz, 2 H), 1.90 (s, 3 H), 2.63 (td, *J* = 7.3, 1.2 Hz, 2 H), 2.85 (d, *J* = 6.2 Hz, 2 H), 3.44 (t, *J* = 7.3 Hz, 1 H), 3.72 (s, 6 H), 5.46 (dtt, *J* = 15.4, 7.3, 1.5 Hz, 1 H), 5.57 (dtt, *J* = 15.4, 6.2, 1.5 Hz, 1 H), 7.09 (dd, *J* = 7.5, 1.4 Hz, 2 H), 7.19 (tt, *J* = 7.5, 1.4 Hz, 1 H), 7.29 (td, *J* = 7.5, 1.4 Hz, 2 H).

^1H NMR (400 MHz, $CDCl_3$): δ (minor) = 0.90 (t, *J* = 7.4 Hz, 3 H), 1.75 (s, 3 H), 1.91 (q, *J* = 7.4 Hz, 2 H), 2.55 (td, *J* = 7.3, 1.2 Hz, 2 H), 2.98 (d, *J* = 6.2 Hz, 2 H), 3.35 (t, *J* = 7.3 Hz, 1 H), 3.69 (s, 6 H), 5.32 (dtt, *J* = 15.4, 7.3, 1.5 Hz, 1 H), 5.45 (dtt, *J* = 15.4, 6.2, 1.5 Hz, 1 H), 7.03 (dd, *J* = 7.5, 1.4 Hz, 2 H), 7.19 (tt, *J* = 7.5, 1.4 Hz, 1 H), 7.27 (td, *J* = 7.5, 1.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) = 13.4, 20.9, 26.1, 31.9, 34.1, 52.0, 52.3, 125.5, 125.7, 127.7, 127.9, 128.5, 131.2, 134.5, 145.0, 169.2.

^{13}C NMR (100 MHz, $CDCl_3$): δ (minor) = 13.2, 17.0, 28.5, 31.8, 37.9, 52.0, 52.3, 125.4, 125.7, 127.9, 128.5, 130.7, 131.9, 134.4, 143.8, 169.2.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{20}H_{26}O_4$: 330.1831; found (%): 371 ($[M + 1]^+$, 23), 330.1832 (M^+, 100), 315 (2), 301 (4), 299 (4).

Dimethyl 2-[(2*E*,5*E*)-5-Methyl-6-(trimethylsilyl)hepta-2,5-dienyl]malonate (3e)
Following typical procedure 2. Purification by flash chromatography (hexane–EtOAc, 20:1) afforded **3e** (4.26 g, 91%) as a colorless oil; bp 120 °C/0.13 mbar.

IR (neat): 2955 (s), 1740 (s), 1612 (w), 1437 (m), 1248 (m), 1155 (m), 972 (w), 856 (m), 837 (m), 756 (w), 689 cm^{-1} (w).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 9 H), 1.62 (d, *J* = 1.2 Hz, 3 H), 1.74 (q, *J* = 1.2 Hz, 3 H), 2.58 (ddd, *J* = 1.2, 6.8, 7.6 Hz, 2 H), 2.76 (d, *J* = 6.3 Hz, 2 H), 3.41 (t, *J* = 7.6 Hz, 1 H), 3.71 (s, 6 H), 5.34 (dt, *J* = 15.1, 6.8 Hz, 1 H), 5.46 (dtt, *J* = 15.1, 6.3, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.40, 17.4, 22.9, 26.8, 31.9, 38.1, 52.0, 52.3, 125.5, 127.6, 130.6, 143.2, 169.2.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{28}O_4Si$: 312.1757; found (%): 313 (M^+, 22), 312.1743 (M^+, 100), 297 (81).

Dimethyl 2-[(2*E*,5*Z*)-6,8-Diphenylocta-2,5-dien-7-ynyl]malonate (4f)
Following typical procedure 2 using $Ni(acac)_2$ (38.5 mg, 0.15 mmol), vinylcyclopropane (2.76 g, 15 mmol), phenylacetylene (4.60 g, 45 mmol), and 1.0 M Me_2Zn in hexane (15 mmol) in anhyd THF (30 mL). Purification by flash column chromatography (hexane–EtOAc, 16:1) afforded **4f** (3.80 g, 65%) as a yellow-colored oil; R_f = 0.55 (hexane–EtOAc, 4:1).

IR (neat): 3028 (s), 2953 (s), 2843 (m), 1738 (s), 1597 (m), 1489 (s), 1435 (s), 1155 (s), 1028 (s), 970 (m), 914 (m), 758 (s), 692 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (td, *J* = 7.6, 1.0 Hz, 2 H), 3.25 (td, *J* = 6.9, 1.0 Hz, 2 H), 3.43 (t, *J* = 7.6 Hz, 1 H), 3.71 (s, 6 H), 5.53 (dtt, *J* = 15.4, 6.9, 1.3 Hz, 1 H), 5.65 (dtt, *J* = 15.4, 7.6, 1.3 Hz, 1 H), 6.37 (t, *J* = 7.6 Hz, 1 H), 7.27–7.37 (m, 6 H), 7.50–7.55 (m, 2 H), 7.62–7.65 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9, 34.4, 51.8, 52.4, 86.4, 95.5, 123.3, 124.1, 125.9, 126.8, 127.5, 128.2, 130.4, 131.4, 135.2, 137.9, 169.1.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{25}H_{24}O_4$: 388.1675; found (%): 389 ($[M + 1]^+$, 28), 388.1689 (M^+, 100), 373 (6), 357 (92), 329 (22).

Acknowledgement

This work was supported by Grants-in Aid for Scientific Research (B) (21350055) and Scientific Research on Innovative Areas 'Molecular Activation Directed toward Straightforward Synthesis' from MEXT, Japan.

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