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Pentadienyl transfer reagents based on zirconium: preparation and reactions with carbonyl compounds

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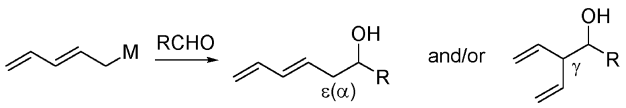
Abstract—A variety of 2,4-pentadienylzirconiums were generated by reacting pentadienyl ethers with zirconocene 'Cp_2Zr'. These complexes underwent a highly γ-regioselective and *anti*-stereoselective in situ addition with carbonyl compounds to afford bis(homoallylic) alcohols in good yields. The reversal of *anti* vs *syn* selectivity was simply achieved with BF_3, thus expanding the synthetic potential of the reaction.

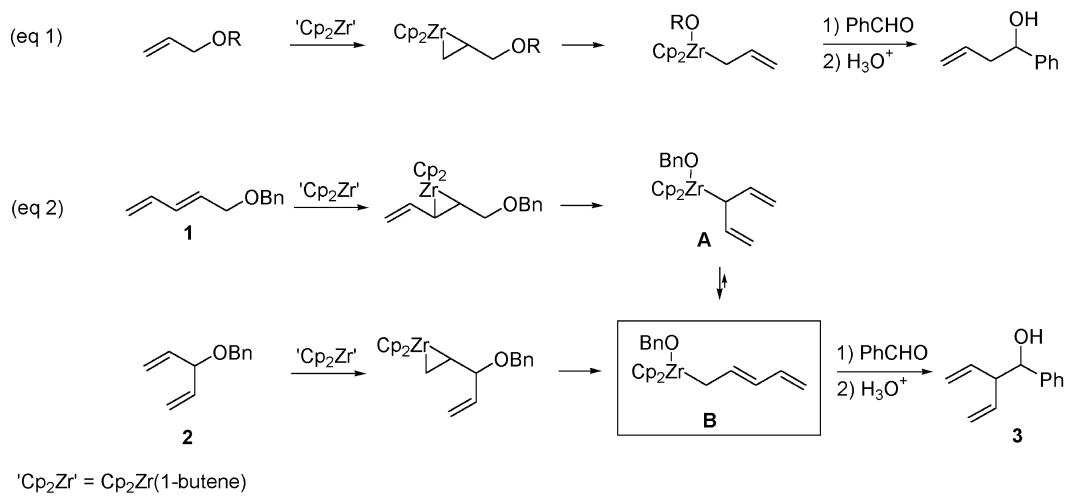
1. Introduction

Allylmetals are important reagents for the stereoselective carbon–carbon bond-forming reactions.[1] Particularly, they react with carbonyl compounds to produce homoallylic alcohols, which are useful synthetic intermediates. In contrast, the analogous 2,4-pentadienylmetals employing reactions have been much less investigated.[2] The regiochemical outcome of the pentadienylation reactions is shown in Scheme 1.



Scheme 1.

When the reaction occurs at the ε (or α)-carbon in the complex, a linear alcohol is formed, whereas at the γ-carbon a branched alcohol is obtained. The regioselectivity of these reactions has been demonstrated to vary with the metal.[2] Whereas lithium, potassium and magnesium generally give poor regioselectivity, the addition at the γ-position preferentially occurs with indium, titanium, boron, zinc or chromium, and at the ε-position with silicon and tin. Furthermore, the stereoselectivity of the pentadienylation reactions have not been studied systematically. Both *anti*



Scheme 2.

Keywords: Homoallylic alcohols; Pentadienylation reaction; Stereocontrol; Zirconium.
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and/or *syn* diastereoselectivity have been observed depending on the metal.

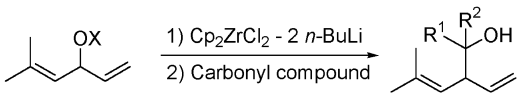
Pentadienylmetals are typically prepared by transmetalation from lithium or potassium pentadienyl precursors or by Barbier-type reactions from the corresponding pentadienyl bromides. The synthetic potential of pentadienylmetals would be considerably enhanced if these complexes could be prepared from chemically more stable and readily available starting materials.[3] With this aim in view we have reported a preliminary work on a simple and practical way of preparing pentadienylzirconocenes from dienyl ethers.[4] These complexes proved to react with aldehydes in the γ-selective manner. We disclose herein a full account on the reactions involving pentadienylzirconium reagents.

2. Results and discussion

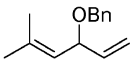
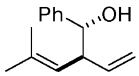
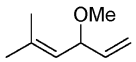
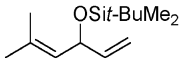
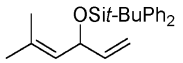
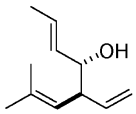
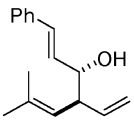
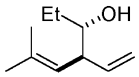
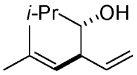
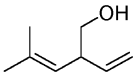
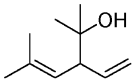
It is known that allylic ethers react with (1-butene)zirconocene[5] to afford allylzirconium derivatives.[6] The reaction occurs through ligand exchange, formation of a zirconacyclopropane and the successive β-elimination of the alkoxy group (Scheme 2, Eq. (1)).

We have demonstrated that, analogously, pentadienylzirconium compounds could be generated from dienyl ethers (Scheme 2, Eq. (2)).[7] It is noteworthy that the same complex **B** was solely obtained from both the linear ether **1** and the ramified ether **2**. We assumed the zirconium fragment (Cp_2ZrOBn) would migrate in **A** to a less hindered site of the allyl moiety, leading to the thermodynamically more favorable complex **B**.[8] Accordingly, both linear and

Table 1. Zr-mediated pentadienylation of carbonyl compounds



4a-d **5a-g**

Entry	Ether	Carbonyl compound	*T* (°C)	Product[a]	Yield (%)[b] (*anti*/*syn*)[c]
1	**4a** 	PhCHO	20	**5a** 	96 (86:14)
2	**4b** 	PhCHO	20	**5a**	55 (84:16)
3	**4c** 	PhCHO	20	**5a**	94 (87:13)
4	**4d** 	PhCHO	20	**5a**	93 (94:6)
5	**4a**	PhCHO	−78	**5a**	78 (92:8)
6	**4a**	MeCH=CHCHO	−78	**5b** 	83 (93:7)
7	**4a**	PhCH=CHCHO	−78	**5c** 	93 (92:8)
8	**4a**	EtCHO	−78	**5d** 	57 (>95:5)
9	**4a**	*i*-PrCHO	−78	**5e** 	64 (>95:5)
10	**4a**	$(HCHO)_n$[d]	−78	**5f** 	81 (−)
11	**4a**	Me_2CO	−78	**5g** 	70 (−)

[a] Only the major stereoisomer is shown.
[b] Isolated yield.
[c] *anti*/*syn* Ratio determinated by ^1H NMR.
[d] Paraformaldehyde was used.

ramified pentadienyl ethers can be employed as starting materials to form the unique penta-2,4-dienylzirconium species.

The pentadienylzirconocenes were typically formed from the pentadienyl ether, Cp_2ZrCl_2 and 2*n*-BuLi by applying the Taguchi protocol for the formation of allylzirconocenes[6d] or better by a modified procedure.[4,9] The zirconium species thus generated were further used for the pentadienylation reactions. In the first experiment, the preformed complex **B** was reacted with benzaldehyde to produce the alcohol **3** regioselectively, in 60–70% yield (Scheme 2).[4] To investigate both the regio- and the stereoselectivity of the reaction we next used the pentadienyl ethers **4a–d** and various carbonyl compounds as substrates. The results are summarized in Table 1.

2.1. Temperature and structure effects on stereoselectivity

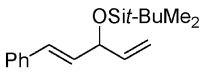
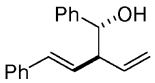
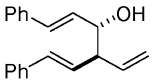
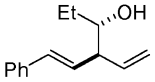
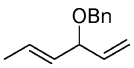
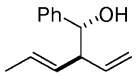
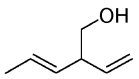
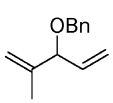
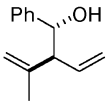
In all cases the reaction occurred regioselectively at the γ-carbon of the complex to afford the branched alcohols **5a–g** solely. Furthermore, the pentadienylation of the aldehydes appeared to be markedly *anti*-stereoselective.[10] The stereoselectivity of the reaction employing PhCHO can slightly be increased by introducing a bulky OX group in the ether. Whereas the diastereomeric ratio remains almost constant for X=Bn, Me and Si*t*-BuMe$_2$ (entries 1–3), an improvement in the *anti* diastereoselection was observed for X=Si*t*-BuPh$_2$ (entry 4). The stereoselectivity of the reaction was increased further by adding the aldehyde at −78 °C rather than at 20 °C. Two examples employing the ether **4a** and benzaldehyde are given (entries 1 and 5). In these conditions, a high *anti*/*syn* ratio remains almost constant (92:8 to >95:5) for the aromatic, α,β-unsaturated as well as the aliphatic aldehydes (entries 5–9). Both regio- and stereochemistry of the reaction are consistent with a conventional six-membered chair-like transition state, as proposed for the simpler allylzirconation reactions.[1] The primary alcohol **5f** and the tertiary alcohol **5g** (a terpene, santolina alcohol) can finally be obtained by employing respectively paraformaldehyde and acetone (entries 10 and 11).

2.2. Ether components

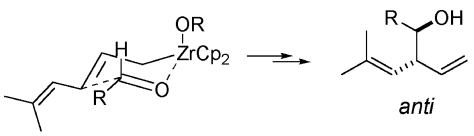
The synthetic utility of the reaction is also displayed by the possible use of various penta-1,4-dienyl ethers as substrates. Both 1- and 2-substituted pentadienyl ethers were employed, and the examples of these reactions are depicted in Table 2.

As for the non-substituted and 1,1-disubstituted pentadienyl ether, also in these cases γ-regioisomers were obtained solely in good yields. All the reactions involving 1-substituted ethers (entries 1–4) proceeded with a high *anti* diastereoselectivity (*anti*/*syn*≅ 95:5). The high level of *anti* selection appeared to be independent both of the nature of the aldehyde (aromatic, α,β-unsaturated or aliphatic, entries 1–3, respectively), and of the alkoxy group in the ether (X=Si*t*-BuMe$_2$ or Bn, entries 1–3 vs 4). We observed a partial *E* to *Z* isomerization of the double bond in alcohols **7d** and **7e** derived from the ether **6b**. Finally, only a moderate decrease in *anti* selectivity has been noticed when using a 2-substituted ether instead of the 1-substituted analogue (alcohols **7d** and **7f**, entries 4 and 6).

Table 2. Zr-mediated pentadienylations (following)

Entry	Ether	Aldehyde	Product[a]	Yield (%)[b] (*anti*/*syn*)[c]
1	**6a** 	PhCHO	**7a** 	90 (>95:5)
2	**6a**	PhCH=CHCHO	**7b** 	81 (>95:5)
3	**6a**	EtCHO	**7c** 	90 (93:7)
4	**6b** 	PhCHO	**7d** 	85 (>95:5)[d]
5	**6b**	$(HCHO)_n$	**7e** 	62 (−)[e]
6	**6c** 	PhCHO	**7f** 	76 (88:12)

[a] Only the major stereoisomer is shown.
[b] Isolated yield.
[c] *anti*/*syn* Ratio determinated by ^{1}H NMR.
[d] *E*/*Z* isomers=80:20.
[e] *E*/*Z* isomers=71:29.



Scheme 3.

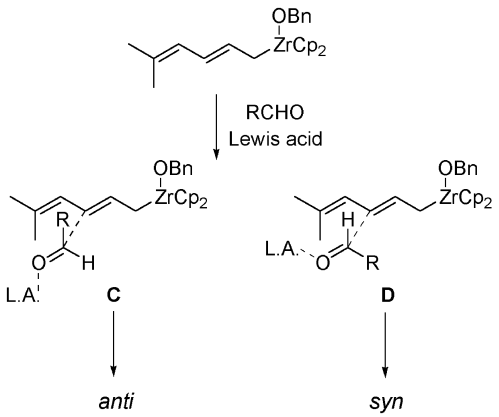
2.3. Reversal of *anti* to *syn* diastereoselectivity

At this stage, the synthetic limitation of the pentadienylation reactions lied in their invariably predominant *anti* stereochemistry. We made efforts to control the stereochemistry of these reactions, i.e. to ensure that it could be reversed leading mainly to the *syn* configurated alcohols. The *anti* stereochemistry can be explained by assuming a conventional six-membered chair-like transition state, as for the simpler allylzirconation reactions (Scheme 3). We then examined whether it was possible to modify the reaction conditions to favour a non-cyclic mechanism[1] over the cyclic one.

Lewis acids[11] and polar solvents, especially HMPA,[12] have been shown to affect the stereochemistry of the reactions originally proceeding through a six-membered transition state. We first examined the effect of HMPA as co-solvent and noticed that no change in stereochemistry took place. To promote a non-cyclic mechanism for the pentadienylation reactions, we then turned to the use of a Lewis acid. After the complex had been generated, $BF_3{\cdot}OEt_2$ (1 equiv.) was added at −78 °C, followed by the aldehyde, and the reaction mixture was allowed to warm to 20 °C. We noticed that a reversal of *anti* to *syn* stereoselectivity took place by applying this modified procedure (Procedure B, Section 3).[13] The results of the reactions with or without BF_3, employing ethers **4a** and **6a**–**c**, as well as the aromatic, α,β-unsaturated and aliphatic aldehydes are summarized in Table 3.

We noticed that a spectacular reversal of *anti* to *syn* stereoselectivity invariably took place when using the aromatic or α,β-unsaturated aldehydes, i.e. benzaldehyde (entries 1, 6, 9, and 10), cinnamaldehyde (entries 3 and 7) and crotonaldehyde (entry 2). In contrast, the effect of modifying the stereoselectivity was only moderate for the aliphatic aldehydes (entries 4, 5, and 8).

The Lewis acid-induced reversal of *anti* to *syn* stereoselectivity in the reactions of η^1-allyltitaniums with



Scheme 4.

carbonyl compounds was observed by Reetz.[11] The predominant *syn* selectivity in the presence of a Lewis acid was considered to be consistent with a non-cyclic antiperiplanar transition state.[14] We assumed tentatively, that also in our case, the reversal of *anti* to *syn* selectivity can be explained by a non-cyclic mechanism operating with BF_3 as presented in Scheme 4.[15]

A higher *syn* selectivity for the aromatic or unsaturated than for the aliphatic aldehydes is not entirely clear at present. This could possibly be rationalized by additional destabilizing π–π interactions in the transition structure **C**, thus favouring all the more **D**. However, the mechanism of the Lewis acid-mediated reactions could even be more complicated.[16] Systematic mechanistic studies are needed to fully elucidate the effect of Lewis acids on the stereoselectivity.

In summary, we have presented a practical procedure for preparing bis(homoallylic) alcohols in a highly γ-regioselective and *anti*-stereoselective manner. Furthermore, in the presence of a Lewis acid, the stereochemistry can be reversed leading predominantly to the *syn*-configurated products.

3. Experimental

3.1. General

All reactions were conducted under an atmosphere of dry

Table 3. Effect of $BF_3{\cdot}OEt_2$ on the *anti* vs *syn* diastereoselectivity

Entry	Ether	Carbonyl compound	Product	*anti*/*syn*[a]	$BF_3{\cdot}OEt_2$ *anti*/*syn*[a]
1	**4a**	PhCHO	**5a**	92:8	26:74
2	**4a**	MeCH=CHCHO	**5b**	93:7	18:82
3	**4a**	PhCH=CHCHO	**5c**	92:8	20:80
4	**4a**	EtCHO	**5d**	>95:5	68:32
5	**4a**	*i*-PrCHO	**5e**	>95:5	57:43
6	**6a**	PhCHO	**7a**	>95:5	16:84
7	**6a**	PhCH=CHCHO	**7b**	>95:5	18:82
8	**6a**	EtCHO	**7c**	93:7	50:50
9	**6b**	PhCHO	**7d**	>95:5	21:79
10	**6c**	PhCHO	**7f**	88:12	35:65[b]

[a] *anti*/*syn* Ratio determinated by ^{1}H NMR.
[b] ε-Addition product, i.e. 3-methyl-1-phenylhexa-3,5-dien-1-ol (**8**), was also formed in 29% yield.

argon using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-250 or DRX-500 spectrometer. IR spectra were recorded on a Nicolet Avatar 320 instrument. Mass spectra were recorded on a ThermoFinnigan Trace MS spectrometer. Cp_2ZrCl_2 and vinylmagnesium bromide reagents were used as received. *n*-BuLi was titrated with diphenylacetic acid in THF prior to use. Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use.

3.2. Preparation of ethers

3.2.1. 4-Benzyloxy-2-methylhexa-2,5-diene (4a). A solution of 3-methylbut-2-enal (7.7 mL, 80 mmol) in THF (20 mL) was added dropwise at room temperature to a solution of vinylmagnesium bromide (100 mL, 100 mmol, 1.0 M in THF) in THF (50 mL). After stirring for 1 h, 5 mL of water was added to the reaction mixture to produce a viscous paste in the walls of the flask. The organic layer was separated. The paste was washed twice with Et_2O. The combined organic phases were dried over $MgSO_4$. Filtration and removal of the solvent gave 8.5 g (95%) of the crude alcohol which was sufficiently pure (according to NMR) to be used in the next step. NaH (0.87 g, 36 mmol, oil removed by washing with pentane) was added to a solution of the crude alcohol (3.36 g, 30 mmol) in THF (30 mL). After stirring for 1 h, benzyl bromide (3.36 mL, 30 mmol) was added. After stirring overnight, water was poured into the mixture and extracted twice with Et_2O. The combined organic phases were dried over $MgSO_4$. Filtration and removal of the solvent gave a light yellow oil which was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 99:1). Yield 4.36 g (72%). ^{1}H NMR (250 MHz): δ (ppm)=1.65 (s, 3H), 1.79 (s, 3H), 4.51 (s, 2H), 4.52–4.58 (m, 1H), 5.15–5.29 (m, 3H), 5.86 (ddd, J=17.3, 10.3, 6.7 Hz, 1H), 7.25–7.39 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=18.3 (CH_3), 25.9 (CH_3), 69.3 (CH_2), 76.5 (CH), 115.7 (CH_2), 124.3 (CH), 127.3 (CH), 127.7 (CH), 128.2 (CH), 136.2 (C), 138.1 (CH), 138.7 (C). IR (film): ν (cm^{-1})=3064, 2859, 1672, 1454, 1380. MS (EI): *m*/*z* (%)=202 (1, $M^{+\cdot}$), 108 (64), 94 (64), 79 (100).

Ethers **4b**–**d** were obtained following the procedure described for the preparation of the ether **4a**, by using MeI, *t*-$BuMe_2SiCl$ and *t*-$BuPh_2SiCl$, respectively, instead of BnBr.

3.2.2. 4-Methoxy-2-methylhexa-2,5-diene (4b). ^{1}H NMR (250 MHz): δ (ppm)=1.70 (s, 3H), 1.77 (s, 3H), 3.28 (s, 3H), 4.32 (t, J=7.7 Hz, 1H), 5.08–5.27 (m, 3H), 5.77 (ddd, J=17.2, 10.3, 6.8 Hz, 1H). ^{13}C NMR (63 MHz): δ (ppm)=18.3 (CH_3), 25.8 (CH_3), 55.4 (CH_3), 79.0 (CH), 115.7 (CH_2), 124.2 (CH), 136.3 (C), 137.9 (CH). IR (film): ν (cm^{-1})=2975, 1686, 1449, 1378. MS (EI): *m*/*z* (%)=126 (6, $M^{+\cdot}$), 111 (28), 94 (85), 79 (100).

3.2.3. 4-*t*-Butyldimethylsilyloxy-2-methylhexa-2,5-diene (4c). ^{1}H NMR (250 MHz): δ (ppm)=0.05 (s, 6H), 0.89 (s, 9H), 1.65 (s, 3H), 1.71 (s, 3H), 4.80–4.87 (m, 1H), 4.99 (dd, J=10.3, 1.4 Hz, 1H), 5.08–5.22 (m, 2H), 5.80 (ddd, J=17.1, 10.3, 5.2 Hz, 1H). ^{13}C NMR (63 MHz): δ (ppm)=−4.7 (CH_3), −4.5 (CH_3), 18.2 (CH_3), 18.3 (C), 25.7 (CH_3), 25.9 (CH_3), 70.8 (CH), 112.4 (CH_2), 127.6 (CH), 131.9 (C), 140.7 (CH). IR (film): ν (cm^{-1})=2947, 2864, 1466 cm^{-1}. MS (EI): *m*/*z* (%)=211 (3, M−Me), 169 (50, M−*t*-Bu), 95 (22), 75 (100).

3.2.4. 4-*t*-Butyldiphenylsilyloxy-2-methylhexa-2,5-diene (4d). ^{1}H NMR (250 MHz): δ (ppm)=1.05 (s, 9H), 1.14 (s, 3H), 1.57 (s, 3H), 4.76–4.84 (m, 1H), 4.99 (dt, J=10.3, 1.5 Hz, 1H), 5.10–5.20 (m, 2H), 5.82 (ddd, J=17.1, 10.3, 5.2 Hz, 1H), 7.30–7.46 (m, 6H), 7.65–7.74 (m, 4H). ^{13}C NMR (63 MHz): δ (ppm)=17.8 (CH_3), 19.3 (C), 25.5 (CH_3), 26.9 (CH_3), 71.5 (CH), 112.7 (CH_2), 127.0 (CH), 127.2 (CH), 127.4 (CH), 129.3 (CH), 129.4 (CH), 132.5 (C), 134.2 (C), 134.3 (C), 135.9 (CH), 136.0 (CH), 140.3 (CH). IR (film): ν (cm^{-1})=3072, 2926, 2844, 1676, 1641, 1591. MS (EI): *m*/*z* (%)=293 (30, M−*t*-Bu), 199 (100).

3.2.5. 3-*t*-Butyldimethylsilyloxy-1-phenylpenta-1,4-diene (6a). A solution of cinnamaldehyde (7.5 mL, 60 mmol) in THF (20 mL) was added dropwise at room temperature to a solution of vinylmagnesium bromide (80 mL, 80 mmol, 1.0 M in THF) in THF (15 mL). After stirring for 1 h, ca. 5 mL of water was added to the reaction mixture to produce a viscous paste in the walls of the flask. The organic layer was separated. The paste was washed twice with Et_2O. The combined organic phases were dried over $MgSO_4$. Filtration and removal of the solvent followed by purification by column chromatography (silica gel, petroleum ether/ethyl acetate 90:10) gave 14.6 g (89%) of 1-phenylpenta-1,4-dien-3-ol. ^{1}H NMR (250 MHz): δ (ppm)=1.83 (br s, OH), 4.78–4.85 (m, 1H), 5.21 (dd, J=10.3, 1.0 Hz, 1H), 5.36 (dd, J=17.3, 1.0 Hz, 1H), 5.98 (ddd, J=17.3, 10.3, 6.2 Hz, 1H), 6.25 (dd, J=16.0, 6.5 Hz, 1H), 6.63 (d, J=16.0 Hz, 1H), 7.20–7.45 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=73.5 (CH), 115.2 (CH_2), 126.4 (CH), 127.6 (CH), 128.4 (CH), 130.3 (CH), 130.5 (CH), 136.4 (C), 139.1 (CH). IR (film): ν (cm^{-1})=3356, 1655, 1597, 1495, 1454. To the alcohol (0.96 g, 6 mmol) in Et_2O (20 mL) was added *t*-$BuMe_2SiCl$ (1.0 g, 6.6 mmol) and 4-(dimethylamino)pyridine (0.85 g, 6.6 mmol). After stirring overnight, the precipitate was eliminated by filtration. Removal of the solvent and purification by column chromatography (silica gel, petroleum ether/ethyl acetate 99:1) furnished 1.38 g (84%) of **6a**. ^{1}H NMR (250 MHz): δ (ppm)=0.11 (s, 6H), 0.91 (s, 9H), 4.78 (br t, J=5.6 Hz, 1H), 5.12 (d, J=10.3 Hz, 1H), 5.29 (d, J=17.1 Hz, 1H), 5.89 (ddd, J=17.1, 10.3, 5.4 Hz, 1H), 6.18 (dd, J=15.9, 5.9 Hz, 1H), 6.56 (d, J=15.9 Hz, 1H), 7.20–7.41 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=−4.7 (CH_3), −4.6 (CH_3), 18.4 (C), 25.9 (CH_3), 74.4 (CH), 113.8 (CH_2), 126.4 (CH), 127.4 (CH), 128.5 (CH), 129.0 (CH), 131.6 (CH), 136.9 (C), 140.1 (CH). IR (film): ν (cm^{-1})=2956, 2857, 1472, 1252. MS (EI): *m*/*z* (%)=217 (13, M−*t*-Bu), 143 (35), 142 (30), 81 (100).

3.2.6. (*E*)-3-Benzyloxyhexa-1,4-diene (6b). Ether **6b** was obtained in 82% yield from crotonaldehyde (two steps) following the procedure described for the preparation of ether **4a**. ^{1}H NMR (250 MHz): δ (ppm)=1.75 (d, J=6.3 Hz, 3H), 4.23 (t, J=6.8 Hz, 1H), 4.51 (s, 2H), 5.20 (d, J=10.3 Hz, 1H), 5.26 (d, J=17.3 Hz, 1H), 5.50 (ddq, J=15.4, 7.1, 1.5 Hz, 1H), 5.71 (dq, J=15.4, 6.3 Hz, 1H), 5.85 (ddd, J=17.3, 10.3, 6.6 Hz, 1H), 7.25–7.35 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=17.8 (CH_3), 69.5 (CH_2), 80.6 (CH), 116.3 (CH_2), 127.3 (CH), 127.6 (CH), 128.2 (CH), 128.7

(CH), 130.5 (CH), 138.1 (CH), 138.6 (C). IR (film): ν (cm^{-1})=3029, 2857, 1668, 1454. MS (EI): *m/z* (%)=170 (1, M−H_2O), 144 (6), 130 (10), 91 (90), 79 (100).

3.2.7. 3-Benzyloxy-2-methylhexa-1,4-diene (6c). Ether **6c** was obtained in 78% yield from methacroleine (2 steps), following the procedure described for the preparation of **4a**. ^1H NMR (250 MHz): δ (ppm)=1.72 (s, 3H), 4.24 (d, *J*=6.1 Hz, 1H), 4.46 (d, *J*=12.0 Hz, 1H), 4.52 (d, *J*=12.0 Hz, 1H), 4.98 (s, 1H), 5.05 (s, 1H), 5.23 (d, *J*=10.4 Hz, 1H), 5.31 (d, *J*=17.3 Hz, 1H), 5.84 (ddd, *J*=17.3, 10.4, 6.1 Hz, 1H), 7.25–7.45 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=17.6 (CH_3), 69.6 (CH_2), 83.5 (CH), 113.0 (CH_2), 116.5 (CH_2), 127.3 (CH), 127.5 (CH), 128.3 (CH), 137.3 (CH), 138.6 (C), 144.1 (C). IR (film): ν (cm^{-1})=3070, 2859, 1644, 1454. MS (EI): *m/z* (%)=170 (4, M−H_2O), 97 (28), 91 (100).

4. Zr-mediated pentadienylation of carbonyl compounds

4.1. General procedure for the preparation of bis(homoallylic) alcohols (procedure A)

To a solution of the dienyl ether (1 mmol) and Cp_2ZrCl_2 (321 mg, 1.1 mmol) in THF (5 mL) at 0 °C, was added dropwise *n*-BuLi (2.2 mmol, 2–2.5 M in hexanes). After stirring for 10 min at this temperature, the yellow solution was refluxed for 0.5 h, and cooled to −78 °C (or 20 °C, see Table 1). The carbonyl compound (1.5 mmol) was added, and the mixture warmed slowly to room temperature (about 1 h). HCl 1N (5 mL) and Et_2O (10 mL) were added to the solution. The organic layer was separated and washed with aq. $NaHCO_3$, then dried over $MgSO_4$. Filtration and removal of the solvent gave a yellow oil, which was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 92:8).

4.2. General procedure for the preparation of bis(homoallylic) alcohols in the presence of $BF_3{\cdot}OEt_2$ (procedure B)

Procedure A was modified by the addition of $BF_3{\cdot}OEt_2$ (125 L, 1 mmol) at −78 °C; the mixture was stirred for 15 min at this temperature before the addition of the carbonyl compound.

4.2.1. 4-Methyl-1-phenyl-2-vinylpent-3-en-1-ol (5a).[4] *Procedure A*. Yield 78% from **4a** (*anti*/*syn* 92:8).

Procedure B. Yield 72% from **4a** (*anti*/*syn* 26:74). IR (film): ν (cm^{-1})=3428, 1636, 1453, 1380. MS (EI): *m/z* (%)=184 (4, M−H_2O), 169 (10), 106 (48), 105 (52), 94 (39), 77 (100).

anti-**5a**. ^1H NMR (500 MHz): δ (ppm)=1.33 (s, 3H), 1.61 (s, 3H), 2.25 (br s, OH), 3.24 (br q, *J*=8.3 Hz, 1H), 4.49 (d, *J*=7.6 Hz, 1H), 5.02 (d, *J*=9.4 Hz, 1H), 5.16 (d, *J*=16.0 Hz, 1H), 5.17 (d, *J*=11.3 Hz, 1H), 5.78 (ddd, *J*=16.0, 11.3, 8.0 Hz, 1H), 7.20–7.35 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=17.9 (CH_3), 26.8 (CH_3), 51.6 (CH), 76.4 (CH), 117.0 (CH_2), 122.0 (CH), 126.7 (CH), 127.3 (CH), 127.8 (CH), 134.5 (C), 138.0 (CH), 142.1 (C).

Syn-**5a**. ^1H NMR (250 MHz): δ (ppm)=1.61 (s, 3H), 1.78 (s, 3H), 2.25 (br s, OH), 3.27 (br q, *J*=7.7 Hz, 1H), 4.46 (d, *J*=7.5 Hz, 1H), 4.88–5.16 (m, 3H), 5.60 (ddd, *J*=17.2, 10.4, 6.9 Hz, 1H), 7.20–7.35 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=18.3 (CH_3), 26.1 (CH_3), 51.0 (CH), 77.0 (CH), 116.1 (CH_2), 122.3 (CH), 127.0 (CH), 127.5 (CH), 128.0 (CH), 136.6 (C), 137.4 (CH), 141.9 (C).

4.2.2. (*E*)-7-Methyl-5-vinylocta-2,6-dien-4-ol (5b). *Procedure A*. Yield 83% (*anti*/*syn* 93:7).

Procedure B. Yield 93% (*anti*/*syn* 18:82). IR (film): ν (cm^{-1})=3405, 672, 1636, 1451, 1376. MS (EI): *m/z* (%)=148 (5, M−H_2O), 133 (8), 96 (59), 81 (100).

anti-**5b**. ^1H NMR (250 MHz): δ (ppm)=1.63 (s, 3H), 1.70 (d, *J*=6.5 Hz, 3H), 1.74 (s, 3H), 1.78 (br s, OH), 3.06 (br q, *J*=8.0 Hz, 1H), 3.94 (t, *J*=6.7 Hz, 1H), 5.03–5.13 (m, 3H), 5.47 (ddq, *J*=15.3, 6.8, 1.6 Hz, 1H), 5.69 (dq, *J*=15.3, 6.5 Hz, 1H), 5.69–5.77 (m, 1H). ^{13}C NMR (63 MHz): δ (ppm)=17.6 (CH_3), 18.1 (CH_3), 25.8 (CH_3), 49.6 (CH), 74.8 (CH), 116.0 (CH_2), 122.1 (CH), 127.2 (CH), 131.3 (CH), 134.3 (C), 137.9 (CH).

syn-**5b**. ^1H NMR (250 MHz): δ (ppm)=1.66 (s, 3H), 1.71 (d, *J*=6.3 Hz, 3H), 1.73 (br s, OH), 1.78 (s, 3H), 3.06 (br q, *J*=7.8 Hz, 1H), 3.90 (t, *J*=7.0 Hz, 1H), 5.01–5.15 (m, 3H), 5.48 (ddq, *J*=15.3, 7.2, 1.4 Hz, 1H), 5.62–5.81 (m, 2H). ^{13}C NMR (63 MHz): δ (ppm)=17.5 (CH_3), 18.0 (CH_3), 25.8 (CH_3), 49.2 (CH), 75.0 (CH), 115.5 (CH_2), 122.3 (CH), 128.0 (CH), 131.3 (CH), 135.0 (C), 137.5 (CH).

4.2.3. (*E*)-6-Methyl-1-phenyl-4-vinylhepta-1,5-dien-3-ol (5c). *Procedure A*. Yield 93% (*anti*/*syn* 92:8).

Procedure B. Yield 84% (*anti*/*syn* 20:80). IR (film): ν (cm^{-1})=3413, 1671, 1635, 1495, 1449, 1376. MS (EI): *m/z* (%)=228 (2, $M^{+\cdot}$), 210 (9), 132 (58), 131 (100).

anti-**5c**. ^1H NMR (250 MHz): δ (ppm)=1.64 (s, 3H), 1.74 (s, 3H), 1.85 (br s, OH), 3.19 (br q, *J*=7.9 Hz, 1H), 4.19 (t, *J*=6.4 Hz, 1H), 5.08–5.21 (m, 3H), 5.80 (ddd, *J*=17.6, 9.7, 7.6 Hz, 1H), 6.23 (dd, *J*=15.9, 6.0 Hz, 1H), 6.62 (d, *J*=15.9 Hz, 1H), 7.20–7.45 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=18.3 (CH_3), 25.9 (CH_3), 49.8 (CH), 74.6 (CH), 116.5 (CH_2), 121.7 (CH), 126.3 (CH), 127.4 (CH), 128.4 (CH), 129.8 (CH), 130.6 (CH), 135.0 (C), 136.8 (C), 137.7 (CH).

syn-**5c**. ^1H NMR (250 MHz): δ (ppm)=1.68 (d, *J*=1.3 Hz, 3H), 1.79 (d, *J*=1.2 Hz, 3H), 1.96 (br d, *J*=3.3 Hz, OH), 3.19 (br q, *J*=7.7 Hz, 1H), 4.15 (td, *J*=6.1, 3.3 Hz, 1H), 5.06–5.20 (m, 3H), 5.79 (ddd, *J*=17.6, 9.8, 7.3 Hz, 1H), 6.23 (dd, *J*=15.9, 6.6 Hz, 1H), 6.62 (d, *J*=15.9 Hz, 1H), 7.20–7.45 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=18.2 (CH_3), 25.9 (CH_3), 49.6 (CH), 74.9 (CH), 116.0 (CH_2), 122.1 (CH), 126.3 (CH), 127.3 (CH), 128.3 (CH), 129.9 (CH), 131.1 (CH), 135.4 (C), 136.7 (C), 137.4 (CH).

4.2.4. 6-Methyl-4-vinylhept-5-en-3-ol (5d). *Procedure A*. Yield 57% (*anti*/*syn* >95:5).

Procedure B. Yield 61% (*anti*/*syn* 68:32). IR (film): ν

(cm^{-1})=3403, 1635, 1454, 1379. MS (EI): *m/z* (%)=136 (1, M−H_2O), 107 (3), 96 (84), 81 (100).

anti-**5d**. ^1H NMR (250 MHz): δ (ppm)=0.96 (t, *J*=7.4 Hz, 3H), 1.28–1.36 (m, 1H), 1.56–1.65 (m, 1H), 1.63 (s, 3H), 1.71 (br s, OH), 1.73 (s, 3H), 2.97 (br q, *J*=8.3 Hz, 1H), 3.35 (td, *J*=7.9, 3.2 Hz, 1H), 5.05 (d, *J*=9.4 Hz, 1H), 5.09–5.12 (m, 2H), 5.72 (ddd, *J*=15.9, 10.7, 8.3 Hz, 1H). ^{13}C NMR (63 MHz): δ (ppm)=10.1 (CH_3), 18.1 (CH_3), 25.9 (CH_3), 26.9 (CH_2), 49.7 (CH), 75.1 (CH), 116.0 (CH_2), 123.0 (CH), 133.6 (C), 138.3 (CH).

syn-**5d**. ^1H NMR (250 MHz): δ (ppm)=0.96 (t, *J*=7.4 Hz, 3H), 1.20–1.40 (m, 2H), 1.66 (s, 3H), 1.71 (br s, OH), 1.77 (s, 3H), 3.02 (br q, *J*=8.2 Hz, 1H), 3.35 (td, *J*=7.9, 3.2 Hz, 1H), 5.02–5.16 (m, 3H), 5.65–5.82 (m, 1H). ^{13}C NMR (63 MHz): δ (ppm)=10.0 (CH_3), 18.1 (CH_3), 26.0 (CH_3), 26.8 (CH_2), 48.9 (CH), 75.2 (CH), 115.4 (CH_2), 122.4 (CH), 135.2 (C), 138.4 (CH).

4.2.5. 2,6-Dimethyl-4-vinylhept-5-en-3-ol (5e). *Procedure A*. Yield 64% (*anti*/*syn* >95:5).

Procedure B. Yield 50% (*anti*/*syn* 57:43). IR (film): ν (cm^{-1})=3437, 1630, 1466, 1379. MS (EI): *m/z* (%)=150 (12, M−H_2O), 135 (24), 107 (50), 96 (52), 79 (100).

anti-**5e**. ^1H NMR (250 MHz): δ (ppm)=0.85 (d, *J*=6.7 Hz, 3H), 0.97 (d, *J*=6.9 Hz, 3H), 1.58 (br s, OH), 1.62 (s, 3H), 1.71 (s, 3H), 1.65–1.80 (m, 1H), 3.03 (br q, *J*=8.5 Hz, 1H), 3.22 (dd, *J*=7.8, 4.0 Hz, 1H), 4.99–5.15 (m, 3H), 5.73 (ddd, *J*=17.7, 9.8, 8.3 Hz, 1H). ^{13}C NMR (63 MHz): δ (ppm)= 15.6 (CH_3), 18.1 (CH_3), 20.2 (CH_3), 25.9 (CH_3), 30.0 (CH), 47.6 (CH), 77.9 (CH), 116.0 (CH_2), 123.3 (CH), 132.9 (C), 138.5 (CH).

syn-**5e**. ^1H NMR (250 MHz): δ (ppm)=0.94 (d, *J*=6.6 Hz, 6H), 1.58 (br s, OH), 1.65 (d, *J*=1.4 Hz, 3H), 1.77 (d, *J*= 1.3 Hz, 3H), 1.65–1.82 (m, 1H), 3.12 (br q, *J*=8.2 Hz, 1H), 3.20–3.28 (m, 1H), 4.99–5.17 (m, 3H), 5.72 (ddd, *J*=17.0, 10.3, 7.2 Hz, 1H). ^{13}C NMR (63 MHz): δ (ppm)=16.3 (CH_3), 18.2 (CH_3), 19.9 (CH_3), 26.0 (CH_3), 30.1 (CH), 46.8 (CH), 78.3 (CH), 115.3 (CH_2), 122.3 (CH), 135.2 (C), 138.7 (CH).

4.2.6. 4-Methyl-2-vinylpent-3-en-1-ol (5f). *Procedure A*. Yield 81%. ^1H NMR (250 MHz): δ (ppm)=1.52 (br s, OH), 1.67 (s, 3H), 1.74 (s, 3H), 3.18 (quint., *J*=7.6 Hz, 1H), 3.45 (dd, *J*=10.3, 6.9 Hz, 1H), 3.52 (dd, *J*=10.3, 7.3 Hz, 1H), 5.00 (d, *J*=9.1 Hz, 1H), 5.11 (d, *J*=10.3 Hz, 1H), 5.12 (d, *J*=17.2 Hz, 1H), 5.69 (ddd, *J*=17.2, 10.3, 7.2 Hz, 1H). ^{13}C NMR (63 MHz): δ (ppm)=18.1 (CH_3), 25.9 (CH_3), 45.7 (CH), 65.4 (CH_2), 115.8 (CH_2), 122.6 (CH), 135.3 (C), 138.1 (CH). MS (EI): *m/z* (%)=126 (2, $M^{+\cdot}$), 108 (23), 93 (65), 91 (68), 79 (100).

4.2.7. 2,5-Dimethyl-3-vinylhex-4-en-2-ol (5g).[2i] *Procedure A*. Yield 70%. ^1H NMR (250 MHz): δ (ppm)=1.17 (s, 3H), 1.18 (s, 3H), 1.65 (s, 3H), 1.70 (br s, OH), 1.78 (s, 3H), 2.98 (dd, *J*=9.4, 8.8 Hz, 1H), 5.05–5.20 (m, 3H), 5.72–5.86 (m, 1H). ^{13}C NMR (63 MHz): δ (ppm)=18.2 (CH_3), 26.1 (CH_3), 26.5 (CH_3), 26.9 (CH_3), 54.4 (CH), 72.5 (C), 116.3 (CH_2), 122.5 (CH), 134.6 (C), 137.9 (CH). MS (EI): *m/z* (%)=136 (18, M−H_2O), 121 (65), 93 (81), 91 (65), 79 (100).

4.2.8. (*E*)-1,4-Diphenyl-2-vinylbut-3-en-1-ol (7a).[2o] *Procedure A*. Yield 90% (*anti*/*syn* >95:5).

Procedure B. Yield 80% (*anti*/*syn* 16:84). IR (film): ν (cm^{-1})=3423, 1636, 1599, 1494, 1451. MS (EI): *m/z* (%)= 232 (2, M−H_2O), 144 (42), 129 (94), 128 (66), 77 (100).

anti-**7a**. ^1H NMR (500 MHz): δ (ppm)=2.31 (br s, OH), 3.25 (br q, *J*=7.4 Hz, 1H), 4.67 (d, *J*=6.8 Hz, 1H), 5.22 (d, *J*=17.2 Hz, 1H), 5.26 (d, *J*=10.2 Hz, 1H), 5.91 (ddd, *J*= 17.2, 10.2, 8.1 Hz, 1H), 6.06 (dd, *J*=16.0, 7.4 Hz, 1H), 6.33 (d, *J*=16.0 Hz, 1H), 7.18–7.33 (m, 10H). ^{13}C NMR (125 MHz): δ (ppm)=55.4 (CH), 76.4 (CH), 118.4 (CH_2), 126.1 (CH), 126.7 (CH), 127.3 (CH), 127.6 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 132.0 (CH), 136.9 (CH), 137.1 (C), 141.7 (C).

syn-**7a**. ^1H NMR (250 MHz): δ (ppm)=2.26 (br d, *J*= 3.0 Hz, OH), 3.27 (br q, *J*=8.0 Hz, 1H), 4.69 (dd, *J*=6.9, 3.0 Hz, 1H), 5.07 (d, *J*=17.1 Hz, 1H), 5.09 (d, *J*=10.8 Hz, 1H), 5.78 (ddd, *J*=17.1, 10.8, 7.1 Hz, 1H), 6.23 (dd, *J*=16.0, 8.0 Hz, 1H), 6.50 (d, *J*=16.0 Hz, 1H), 7.20–7.41 (m, 10H). ^{13}C NMR (63 MHz): δ (ppm)=55.4 (CH), 76.5 (CH), 117.2 (CH_2), 126.3 (CH), 126.8 (CH), 127.5 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.5 (CH), 133.2 (CH), 136.9 (CH), 137.0 (C), 141.8 (C).

4.2.9. (1*E*,6*E*)-1,6-Diphenyl-4-vinylhexa-1,5-dien-3-ol (7b). *Procedure A*. Yield 81% (*anti*/*syn* >95:5).

Procedure B. Yield 68% (*anti*/*syn* 18:82). IR (film): ν (cm^{-1})=3412, 1637, 1599, 1495, 1449. MS (EI): *m/z* (%)=276 (3, $M^{+\cdot}$), 258 (3), 172 (6), 144 (16), 143 (100), 128 (75).

anti-**7b**. ^1H NMR (250 MHz): δ (ppm)=2.00 (br s, OH), 3.17 (br q, *J*=7.3 Hz, 1H), 4.34 (br t, *J*=5.7 Hz, 1H), 5.24 (d, *J*=16.9 Hz, 1H), 5.26 (d, *J*=10.5 Hz, 1H), 5.95 (ddd, *J*=16.9, 10.5, 7.7 Hz, 1H), 6.24 (dd, *J*=15.9, 7.8 Hz, 1H), 6.28 (dd, *J*=15.9, 6.3 Hz, 1H), 6.50 (d, *J*=15.9 Hz, 1H), 6.64 (d, *J*=15.9 Hz, 1H), 7.15–7.45 (m, 10H). ^{13}C NMR (63 MHz): δ (ppm)=54.2 (CH), 74.7 (CH), 118.1 (CH_2), 126.2 (CH), 126.5 (CH), 127.4 (CH), 127.7 (CH), 127.9 (CH), 128.5 (CH), 128.5 (CH), 129.5 (CH), 131.6 (CH), 132.7 (CH), 136.6 (C), 136.8 (CH), 137.0 (C).

syn-**7b**. ^1H NMR (250 MHz): δ (ppm)=2.04 (br s, OH), 3.16 (br q, *J*=6.9 Hz, 1H), 4.30–4.38 (m, 1H), 5.17–5.25 (m, 2H), 5.94 (ddd, *J*=17.7, 9.5, 7.5 Hz, 1H), 6.26 (dd, *J*= 16.0, 8.0 Hz, 1H), 6.27 (dd, *J*=16.0, 6.4 Hz, 1H), 6.52 (d, *J*=16.0 Hz, 1H), 6.64 (d, *J*=16.0 Hz, 1H), 7.18–7.41 (m, 10H). ^{13}C NMR (63 MHz): δ (ppm)=54.2 (CH), 74.8 (CH), 117.7 (CH_2), 126.3 (CH), 126.5 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH), 128.5 (CH), 128.5 (CH), 129.6 (CH), 131.6 (CH), 132.9 (CH), 136.6 (C), 136.8 (CH), 137.0 (C).

4.2.10. (*E*)-6-Phenyl-4-vinylhex-5-en-3-ol (7c). *Procedure A*. Yield 90% (*anti*/*syn* 93:7).

Procedure B. Yield 80% (*anti*/*syn* 50:50). IR (film): ν

(cm^{-1})=3415, 1637, 1599, 1495, 1449. MS (EI): *m/z* (%)= 184 (2, M−H_2O), 144 (91), 129 (100), 128 (96), 115 (85).

anti-**7c**. ^1H NMR (250 MHz): δ (ppm)=1.00 (t, *J*=7.4 Hz, 3H), 1.60–1.75 (m, 3H), 2.98 (br q, *J*=8.0 Hz, 1H), 3.51–3.60 (m, 1H), 5.21 (d, *J*=17.0 Hz, 1H), 5.23 (d, *J*=10.5 Hz, 1H), 5.90 (ddd, *J*=17.0, 10.5, 8.0 Hz, 1H), 6.19 (dd, *J*=16.0, 8.0 Hz, 1H), 6.47 (d, *J*=16.0 Hz, 1H), 7.17–7.38 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=10.1 (CH_3), 27.2 (CH_2), 53.9 (CH), 74.9 (CH), 117.6 (CH_2), 126.1 (CH), 127.3 (CH), 128.5 (CH), 129.1 (CH), 131.8 (CH), 137.2 (C), 137.2 (CH).

syn-**7c**. ^1H NMR (250 MHz): δ (ppm)=1.00 (t, *J*=7.4 Hz, 3H), 1.56–1.71 (m, 2H), 1.74 (br s, OH), 2.94–3.02 (m, 1H), 3.51–3.60 (m, 1H), 5.18 (d, *J*=17.5 Hz, 1H), 5.22 (d, *J*=10.3 Hz, 1H), 5.89 (ddd, *J*=17.5, 10.3, 8.4 Hz, 1H), 6.23 (dd, *J*=16.0, 8.4 Hz, 1H), 6.49 (d, *J*=16.0 Hz, 1H), 7.17–7.38 (m, 5H). ^{13}C NMR (63 MHz): δ (ppm)=10.1 (CH_3), 27.2 (CH_2), 53.6 (CH), 75.0 (CH), 116.9 (CH_2), 126.2 (CH), 127.4 (CH), 128.2 (CH), 128.5 (CH), 132.6 (CH), 137.1 (C), 137.9 (CH).

4.2.11. 1-Phenyl-2-vinylpent-3-en-1-ol (7d).[2o] *Procedure A*. Yield 85% ((*E*)-*anti*/(*Z*)-*anti*/(*E*)-*syn*/(*Z*)-*syn* 76:20:4:0).

Procedure B. Yield 70% (20:1:60:19). IR (film): ν (cm^{-1})= 3412, 1630, 1454. MS (EI): *m/z* (%)=170 (4, M−H_2O), 155 (10), 106 (61), 105 (61), 79 (80), 77 (100).

(*E*)-*anti*-**7d**. ^1H NMR (500 MHz): δ (ppm)=1.59 (d, *J*= 6.3 Hz, 3H), 2.32 (br s, OH), 3.02 (br q, *J*=7.4 Hz, 1H), 4.57 (d, *J*=6.9 Hz, 1H), 5.11 (d, *J*=17.3 Hz, 1H), 5.16 (d, *J*= 10.2 Hz, 1H), 5.28 (ddq, *J*=15.4, 7.2, 1.3 Hz, 1H), 5.39 (dq, *J*=15.4, 6.3 Hz, 1H), 5.79 (ddd, *J*=17.3, 10.2, 8.1 Hz, 1H), 7.24–7.32 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=18.0 (CH_3), 55.1 (CH), 76.2 (CH), 117.6 (CH_2), 126.8 (CH), 127.3 (CH), 127.8 (CH), 127.9 (CH), 129.1 (CH), 137.4 (CH), 141.9 (C).

(*Z*)-*anti*-**7d**. ^1H NMR (500 MHz): δ (ppm)=1.38 (dd, *J*= 6.8, 1.7 Hz, 3H), 2.25 (br s, OH), 3.41 (br q, *J*=8.3 Hz, 1H), 4.53 (d, *J*=7.7 Hz, 1H), 5.19–5.25 (m, 2H), 5.29 (ddq, *J*= 10.7, 9.7, 1.7 Hz, 1H), 5.47 (dq, *J*=10.7, 6.8 Hz, 1H), 5.80–5.88 (m, 1H), 7.25–7.35 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=12.8 (CH_3), 50.2 (CH), 76.2 (CH), 117.1 (CH_2), 126.3 (CH), 126.8 (CH), 127.4 (CH), 127.9 (CH), 128.0 (CH), 137.6 (CH), 142.0 (C).

(*E*)-*syn*-**7d**. ^1H NMR (500 MHz): δ (ppm)=1.74 (dd, *J*=6.4, 1.5 Hz, 3H), 2.28 (br d, *J*=2.5 Hz, OH), 3.02 (br q, *J*= 7.7 Hz, 1H), 4.49 (dd, *J*=7.5, 2.5 Hz, 1H), 4.92–5.01 (m, 1H), 5.45 (ddq, *J*=15.4, 8.4, 1.5 Hz, 1H), 5.59–5.68 (m, 2H), 7.25–7.34 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)= 18.2 (CH_3), 55.4 (CH), 76.3 (CH), 116.5 (CH_2), 126.9 (CH), 127.5 (CH), 128.0 (CH), 129.3 (CH), 129.6 (CH), 137.3 (CH), 141.9 (C).

(*Z*)-*syn*-**7d**. ^1H NMR (500 MHz): δ (ppm)=1.59 (d, *J*= 6.8 Hz, 3H), 2.23 (br s, OH), 3.44 (br q, *J*=7.8 Hz, 1H), 4.53–4.57 (m, 1H), 4.92–5.02 (m, 2H), 5.40–5.46 (m, 1H), 5.60–5.65 (m, 1H), 5.75 (dq, *J*=10.9, 6.8 Hz, 1H), 7.25–7.35 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=13.2 (CH_3), 49.5 (CH), 76.7 (CH), 116.4 (CH_2), 126.8 (CH), 127.5 (CH), 128.0 (3 CH), 137.0 (CH), 141.9 (C).

4.2.12. 2-Vinylpent-3-en-1-ol (7e). *Procedure A*. Yield 62% (*E*/*Z* 71:29). IR (film): ν (cm^{-1})=3356, 1638, 1453, 1377. MS (EI): *m/z* (%)=95 (2), 81 (54), 79 (100).

(*E*)-**7e**. ^1H NMR (250 MHz): δ (ppm)=1.50 (br s, OH), 1.71 (d, *J*=6.4 Hz, 3H), 2.91 (quint., *J*=7.2 Hz, 1H), 3.46–3.55 (m, 2H), 5.11–5.17 (m, 2H), 5.36 (ddq, *J*=15.4, 7.8, 1.5 Hz, 1H), 5.59 (dq, *J*=15.4, 6.4 Hz, 1H), 5.66–5.76 (m, 1H). ^{13}C NMR (63 MHz): δ (ppm)=18.1 (CH_3), 49.8 (CH), 65.1 (CH_2), 116.4 (CH_2), 128.2 (CH), 129.6 (CH), 137.9 (CH).

(*Z*)-**7e**. ^1H NMR (250 MHz): δ (ppm)=1.65 (br s, OH), 1.67 (dd, *J*=6.8, 1.7 Hz, 3H), 3.33 (quint., *J*=7.5 Hz, 1H), 3.46–3.55 (m, 2H), 5.11–5.17 (m, 2H), 5.27 (ddq, *J*=10.8, 9.4, 1.7 Hz, 1H), 5.66–5.76 (m, 2H). ^{13}C NMR (63 MHz): δ (ppm)=13.2 (CH_3), 44.6 (CH), 65.3 (CH_2), 116.6 (CH_2), 127.4 (CH), 128.5 (CH), 137.5 (CH).

4.2.13. 3-Methyl-1-phenyl-2-vinylbut-3-en-1-ol (7f). *Procedure A*. Yield 76% (*anti*/*syn* 88:12).

Procedure B. Yield 48% (*anti*/*syn* 35:65) accompanied with 29% of the linear isomer **8**. IR (film): ν (cm^{-1})=3424, 1644, 1494, 1453. MS (EI): *m/z* (%)=170 (3, M−H_2O), 155 (8), 106 (98), 105 (99), 77 (100).

anti-**7f**. ^1H NMR (500 MHz): δ (ppm)=1.61 (s, 3H), 2.18 (br d, *J*=2.0 Hz, OH), 2.98 (t, *J*=8.4 Hz, 1H), 4.70 (dd, *J*=7.8, 2.0 Hz, 1H), 4.73 (s, 1H), 4.77 (br s, 1H), 5.18 (d, *J*=17.1 Hz, 1H), 5.21 (dd, *J*=10.2, 1.7 Hz, 1H), 6.01 (ddd, *J*=17.1, 10.2, 9.2 Hz, 1H), 7.25–7.34 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=21.8 (CH_3), 59.9 (CH), 74.9 (CH), 113.1 (CH_2), 118.1 (CH_2), 126.8 (CH), 127.6 (CH), 128.1 (CH), 137.1 (CH), 142.0 (C), 144.5 (C).

syn-**7f**. ^1H NMR (500 MHz): δ (ppm)=1.81 (s, 3H), 2.29 (br d, *J*=2.1 Hz, OH), 3.07 (t, *J*=8.6 Hz, 1H), 4.64 (dd, *J*=9.4, 2.1 Hz, 1H), 4.86 (d, *J*=17.1 Hz, 1H), 4.91 (d, *J*=10.3 Hz, 1H), 5.01 (s, 1H), 5.05 (br s, 1H), 6.01 (ddd, *J*=17.1, 10.3, 8.1 Hz, 1H), 7.25–7.34 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=20.0 (CH_3), 60.3 (CH), 74.5 (CH), 114.1 (CH_2), 117.1 (CH_2), 127.0 (CH), 127.6 (CH), 128.0 (CH), 135.9 (CH), 141.9 (C), 145.0 (C).

4.2.14. 3-Methyl-1-phenylhexa-3,5-dien-1-ol (8). ^1H NMR (500 MHz): δ (ppm)=1.83 (s, 3H), 2.10 (br s, OH), 2.42 (dd, *J*=13.7, 9.1 Hz, 1H), 2.45 (dd, *J*=13.7, 4.4 Hz, 1H), 4.82 (dd, *J*=9.1, 4.4 Hz, 1H), 5.07 (dd, *J*=10.2, 1.5 Hz, 1H), 5.16 (dd, *J*=16.9, 1.5 Hz, 1H), 5.97 (d, *J*=10.0 Hz, 1H), 6.59 (dt, *J*=16.9, 10.5 Hz, 1H), 7.25–7.34 (m, 5H). ^{13}C NMR (125 MHz): δ (ppm)=16.7 (CH_3), 50.3 (CH_2), 71.7 (CH), 116.3 (CH_2), 125.7 (CH), 127.5 (CH), 128.4 (CH), 129.1 (CH), 132.7 (CH), 135.2 (C), 144.0 (C).

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7. The pentadienyl ethers are stable compounds in comparison with pentadienyl bromides.

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9. We have noticed that this procedure is also useful for the preparation of allylzirconocenes from allylic ethers.

10. The *anti* configuration was defined with reference to the simpler allylmetalation reactions, by considering pentadienylzirconiums as alkenyl-substituted allylmetals. The *anti* configuration was undoubtedly assigned to the major isomers by a cyclization method. For an example see Ref. 4.

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13. Similar reversal of *anti* to *syn* stereoselectivity was also obtained with $TiCl_4$. The reversal of *anti* to *syn* selectivity was found to be less stronger when the solution of the aldehyde and BF_3 in THF was added to the reaction mixture.

14. The predominant *syn* diastereoselection in the Lewis acid-mediated allylic tin-aldehyde condensation reactions was rationalized similarly, see Ref. 1.

15. The formation of the ε-regioisomeric by-product **8** from the ether **6c** in the presence of a Lewis acid (see Table 3) also corroborates a non-cyclic mechanism.

16. For example, different open transition structures have been considered for the Lewis acid-mediated allylmetalation reactions, see: (a) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (b) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970.