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$AgAsF_6$ as Safe Alternative to $AgClO_4$ for Generating Cationic Zirconocene Species: Utilities in Lewis Acid-Promoted Selective C–C Bond Forming Reactions

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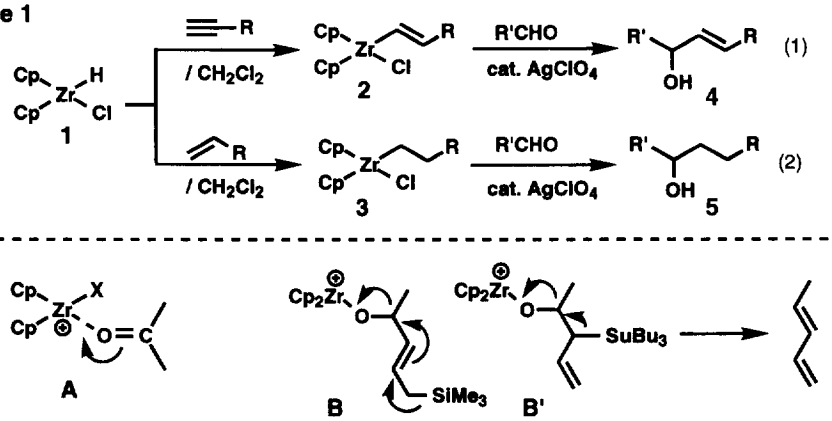
Abstract: For generating cationic zirconocene species that are useful for organic synthesis, $AgAsF_6$ proved to be an efficient catalyst that serves as a safe alternative to $AgClO_4$. Scope and limitation is discussed on this new catalyst in the processes including (1) alkyl/alkenyl transfer reaction from organozirconocene chloride to aldehyde, (2) two- and four-carbon homologation of aldehyde, (3) dual synthetic methods of 1,3-dienes from aldehydes/ketones via 1,3-bimetallic species, and (4) three-component alkylative cycloaddition via *o*-quinodimethane species.

Introduction

We previously reported several new selective C–C bond forming processes that depend on cationic zirconocene complexes as the key active species.[1] Scheme 1 shows two major roles of such cationic species.

Scheme 1



Organozirconocene chlorides, readily accessible by hydrozirconation of alky(e)nes with Schwartz reagent (**1**),[2] generally show poor reactivity toward carbonyl compounds. However, we previously found that it could be remarkably accelerated by employing a catalytic amount of $AgClO_4$ (eqs 1 and 2).[1b] The in situ-generated cationic species accounts for the enhancement via the carbonyl activation as depicted in **A**.[3,4] The catalytic activity is excellent for the *alkenyl* complexes **2** (eq 1), whereas, unfortunately, it is unsatisfactory for the corresponding *alkyl* transfer reaction (eq 2), which remained as a limitation of the process.[1b]

The related addition reactions of (Zr, Si)- or (Zr, Sn)-1,3-bimetallic species offer useful protocols for the synthesis of 1,3-dienes.[1c,e,5] In the Peterson-type[6] elimination reactions of zirconocene alkoxides (**B** and **B'**), the departure of an oxygen function requires the electron deficiency at the zirconium center.

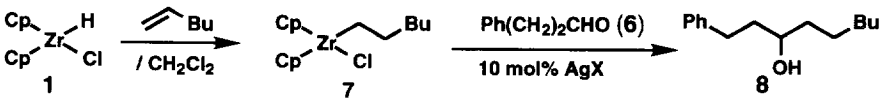
We now report that $AgAsF_6$ serves as a safe (non-explosive) alternative to *potentially explosive* $AgClO_4$[7] for generating such cationic zirconocene species. Efficiency of the new catalyst is remarkable in that it can catalyze not only the *alkenylation* but also the *alkylation* (vide supra). Scope and limitation of the catalyst in the relevant Lewis acid promoted processes are discussed, and also the extension of the reaction pattern to the quinodimethane chemistry is described.

Results and Discussion

(1) Carbonyl Addition Reactions

The poor reactivity of alkylzirconocene chloride is illustrated in run 1 (Table 1). *n*-Hexylzirconocene chloride (**7**), generated by the hydrozirconation of 1-hexene, did not react with aldehyde **6** at all even after long reaction period. As reported previously,[1b] the reaction did proceed by employing $AgClO_4$ as a catalyst, but only slowly (run 2). To overcome the difficulty, we tested various Ag(I) salts with non-nucleophilic anions. It tuned out that $AgAsF_6$ is an exceptionally good catalyst that can promote the alkyl addition with unusual efficiency. The reaction completed almost instantaneously at room temperature by employing $AgAsF_6$ (10 mol%) as the catalyst (run 6). By contrast, other silver salts were totally ineffective, and even the other hexafluoro derivatives of group 15 elements (PF_6^- and SbF_6^-) proved catalytically inactive (runs 5 and 7).

Table 1 Comparison of Ag(I) salts for addition of hexylzirconocene chloride to aldehyde.



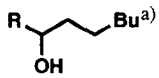
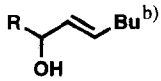
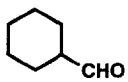
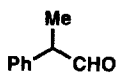
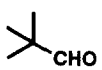
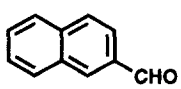
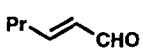
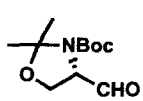
Run	AgX	Time	Yield/%
1	none	10 h	–[a]
2	$AgClO_4$	4 h	54
3	$AgBF_4$	6 h	–[a]
4	AgOTf	20 h	13[b]
5	$AgPF_6$	24 h	–[a]
6	$AgAsF_6$	10 min	95
7	$AgSbF_6$	26 h	62

a) Essentially no reaction was observed.
b) Reduced product [$Ph(CH_2)_2CH_2OH$] was obtained in 50% yield.

The $AgAsF_6$-catalyzed protocol for the alkyl transfer reaction is widely applicable as demonstrated by the reactions of *n*-hexylzirconocene chloride with various aldehydes (Table 2; the left column). The results shown here are obtained by employing 10 mol% of $AgAsF_6$ (CH_2Cl_2, room temperature, 10 min; see experimental). The reaction proceeded for a wide range of aldehydes including aliphatic ones of varying steric demands (runs 1–4), or an aromatic aldehyde (run 5). 1,2-Addition was the sole reaction mode observed for the reaction with an α,β-unsaturated aldehyde (run 6). As for the chemoselectivity, the aldehyde with an ester function underwent clean reaction exclusively at its formyl group (run 7). Although not described in the table, it should be noted that, either for the alkyl or the alkenyl transfer, *the addition reaction did not proceed with ketones.* A limitation turned out to be the failure of the reaction of a serine-derived aldehyde (run 8). This is presumably due to the inactivation of the cationic center by the Lewis basic functionality of the substrate. The aldehyde was fully recovered unchanged.

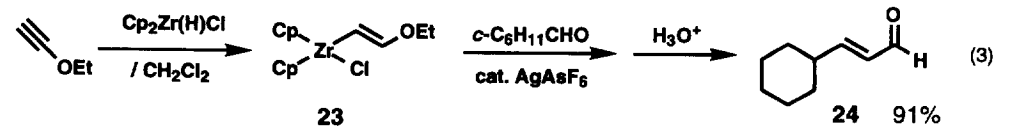
$AgAsF_6$ proved to be catalytically active also for the corresponding *alkenyl transfer reactions*,. The right column of Table 2 shows the results of the reactions of (*E*)-1-hexenylzirconocene chloride with the same series of aldehydes. The reaction conditions were the same as those of the alkyl counterpart, except that a smaller amount of the catalyst (5 mol%) was employed. The alkenyl complex is more reactive than the corresponding alkyl complex, and the serine-derived aldehyde underwent the addition (run 8), although no useful level of diastereoselectivity was attained.

Table 2 $AgAsF_6$-Promoted addition of organozirconocene chloride to aldehyde.

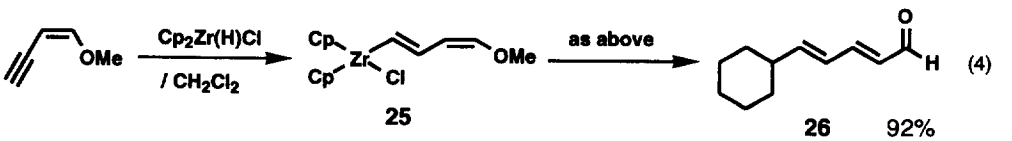
Run	Aldehyde RCHO	 a) (Yield/%)	 b) (Yield/%)
1		**8** (95)	**15** (91)
2		**9** (99)	**16** (96)
3		**10** c) (98)	**17** c) (91)
4		**11** (89)	**18** (88)
5		**12** (89)	**19** (91)
6		**13** (91)	**20** (85)
7		**14** (95)	**21** (94)
8		—d)	**22** c) (70)

a) Product of the reaction of aldehyde with *n*-hexylzirconocene chloride.
b) Product of the reaction of aldehyde with (*E*)-1-hexenylzirconocene chloride.
c) The product was ca. 1:1 diastereomeric mixture.
d) No reaction occurred even after prolonged reaction period.

The alkenyl transfer reaction proved applicable to the two- and four-carbon homologation of aldehyde.[1d] Alkoxy complex **23**,[8, 9] generated from ethoxyethyne, cleanly added to cyclohexanecarbaldehyde in the presence of catalytic $AgAsF_6$. As reported previously,[1d] mild acid hydrolysis of the crude adduct gave (*E*)-enal **24** (eq 3). Similarly, the four-carbon homologation by using a commercially available methoxyenyne,[10] gave (*E*, *E*)-dienal **26** in high yield (eq 4). In principle, these protocols would be applicable to higher polyenal synthesis.[1d, 11]



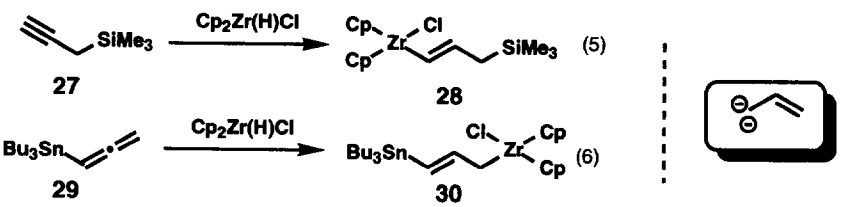
(3)



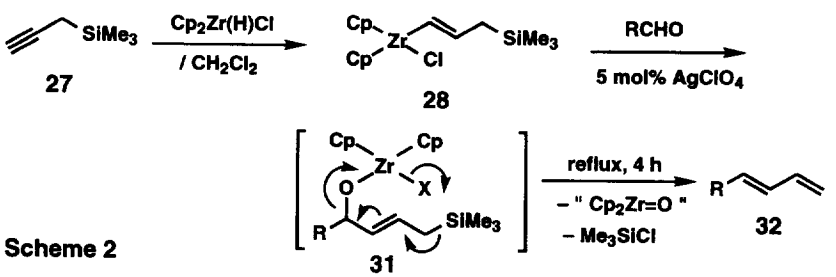
(4)

(2) Dual Methods for 1,3-Diene Synthesis[1c, e]

This section features dual methods for selective synthesis of 1,3-dienes by utilizing 1,1-dianion equivalents (see below). The key elements are two related 1,3-bimetallic species,[12] **28** and **30**, which can be generated by the hydrozirconation of propargylsilane **27**[13] and allenylstannane **29**,[14] respectively (eqs 5 and 6). These studies suggested another mechanistic importance of cationic zirconocene species.



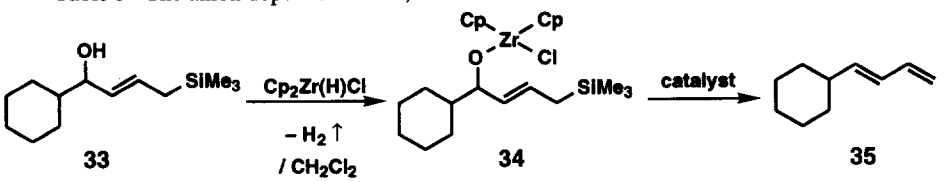
Method 1:[1c] The first method consists of two steps (Scheme 2); the addition of γ-silyl alkenyl-Zr **28** to aldehyde (Step 1) and the cascade elimination of $Cp_2Zr{=}O$[15] and Me_3SiCl (Step 2). As reported previously, $AgClO_4$ serves as the catalyst to achieve this two-step conversion, whereas $AgAsF_6$ turned out to be inefficient in this particular instance. Although the first addition step proceeded without event, the elimination step was totally retarded. Thus, the elimination step proved to be markedly anion dependent, which could be highlighted in the following experiments.



Scheme 2

Simple heating of the possible intermediate **34**, prepared by alcoholysis of Schwartz reagent with **33**, did not give diene **35**, but resulted in the recovery of alcohol **33** (run 1). The difference from Scheme 2 is the presence/absence of the catalytic $AgClO_4$, and, indeed its addition to this mixture led to the elimination reaction (run 2). We could reasonably assume that the Ag(I) ion is out of the scene so that the ClO_4^- ion is essential. Then the perchlorate carrier would be Me_3SiClO_4,[16] which indeed induced the elimination reaction (run 3). The inability of AsF_6^- to induce the elimination step was clearly shown by this study (run 4). Presumably, an equilibrium ($Me_3SiAsF_6 \rightleftarrows Me_3SiF + AsF_5$) hampers the regeneration of the cationic zirconocene species.

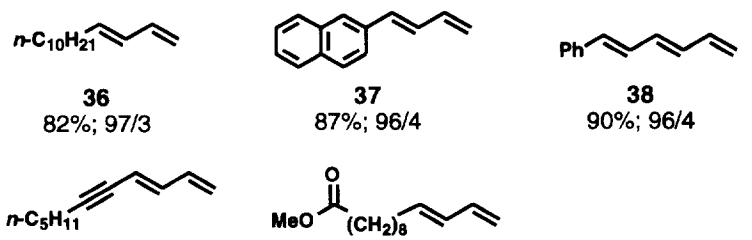
Table 3 The anion dependence of 1,4-elimination



Run	Catalyst[a]	Reaction Period/h	Yield of **35**/%
1	none	4	trace
2	$AgClO_4$	4	78
3	Me_3SiClO_4	2	76
4	$AgAsF_6$	5	8

a) 5 Mol% amount of the catalyst was employed.

Figure 1 summarizes some 1,3-dienes obtained by Method 1. One of the notable points is the high (*E*)-selectivity for the newly formed double bond, which stands in contrast to the Wittig reaction, where the semi-stabilized ylide provides generally a mixture of *E/Z* isomers (eq 7).[17] One exception is the poor selectivity of **39** derived from an alkynal (n-$C_5H_{11}C{\equiv}CCHO$). Another notable point is the chemoselectivity: the reaction is limited to aldehydes, and either esters or ketones are inert toward the first alkenylation (Cf. Method 2).

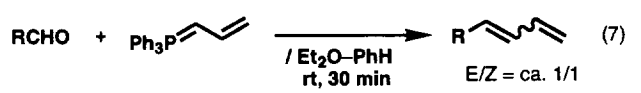


36 82%; 97/3 **37** 87%; 96/4 **38** 90%; 96/4

39 74%; 74/26 **40** 80%; 98/2

Figure 1

Cf



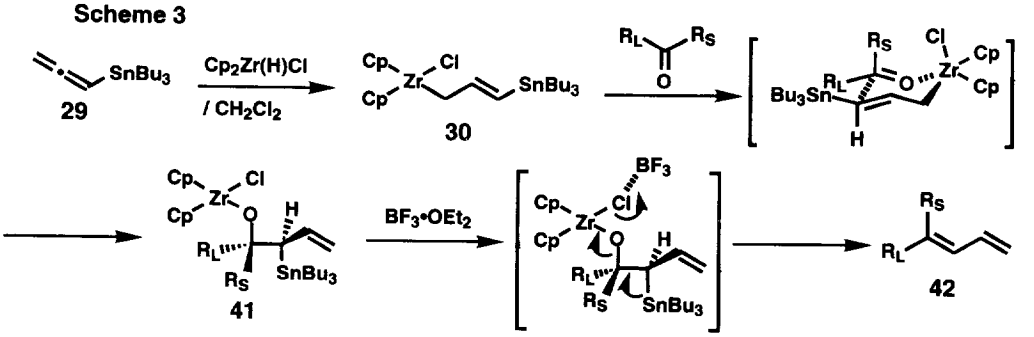
(7)

E/Z = ca. 1/1

Method 2:[1e] The second method depends on the hydrozirconation[18] of allenylstannane to generate 1,3-(Sn, Zr)-bimetallic species followed by 1,2-elimination of $Cp_2Zr{=}O$ and Bu_3SnCl.[18] For its ready

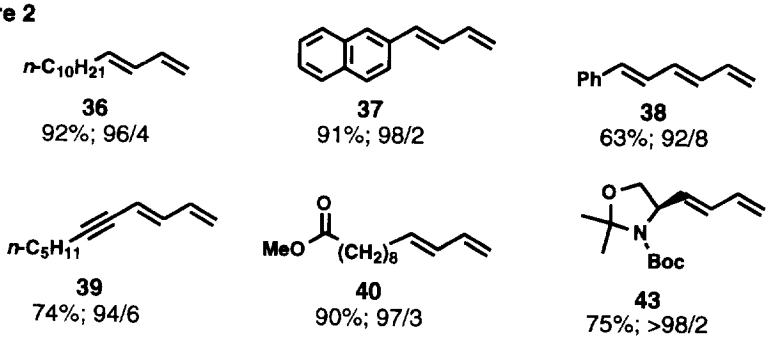
accessibility, stannane **29** was employed rather than the corresponding silane. The (*E*)-geometry of **30** was clearly deduced from the NMR measurement (J=17.6 Hz, 27 °C). The allylic zirconium **30**[18, 19] attacks aldehydes without resort to the AgX catalysis in S_E2' manner (Cf. Method 1), and direct treatment of the mixture with stoichiometric BF_3•OEt_2 furnished the 1,3-diene in high yield. The role of BF_3•OEt_2 could be to polarize the Zr–Cl bond to trigger the C–O bond cleavage. The (*E*)-selectivity originates from the steric constraint at the six-membered transition state to provide stereo-defined adduct **41**, which, upon treatment with BF_3•OEt_2, undergoes the *anti*-elimination.[6d]

Scheme 3



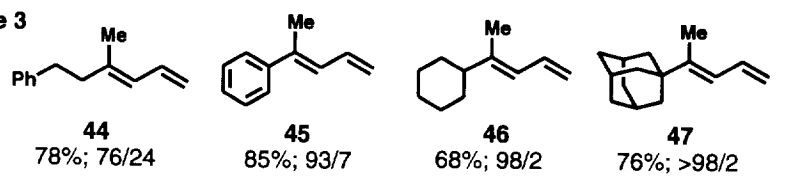
This method proved useful in terms of yield, chemoselectivity, and stereoselectivity. The reaction worked nicely with a wide range of aldehydes including aliphatic, aromatic, α,β-unsaturated or functionalized ones, giving the corresponding 1,3-dienes **36–40** and **43** uniformly in high yields and high (*E*)-selectivities. Notably, a high (*E*)-selectivity was achieved also for an alkynal (*n*-$C_5H_{11}C{\equiv}CCHO$; cf. Method 1).

Figure 2



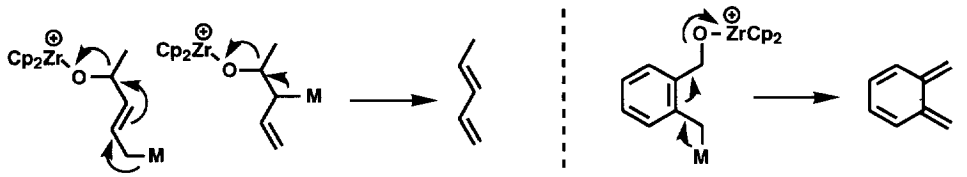
Different from Method 1, the reaction proved to work also for ketones. Notably, high (*E*)-selectivity could be achieved, given the size difference in two groups (R_L vs. R_S) was sufficient, as illustrated by the change of the *E/Z* selectivities of the reactions with a series of methyl ketones: products **44–47**.

Figure 3

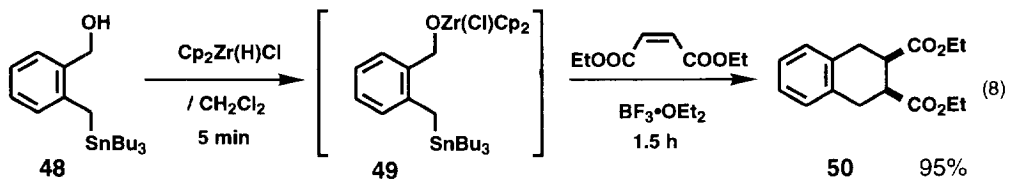


(3) Quinodimethane Generation and Sequential Reaction[20]

The dual methods for 1,3-diene synthesis stated above could be viewed as the 1,4- or 1,2-elimination triggered by cationic zirconocene alkoxide. Application of such elimination process across an aromatic ring would generate quinodimethane species,[21] which proved indeed the case.

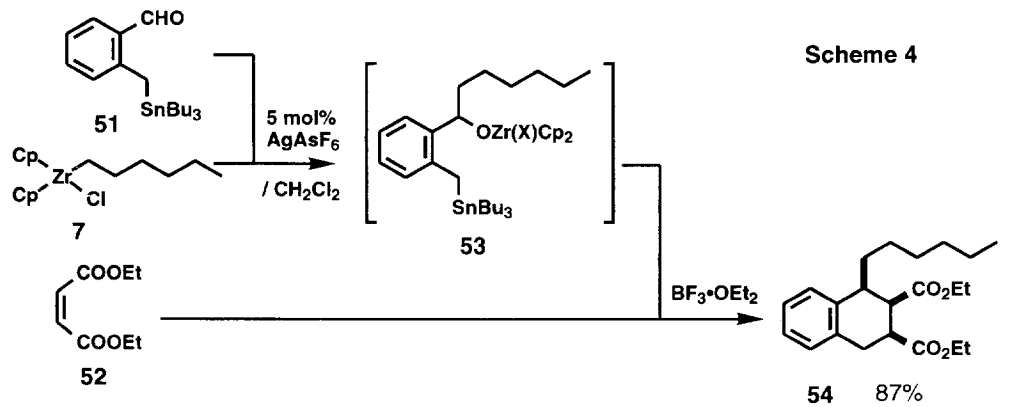


Treatment of stannyl alcohol **48**[22] with Schwartz reagent in CH_2Cl_2 to generate Zr-alkoxide **49** in situ. Subsequent addition of diethyl maleate followed by BF_3•OEt_2 (2 equiv.) led quickly to the formation of cycloadduct **50**, resulting from the quinodimethane generation followed by [4+2] cycloaddition (eq 8). This is the Lewis acid-promoted version of the Sano reaction,[22] where the stoichiometric use of BF_3•OEt_2 proved favorable for the quinodimethane generation. Catalytic use of $AgClO_4$ or $AgAsF_6$ proved ineffective.

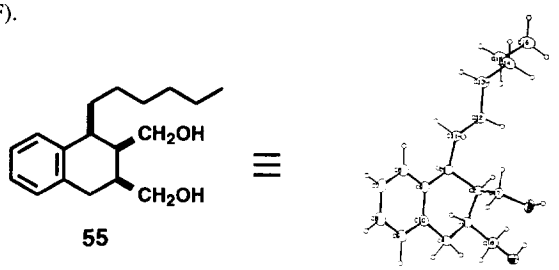


Thus, the quinodimethane generation and the aforementioned alkylation reaction differ in the reaction conditions for generating the key cationic zirconium species, that is, stoichiometric BF_3•OEt_2 for the former, whereas catalytic $AgAsF_6$ for the latter. Such an orthogonal nature of the reaction conditions enables the Lewis acid-promoted sequential addition–cycloaddition (Scheme 4). A triad mixture of aldehyde **51**,[23] hexyl-zirconocene chloride (**7**), and diethyl maleate (**52**) stayed unchanged in CH_2Cl_2 at room temperature. However, upon addition of $AgAsF_6$ (5 mol%), the alkylation reaction immediately occurred in high yield, which cleanly stopped at this stage. The mixture was, in turn, treated with BF_3•OEt_2 to generate a quinodimethane that was trapped by the third component **52**, giving cycloadduct **54** as the sole detectable isomer.

Scheme 4



The stereostructure of **54** was determined by the single X-ray analysis of **55**, which was obtained by the reduction of **54** ($LiAlH_4$/THF).



55

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Experimental

General: All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon. Schwartz reagent [$Cp_2Zr(H)Cl$] was prepared by the method of Buchwald.[24] Ethereal solvents were distilled from benzophenone ketyl immediately before use. CH_2Cl_2 was distilled successively from P_2O_5 and CaH_2 and stored over molecular sieves 4A. For thin-layer chromatography (TLC) analysis, Merck precoated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. Silica-gel 60 K070-WH (70–230 mesh; Katayama Chemical) was used for flash column chromatography. Preparative TLC (PTLC) was performed on Merck Kieselgel 60 PF_{254} (Art 7747). Melting points (mp) were measured by using a Yanaco MP-S3 instrument and are uncorrected. Boiling points (bp) refer to the oven temperature of bulb-to-bulb distillations with a Kugelrohr apparatus. ^1H and ^{13}C NMR spectra were measured, otherwise noted, in $CDCl_3$ on a JEOL JNM GX-400 (400/100 MHz) or EX-270 (270/67.5 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane (δ=0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Jasco IRA-202 spectrometer. High resolution mass spectra (HRMS) were obtained with a JEOL JMS DX 302 spectrometer. X-Ray data was obtained on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo K_α radiation. The X-ray intensities up to 2θ=50° were measured. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced.

*Representative Procedure for the $AgAsF_6$-catalyzed addition is described for the reaction of n-hexylzirconocene chloride to 3-phenylpropanal (**6**) (Table 1, Run 6):* A mixture of $Cp_2Zr(H)Cl$ (270 mg, 1.05 mmol) and 1-hexene (93.1 mg, 1.11 mmol) in CH_2Cl_2 (3 mL) was stirred for 10 min. To the resulting solution was added **6** (83.1 mg, 0.619 mmol) in CH_2Cl_2 (3 mL) followed by $AgAsF_6$ (20.1 mg, 67.7 μmol, 10 mol%). The reaction mixture gradually turned dark brown. After 10 min, the mixture was poured into sat. aq. $NaHCO_3$. Extractive workup (EtOAc) followed by purification with PTLC (hexane/EtOAc = 4/1) gave allylic alcohol **8** as a colorless oil (129 mg, 94.5%); ^1H NMR: δ 7.14–7.30 (m, 5H), 3.56–3.65 (br, 1H), 2.60–2.84 (m, 2H), 1.63–1.85 (m, 2H), 1.61–1.63 (br, 1H), 1.27–1.47 (m, 10H), 0.88 (t, 3H, J=6.6 Hz); ^{13}C NMR: δ 142.2, 128.6, 128.3, 125.7, 71.4, 39.1, 37.6, 32.0, 31.8, 29.3, 25.5, 22.6, 14.0; IR (neat): 3360, 2930, 2860, 1600 1500, 1450, 1380, 1125, 740, 700 cm^{-1}; HRMS: *m/z* 220.1844 (220.1828 calcd for $C_{15}H_{24}O$, M^+).

Data for other adducts **9**–**22** (Table 2) are as follows:

9: ^1H NMR: δ 3.29–3.39 (br, 1H), 1.01–1.85 (m, 22H), 0.89 (t, 3H, J=6.9 Hz); ^{13}C NMR: δ 76.1, 43.6, 34.1, 31.9, 29.4, 29.3, 27.7, 26.6, 26.4, 26.2, 25.9, 22.6, 14.0; IR (neat): 3350, 2900, 2850, 1450, 1380, 1125, 1080, 1060, 1030, 970, 890 cm^{-1}; HRMS: *m/z* 199.2070 (199.2061 calcd for $C_{13}H_{27}O$, M^++1).

10: (as a mixture of diastereomers) ^1H NMR: δ 7.19–7.35 (m, 5H), 3.60–3.68 (br, 1H), 2.69–2.83 (m, 1H), 1.23–1.66 (m, 14H), 0.80–0.89 (m, 3H); ^{13}C NMR: δ 144.7, 143.5, 128.4, 128.3, 128.1, 127.7, 126.5, 126.2, 76.1, 76.0, 46.0, 45.6, 34.7, 34.5, 31.8, 29.3, 29.2, 25.9, 25.7, 22.5, 17.5, 15.4, 14.0; IR (neat): 3400, 2920, 2850, 1490, 1450, 1370, 1220, 1080, 1010, 760, 700 cm^{-1}; HRMS: *m/z* 220.1822 (220.1827 calcd for $C_{15}H_{24}O$, M^+).

11[25]: ^1H NMR: δ 3.14–3.20 (m, 1H), 1.19–1.53 (m, 11H), 0.88 (s, 9H), 0.85–0.93 (m, 3H); ^{13}C NMR: δ 80.0, 34.9, 31.9, 31.5, 29.4, 27.1, 25.7, 22.6, 14.0; IR (neat): 3400, 2900, 2850, 1460, 1360, 1070, 1020, 960 cm^{-1}.

12: ^1H NMR: δ 7.74–7.82 (m, 4H), 7.23–7.49 (m, 3H), 4.77–4.81 (t, 1H, J=6.6 Hz), 2.09 (s, 1H), 1.66–1.90 (m, 2H), 1.25–1.47 (m, 8H), 0.85 (t, 3H, J=6.6 Hz); ^{13}C NMR: δ 142.3, 133.3, 133.0, 128.2, 127.9, 127.7, 126.1, 125.7, 124.6, 124.1, 74.8, 39.0, 31.8, 29.2, 25.8, 22.6, 14.1; IR (KBr): 3275, 2920, 2850, 1600, 1505, 1460, 1320, 1040, 950, 890, 860, 825, 745 cm^{-1}, HRMS: *m/z* 242.1689 (242.1671 calcd for $C_{17}H_{22}O$, M^+).

13: ^{1}H NMR: δ 5.63 (dt, 1H, J_1=15.5, J_2=6.9 Hz), 5.45 (dd, 1H, J_1=15.5, J_2=6.9 Hz), 3.99–4.07 (dt, 1H, J_1=J_2=6.9 Hz), 1.96–2.05 (dt, 2H, J_1=J_2=6.9 Hz), 1.21–1.63 (m, 13H), 0.86–0.99 (m, 6H); ^{13}C NMR: δ 133.3, 131.8, 73.1, 37.4, 34.2, 31.8, 29.2, 25.4, 22.6, 22.3, 14.0, 13.6; IR (neat): 3350, 2930, 2860, 1460, 965 cm^{-1}; HRMS: *m/z* 184.1824 (184.1828 calcd for $C_{12}H_{24}O$, M$^+$).

14: ^{1}H NMR: δ 3.64 (s, 3H), 3.54–3.58 (br, 1H), 2.28 (t, 2H, J=7.6 Hz), 1.27–1.63 (m, 25H), 0.8 (t, 3H, J=6.6 Hz); ^{13}C NMR: δ 174.1, 71.8, 51.3, 37.4, 34.0, 31.8, 29.6, 29.3, 29.1, 29.0, 25.5, 24.9, 22.5, 14.0; IR (KBr): 3400, 2900, 2850, 1735, 1460, 1430, 1410, 1380, 1340, 1310, 1285, 1260, 1240, 1205, 1175, 1130, 1075, 1040, 1010, 990, 900, 880, 860, 725 cm^{-1}; HRMS: *m/z* 286.2468 (286.2508 calcd for $C_{17}H_{34}O_3$, M$^+$).

15: ^{1}H NMR: δ 7.31–7.18 (m, 5H), 5.67 (dt, 1H, J_1=15.2, J_2=6.6 Hz), 5.50 (dd, 1H, J_1=15.2, J_2=6.6 Hz), 4.08 (dt, 1H, J_1=J_2=6.6 Hz), 2.65–2.73 (m, 2H), 2.05 (dt, 2H, J_1=J_2=6.6 Hz), 1.76–1.91 (m, 2H), 1.30–1.40 (m, 5H), 0.91 (t, 3H, J=6.9 Hz); ^{13}C NMR: δ 142.0, 132.8, 132.5, 128.4, 128.3, 125.8, 72.4, 38.8, 31.9, 31.8, 31.3, 22.2, 13.9; IR (neat): 3350, 3100, 3060, 3030, 2960, 2930, 2860, 1670, 1600, 1500, 1450, 970, 740, 700 cm^{-1}; HRMS: *m/z* 218.1667 (218.1670 calcd for $C_{15}H_{22}O$, M$^+$).

16: ^{1}H NMR: δ 5.61 (dt, 1H, J_1=15.2, J_2=6.6 Hz), 5.45 (dd, 1H, J_1=15.2, J_2=7.3 Hz), 3.77 (dd, 1H, J_1=J_2=7.3 Hz), 2.04 (dt, 2H, J_1=J_2=6.6 Hz), 0.87–1.89 (m, 16H), 0.90 (t, 3H, J=6.9 Hz); ^{13}C NMR: δ 132.8, 131.5, 77.6, 43.7, 31.9, 31.4, 28.8, 28.7, 26.5, 26.1, 26.0, 22.2, 13.8; IR (neat): 3350, 2900, 2850, 1680, 1440, 1375, 1300, 1250, 1080, 1000, 970, 890, 760 cm^{-1}; HRMS: *m/z* 196.1805 (196.1828 calcd for $C_{13}H_{24}O$, M$^+$).

17: (as a mixture of diastereomers) ^{1}H NMR: δ 7.16–7.36 (m, 5H), 5.30–5.75 (m, 2H), 4.05–4.17 (m, 1H), 2.70–2.93 (m, 1H), 1.92–2.10 (m, 2H), 1.50 (s, 1H), 1.19–1.50 (m, 7H), 0.82–0.93 (m, 3H); ^{13}C NMR: δ 143.5, 143.4, 134.0, 132.8, 130.7, 128.5, 128.2, 128.0, 126.6, 126.3, 77.8, 77.1, 46.4, 45.9, 31.9, 31.8, 31.3, 22.2, 22.0, 18.0, 16.0, 13.9; IR (neat): 3450, 3080, 3050, 2980, 2950, 2895, 1670, 1605, 1500, 1455, 1380, 1100, 1010, 975, 765, 705 cm^{-1}; HRMS: *m/z* 219.1725 (219.1749 calcd for $C_{15}H_{23}O$, M$^+$+1).

18: ^{1}H NMR: δ 5.64 (dt, 1H, J_1=15.2, J_2=6.6 Hz), 5.55 (dd, 1H, J_1=15.2, J_2=7.3 Hz), 3.69 (d, 1H, J=7.3 Hz), 2.05 (dt, 2H, J_1=J_2=6.6 Hz), 1.47 (s, 1H), 1.23–1.44 (m, 4H), 0.90 (s, 9H), 0.87–0.92 (m, 3H); ^{13}C NMR: δ 133.7, 129.7, 81.1, 34.7, 32.0, 31.4, 25.7, 22.2, 13.9; IR (neat): 3400, 2950, 2920, 2850, 1680, 1460, 1360, 1035, 990, 970 cm^{-1}; HRMS: *m/z* 170.1699 (170.1670 calcd for $C_{11}H_{22}O$, M$^+$).

19: ^{1}H NMR: δ 7.80–7.84 (m, 4H), 7.44–7.50 (m, 3H), 5.81 (dd, 1H, J_1=15.2, J_2=5.9 Hz), 5.72 (dt, 1H, J_1=15.2, J_2=5.9 Hz), 5.30–5.34 (m, 1H), 2.00–2.10 (m, 3H), 1.25–1.45 (m, 4H), 0.89 (t, 3H, J=6.9 Hz); ^{13}C NMR: δ 140.8, 133.4, 133.0, 132.9, 132.2, 128.1, 128.0, 127.6, 125.8, 75.2, 31.9, 31.2, 22.2, 13.9; IR (neat): 3350, 2930, 2850, 1670, 1600, 1510, 1460, 1080, 1010, 965, 860, 820, 735 cm^{-1}; HRMS: *m/z* 240.1479 (240.1514 calcd for $C_{17}H_{20}O$, M$^+$).

20: ^{1}H NMR: δ 5.45–5.72 (m, 4H), 4.52 (dd, 1H, J_1=J_2=6.6 Hz), 1.96–2.07 (m, 4H), 1.24–1.44 (m, 7H), 0.83–0.95 (m, 6H); ^{13}C NMR: δ 132.0, 131.9, 131.7, 130.8, 73.5, 34.2, 31.8, 31.2, 22.2, 22.1, 13.8, 13.5; IR (neat): 3400, 2960, 2940, 2870, 1665, 1460, 1380, 990, 970 cm^{-1}; HRMS: *m/z* 182.1643 (182.1670 calcd for $C_{12}H_{22}O$, M$^+$).

21: ^{1}H NMR: δ 5.64 (dt, 1H, J_1=15.2, J_2=6.6 Hz), 5.41 (dd, 1H, J_1=15.2, J_2=6.6 Hz), 4.02 (dt, 1H, J_1=J_2=6.6 Hz), 3.66 (s, 3H), 2.29 (t, 2H, J=7.6 Hz), 2.02 (dt, 2H, J_1=J_2=6.6 Hz), 1.25–1.68 (m, 19H), 0.89 (t, 3H, J=6.9 Hz); ^{13}C NMR: δ 174.2, 133.1, 131.9, 73.0, 51.3, 37.3, 34.0, 31.8, 31.3, 29.4, 29.3, 29.1, 29.0, 25.4, 24.9, 22.1, 13.8; IR (neat): 3400, 2910, 2850, 1735, 1670, 1450, 1430, 1360, 1195, 1165, 1100, 1000, 965 cm^{-1}; HRMS: *m/z* 285.2416 (285.2430 calcd for $C_{17}H_{33}O_3$, M$^+$+1).

22: (as a diastereomer mixture) ^{1}H NMR: δ 5.68–5.79 (m, 1H), 5.38–5.49 (m, 1H), 3.69–4.36 (m, 4H), 2.01–2.10 (m, 2H), 1.32–1.65 (m, 20H), 0.86–0.91 (m, 3H); ^{13}C NMR: δ 199.4, 135.3, 133.4, 95.1, 94.5, 81.4, 81.2, 77.3, 74.0, 73.7, 64.8, 32.1, 32.0, 31.3, 31.2, 28.4, 28.3, 26.3, 22.2, 13.9; IR (neat): 3130, 3000, 1700, 1670, 1390, 1255, 1170, 1100, 850, 760 cm^{-1}; HRMS: *m/z* 313.2253 (313.2251 calcd for $C_{17}H_{31}NO_4$, M$^+$).

Synthesis of enal ***24*** *via two-carbon homologation (eq 3):* A solution of ethoxyethyne (40% in hexane, 171 mg, 0.976 mmol) in CH_2Cl_2 (2 mL) was added to $Cp_2Zr(H)Cl$ (228 mg, 0.884 mmol) at room temperature. After 10 min, to the resulting red solution was added cyclohexanecarbaldehyde (64.0 mg, 0.568 mmol) in CH_2Cl_2 (3 mL) was added followed by $AgAsF_6$ (9.0 mg, 30 μmol, 5 mol%). After 10 min, the mixture was diluted with Et_2O, to which sat. aq. $NaHCO_3$ was added. After filtration (Celite), the products were extracted with Et_2O. To the combined extracts was added 3 N HCl (30 mL) and the two-phase mixture was placed in an oil bath (50 °C) with a reflux condenser for 1 h. After separation, the organic layer was washed with sat. aq. $NaHCO_3$ and brine, and dried (Na_2SO_4). Column chromatography (hexane/EtOAc=4/1) gave **24** (71.2 mg, 90.7%; >95% isomeric purity by GLC); ^{1}H NMR: δ 9.49 (d, 1H, J=7.6 Hz), 6.77 (dd, 1H, J_1=6.6, J_2=15.5 Hz), 6.06 (ddd, 1H, J_1=7.6, J_2=15.5, J_3=1.3 Hz), 2.20–2.34 (m, 1H), 1.62–1.87 (m, 5H), 1.09–1.43 (m, 5H); ^{13}C NMR: δ 194.4, 163.7, 130.5, 40.8, 31.4, 25.8, 25.5; IR (neat): 2920, 2850, 2800, 1685, 1630, 1445, 1120, 1100, 975 cm^{-1}; HRMS: *m/z* 138.1040 (138.1044 calcd for $C_9H_{14}O$, M$^+$).

Synthesis of dienal ***26*** *via four-carbon homologation (eq 4):* A solution of (*Z*)-1-methoxy-1-buten-3-yne (0.83 M in CH_2Cl_2, 0.87 mL, 0.72 mmol) was added to $Cp_2Zr(H)Cl$ (169 mg, 0.655 mmol) at room temperature. After 10 min, to the resulting red solution was added cyclohexanecarbaldehyde (48.8 mg, 0.433 mmol) in CH_2Cl_2 (2 mL) was added followed by $AgAsF_6$ (6.9 mg, 23 μmol, 5 mol%). After 10 min, the reaction mixture was diluted with Et_2O, to which sat. aq. $NaHCO_3$ was added. After filtration through a Celite pad, the products were extracted with Et_2O. To the combined extracts was added 3 N HCl (30 mL) and the two-phase mixture was placed in an oil bath (50 °C) with a reflux condenser for 1 h. After separation, the organic layer was washed with sat. aq. $NaHCO_3$ and brine, and dried (Na_2SO_4). Purification with column chromatography (hexane/EtOAc=9/1) gave **26** (65.5 mg, 92.1%; 96% isomeric purity by GLC); ^1H NMR: δ 9.53 (d, 1H, J=8.1 Hz), 7.08 (dd, 1H, J_1=9.9, J_2=15.4 Hz), 6.29 (dd, 1H, J_1=9.9, J_2=15.4 Hz), 6.22 (dd, 1H, J_1=6.2, J_2=15.4 Hz), 6.09 (dd, 1H, J_1=8.1, J_2=15.4 Hz), 2.11–2.18 (m, 1H), 1.65–1.80 (m, 5H), 1.10–1.36 (m, 5H); ^{13}C NMR: δ 193.7, 153.1, 152.4, 130.0, 126.1, 41.2, 32.0, 25.8, 25.6; IR (neat): 2920, 2850, 1680, 1635, 1600, 1445, 1160, 1120, 1010, 985, 760 cm^{-1}; HRMS: *m/z* 164.1203 (164.1201 calcd for $C_{11}H_{16}O$, M^+).

Method 1 for 1,3-diene synthesis: *Representative procedure is described for the synthesis of* ***37*** *(Figure 1):* To a suspension of $Cp_2Zr(H)Cl$ (234 mg, 0.907 mmol) in CH_2Cl_2 (3 mL) was added propargylsilane **27**[12] (106 mg, 0.942 mmol), and the mixture was stirred at room temperature for 10 min. To this solution was sequentially added 2-naphthalenecarbaldehyde (118 mg, 0.754 mmol) in CH_2Cl_2 (1 mL) and $AgClO_4$ (8.1 mg, 39 μmol, 5 mol%), and the solution was stirred for further 30 min. After the reaction mixture was poured into sat. aq. $NaHCO_3$ extractive workup (EtOAc) followed by purification on preparative TLC (hexane/EtOAc=9/1) gave 1,3-diene **37** (119 mg, 87.2%): ^1H NMR: δ 7.74–7.80 (m, 4H), 7.62 (m, 1H), 7.40–7.47 (m, 2H), 6.92 (dd, 1H, J_1=10.3, J_2=15.6 Hz), 6.72 (d, 1H, J=15.6 Hz), 6.56 (ddd, 1H, J_1=J_2=10.3, J_3=17.1 Hz), 5.38 (d, 1H, J=17.1 Hz), 5.21 (d, 1H, J=10.3 Hz); ^{13}C NMR: δ 137.2, 134.6, 133.6, 132.9, 130.0, 128.2, 127.9, 127.6, 126.5, 126.2, 125.8, 123.4, 117.7; IR (KBr): 1600, 1000, 950, 890, 820, 740 cm^{-1}; HRMS: *m/z* 180.0939 (180.0939 calcd for $C_{14}H_{12}$, M^+).

Data for other dienes **36**, **38**, **39**, and **40** follow (The data of the (*E*)-isomer are shown, respectively):

36: ^1H NMR: δ 6.32 (ddd, 1H, J_1=J_2=10.3, J_3=17.1 Hz), 6.05 (dd, 1H, J_1=10.3, J_2=15.1 Hz), 5.72 (dt, 1H, J_1=15.1, J_2=7.3 Hz), 5.09 (d, 1H, J=17.1 Hz), 4.96 (d, 1H, J=10.3 Hz), 2.08 (dt, 2H, J_1=J_2=7.3 Hz), 1.24–1.41 (m, 16H), 0.89 (t, 3H, J=6.8 Hz); ^{13}C NMR: δ 137.4, 135.5, 130.9, 114.5, 32.6, 32.0, 29.7, 29.6, 29.4, 29.3, 22.7, 14.1; IR (neat): 2920, 2850, 1645, 1600, 1460, 1000, 950, 890, 720 cm^{-1}; HRMS: *m/z* 194.2029 (194.2035 calcd for $C_{14}H_{26}$, M^+).

38: ^1H NMR: δ 7.19–7.46 (m, 5H), 6.82 (dd, 1H, J_1=9.8, J_2=15.6 Hz), 6.57 (d, 1H, J=15.6 Hz), 6.32–6.50 (m, 3H), 5.27 (dd, 1H, J_1=1.5, J_2=17.1 Hz), 5.13 (dd, 1H, J_1=1.5, J_2=9.8 Hz); ^{13}C NMR: δ 137.3, 137.0, 133.8, 133.4, 132.9, 128.8, 128.6, 127.6, 126.4, 117.5; IR (KBr): 3030, 2350, 1615, 1490, 1465, 1015, 990, 980, 905, 750 cm^{-1}.

39: ^1H NMR: δ 6.51 (dd, 1H, J_1 = 10.3, J_2 = 15.4 Hz), 6.35 (ddd, 1H, J_1=J_2=10.3, J_3=16.6 Hz), 5.62 (dt, 1H, J_1=2.0, J_2=15.4 Hz), 5.25 (d, 1H, J=16.6 Hz), 5.12 (d, 1H, J=10.3 Hz), 2.32 (dt, 2H, J_1=2.0, J_2=7.3 Hz), 1.50–1.57 (m, 2H), 1.26–1.42 (m, 4H), 0.91 (t, 3H, J=7.1 Hz); ^{13}C NMR: δ 140.8, 136.4, 118.4, 112.7, 93.6, 79.5, 31.1, 28.5. 22.2, 19.6, 13.9; IR (neat): 2920, 2850, 2200, 1620, 1455, 995, 940, 900, 840, 760 cm^{-1}; HRMS: *m/z* 148.1261 (148.1252 calcd for $C_{11}H_{16}$, M^+).

40: ^1H NMR: δ 6.31 (ddd, 1H, J_1=J_2=10.3, J_3=17.1 Hz), 6.04 (dd, 1H, J_1=10.3, J_2=15.1 Hz), 5.70 (dt, 1H, J_1=15.1, J_2=7.3 Hz), 5.08 (d, 1H, J=17.1 Hz), 4.95 (d, 1H, J=10.3 Hz), 3.67 (s, 3H), 2.30 (t, 2H, J=7.3 Hz), 2.07 (dt, 2H, J_1=J_2=7.3 Hz), 1.55–1.68 (m, 2H), 1.20–1.45 (m, 10H); ^{13}C NMR: δ 174.1, 137.2, 135.3, 130.8, 114.4, 51.2, 34.0, 32.4, 29.2, 29.0, 24.9; IR (neat): 2930, 2850, 1735, 1640, 1600, 1430, 1360, 1240, 1200, 1170, 1000, 950, 890, 720 cm^{-1}; HRMS: *m/z* 224.1776 (224.1776 calcd for $C_{14}H_{24}O_2$, M^+).

Method 2 for 1,3-diene synthesis: *Representative procedure is described for the synthesis of* ***36*** *(Figure 2):* To $Cp_2Zr(H)Cl$ (316 mg, 1.23 mmol) was added stannylallene **29**[13] (271 mg, 0.823 mmol) in CH_2Cl_2 (3 mL), and a clear red solution resulted in 10 min. *n*-Undecanal (100 mg, 0.587 mmol) in CH_2Cl_2 (3 mL) was added, where the solution turned yellow. After consumption of the aldehyde (room temperature, 30 min; by TLC), BF_3•OEt_2 (118 mg, 0.831 mmol) in CH_2Cl_2 (1 mL) was added, where a white suspension formed within 10 min. After quenching with sat. aq. $NaHCO_3$, the mixture was stirred for 10 min, where white precipitates appeared. After filtration through a Celite pad, products were extracted with Et_2O, and the combined extracts were washed with brine and dried (Na_2SO_4). Purification with PTLC (hexane/EtOAc=9/1) followed by bulb-to-bulb distillation (75–105 °C/2 mmHg) gave 1,3-diene **36** (105 mg, 92.3%).

Data for other dienes **43**–**47** follow (The data of the (*E*)-isomer are shown, respectively):

43: ^1H NMR: δ 6.32 (ddd, 1H, J_1=9.8, J_2=10.3, J_3=16.6 Hz), 6.11–6.22 (br, 1H), 5.66 (dd, 1H, J_1=7.8, J_2=15.1 Hz), 5.19 (d, 1H, J=16.6 Hz), 5.08 (d, 1H, J=9.8 Hz), 4.25–4.43 (br, 1H), 4.05 (dd, 1H, J_1=6.3, J_2=8.8 Hz), 3.75 (dd, 1H, J_1=2.4, J_2=8.8 Hz), 1.61 (s, 3H), 1.52 (s, 3H), 1.45 (s, 9H); ^{13}C NMR: δ 151.9,

136.1, 132.5, 117.3, 93.9, 79.6, 68.2, 58.9, 28.4, 26.5, 23.8; IR (neat): 2970, 1690, 1600, 1475, 1450, 1380, 1250, 1175, 1095, 1055, 1000, 860, 770 cm^{-1}; HRMS: *m/z* 253.1671 (253.1678 calcd for $C_{14}H_{23}O_3N$, M^+).

44: ^1H NMR: δ 7.15–7.30 (m, 5H), 6.58 (ddd, 1H, J_1=10.3, J_2=10.8, J_3=17.1 Hz), 5.88 (d, 1H, J=10.8 Hz), 5.10 (dd, 1H, J_1=1.5, J_2=17.1 Hz), 5.00 (dd, 1H, J_1=1.5, J_2=10.3 Hz), 2.73–2.77 (m, 2H), 2.33–2.37 (m, 2H), 1.81 (s, 3H); IR (neat): 3040, 2940, 1650, 1600, 1500, 1455, 990, 900, 750, 700 cm^{-1}; HRMS: *m/z* 172.1234 (172.1252 calcd for $C_{13}H_{16}$, M^+).

45: ^1H NMR: δ 7.43–7.47 (m, 2H), 7.30–7.35 (m, 2H), 7.23–7.27 (m, 1H), 6.77 (ddd, 1H, J_1=J_2=10.3, J_3=16.6 Hz), 6.46 (d, 1H, J=10.3 Hz), 5.32 (dd, 1H, J_1=1.5, J_2=16.6 Hz), 5.19 (dd, 1H, J_1=1.5, J_2=10.3 Hz), 2.18 (s, 3H); ^{13}C NMR: δ 143.0, 136.7, 133.5, 128.2, 127.7, 127.1, 125.7, 117.5, 16.0; IR (neat): 3400, 3090, 3060, 3030, 2930, 2855, 1625, 1590, 1495, 1440, 985, 900, 760 cm^{-1}; HRMS: *m/z* 144.0912 (144.0939 calcd for $C_{11}H_{12}$, M^+).

46: ^1H NMR: δ 6.31 (ddd, 1H, J_1=J_2=10.3, J_3=17.1 Hz), 5.86 (d, 1H, J=10.3 Hz), 4.98 (dd, 1H, J_1=2.0, J_2=10.3 Hz), 4.10 (dd, 1H, J_1=2.0, J_2=17.1 Hz), 1.85–1.93 (m, 1H), 1.65–1.80 (m, 5H), 1.80 (s, 3H), 1.10–1.34 (m, 5H); ^{13}C NMR: δ 144.7, 133.6, 123.5, 114.5, 47.5, 31.7, 26.7, 26.4, 15.0; IR (neat): 2950, 2870, 1650, 1455, 990, 895 cm^{-1}; HRMS: *m/z* 150.1391 (150.1408 calcd for $C_{11}H_{18}$, M^+).

47: ^1H NMR: δ 6.50 (ddd, 1H, J_1=J_2=10.3, J_3=17.1 Hz), 5.88 (d, 1H, J=10.3 Hz), 5.14 (dd, 1H, J_1=2.0, J_2=17.1 Hz), 5.01 (dd, 1H, J_1=2.0, J_2=10.3 Hz), 2.01 (m, 3H), 1.74 (s, 3H), 1.63–1.78 (m, 12H); ^{13}C NMR: δ 147.7, 134.1, 122.1, 115.1, 40.7, 38.0, 37.0, 28.7, 12.2; IR (neat): 2910, 2850, 1635, 1450, 1345, 1105, 990, 895, 795 cm^{-1}; HRMS: *m/z* 202.1745 (202.1721 calcd for $C_{15}H_{22}$, M^+).

Model reaction for quinodimethane generation (eq 8): To $Cp_2Zr(H)Cl$ (121 mg, 0.469 mmol) was added alcohol **48**[22] (197 mg, 0.479 mmol) in CH_2Cl_2 (3 mL) at room temperature. After 5 min, to the resulting pale yellow solution was added diethyl maleate (163 mg, 0.947 mmol) in CH_2Cl_2 (2 mL) followed by BF_3•OEt_2 (133 mg, 0.937 mmol) in CH_2Cl_2 (1 mL). After 15 min, the mixture was poured into sat. aq. KF. Extractive workup (EtOAc) followed by purification with PTLC (hexane/EtOAc=4/1) gave cycloadduct **50**[26] (126 mg, 95.2%): ^1H NMR: δ 7.05–7.15 (m, 4H), 4.10–4.23 (m, 4H), 2.87–3.32 (m, 6H), 1.27 (t, 3H, J=7.3 Hz), 1.23 (t, 3H, J=7.3 Hz); ^{13}C NMR: δ 174.3, 172.8, 133.9, 128.9, 128.5, 126.2, 126.0, 117.8, 60.7, 60.6, 42.1, 40.5, 31.8, 29.5, 14.1, 14.0; IR (neat): 3000, 1730, 1440, 1375, 1180, 1110, 1035, 860 cm^{-1}.

*Synthesis of **54** via tandem reaction (Scheme 4):* To $Cp_2Zr(H)Cl$ (112 mg, 0.434 mmol) was added 1-hexene (46.1 mg, 0.549 mmol) in CH_2Cl_2 (3 mL). After 10 min, to the resulting yellow solution was added aldehyde **51** (88.2 mg, 0.216 mmol) and diethyl maleate **52** (83.6 mg, 0.486 mmol) in CH_2Cl_2 (3 mL). After 5 min, $AgAsF_6$ (10.5 mg, 0.0354 mmol) was added, where a black suspension formed. TLC monitoring showed the consumption of the aldehyde and formation of a new spot. After 15 min, BF_3•OEt_2 (69 mg, 0.49 mmol) in CH_2Cl_2 (1.0 mL) was added, where the above-stated spot immediately disappeared, and a new spot appeared on tlc. After 10 min, the reaction was stopped by adding sat. aq. KF, and the mixture was stirred for 10 min, where white precipitates appeared. After filtration through a Celite pad, products were extracted with EtOAc, and the combined extracts were washed with brine and dried (Na_2SO_4). Purification with PTLC (hexane/EtOAc=9/1) gave **54** (67.2 mg, 86.5%); ^1H NMR (C_6D_6): δ 7.27 (d, 1H, J=7.8 Hz), 7.01–7.13 (m, 3H), 3.99–4.13 (m, 2H), 3.82–3.90 (m, 2H), 3.65 (dd, 1H, J_1=11.7, J_2=17.1 Hz), 3.53 (dd, 1H, J_1=J_2=4.4 Hz), 2.99 (dd, 1H, J_1=6.4, J_2=17.1 Hz), 2.73–2.82 (m, 2H), 2.01–2.10 (m, 1H), 1.81–1.91 (m, 1H), 1.61–1.68 (m, 1H), 1.20–1.31 (m, 7H), 1.04 (t, 3H, J=6.8 Hz), 0.94 (t, 3H, J=6.8 Hz), 0.88 (t, 3H, J=7.3 Hz); ^{13}C NMR: δ 173.4, 171.3, 137.9, 135.0, 128.7, 126.0, 125.8, 125.6, 60.7, 60.1, 43.6, 42.4, 41.1, 31.8, 31.1, 29.6, 28.6, 27.7, 22.6, 14.1, 14.0; IR (neat): 2940, 2860, 1730, 1490, 1450, 1380, 1300, 1190, 1030, 750 cm^{-1}; Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95; Found: C, 73.15; H, 9.30.

*Reduction of cycloadduct **54**:* To a suspension of $LiAlH_4$ (45.3 mg, 1.19 mmol) in THF (1 mL) was added diester **54** (207 mg, 0.575 mmol) in THF (8 mL) at –78 °C, and stirring was continued for 3.5 h. After the mixture was poured into sat. aq. NH_4Cl, 1.5 N HCl was added to the mixture until the gray suspension became a clear solution. Extractive workup (Et_2O) followed by purification with PTLC (hexane/EtOAc = 3/2) gave diol **55** (single isomer, 114 mg, 72.1%); mp (71–72 °C; hexane); ^1H NMR (C_6D_6): δ 6.98–7.23 (m, 4H), 3.63 (dd, 1H, J_1=11.2, J_2=4.4 Hz), 3.58 (dd, 1H, J_1=11.2, J_2=6.8 Hz), 3.31 (dd, 1H, J_1=10.7, J_2=3.4 Hz), 3.23 (dd, 1H, J_1=J_2=10.7 Hz), 2.78 (dd, 1H, J_1=17.6, J_2=11.7 Hz), 2.67–2.71 (m, 1H), 2.62 (dd, 1H, J_1=17.6, J_2=6.4 Hz), 2.21 (dt, 1H, J_1=12.2, J_2=3.4 Hz), 1.90–2.05 (m, 2H), 1.24–1.58 (m, 10H), 0.93 (t, 3H, J=6.8 Hz), 0.53 (s, 1H); ^{13}C NMR: δ 139.2, 135.9, 128.9, 125.7, 125.5, 65.9, 57.8, 42.2, 40.9, 40.5, 31.8, 30.7, 29.7, 28.2, 27.7, 22.7, 14.1; IR (KBr): 3200, 2900, 1450, 1330, 1220, 1100, 1040, 950, 910, 840, 760 cm^{-1}; Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.97; H, 10.17. Crystallographic data: orthorhombic (Spontaneous resolution was observed.), $P2_12_12_1$, a=10.597(3), b=19.149(2), c=8.033(5) Å, V=1630.1(5) $Å^3$, Z=4, D_X=1.13 gcm^{-3}, μ(Mo Kα)=0.066 mm^{-1}. Final R is 0.057 for 1144 reflections.

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