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Reactions of Trimethylsilyl Dienol Ethers with Palladium(II) Salts: Formation of Formyl-Substituted η^3-Allylpalladium Complexes and 4-Acyloxy-2-Alkenals

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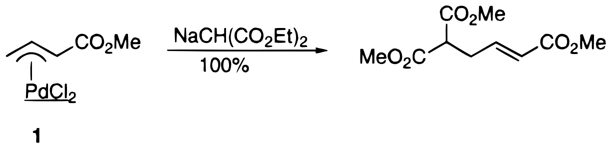
Reaction of acyclic 1-(trimethylsilyloxy)-1,3-dienes with bis(acetonitrile)palladium dichloride, in benzene, affords formyl-substituted η^3-allylpalladium complexes in good to excellent yield. In contrast, using palladium diacetate as the palladium(II) source produces 4-acetyloxy-substituted 2-alkenals. Excellent stereoselection in favor of the *E*-alkenal is usually observed. The corresponding benzoic acid esters can be prepared, with similar stereoselection, using 1-(trimethylsilyloxy)-1,3-dienes and palladium diacetate in the presence of an excess sodium benzoate.

Introduction

Reactions of η^3-allylmetal complexes in general and η^3-allylpalladium complexes in particular have been extensively studied over the last few decades. A number of important catalytic and stoichiometric reactions involving these intermediates have been developed. In the vast majority of cases, the η^3-allyl group is substituted with alkyl groups without any functionality on the adjacent carbons. In contrast, reactions of η^3-allylpalladium complexes having an electrophilic functional group, such as a carbonyl group, directly attached remain to be studied in more detail. Complexes of this type have, in principle, five potentially electrophilic sites. The two terminal carbons of the allylic group, the central carbon, the carbonyl carbon, and the metal all have electrophilic character; thus, a number of different products may arise upon reaction of these complexes with nucleophiles. Utilization of such carbonyl-substituted complexes is relatively scarce in the literature, but a few examples of nucleophilic addition of carbanions and heteronucleophiles to η^3-allylpalladium complexes of this type can be found.[3] For example, reaction of the ester complex 1[4] with sodium diethyl malonate gave the γ-substituted product in high yield (Scheme 1). *E*-Stereochemistry in the final product is generally observed starting from syn complexes. Related catalytic reactions of the allylic substrates **2**[5] and **3**[6] with vinyltin reagents and stabilized carbanions, respectively, again produced γ-substituted products, probably via an η^3-allylpalladium intermediate (Schemes 2 and 3).[6b,7]

Scheme 1



The transformation of silyl enol ethers to α,β-unsaturated ketones using a catalytic amount of palladium diacetate, a reaction originally developed by Saegusa et al.,[8] has been of substantial use in organic synthesis. Intermediately formed, highly reactive, oxa-η^3-allylpalladium species have been proposed for this transformation. The presence of an additional double bond, i.e., employing silyl dienol ethers as starting materials, should produce a more stable η^3-allylpalladium complex having an adjacent formyl group. Murai et al. recently reported that upon reaction of 1-(trimethylsilyloxy)-1,3-butadiene (**4a**) with bis(acetonitrile)palladium dichloride ($PdCl_2(MeCN)_2$), the η^3-allylpalladium complex **5a** was isolated as an 87:13 *syn*/*anti* mixture in almost quantitative yield (Scheme 4).[9,10] In addition to this single example employing palladium,

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(3) For references to synthesis and reactions of related η^3-allyl complexes substituted with an electron-withdrawing group for Mo, see: (a) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 897. (b) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132. (c) Yu, R. H.; McCallum, J. S.; Liebeskind, L. S. *Organometallics* **1994**, *13*, 1476. (d) Lin, S.-H.; Lush, S.-F.; Cheng, W.-J.; Lee, G.- H.; Peng, S.-M.; Liao, Y.-L.; Wang, S.-L.; Liu, R.-S. *Organometallics* **1994**, *13*, 171. (e) Rubio, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 891. (f) Lin, S.-H.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1993**, *12*, 2187. (g) Lin, S.-H.; Cheng, W.-J.; Liao, Y.-L.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1391. (h) Vong, W.-J.; Peng, S.-M.; Lin, S.-H.; Lin, W.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **1991**, *113*, 573. (i) Lin, S.-H.; Vong, W.-J.; Cheng, C.-Y.; Wang, S.-L.; Liu, R.-S. *Tetrahedron Lett.* **1990**, *31*, 7645. (j) Vong, W.-J.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 2187. For W, see: (k) Liang, K.-W.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1995**, *14*, 2353. (l) Kwei-Wen, L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2705. For Fe, see: (m) Enders, D.; Frank, U.; Fey, P.; Jandeleit, B.; Lohray, B. B. *J. Organomet. Chem.* **1996**, *519*, 147. (n) Enders, D.; Fey, P.; Schmitz, T.; Lohray, B. B.; Jandeleit, B. *J. Organomet. Chem.* **1996**, *514*, 227. (o) Ley, S. V.; Meek, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1751. (p) Enders, D.; Jandeleit, B.; Prokopenko, O. F. *Tetrahedron* **1995**, *51*, 6273.

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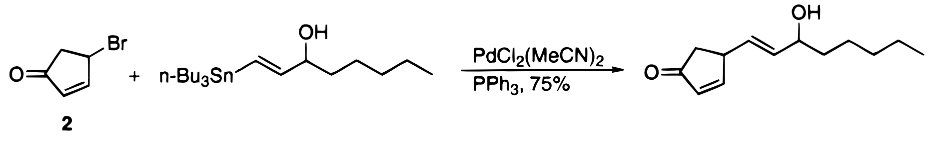
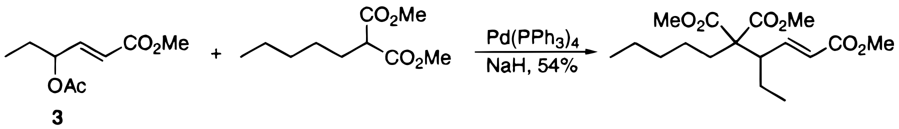
S0276-7333(97)01048-0 CCC: $15.00

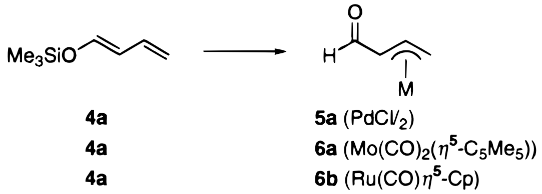
Scheme 2



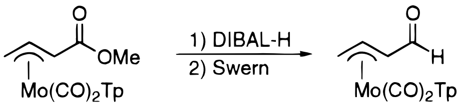
Scheme 3



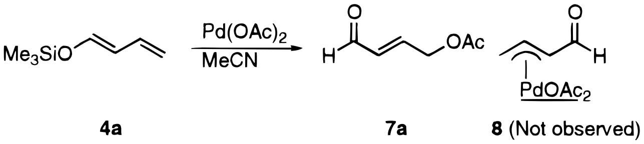
Scheme 4



Scheme 5



Scheme 6



some related molybdenum[11] and ruthenium[12] complexes (e.g., **6a**[11c] and **6b**) have been isolated from similar reactions of 1-(trimethylsilyloxy)-1,3-butadienes with $[(\eta^5\text{-}C_5Me_5)(MeCN)_2(CO)Mo]^+BF_4^-$ or $[Cp(MeCN)_2(CO)Ru]^+BF_4^-$, respectively (Scheme 4). Pearson et al. recently reported the synthesis of an additional member of this family by a reduction−oxidation sequence (Scheme 5, Tp = hydridotris(1-pyrazolyl)borato).[13]

We have also, independently, observed this facile formation of η^3-allylpalladium complexes from 1-(trimethylsilyloxy)-1,3-butadiene and bis(acetonitrile)palladium dichloride. Attempts to prepare the closely related acetate complex **8** by reaction of **4a** with palladium diacetate proved to be futile. However, the synthetically interesting building block *E*-4-acetoxy-2-butenal (**7a**) was isolated as the sole product (Scheme 6). Compounds of this type, 4-acyloxy-2-alkenals, have been used in the total synthesis of natural products, such as geissoschzine methyl ester,[14] isotopically labeled carotenoids,[15] vitamin A acetate,[16] the methyl ester of the seed pigment bixine,[17] and in the synthesis toward the dolabellan diterpene skeleton.[18]

Herein is reported the synthesis and characterization of a number of novel formyl-substituted η^3-allylpalladium complexes together with a full account of the palladium diacetate-mediated reaction of 1-(trimethylsilyloxy)-1,3-dienes affording 4-acetoxy- and 4-benzoyloxy-substituted 2-alkenals.[19]

Results and Discussion

A number of 1-(trimethylsilyloxy)-1,3-dienes were prepared from 2-alkenals and trimethylsilyl chloride in the presence of triethylamine using standard literature procedures. The dienes were reacted with a stoichiometric amount of bis(acetonitrile)palladium dichloride, $(MeCN)_2PdCl_2$, forming η^3-allylpalladium complexes in good to excellent yield. The results thereof are summarized in Table 1. In contrast to the relatively stable parent complex **5a** studied by Murai et al., the more

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(6) Tsuji, J.; Ueno, H.; Kobayashi, Y.; Okumoto, H. *Tetrahedron Lett.* **1981**, *22*, 2573. For other related examples using C-nucleophiles, see: (a) Nakami, J.; Ohkura, M.; Dan-oh, Y.; Sakamoto, Y. *Tetrahedron Lett.* **1991**, *32*, 2409. (b) Huggenberg, W.; Hesse, M. *Tetrahedron Lett.* **1989**, *30*, 5119. For O-nucleophiles, see: (c) Panek, J.-S.; Yang, M.; Solomon, J. S. *J. Org. Chem.* **1993**, *58*, *8*, 1003. (d) Suzuki, T.; Sato, O.; Hirama, M.; Yamamoto, Y.; Murata, M.; Yasumoto, T.; Harada, N. *Tetrahedron Lett.* **1991**, *32*, 4505. (e) Suzuki, T.; Sato, O.; Hirama, M. *Tetrahedron Lett.* **1990**, *31*, 4747. For N-nucleophiles, see: (f) Öhler, E.; Kanzler, S. *Synthesis* **1995**, 539. (g) Tsuda, T.; Horii, Y.; Nakagawa, Y.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1989**, *54*, 977. (h) Tanikaga, R.; Takeuchi, J.; Takyu, M.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1987**, 386. For hydride addition, see: (i) Tsuji, J.; Mandai, T. *Synthesis* **1996**, 1 and references therein. (j) Nagasawa, K.; Shimizu, I.; Nakata, T. *Tetrahedron Lett.* **1996**, *37*, 6881. (k) Satake, A.; Shimizu, I. *Tetrahedron: Asymmeth.* **1993**, 4, 1405. (l) Nagasawa K.; Ishihara, H.; Zako, Y.; Shimizu, I. *J. Org. Chem.* **1993**, *58*, 2523. (m) Jung, M.; Trifunovich, I. D. *Tetrahedron Lett.* **1992**, *33*, 2921. (n) Mori, K.; Harashima, S. *Tetrahedron Lett.* **1992**, *33*, 2921. (o) Nagasawa, K.; Zako, Y.; Ishihara, H.; Shimizu, I. *Tetrahedron Lett.* **1991**, *32*, 4937. (p) Shimizu, I.; Hayashi, K.; Ide, N.; Oshima, M. *Tetrahedron Lett.* **1991**, *47*, 2991.

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(9) Ogoshi, S.; Hirako, K.; Nakanishi, J.; Ohe, K.; Murai, S. *J. Organomet. Chem.* **1993**, *445*, C13. See also: Andri, M. K.; Krylov, A. V.; Averochkin, N. E.; Belov, A. P. *Koord. Khim.* **1984**, *10*, 540.

(10) For a related reaction of 1-(trimethylsilyl)-1-(trimethylsilyloxy)-1,3-butadiene, see: Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Murai, S. *Organometallics* **1991**, *10*, 3813.

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(15) Jansen, F. J. H. M.; Lugtenburg, J. *Pure Appl. Chem.* **1994**, *66*, 963.

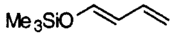
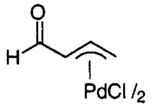
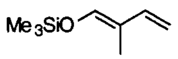
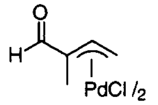
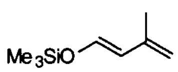
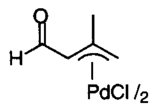
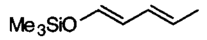
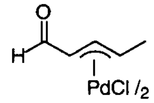
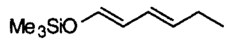
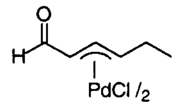
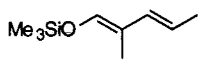
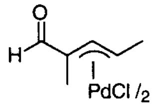
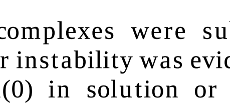
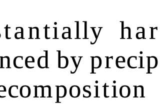
(16) (a) Soukup, M.; Widmer, E. *Tetrahedron Lett.* **1991**, *32*, 4117. (b) Reif, W.; Grassner, H. *Chem.-Ing.-Technol.* **1973**, *45*, 646.

(17) Pattenden, G.; Way, J. E.; Weedon, B. C. L. *J. Chem. Soc. C.* **1970**, 235.

(18) Williams, D. R.; Coleman, P. J.; Nevill, C. R.; Robinson, L. A. *Tetrahedron Lett.* **1994**, *34*, 7895.

(19) Presented in part by A.K.B. at the 213th American Chemical Society National Meeting, San Francisco, CA, April, 1997 (Abstract ORGN 419).

Table 1. η^3-Allylpalladium Complexes from Silyl Dienol Ethers

Entry	Dienol Ether	Product (yield, syn:anti)[a]
1	 **4a**	 **5a** (99%, 87:13)[b]
2	 **4b**	 **5b** (100%, 34:66)
3	 **4c**	 **5c** (84%, 31:69)
4	 **4d**	 **5d** (66%, 87:13)
5	 **4e**	 **5e** (80%, 89:11)
6	 **4f**	 **5f** (87%, 29:71)
7	 **4g**	 **5g** (not isolated)[c]

[a] Yield of isolated products. The syn isomer is depicted. [b] Reference 9. [c] Rapidly decomposes at room temperature. Partial ^{1}H NMR from a 63:37 mixture of isomers: δ 10.09 (d, $J = 7.5$ Hz, 1H), 9.52 (d, $J = 5.5$ Hz, 1H), 4.89 (d, $J = 5.7$ Hz, 1H), 3.87 (d, $J = 7.5$ Hz, 1H).

substituted complexes were substantially harder to handle. Their instability was evidenced by precipitation of palladium(0) in solution or decomposition of the complexes in the solid state. Employing the more complex silyl dienol ether **4g**, the corresponding η^3-allylpalladium complex **5g** (entry 7) was probably formed, but we were unable to isolate this complex due to rapid decomposition at ambient temperature.

The complexes were obtained as inseparable mixtures of the syn and anti isomers, which were readily distinguished from each other by ^{1}H NMR. Especially diagnostic were the aldehyde protons shielded by the palladium in the anti complexes and substantially shifted upfield compared to the syn complexes.[11] The largest upfield shift was observed for complex **5c** (1.05 ppm); shifts for all other complexes ranged from 0.51 to 0.68 ppm. It is interesting to note the almost identical isomer ratio of complexes **5a**, **5d**, and **5e**, all unsubstituted on the central carbon or on the formyl-substituted terminus of the allylic system. Introduction of an alkyl group in either of these two positions resulted in an inversion of the isomer ratio with the anti isomer being the major product (entries 2, 3, and 6). Unfavorable steric interactions between the central methyl group and the formyl substituent in **5c** and between the palladium moiety and the larger methyl group (compared to the formyl group) for complexes **5b** and **5f** offer a plausible explanation for the observed anti preference in these complexes.

Of the four possible stereoisomers of **5d**, only two were isolated. No additional isomers were observed by ^{1}H NMR of the crude reaction mixture. For the major isomer of **5d**, a triplet resonance for the central proton of the allylic system was found at δ 5.78 ppm having a spin–spin coupling constant $J = 11.1$ Hz, typical of a trans configuration of protons in an η^3-allyl complex.[3b] For the minor isomer, the corresponding resonance was observed at δ 5.48 ppm as a doublet of doublets ($J = 12.1$ and 7.2 Hz), indicating both a cis and a trans relationship. Moreover, the resonance for the proton adjacent to the methyl group in the minor isomer appears as a doublet of quartets ($J = 12.1$ and 7.2 Hz). Homonuclear decoupling of the methyl group of the minor isomer results in a collapse of the doublet of quartets to a doublet ($J = 12$ Hz). Thus, it is evident from the above data that **5d** is isomeric on the aldehyde side of the η^3-allyl moiety and not on the alkyl side. Similar ^{1}H NMR data were also observed for **5e** and **5f**, establishing these as isomeric on the aldehyde side of the complex.

In an attempt to prepare the related acetate complex **8** employing palladium diacetate (Pd(OAc)$_2$) in place of PdCl$_2$(MeCN)$_2$, *E*-4-acetoxy-2-butenal (**7a**) was isolated in 51% yield (Scheme 6). The reaction proceeds rapidly, as evident by the immediate precipitation of palladium(0) after addition of the silyl dienol ether to a slurry of Pd(OAc)$_2$ in acetonitrile. The regioselective formation of the γ-substituted alkenal is consistent with previous results employing stabilized anions (Schemes 1–3). Related examples of palladium-mediated acetoxylations of intermediately formed η^3-complexes having an sulfone[20] or an carboxylic ester substituent[21] have been reported.

To evaluate the scope and limitation of the palladium(II)-mediated oxidation reaction, several silyl dienol ethers were reacted with a stoichiometric amount of Pd(OAc)$_2$ as described above. The results thereof are summarized in Table 2. Addition of 1 equiv of sodium acetate to the reaction of **4a** resulted in a substantially higher isolated yield of **7a** (entry 1). Addition of NaOAc had, in most cases, a similar but not as dramatic effect on the yield. Moreover, both a higher yield and improved *E*/*Z* ratio of **7b** was observed upon reaction of silyl dienol ether **4b** with Pd(OAc)$_2$ in the presence of NaOAc (entries 8 and 9). It should be noted that most if not all of the products depicted in Table 2 are volatile. The amount of product before workup and chromatographic purification is probably higher than what is

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Table 2. Pd(OAc)$_2$-Mediated Oxidation of Silyl Dienol Ethers

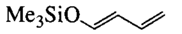
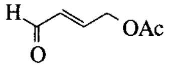
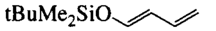
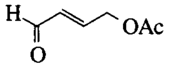
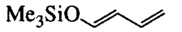
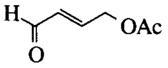
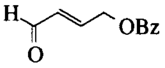
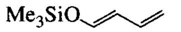
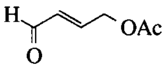
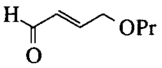
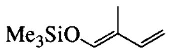
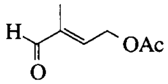
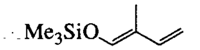
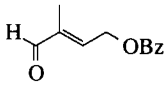
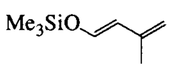
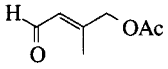
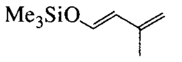
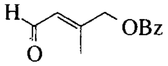
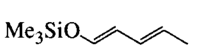
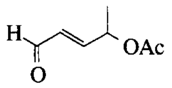
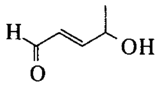
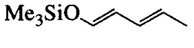
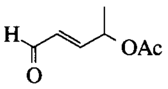
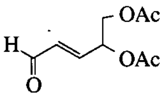
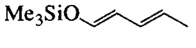
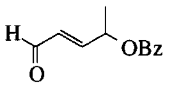
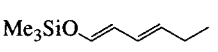
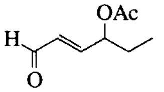
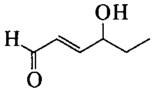
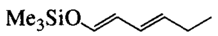
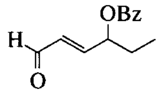
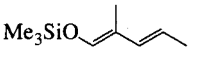
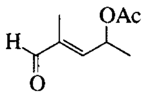
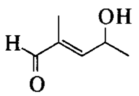
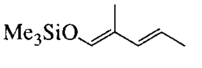
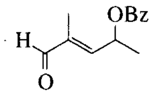
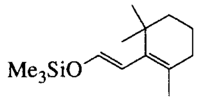
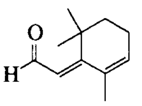
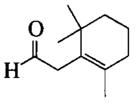
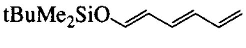
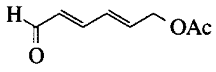
Entry[a]	Dienolether	Product (yield, *E*:*Z*)[b]	
			
1	**4a**	**7a** (97%, >95:5)	
2[c]	**4a**	**7a** (51%, >95:5)	
			
3	**15**	**7a** (51%, 92:8)	
			
4	**4a**	**7a** (8%, >95:5)	**9a** (64%, >95:5)
5[d]	**4a**	**7a** (62%, >95:5)	**9a** (20%, >95:5)
6[e]	**4a**	**7a** (10%, >95:5)	**9a** (55%, >95:5)
			
7[f]	**4a**	**7a** (15%, >95:5)	**10a** (16%, >95:5)
			
8	**4b**	**7b** (62%, 91:9)	
9[c]	**4b**	**7b** (44%, 76:24)	
			
10	**4b**	**9b** (62%, 70:30)[g]	
			
11	**4c**	**7c** (50%, 40:60)	
12[c]	**4c**	**7c** (40%, 38:62)	
			
13	**4c**	**9c** (42%, 33:67)	
			
14	**4d**	**7d** (64%, >95:5)	**11d** (3%, >95:5)
15[c]	**4d**	**7d** (27%, >95:5)	**11d** (6%, >95:5)
			
16[h]	**4d**	**7d** (21%, >95:5)	**12** (4%, >95:5)
			
17	**4d**	**9d** (35%, >95:5)	

Table 2 (Continued)

Entry[a]	Dienolether	Product (yield, *E*:*Z*)[b]	
			
18	**4e**	**7e** (24%, >95:5)	**11e** (3%, >95:5)
19[c]	**4e**	**7e** (28%, ~95:5)	**11e** (40%, >95:5)
			
20	**4e**	**9e** (25%, >95:5)[i]	
21[j]	**4e**	**9e** (17%, >95:5)[k]	
			
22	**4f**	**7f** (4%, >95:5)	**11f** (26%, >95:5)
			
23	**4f**	**9f** (22%, 97:3)	
			
24	**4g**	**13** (19%, 50:50)	**14** (49%)
25[l]	**4g**	**13** (56%, 50:50)	**14** (19%)
			
26	**4h**	**7h** (21%, >95:5)	

[a] Typical reaction conditions: 1 mmol of $Pd(OAc)_2$, 1.1 mmol of diene, 1 mmol of NaOAc (or 4 mmol of NaOBz), 10 mL of MeCN, ambient temperature to 45 °C, 0.5–5 h unless otherwise stated. [b] Pure isolated products. The *E*/*Z* ratio was determined by ^{1}H NMR, and a ratio of >95:5 indicates that only the *E* isomer was detected. [c] No NaOAc was added. [d] Only 1 equiv of NaOBz was used. [e] A 1 mmol amount of $Pd(OBz)_2$, 1.1 mmol of diene, 4 mmol of NaOAc were used. [f] Four equivalents of $CH_3CH_2CO_2Na$ was used in place of NaOAc. [g] Traces (~5%) of **7b** were observed in the crude mixture. [h] After 20 h at 40 °C. [i] There was 7% of a 71:24:5 mixture of *E,E*/*E,Z*/*Z,E*-2,4-hexadienal isolated. [j] Four equivalents of Na_2CO_3 was added. [k] There was 31% of a 74:26 mixture of *E,E*/*E,Z*-2,4-hexadienal isolated. [l] Heated at reflux for 1 h.

reflected in the reported isolated yield. In contrast to the $Pd(OAc)_2$-catalyzed oxidation of trimethylsilyl enol ethers producing α,β-unsaturated ketones developed by Saegusa,[8,22] the presence of a *tert*-butyldimethylsilyl group does not appear to interfere with the reaction. For example, the ester **7a** was isolated in 51% yield from **15**, although a lower isomer ratio was observed compared to the trimethylsilyl ether (entry 3). Excellent selectivity in favor of the *E* isomer was obtained from all but two of the dienes examined. A lower *E*/*Z* selectivity was observed for 2-methyl-1-(trimethylsilyloxy)-1,3-butadiene (**4b**), and in the case of 3-methyl-1-(trimethylsilyloxy)-1,3-butadiene (**4c**), a slight excess of the *Z* isomer was isolated (entries 8 and 9 and 11 and 12, respectively). The isomers were identified by comparison with literature ^{1}H NMR data, and the isomeric ratio was determined by integration of the aldehyde or the allylic C-4 proton resonances.[23]

The yield of esters decreased when silyl dienol ethers derived from pentenals and hexenals were used as the substrates for the oxidation reaction. In addition to the expected esters, 4-hydroxy-2-alkenals (**11d–f**), 2-alkenals, and 2,4-dienals were formed from silyl dienol ethers **4d–f**. Although usually lost during workup and chromatography, a substantial amount of the latter two products was observed by ^{1}H NMR of the crude reaction mixtures. The dienals may be formed via β-hydride elimination from a putative η³-allylpalladium complex[24] or by base-induced elimination of acetic acid from the

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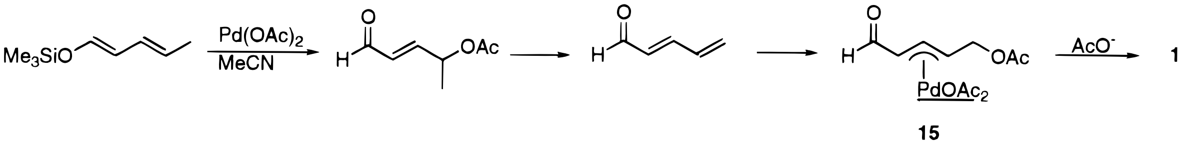
(22) (*tert*-Butyldimethylsilyl)enol ethers undergo this reaction in the presence of $TiCl_4$ and a stoichiometric amount of $Pd(OAc)_2$, see: Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, *107*, 5495.

(23) The ^{1}H resonances for the allylic C-4 proton(s) of the *E* isomers are found upfield relative to the *Z* isomers, see: (a) Traas, P. C.; Boelens, H.; Takken, H. J. *Recl. Trav. Chim.* **1976**, *95*, 57. (b) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161.

(24) Andersson, P. G.; Schab, S. *Organometallics* **1995**, *14*, 1 and references therein. See also: Dorman, G.; Roberts, S. M.; Wakefield, B. J.; Winders, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1543.

Scheme 7



expected ester (e.g., **7d**).[25] This represents, at least in a formal sense, the products derived from a homologous Saegusa reaction. The 2,4-dienal **13** and the β,γ-unsaturated aldehyde **14** were the sole products isolated from the reaction of **4g** (entry 24). A substantial yield increase of the elimination product **13** was realized when the reaction mixture was heated at reflux (entry 25).

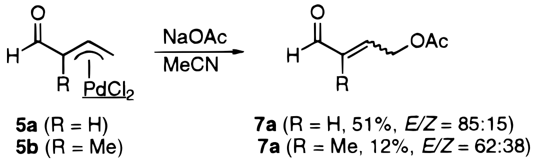
A new product, the diacetate **12**, was isolated in low yield upon reaction of dienol **4d** over an extended period of time (Table 2, entry 16). Formation of diacetate **12** can be envisioned to occur via elimination of acetic acid from **7d** to give 2,4-pentadienal followed by acetoxypalladation to form η^3-allyl complex **15** and nucleophilic addition (Scheme 7).

As a final example of acetate addition, the silyl trienol ether **4h** was reacted as described above, exclusively furnishing *E*,*E*-6-acetoxy-2,4-hexadienal **7h** in low yield (entry 26). This represents a two-step formal synthesis of *E*,*E*-6-hydroxy-2,4-hexadienal, an antimicrobial stress metabolite isolated from *Hypochoeris radicata*.[26] It is interesting to note the exclusive ϵ-selectivity; no trace of additional isomers was observed.

In addition to the acetates, esters can be obtained employing other carboxylic acid anions. For example, reaction of **4a** with Pd(OAc)$_2$ in the presence of 4 equiv of sodium benzoate gave a mixture of the esters **7a** and **9a** in a $\sim$1:6 ratio, as determined by ^{1}H NMR of the crude reaction mixture. Purification by column chromatography gave **7a** and **9a** in 8% and 62% yield, respectively (entry 3). An excess of nucleophile is required to suppress the formation of **7a**. For example, performing the same reaction using only 1 equiv of sodium benzoate gave a 3:1 mixture of **7a** and **9a** (entry 5). Benzoate esters were isolated from reactions of dienes **4b**−**f** with Pd(OAc)$_2$ in the presence of an excess of sodium benzoate. Although the corresponding alcohols were not observed in these reactions, the major byproducts were again 2-alkenals and 2,4-dienals. Reaction of 1-(trimethylsilyloxy)-1,3-hexadiene (**4e**) with sodium benzoate in the presence of an excess of sodium carbonate resulted in a somewhat decreased yield of **9e** but substantially increased the yield of the elimination product 2,4-hexadienal. Sodium propionate was also used as the nucleophile, but a lower selectivity and yield of the product was observed (entry 7).

Nucleophilic addition of acetate to an intermediately formed η^3-allylpalladium complex (**8**) appears to be a plausible mechanistic rationale for the formation of **7a**. Reaction of η^3-allylpalladium chloride complex **5a** with 2 equiv of NaOAc in MeCN at 50 °C produced **7a** in 51% yield.[27] The ratio of ***(E)*-7a** to ***(Z)*-7a** was 85:15, almost identical to the isomer ratio observed for the starting palladium complex **5a** (Scheme 8). However, reaction of complex **5b** under the same conditions gave **7b** (*E*/*Z* = 62:38) in low yield having the opposite stereochemistry compared to the starting material.

Scheme 8



The question of whether the acetate (or benzoate) adds to the η^3-allyl complex by external attack or migration from palladium is not easily addressed. Both external and internal delivery of acetate to η^3-allylpalladium complexes have been previously documented.[28] Using palladium dibenzoate in place of Pd(OAc)$_2$, in the presence of 4 equiv of sodium acetate, gave a mixture of **9a** and **7a** in a 5:1 ratio. The small change in the product ratio between this experiment and entry 4 (Table 2) perhaps indicates an initial formation of an η^3-allyl acetate complex from **4a** and Pd(OAc)$_2$ followed by an exchange reaction affording an η^3-allyl benzoate complex, terminated by internal delivery of the nucleophile. Formation of Pd(OBz)$_2$ from Pd(OAc)$_2$ prior to complexation does not appear to occur at ambient temperature. An NMR experiment was performed wherein Pd(OAc)$_2$ was dissolved in benzene-d_6; 2 equiv of sodium benzoate was added, and a spectrum was recorded every 5 min for 2 h. No formation of Pd(OBz)$_2$ was observed.

In summary, a novel palladium-mediated oxidation reaction of substituted 1-(trimethylsilyloxy)-1,3-dienes to afford 4-acetoxy- and 4-benzoyloxy-substituted 2-alkenals has been developed. The *E* product is formed predominately. We are presently pursuing a catalytic reaction using a catalytic amount of palladium diacetate and a reoxidant.

Experimental Section

General Procedures. All NMR spectra were determined in CDCl$_3$ at 270 (^{1}H NMR) and 67.5 MHz (^{13}C NMR). The chemical shifts are expressed in δ values relative to Me$_4$Si (0.00 ppm, ^{1}H and ^{13}C) or CDCl$_3$ (77.00 ppm, ^{13}C) internal standards. ^{1}H−^{1}H coupling constants are reported as calculated from the spectra; thus, a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained. The results of the APT (attached proton test) ^{13}C NMR experiments are shown in parentheses where, relative to CDCl$_3$, (−) denotes CH$_3$ or CH and (+) denotes CH$_2$ or C. Although all organic products described herein have been previously prepared, apart from compounds **7f**, **9f**, and **11f**, little or no spectroscopic data can be found in the literature.

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(25) A similar reaction of 1,3-dienol acetate has been reported, see: Minami, I.; Takahashi, K.; Shimizu, I.; Kimura, T.; Tsuji, J. *Tetrahedron Lett.* **1986**, *42*, 2971.

(26) Maruta, Y.; Fukushi, Y.; Ohkawa, K.; Nakanishi, Y.; Tahara, S.; Mizutani, J. *Phytochemistry* **1995**, *38*, 1169.

(27) The complex reacted very slowly with NaOAc at ambient temperature.

(28) For examples, see: Bäckvall, J.-E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892.

To support the assigned structures, IR and ^{1}H and ^{13}C NMR spectra have been reported.

Tetrahydrofuran (THF), 1,4-dioxane, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Toluene, pyridine, hexanes, benzene, acetonitrile, and ethyl acetate were distilled from calcium hydride. Chemicals prepared according to the literature procedures have been footnoted at the first time used; all other reagents were obtained from commercial sources and used as received. All reactions were performed in oven-dried glassware. Solvents were removed from crude reaction mixtures and products on a rotary evaporator at water-aspirator pressure unless otherwise stated. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

Dichlorobis[(1,2,3-η)-3-methyl-4-oxo-2-buten-1-yl]dipalladium (5b). To a slurry of of PdCl(MeCN)$_2$[29] (65 mg, 0.25 mmol) in benzene (3 mL) was added a solution of 2-methyl-1-(trimethylsilyloxy)-1,3-butadiene[30] (53 mg, 0.24 mmol) in benzene (2 mL). A clear orange solution was formed within a few minutes. The solution was stirred at ambient temperature for 2 h, whereafter 1 Tbsp of silica (SiO$_2$) was added, and the solvent was removed using a high-vacuum pump. The solid residue was purified by chromatography (EtOAc−EtOH, 9:1), affording **5b** (57 mg, 0.25 mmol, 100%) as a yellow solid. Spectral data were obtained from a 34:66 mixture of *syn*- and *anti*-**5b**. Mp 116−119 °C (decomp); IR (CDCl$_3$) 1692, 1669 cm $^{-1}$ *syn*-**5b**: ^{1}H NMR δ 9.32 (s, 1H), 5.68 (dd, $J = 12.9$, 7.5 Hz, 1H), 4.42 (d with further fine splitting, $J = 7.5$ Hz, 1H), 3.76 (d partially overlapped, $J = 15$ Hz, 1H), 1.14 (s, 3H); ^{13}C NMR δ 194.4 (−), 110.6 (−), 85.9 (+), 64.4 (+), 12.8(−). *anti*-**5b**: ^{1}H NMR δ 8.76 (s, 1H), 5.74 (dd, $J =$ 13.2, 8.1 Hz, 1H), 4.14 (dd, $J = 7.9$, 2.2 Hz, 1H), 3.71 (dd, $J =$ 12.9, 2.4 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR δ 184.4 (−), 112.1 (−), 88.9 (+), 60.6 (+), 17.0 (−).

Dichlorobis[(1,2,3-η)-2-methyl-4-oxo-2-buten-1-yl]dipalladium (5c). A slurry of PdCl$_2$(MeCN)$_2$ (260 mg, 1.00 mmol) in benzene (8 mL) was reacted with 3-methyl-1-(trimethylsilyloxy)-1,3-butadiene[23b] (160 mg, 1.02 mmol) dissolved in benzene (2 mL) as described above (2 h). Hexanes (10 mL) were added at 0 °C to precipitate the product. After a few hours, the precipitate was filtered off and dried using a high-vacuum pump to afford **5c** (190 mg, 0.84 mmol, 84%) as a yellow solid. Spectral data were obtained from a 34:66 mixture of *syn*- and *anti*-**5c**. Mp 112−115 °C; IR (neat) 1674 cm^{-1}. *anti*-**5c**: ^{1}H NMR δ 8.80 (d, $J = 5.9$ Hz, 1H), 4.90 (d, J = 5.9 Hz, 1H), 4.15 (s, 1H), 3.75 (d, $J = 1.5$ Hz, 1H), 2.24 (s, 3H); ^{13}C NMR δ 185.7 (−), 126.5 (+), 76.3 (−), 64.5 (+), 23.4 (−). *syn*-**5c**: ^{1}H NMR δ 9.85 (d, $J = 6.2$ Hz, 1H), 4.05 (s, 1H), 3.62 (d, $J = 5.9$ Hz, 1H), 3.17 (s, 1 H), 2.47 (s, 3 H); ^{13}C NMR δ 194.2 (−), 127.6 (+), 71.4 (−), 66.6 (+), 19.2 (−). Anal. Calcd for $C_{10}H_{14}Cl_2O_2Pd_2$: C, 26.69; H, 3.14. Found: C, 26.78; H, 3.13.

Dichlorobis[(2,3,4-η)-1-oxo-3-penten-2-yl]dipalladium (5d). A slurry of PdCl$_2$(MeCN)$_2$ (261 mg, 1.00 mmol) in benzene (8 mL) was reacted with 1-(trimethylsilyloxy)-1,3-pentadiene[30] (169 mg, 1.08 mmol) dissolved in benzene (2 mL) as described above (5 h). Hexanes (10 mL) were added at 0 °C to precipitate the product. After a few hours, the precipitate was filtered off and dried using a high-vacuum pump to afford **5d** (149 mg, 0.66 mmol, 66%) as a yellow solid. Spectral data were obtained from a 87:13 mixture of *syn*- and *anti*-**5d**. Mp 77−80 °C (decomp); IR (neat) 1691 cm^{-1}. *syn*-**5d**: ^{1}H NMR δ 9.65 (d, $J = 5.4$ Hz, 1H), 5.78 (t, $J = 11.1$ Hz, 1H), 4.42 (qd, J = 11.9, 5.7 Hz, 1H), 3.73 (dd, $J = 10.6$, 5.2 Hz, 1H), 1.39 (d, J = 6.2 Hz, 3H); ^{13}C NMR δ 194.9 (−), 110.0 (−), 86.9 (−), 69.0 (−), 18.4 (−). *anti*-**5d**: ^{1}H NMR δ 9.02 (d, $J = 4.9$ Hz, 1H), 5.48 (dd, $J = 12.1$, 7.2 Hz, 1H), 4.98 (qd, $J = 12.4$, 6.2 Hz, 1H), 4.86 (t, $J = 5.4$ Hz, 1H), 1.27 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR δ 186.6 (−), 108.4 (−), 86.9 (−), 70.9 (−), 18.9 (−).

Dichlorobis[(2,3,4-η)-1-oxo-3-hexen-2-yl]dipalladium (5e). A slurry of PdCl$_2$(MeCN)$_2$ (262 mg, 1.01 mmol) in benzene (8 mL) was reacted with 1-(trimethylsilyloxy)-1,3-hexadiene[23b] (183 mg, 1.07 mmol) dissolved in benzene (2 mL) as described above (2 h). Hexanes (10 mL) were added at 0 °C to precipitate the product. After a few hours, the precipitate was filtered off and dried using a high-vacuum pump to afford **5e** (194 mg, 0.81 mmol, 80%) as a yellow solid. Spectral data were obtained from a 89:11 mixture of *syn*- and *anti*-**5e**. Mp 68−70 °C (decomp); IR (neat) 1693 cm^{-1}. *syn*-**5e**: ^{1}H NMR δ 9.62 (d, $J = 5.4$ Hz, 1H), 5.75 (t, $J = 11.2$ Hz, 1H), 4.37 (td, J = 11.7, 5.8 Hz, 1H), 3.67 (dd, $J = 10.5$, 5.3 Hz, 1H), 1.72 (apparent quintet, $J = 7.0$ Hz, 2H), 1.14 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR δ 195.2 (−), 107.2 (−), 92.9 (−), 68.6 (−), 68.6 (−), 25.4 (+), 12.4 (−). *anti*-**5e**: ^{1}H NMR δ 8.99 (d, $J = 5.9$ Hz, 1H), 5.46 (dd, $J = 12.3$, 6.9 Hz, 1H), 4.92 (td, $J = 11.7$, 6.5 Hz, 1H), 4.81 (d, $J = 5.3$ Hz, 1H); ^{13}C NMR δ 186.7 (−), 105.8 (−), 92.8 (−), 70.6 (−), 25.9 (+), 12.3 (−).

Dichlorobis[(2,3,4-η)-2-methyl-1-oxo-3-penten-2-yl]dipalladium (5f). A slurry of PdCl$_2$(MeCN)$_2$ (260 mg, 1.00 mmol) in benzene (8 mL) was reacted with 2-methyl-1-(trimethylsilyloxy)-1,3-pentadiene[30] (183 mg, 1.07 mmol) dissolved in benzene (2 mL) as described above (1 h). Hexanes (10 mL) were added at 0 °C to precipitate the product. After a few hours, the precipitate was filtered off and dried using a high-vacuum pump to afford **5c** (208 mg, 0.87 mmol, 87%) as a yellow solid. Spectral data were obtained from a 29:71 mixture of *syn*- and *anti*-**5f**. Mp 120−123 °C (decomp); IR (neat) 1673 cm^{-1}. *anti*-**5f**: ^{1}H NMR δ 8.77 (s, 1H), 6.10 (d, J = 12.9 Hz, 1H), 5.24 (m partially overlapped, $J = 12.6$, 6.1 Hz, 1H), 1.50 (d, $J = 6.3$ Hz, 3H), 1.48 (s, 3H); ^{13}C NMR δ 184.9 (−), 112.8 (−), 85.2 (+), 80.2 (−), 18.7 (−), 17.1 (−). *syn*-**5f**: ^{1}H NMR δ 9.28 (s, 1H), 6.03 (d, $J = 12.9$ Hz, 1H), 5.20 (m partially overlapped, $J = 12.8$, 6.3 Hz, 1H), 1.60 (d, $J = 6.3$ Hz, 3H), 1.13 (s, 3H); ^{13}C NMR δ 195.0 (−), 110.7 (−), 84.8 (−), 81.8 (+), 18.6 (−), 13.6 (−).

(*E*)-4-Acetoxy-2-butenal (7a).[26] Under a positive flow of argon, Pd(OAc)$_2$ (229 mg, 1.02 mmol) was added to a slurry of 1-(trimethylsilyloxy)-1,3-butadiene (**4a**) (200 μL, 1.14 mmol) and sodium acetate (84 mg, 1.03 mmol) in MeCN (10 mL). The reaction was stirred at ambient temperature for 2 h. The black slurry was diluted with ether (10 mL) and water (10 mL), and the phases were separated. The aqueous layer was extracted with ether (2 × 10 mL), and the combined organic phases were washed with Na$_2$CO$_3$ (10% aq, 10 mL). The combined organic phases were dried (MgSO$_4$) and filtered, and the solvent was removed. The crude product was purified by chromatography (pentane−ether, 7:3) to give **(*E*)-7a** (127 mg, 0.97 mmol, 97%) as a colorless oil. IR (neat) 1745, 1693 cm^{-1}. ^{1}H NMR δ 9.56 (d, $J = 7.7$ Hz, 1H), 6.78 (td, $J = 15.8$, 4.3 Hz, 1H), 6.25 (tdd, $J = 15.8$, 7.9, 1.9 Hz, 1H), 4.83 (dd, $J = 4.2$, 1.8 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR δ 192.7 (−), 170.1 (+), 149.5 (−), 132.0 (−), 62.3 (+), 20.6 (−).

Reaction of Pd(OAc)$_2$ (224 mg, 1.00 mmol) with **4a** (200 μL, 1.14 mmol) in MeCN (10 mL) as described above (2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-7a** (65 mg, 0.51 mmol, 51%).

Under a positive flow of argon, Pd(OAc)$_2$ (226 mg, 1.01 mmol) was added to a slurry of 1-(*tert*-butyldimethylsilyloxy)-1,3-butadiene (**15**) (196 mg, 1.06 mmol) and sodium acetate (84 mg, 1.03 mmol) in MeCN (10 mL). The reaction was stirred at ambient temperature for 2 h. Similar workup to that described above, gave after chromatography (pentane−ether, 7:3), a 92:8 mixture of **(*E*)**- and **(*Z*)-7a** (66 mg, 0.51 mmol, 51%) as a colorless oil. **(*Z*)-7a**: ^{1}H NMR δ 10.03 (d, J = 6.3 Hz, 1H), 6.53 (td, $J = 11.5$, 6.1 Hz, 1H), 6.12 (tdd, $J =$ 11.3, 6.1, 1.8 Hz, 1H), 5.10 (dd, $J = 6.0$ and 1.8 Hz, 2H), 2.11 (s, 3H).

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Under a positive flow of argon, sodium acetate (208 mg, 2.54 mmol) was added to a solution of complex **5a** (268 mg, 1.27 mmol) in MeCN (14 mL). The reaction mixture was stirred at 50 °C for 16 h. Similar workup to that described above gave, after chromatography (pentane−ether, 7:3), a 85:15 mixture of **(*E*)-** and **(*Z*)-7a** (65 mg, 0.51 mmol, 40%) as a colorless oil.

(*E*)-4-Benzoyloxy-2-butenal (9a)[31] **and (*E*)-4-Acetoxy-2-butenal (7a).** Reaction of $Pd(OAc)_2$ (225 mg, 1.00 mmol), **4a** (200 μL, 1.14 mmol), and sodium benzoate (576 mg, 4.00 mmol) in MeCN (10 mL) as described above (2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-9a** (123 mg, 0.64 mmol, 64%) followed by **(*E*)-7a** (10 mg, 0.08 mmol, 8%), both as colorless oils. IR (neat) 1723, 1692 cm^{-1}. ^{1}H NMR δ 9.59 (d, J = 7.7 Hz, 1H), 8.07 (dd, J = 7.1, 1.6 Hz, 2H), 7.57 (dt, J = 7.3, 2.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.92 (td, J = 15.8, 4.1 Hz, 1H), 6.37 (tdd, J = 15.8, 7.9, 1.8 Hz, 1H), 5.08 (dd, J = 4.1, 2.0 Hz, 2H); ^{13}C NMR δ 192.6 (−), 165.6 (+), 149.5 (−), 133.3 (−), 131.9 (−), 129.5 (−), 129.1 (+), 128.4 (−), 62.6 (+).

Reaction of $Pd(OAc)_2$ (225 mg, 1.00 mmol), **4a** (200 μL, 1.14 mmol), and sodium benzoate (146 mg, 1.02 mmol) in MeCN (10 mL) as described above (1 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-9a** (39 mg, 0.20 mmol, 20%) followed by **(*E*)-7a** (80 mg, 0.62 mmol, 62%).

Reaction of palladium dibenzoate[32] (350 mg, 1.00 mmol), **4a** (200 μL, 1.14 mmol), and NaOAc (330 mg, 4.02 mmol) in MeCN (10 mL) as described above (2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-9a** (104 mg, 0.55 mmol, 55%) followed by **(*E*)-7a** (13 mg, 0.10 mmol, 10%).

(*E*)-4-Propionyloxy-2-butenal (10a)[33] **and (*E*)-4-Acetoxy-2-butenal (7a).** Reaction of **4a** (200 μL, 1.14 mmol), $Pd(OAc)_2$ (225 mg, 1.00 mmol), and sodium propionate (385 mg, 4.00 mmol) in MeCN (10 mL) as described above (ambient temperature, 20 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-10a** (23 mg, 0.16 mmol, 16%) followed by **(*E*)-7a** (20 mg, 0.15 mmol, 15%), both as colorless oils. **(*E*)-10a**: IR (neat) 1740, 1685 cm^{-1}; ^{1}H NMR δ 9.59 (d, J = 7.7 Hz, 1H), 6.83 (td, J = 15.8, 4.3 Hz, 1H), 6.29 (tdd, J = 15.8, 7.7, 1.8 Hz, 1H), 4.86 (dd, J = 4.1, 1.5 Hz, 2H), 2.42 (q, J = 7.5 Hz, 2H), 1.18 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 192.8 (−), 173.6 (+), 149.7 (−), 132.1 (−), 62.2 (+), 27.3 (+), 9.0 (−).

4-Acetoxy-2-methyl-2-butenal (7b).[17,34] Reaction of $Pd(OAc)_2$ (230 mg, 1.02 mmol), 2-methyl-1-(trimethylsiloxy)-1,3-butadiene (**4b**) (176 mg, 1.12 mmol), and sodium acetate (82 mg, 1.00 mmol) in MeCN (10 mL) as described above (3 h, 40 °C) gave, after purification by chromatography (pentane−ether, 7:3), **7b** (90 mg, 0.63 mmol, 62%) as a colorless oil. Spectral data were obtained from a 90:10 *E*/*Z*-mixture of isomers. IR (neat) 1739, 1682 cm^{-1}. **(*E*)-7b**: ^{1}H NMR δ 9.40 (s, 1H), 6.46 (t, J = 5.9 Hz, 1H), 4.86 (d, J = 5.9 Hz, 1H), 2.07 (s, 3H), 1.75 (s, 3H); ^{13}C NMR δ 193.9 (−), 170.5 (+), 145.6 (−), 140.2 (+), 60.7 (+), 20.6 (−), 9.3 (−). **(*Z*)-7b**: ^{1}H NMR δ 10.08 (s, 1H), 5.02 (d, J = 6.9 Hz, 1H), 2.05 (s, 3H), 1.80 (s, 3H), resonance for OCH_2 obscured by OCH_2 for the major isomer; ^{13}C NMR δ 190.5 (−), 170.4 (+), 139.9 (−), 138.2 (+), 58.7 (+), 20.6 (−), 16.2 (−).

Reaction of $Pd(OAc)_2$ (225 mg, 1.00 mmol) with **4b** (169 mg, 1.08 mmol) in MeCN (10 mL) as described above (40 °C, 2 h) gave, after purification by chromatography (pentane−ether, 7:3), a 76:24 mixture of **(*E*)-7b** (63 mg, 0.44 mmol, 44%) followed by **(*E*)-7a** (80 mg, 0.62 mmol, 62%).

Under a positive flow of argon, sodium acetate (208 mg, 2.54 mmol) was added to a solution of complex **5b** (122 mg, 0.54 mmol) in MeCN (14 mL). The reaction mixture was stirred at 50 °C for 2 h. Similar workup to that described above gave, after chromatography (pentane−ether, 7:3), a 62:38 mixture of **(*E*)-** and **(*Z*)-7b** (10 mg, 0.067 mmol, 12%) as a colorless oil.

4-Benzoyloxy-2-methyl-2-butenal (9b).[35] Reaction of $Pd(OAc)_2$ (224 mg, 1.00 mmol), **4b** (171 mg, 1.10 mmol), and sodium benzoate (577 mg, 4.00 mmol) in MeCN (10 mL) as described above (2 h, 40 °C) gave, after purification by chromatography (pentane−ether, 7:3), **9b** (127 mg, 0.62 mmol, 62%) as a colorless oil. Spectral data were obtained from a 70:30 *E*:*Z*-mixture of **9b**. IR (neat) 1721, 1691 cm^{-1}. ^{13}C NMR δ 194.1 (−), 190.7 (−), 166.2 (+), 166.2 (+), 145.8 (−), 140.7 (+), 140.1 (−), 138.6 (+), 134.6, 133.4 (−), 133.4 (−), 130.6, 129.8 (+), 129.6, 129.5, 128.9 (−), 61.4 (+), 59.4 (+), 16.5 (−), 9.6 (−). **(*E*)-9b**: ^{1}H NMR δ 9.47 (s, 1H), 8.09−8.01 (m, 2H), 7.61−7.52 (m, 1H), 7.49−7.39 (m, 2H), 6.65−6.56 (m, 2H), 5.13 (dd, J = 5.7, 1.0 Hz, 1H), 1.84 (d, J = 1.0 Hz, 3H). Partial spectral data for **(*Z*)-9b**: ^{1}H NMR δ 10.20 (s, 1H), 5.29 (dd, J = 7.1, 1.2 Hz, 1H), 1.86 (d, J = 1.4 Hz, 3H).

4-Acetoxy-3-methyl-2-butenal (7c).[34c] Reaction of $Pd(OAc)_2$ (225 mg, 1.00 mmol), 3-methyl-1-trimethylsiloxy-1,3-butadiene (**4c**) (184 mg, 1.18 mmol), and sodium acetate (83 mg, 1.02 mmol) in MeCN (10 mL) as described above (3 h, 40 °C) gave, after purification by chromatography (pentane−ether, 7:3), **(*Z*)-7c** (42 mg, 0.30 mmol, 30%) followed by **(*E*)-7c** (29 mg, 0.20 mmol, 20%), both as colorless oils. **(*Z*)-7c**: IR (neat) 1742, 1679 cm^{-1}; ^{1}H NMR δ 10.17 (d, J = 7.2 Hz, 1H), 6.00 (d, J = 7.4 Hz, 1H), 5.04 (s, 2H), 2.12 (s, 3H), 2.02 (s, 3H); ^{13}C NMR δ 189.9 (−), 170.4 (+), 155.1 (+), 129.6 (−), 62.2 (+), 22.1 (−), 20.6 (−).

(*E*)-7c: IR (neat) 1743, 1671 cm^{-1}; ^{1}H NMR δ 10.05 (d, J = 7.9 Hz, 1H), 6.03 (d, J = 7.9 Hz, 1H), 4.64 (s, 2H), 2.16 (s, 3H), 2.14 (s, 3H); ^{13}C NMR δ 190.6 (−), 170.2 (+), 155.5 (+), 125.4 (−), 66.4 (+), 20.6 (−), 14.5 (−).

Reaction of $Pd(OAc)_2$ (225 mg, 1.00 mmol) with **4c** (173 mg, 1.11 mmol) in MeCN (10 mL) as described above (40 °C, 3 h) gave, after purification by chromatography (pentane−ether, 7:3), a 38:62 mixture of **7c** (57 mg, 0.40 mmol, 40%).

4-Benzoyloxy-3-methyl-2-butenal (9c).[18] Reaction of $Pd(OAc)_2$ (224 mg, 1.00 mmol), **4c** (179 mg, 1.14 mmol), and sodium benzoate (573 mg, 3.98 mmol) in MeCN (10 mL) as described above (2 h, 40 °C) gave, after purification by chromatography (pentane−ether, 7:3), **(*Z*)-9c** (58 mg, 0.28 mmol, 28%) followed by a 90:10 *E*:*Z*-mixture of **9c** (29 mg, 0.14 mmol, 14%), both as colorless oils. Spectral data for **(*Z*)-9c**: IR (neat) 1722, 1679 cm^{-1}; ^{1}H NMR δ 10.09 (d, J = 7.1 Hz, 1H), 8.04 (d, J = 7.9 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 6.05 (dd, J = 7.1, 1.2 Hz, 1H), 5.31 (s, 2H), 2.09 (d, J = 0.8 Hz, 3H); ^{13}C NMR δ 189.9 (−), 166.0 (+), 155.2 (+), 133.4 (−), 129.7 (−), 129.6 (−), 129.3 (+), 128.5 (−), 62.7 (+), 22.3 (−).

Spectral data for **(*E*)-9c** from a 90:10 *E*:*Z*-mixture: IR (neat) 1724, 1677 cm^{-1}; ^{1}H NMR δ 10.08 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.9 Hz, 2H), 6.15 (dd, J = 7.7, 1.2 Hz, 1H), 4.90 (s, 2H), 2.24 (s, 3H); ^{13}C NMR δ 190.6 (−), 165.6 (+), 155.5 (+), 133.5 (−), 129.7 (−), 129.2 (+), 128.5 (−), 125.5 (−), 66.8 (+), 14.5 (−).

(*E*)-4-Acetoxy-2-pentenal (7d)[36] **and (*E*)-4-Hydroxy-2-pentenal (11d).**[37] Reaction of 1-(trimethylsilyloxy)-1,3-pentadiene (181 mg, 1.15 mmol) with $Pd(OAc)_2$ (226 mg, 1.00 mmol) and NaOAc (82 mg, 4.00 mmol) in MeCN (10 mL) as described above (ambient temperature, 2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-7d** (91

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mg, 0.64 mmol, 64%) followed by **(*E*)-11d** (3 mg, 3 mmol, 3%), both as colorless oils. Spectral data for **(*E*)-7d**: IR (neat) 1740, 1694 cm^{-1}; ^{1}H NMR δ 9.54 (d, J = 7.7 Hz, 1H), 6.73 (dd, J = 15.8, 4.6 Hz, 1H), 6.19 (ddd, J = 15.8, 7.7, 1.6 Hz, 1H), 5.57 (ddq, J = 6.4, 4.4, 1.5, 1H), 2.08 (s, 3H), 1.39 (d, J = 6.7 Hz, 3H); ^{13}C NMR δ 193.0 (−), 169.8 (+), 154.6 (−), 130.9 (−), 68.6 (−), 20.9 (−), 19.3 (−). Partial spectral data for **(*E*)-11d**: ^{1}H NMR δ 9.57 (d, J = 7.7 Hz, 1H), 6.82 (dd, J = 15.8, 4.6 Hz, 1H), 6.29 (ddd, J = 15.6, 7.7, 1.6 Hz, 1H), 4.60 (m, 1H), 2.3 (br s, 1H), 1.36 (d, J = 7.5 Hz, 3H).

Reaction of Pd(OAc)$_2$ (224 mg, 1.00 mmol) with **4d** (165 mg, 1.06 mmol) in MeCN (10 mL) as described above (40 °C, 2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-7d** (38 mg, 0.27 mmol, 27%) followed by **(*E*)-11d** (7 mg, 0.06 mmol, 6%).

(*E*)-4-Benzoyloxy-2-pentenal (9d).[37a] Reaction of **4d** (168 mg, 1.08 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and sodium benzoate (575 mg, 3.99 mmol) in MeCN (10 mL) as described above (ambient temperature, 2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-9d** (72 mg, 0.35 mmol, 35%) as a colorless oil. IR (neat) 1722, 1694 cm^{-1}; ^{1}H NMR δ 9.58 (d, J = 7.7 Hz, 1H), 8.05 (dd, J = 7.1, 1.6 Hz, 2H), 7.58 (dt, J = 7.1, 1.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 6.87 (dd, J = 15.8, 4.5 Hz, 1H), 6.30 (ddd, J = 15.8, 7.7, 1.6 Hz, 1H), 5.84 (ddq, J = 6.4, 4.3, 1.4, 1H), 1.54 (d, J = 6.7 Hz, 3H); ^{13}C NMR δ 193.0 (−), 165.3 (+), 154.7 (−), 133.3 (−), 130.9 (−), 129.6 (−), 129.5 (+), 128.4 (−), 69.1 (−), 19.4 (−).

(*E*)-4-Acetoxy-2-pentenal (7d) and (*E*)-4,5-Diacetoxy-2-pentenal (12).[38] Reaction of 1-(trimethylsilyloxy)-1,3-pentadiene (178 mg, 1.14 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and NaOAc (84 mg, 1.02 mmol) in MeCN (10 mL) as described above (40 °C, 20 h) gave, after purification by chromatography (pentane−ether, 7:3), **7d** (30 mg, 0.21 mmol, 21%) followed by **12** (9 mg, 0.04 mmol, 4%), both as colorless oils.

(*E*)-4-Acetoxy-2-hexenal (7e)[37b] **and (*E*)-4-Hydroxy-2-hexenal (11e).**[37b] Reaction of 1-(trimethylsilyloxy)-1,3-hexadiene (**4e**) (197 mg, 1.15 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and NaOAc (83 mg, 1.01 mmol) in MeCN (10 mL) as described above (40 °C, 2 h) gave, after purification by chromatography (pentane−ether, 7:3), **(*E*)-7e** (38 mg, 0.24 mmol, 24%) followed by **(*E*)-11e** (4 mg, 0.03 mmol, 3%), both as colorless oils.[39]

Similar reaction of **4e** (180 mg, 1.06 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) in MeCN (10 mL) as described above (40 °C, 1 h) gave, after purification by chromatography (pentane−ether, 9:1 followed by pentane−ether, 7:3), **(*E*)-7e** (28 mg, 0.18 mmol, 18%) followed by **(*E*)-11e** (46 mg, 0.40 mmol, 40%), both as colorless oils. A trace amount of a minor isomer tentatively assigned as **(*Z*)-7e** was observed in the crude ^{1}H NMR spectra (δ 10.13 (d, J = 7.5 Hz)).

Spectral data for **(*E*)-7e**: IR (neat) 1741, 1694 cm^{-1}; ^{1}H NMR δ 9.53 (d, J = 7.7 Hz, 1H), 6.70 (dd, J = 15.8, 4.8 Hz, 1H), 6.18 (ddd, J = 15.8, 7.7, 1.4 Hz, 1H), 5.44 (q, J = 6.3 Hz, 1H), 2.08 (s, 3H), 1.73 (dquint, J = 7.7, 2.0 Hz, 2H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 193.0 (−), 170.0 (+), 153.7 (−), 131.6 (−), 73.3 (−), 26.7 (+), 20.8 (−), 9.2 (−). Partial spectral data for **(*E*)-11e**: ^{1}H NMR δ 9.60 (d, J = 7.9 Hz, 1H), 6.82 (dd, J = 15.6, 4.7 Hz, 1H), 6.32 (ddd, J = 15.6, 7.9, 1.6 Hz, 1H), 4.39 (q, J = 5.1 Hz, 1H), 1.69 (quint, J = 7.5 Hz, 2H), 1.25 (s, 1H), 1.00 (t, J = 7.5 Hz, 3H).

(*E*)-4-Benzoyloxy-2-hexenal (9e).[37a] Reaction of **4e** (174 mg, 1.02 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and sodium benzoate (576 mg, 4.00 mmol) in MeCN (10 mL) as described above (ambient temperature, 0.5 h) gave, after purification by chromatography (pentane−ether, 9:1), a 71:24:5 mixture of *E,E*:*E,Z*:*Z,E*-2,4-hexadienal (6 mg, 0.06 mmol, 6%) followed by **(*E*)-9e** (54 mg, 0.25 mmol, 25%) as a colorless oil.[39]

Reaction of Pd(OAc)$_2$ (225 mg, 1.00 mmol), **4e** (200 μL, 1.14 mmol), and sodium benzoate (146 mg, 1.02 mmol) in MeCN (10 mL) in the presence of Na$_2$CO$_3$ (425 mg, 4.01 mmol) as described above (ambient temperature, 1 h) gave, after purification by chromatography (pentane−ether, 7:3), a 74:26 mixture of *E,E*:*E,Z*-2,4-hexadienal (30 mg, 0.31 mmol, 31%) followed by **(*E*)-9e** (37 mg, 0.17 mmol, 17%). IR (neat) 1722, 1693 cm^{-1}; ^{1}H NMR δ 9.59 (d, J = 7.7 Hz, 1H), 8.08 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 6.85 (dd, J = 15.8, 4.5 Hz, 1H), 6.30 (ddd, J = 15.8, 7.7, 1.4 Hz, 1H), 5.73 (q, J = 6.1 Hz, 1 H), 1.91 (quint, J = 7.1 Hz, 2 H), 1.05 (t, J = 7.5 Hz, 3H).

(*E*)-4-Acetoxy-2-methyl-2-pentenal (7f) and (*E*)-4-Hydroxy-2-methyl-2-pentenal (11f). Reaction of 2-methyl-1-(trimethylsilyloxy)-1,3-pentadiene (189 mg, 1.11 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and NaOAc (84 mg, 1.01 mmol) in MeCN (10 mL) as described above (45 °C, 20 h) gave, after purification by chromatography (pentane−ether, 7:3), **7f** (6 mg, 0.04 mmol, 4%) followed by **10f** (29 mg, 0.26 mmol, 26%), both as colorless oils.[40] Spectral data for **(*E*)-7f**: IR (neat) 1731, 1682 cm^{-1}; ^{1}H NMR δ 9.43 (s, 1H), 6.34 (qd, J = 8.1, 1.4 Hz, 1H), 5.73 (quint, J = 7.9 Hz, 1H), 2.07 (s, 3H), 1.81 (d, J = 1.2 Hz, 3H), 1.38 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 194.6 (−), 170.2 (+), 150.6 (−), 139.1 (+), 67.4 (−), 21.1 (−), 19.4 (−), 9.5 (−).

Spectral data for **(*E*)-11f**: IR (neat) 3418, 1686 cm^{-1}; ^{1}H NMR δ 9.41 (s, 1H), 6.42 (qd, J = 6.7, 1.2 Hz, 1H), 4.85 (quint, J = 6.4 Hz, 1H), 2.07 (br s, 1 H), 1.76 (d, J = 1.0 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 195.2 (−), 155.5 (−), 137.8 (+), 64.8 (−), 22.4 (−), 9.3 (−).

4-Benzoyloxy-2-methyl-2-pentenal (9f). Reaction of **4f** (184 mg, 1.08 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and sodium benzoate (578 mg, 4.00 mmol) in MeCN (10 mL) as described above (ambient temperature, 0.5 h) gave, after purification by chromatography (pentane−ether, 9:1), **9f** (49 mg, 0.22 mmol, 22%) as a colorless oil.[41] Spectral data were obtained from a 97:3 mixture of ***(E)*-** and ***(Z)*-9f**. IR (neat) 1715, 1693 cm^{-1}. ^{1}H NMR δ 10.33 (s, minor isomer), 9.45 (s, 1H), 8.05 (dd, J = 8.3, 1.2 Hz, 2H), 7.58 (tt, J = 6.3, 1.2 Hz, 1H), 7.45 (dt, J = 6.3, 1.4 Hz, 2H), 6.47 (qd, J = 8.1, 1.4 Hz, 1H), 5.99 (quint, J = 6.5 Hz, 1H), 1.89 (d, J = 1.4 Hz, 3H), 1.54 (d, J = 6.5 Hz, 3H); ^{13}C NMR δ 194.6 (−), 170.2 (+), 150.6 (−), 139.1 (+), 67.4 (−), 21.1 (−), 19.4 (−), 9.5 (−). Anal. Calcd for C$_{13}$H$_{14}$O$_3$: C, 71.54; H, 6.47. Found: C, 71.43; H, 6.49.

2,6,6-Trimethyl-1-cyclohexen-1-yl Acetaldehyde (13)[42] **and 2,6,6-Trimethyl-2-cyclohexen-1-ylidene Acetaldehyde (14).**[43] Reaction of **4g** (267 mg, 1.12 mmol) with Pd(OAc)$_2$ (225 mg, 1.00 mmol) and NaOAc (83 mg, 1.01 mmol) in MeCN (10 mL) as described above (40 °C, 5 h) gave, in order of elution after purification by chromatography (pentane−ether, 7:3), **13** (82 mg, 0.49 mmol, 49%) and **14** (30 mg, 0.19 mmol, 19%), both as colorless oils.

A similar reaction of **4g** (254 mg, 1.07 mmol) with Pd(OAc)$_2$ (224 mg, 1.00 mmol) and NaOAc (85 mg, 1.03 mmol) in MeCN (10 mL) as described above (reflux, 1 h) gave, in order of elution after purification by chromatography (pentane−ether, 9:1), **13** (30 mg, 0.18 mmol, 18%) and **14** (92 mg, 0.56 mmol, 56%), both as colorless oils. Compound **14** was obtained as a 1:1 mixture of *Z*:*E* isomers in both cases. Spectral data for **14**: IR (neat)

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(38) (a) Tam, S. Y.-K.; Fraser-Reid, B. *Carbohydr. Res.* **1975**, *45*, 29. (b) Esterbauer, H.; Sanders, E. B.; Schubert, J. *Carbohydr. Res.* **1975**, *44*, 126.

(39) A substantial amount of 2,4-hexadienal was observed by ^{1}H NMR of the crude reaction mixture. This compound was lost during purification.

(40) A minor amount (~5%) of an additional product was observed by ^{1}H NMR. The minor product could not be removed, and we were unable to obtain a correct elemental analysis.

(41) A minor amount (~3%) of an additional product, probably the *Z* isomer, was observed by ^{1}H NMR.

(42) Aldrich Library of Spectra, 1993: ^{1}H and ^{13}C NMR spectra **1**,746A, FT-IR spectra **3**,567C.

(43) F. Hoffmann-LaRoche & Co., Akt.-Ges. Brit. 764,122; *Chem. Abstr.* **1957**, *51*, P14798C.

1733, 1663, 1624 cm^{-1}; ^{1}H NMR δ 10.44 (d, $J = 8.1$ Hz, 1H), 10.21 (d, $J = 7.9$ Hz, 1H), 6.14 (t with further fine splitting, $J = 4.5$ Hz, 1H), 6.00 (m, 1H), 5.93 (d, $J = 9.5$ Hz, 1H), 5.90 (d, $J = 8.5$ Hz, 1H), 2.28−2.14 (m, 4H), 2,13 (s with further fine splittings, 3H), 1.83 (s with further fine splittings, 3H), 1.57−1.52 (m, 4H), 1.39 (s, 6H), 1.09 (s, 6H); ^{13}C NMR δ 193.7 (−), 192.9 (−), 165.4 (+), 163.5 (+), 136.5 (−), 136.0 (−), 133.2 (+), 130.7 (+), 124.5 (−), 123.7 (−), 39.4 (+), 36.6 (+), 36.1 (+), 35.7 (+), 30.8 (−, 2C), 27.4 (-, 2C), 27.0 (−), 23.7 (+), 23.0 (+), 21.3 (−).

(*E*,*E*)-6-Acetoxy-2,4-hexadienal (7h).[26] Reaction of 1-(*tert*-butyl-dimethylsilyloxy)-1,3,5-hexadiene (238 mg, 1.13 mmol) with Pd(OAc)$_2$ (226 mg, 1.01 mmol) and NaOAc (83 mg, 1.01 mmol) in MeCN (10 mL) as described above (40 °C, 2.5 h) gave, after purification by chromatography (pentane−ether, 7:3), **7h** (41 mg, 0.27 mmol, 26%) as a colorless oil. Spectral data for **7h**: IR (neat) 1737, 1682 cm^{-1}; ^{1}H NMR δ 9.58 (d, $J = 7.9$ Hz, 1H), 7.10 (dd, $J = 15.2$, 10.8 Hz, 1H), 6.27 (dt, $J = 15.3$, 5.5 Hz, 1H), 6.19 (dd, $J = 15.2$, 7.9 Hz, 1H), 4.71 (d, $J = 5.5$ Hz, 2H), 2.12 (s, 3H); ^{13}C NMR δ 193.6 (−), 170.5 (+), 150.4 (−), 137.4 (−), 132.4 (−), 130.1 (−), 63.5 (+), 20.8 (−).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra (14 pages). Ordering information is given on any current masthead page.

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