Novel Synthesis of Phenol Derivatives by Palladium-Catalyzed Cyclocarbonylation of 2,4-Pentadienyl Acetates

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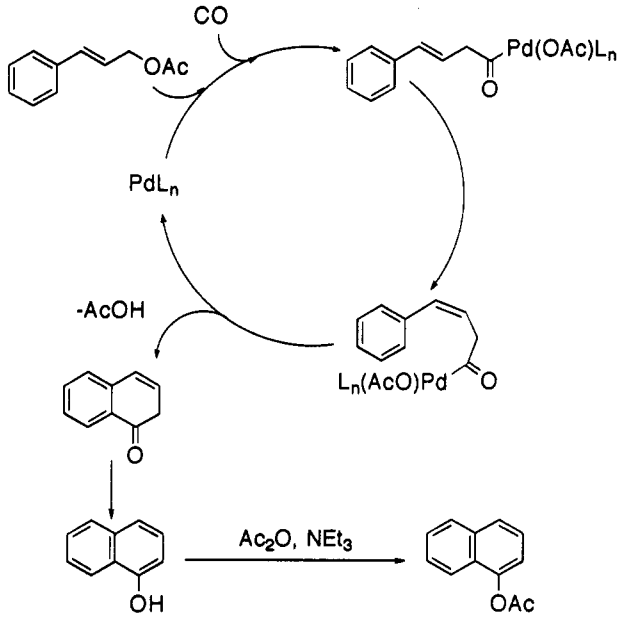
Phenyl acetates were selectively obtained in good yields by cyclocarbonylation of 2,4-pentadienyl acetates in the presence of NEt_3, Ac_2O, and a catalytic amount of palladium complexes such as $PdCl_2(PPh_3)_2$ at 120–140 °C under 50 atm of CO. No five-membered ring products were observed. A platinum complex $PtCl_2(PPh_3)_2$ was also effective as a catalyst. The reaction of 5-phenyl-2,4-pentadienyl bromide with $M(CO)(PPh_3)_3$ (M = Pd or Pt) under CO gave the corresponding 6-phenyl-3,5-hexadienoyl complexes in a high yield, which in turn afforded 2-acetoxybiphenyl in 41–51% yield on heating to 160 °C under 50 atm of CO in the presence of NEt_3 and Ac_2O. Similar 3,5-hexadienoyl complexes are proposed to be intermediates in the catalytic cyclocarbonylation of 2,4-pentadienyl acetates. On the other hand, $PdCl_2(PPh_3)_2$-catalyzed carbonylation of *o*-(bromomethyl)(1-alkenyl)-benzenes in the presence of NEt_3 and Ac_2O gave 2-naphthyl acetates in moderate yields, while the reaction in the absence of Ac_2O gave five-membered ring products such as 2-indanones or a tricyclic lactone by incorporation of one or two CO molecules, respectively.

Introduction

The synthesis of phenols has long been among the major subjects in organic synthesis because of their importance in industrial chemistry and wide occurrence in nature. Recently, much effort has been paid for the application of annulation methods for the synthesis of substituted phenols,[1] in which the aromatic system is assembled from acyclic precursors in a single step to give the desired substituted phenol derivatives. One major advantage of the annulation methodology is that it provides regiochemically unambiguous access to multisubstituted phenols which cannot be obtained by conventional aromatic substitution reactions.

In the course of our continuous study on catalytic carbonylation reactions, we have previously developed a novel catalytic cyclocarbonylation of 3-arylallyl acetates as a synthetic route to fused aromatic compounds having a naphthalene,[2] phenanthrene,[3] benzofuran,[4] benzothiophene,[4] or indole[4] skeleton. These reactions are supposed to proceed via a 4-arylbutenoylpalladium complex (Scheme I).[2,5] Intramolecular acylation of the aryl group on the metal forms a new six-membered ring, which tautomerizes to give a fused aromatic system. The insight into the mechanism of the cyclocarbonylation of 3-arylallyl acetates

Scheme I



leads to a new idea that the carbonylation of 2,4-pentadienyl acetates may give phenol derivatives if the corresponding acylmetal intermediate undergoes cyclization forming a six-membered ring via the acylmetalation of the terminal C=C bond. Such a reaction seems quite interesting in that it provides a new potential and catalytic family of annulation methods for the synthesis of substituted phenol derivatives. On the ground of this prospect, we have investigated the cyclocarbonylation of 2,4-pentadienyl acetates in detail. A part of the study was briefly reported in a previous paper.[6]

Results and Discussion

Synthesis of Phenyl Acetates. We have previously revealed that addition of both Ac_2O and NEt_3 is essential

• Abstract published in *Advance ACS Abstracts,* October 15, 1993.

(1) Recent examples: (a) Krysan, D. J.; Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 1412. (b) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093. (c) Perri, S. T.; Moore, H. W. *J. Am. Chem. Soc.* **1990**, *112*, 1897. (d) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 8617. (e) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (f) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc: Greenwich, CT, 1989; Vol. 1. (g) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

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(4) (a) Iwasaki, M.; Li, J.-P.; Kobayashi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Tetrahedron Lett.* **1989**, *30*, 95. (b) Iwasaki, M.; Li, J.-P.; Kobayashi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *J. Org. Chem.* **1991**, *56*, 1922.

(5) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *Chem. Lett.* **1988**, 377.

(6) Ishii, Y.; Gao, C.; Iwasaki, M.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1991**, 695.

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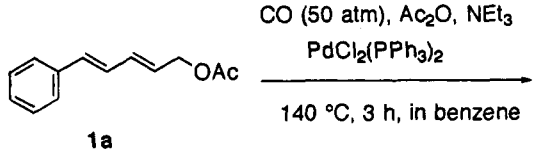
Table I. Effects of Catalysts on Cyclocarbonylation of 2,4-Pentadienyl Acetate[a]

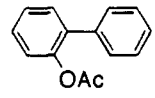
catalyst	conv,[b] %	yield of 2a,[c] %
$PdCl_2(PPh_3)_2$	100	74 (69)
$PdCl_2(PMe_2Ph)_2$	100	75
$Pd(PPh_3)_4$	100	76
$PdCl_2$(dpe)	9	1
$Pd(OAc)_2$	-	0
$NiBr_2(PPh_3)_2$	-	0
$PtCl_2(PPh_3)_2$	91	76
$Fe(CO)_5$	0.5	0
$Co_2(CO)_8$	10	0
$RuCl_2(PPh_3)_3$	44	26
$RhCl(PPh_3)_3$	12	0

[a] Reaction conditions: 2a 3 mmol, catalyst 0.09 mmol, Ac_2O 6 mmol, NEt_3 6.6 mmol, benzene 5 mL, CO 50 atm, 140 °C, 3 h. [b] Determined by GC. [c] GC yield based on the substrate charged. Isolated yield in parentheses.

to obtain fused aromatic products by the palladium-catalyzed cyclocarbonylation of 3-arylallyl acetates. On the basis of these results, we have first examined the effect of addition of Ac_2O and NEt_3 on the catalytic carbonylation of (2*E*,4*E*)-5-phenyl-2,4-pentadienyl acetate (**1a**). As expected, 2-acetoxybiphenyl (**2a**) was obtained in 74% yield by a reaction in the presence of both NEt_3 and Ac_2O, and a catalytic amount of $PdCl_2(PPh_3)_2$ (eq 1). No other



1a (1)

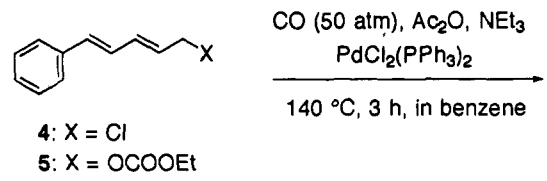


2a 74%

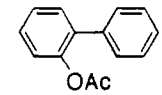
identifiable products including cyclopentenone derivatives were detected by GC analysis. By contrast, a reaction in the absence of Ac_2O gave **2a** in 11% and 2-biphenylol (**3**) in 16% yield (conv 100%), while a reaction in the absence of NEt_3 gave **2a** in 9% yield (based on the starting **1a**, conv 52%).

Effect of catalysts on the cyclocarbonylation of **1a** is summarized in Table I. Palladium and platinum phosphine complexes such as $PdCl_2(PPh_3)_2$, $PdCl_2(PMe_2Ph)_2$, and $PtCl_2(PPh_3)_2$ proved to be effective catalysts, and $RuCl_2(PPh_3)_3$ showed a low catalytic activity. Other group 8 metal compounds such as $Pd(OAc)_2$, $PdCl_2$(dpe) (dpe = $Ph_2PCH_2CH_2PPh_2$), $Co_2(CO)_8$, $NiBr_2(PPh_3)_2$, and $RhCl(PPh_3)_3$ were inactive. Reaction temperatures of 120–140 °C were required to obtain **2a** in good yields (71–74%). Thus, a reaction at 100 °C resulted in a lower yield of **2a** (45%, conv 75%). Use of other reaction solvents such as THF, DMF, MeCN, and Et_2O in place of benzene did not improve the yield of **2a** (55–72%).

Reactions of 5-phenyl-2,4-pentadienyl chloride (**4**) or ethyl carbonate (**5**) instead of acetate **1a** were also examined (eq 2). However, **2a** was obtained in much lower yields from **4** (33%) or from **5** (24%) than from **1a** under the same reaction conditions. Although allylic acetates have been claimed to be poor substrates for carbonylation reactions,[7] 2,4-pentadienyl acetates proved to be preferable as the substrates for the present cyclocarbonylation.



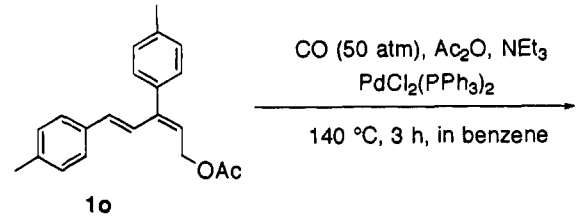
4: X = Cl
5: X = OCOOEt (2)



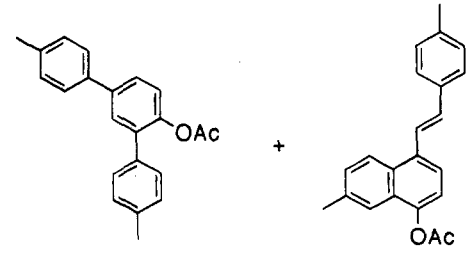
2a 33% from **4**
24% from **5**

A variety of 2,4-pentadienyl acetates **1** were converted to the corresponding phenyl acetates **2** by the cyclocarbonylation. The results are summarized in Table II. 5-Aryl-substituted 2,4-pentadienyl acetates were good substrates for this reaction, but aliphatic substrates also gave the corresponding phenyl esters in moderate yields. Substituents at 2- or 4-position of the substrates somewhat lowered the yields of **2**. Also in the reaction of (2*E*,4*E*,6*E*)-2,4,6-undecatrienyl acetate (**1n**), the six-membered ring formation exclusively occurred, and *o*-(1-hexenyl)phenyl acetate (**2n**) was obtained as the only isolable product. The *E*/*Z* ratio of **2n** obtained was 79/21, indicating the isomerization of the C=C double bonds during the catalytic reaction. It should be pointed out that the cyclocarbonylation is applicable to the synthesis of 2,3- and 3,5-disubstituted phenyl acetates, which are difficult to be prepared by conventional electrophilic substitution reactions of phenol. These results clearly indicates that the present cyclocarbonylation enjoys the effectiveness as a synthetic method for substituted phenols.

When (2*E*,4*E*)-3,5-di(*p*-tolyl)-2,4-pentadienyl acetate (**1o**) was carbonylated under similar reaction conditions, cyclization toward the tolyl group at the 3-position competed with the phenyl acetate formation, and naphthyl acetate **6** was obtained in 17% yield as well as the expected 2,4-di(*p*-tolyl)phenyl acetate (**2o**, 38%) (eq 3).



1o (3)



2o 38% **6** 17%

It is noteworthy that the olefinic double bond and the tolyl group exhibited comparable reactivity in the cyclocarbonylation in spite of the *E* configuration of the substrate,[2] and this may be a limitation of this reaction.

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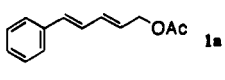
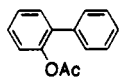
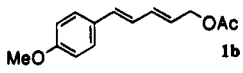
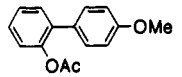
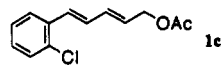
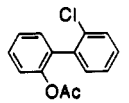
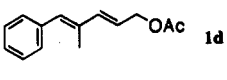
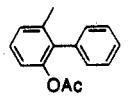
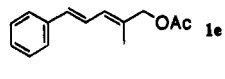
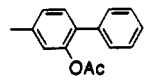
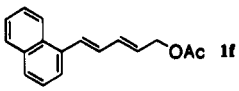
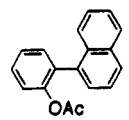
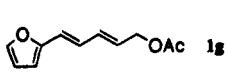
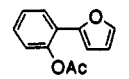
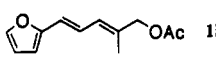
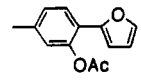
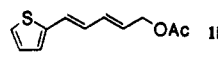
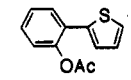
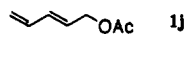
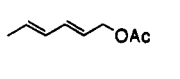
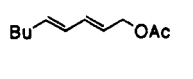
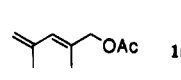
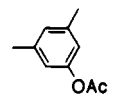
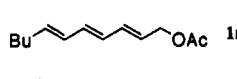
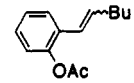
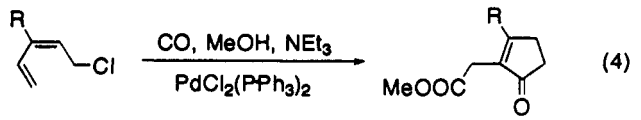
Table II. Cyclocarbonylation of Substituted 2,4-Pentadienyl Acetates[a]

substrate	product	isolated yield, %
 1a	 2a	69
 1b	 2b	73
 1c	 2c	84
 1d	 2d	57
 1e	 2e	46
 1f	 2f	79
 1g	 2g	57
 1h	 2h	24
 1i	 2i	53
 1j	 2j	54[b]
 1k	 2k	51[b]
 1l	 2l	48[b]
 1m	 2m	40
 1n	 2n	52[c]

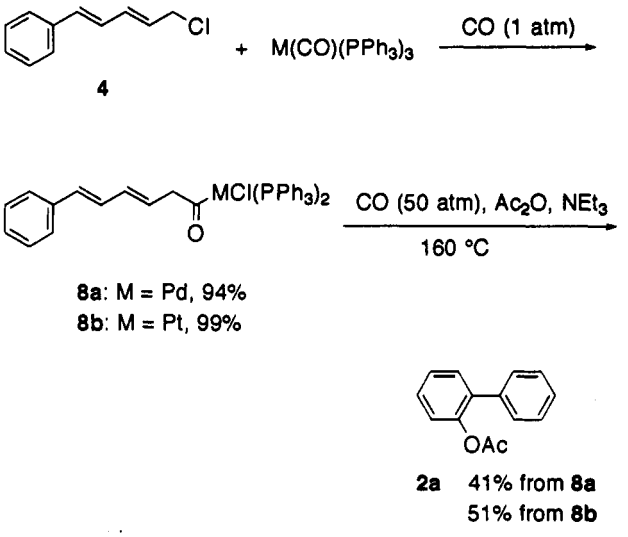
[a] Reaction conditions: substrate 3 mmol, $PdCl_2(PPh_3)_2$ 0.09 mmol, Ac_2O 6 mmol, NEt_3 6.6 mmol, benzene 5 mL, CO 50 atm, 140 °C, 3 h. [b] Benzene (2 mL) was used as a solvent. [c] E/Z = 79/21.

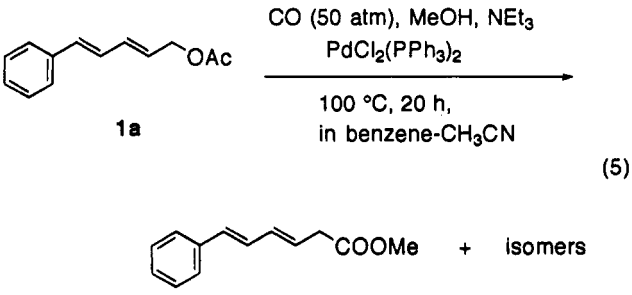
Previously Negishi reported that the cyclocarbonylation of *cis*-2,4-pentadienyl chlorides catalyzed by $PdCl_2(PPh_3)_2$ in the presence of MeOH and NEt_3 yields cyclopentenone derivatives (eq 4).[8] Quite interestingly, our cyclocarbonylation described here is in striking contrast to eq 4 in several aspects, although the catalytic systems are closely related to each other. Thus, in our reaction, only the six-membered products (phenyl acetates), but not the five-membered ones, were selectively obtained, while in eq 4 only the formation of five-membered products (cyclopentenones) was reported. Further, in our system substrates of the trans configuration smoothly undergo the cyclization, but in Negishi's system the cis configuration of the substrates was claimed to be essential for the cyclization. In fact, carbonylation of **1a** under Negishi's conditions did not give any cyclization product but resulted in the formation of methyl (3*E*,5*E*)-6-phenyl-3,5-hexadienoate (7, 60%) and its stereoisomers (13%) (eq 5). From a synthetic point of view, it is particularly advantageous that easily accessible trans substrates can be used in our cyclocarbonylation.



(4)

Scheme II



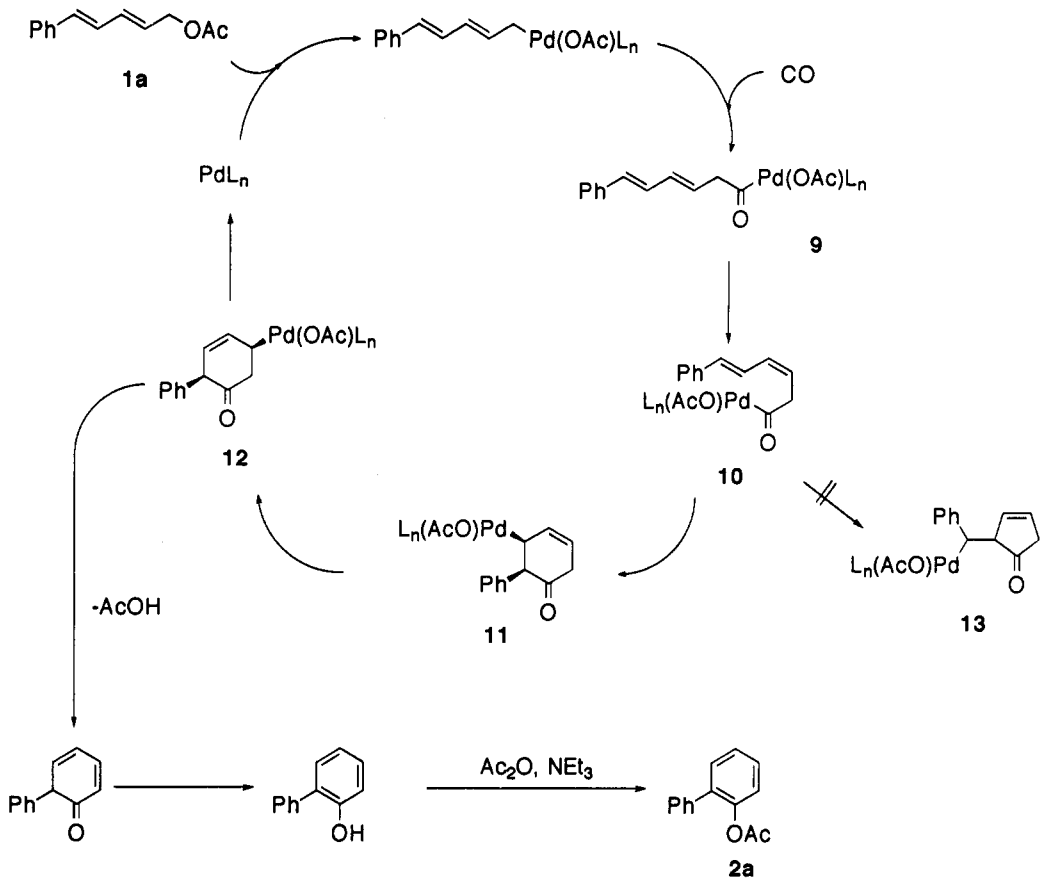


(5)

Reaction Mechanism. In order to shed light on the reaction mechanism of the cyclocarbonylation of 2,4-pentadienyl acetates **1**, stoichiometric model reactions were examined. Thus, the reaction of a palladium or platinum carbonyl complex $M(CO)(PPh_3)_3$ with **4** under CO (1 or 20 atm) in toluene at room temperature gave the corresponding 3,5-hexadienoyl complex ($PhCH{=}CHCH{=}CHCH_2CO$)$MCl(PPh_3)_2$ (**8**) in a nearly quantitative yield. The CO pressure did not affect the yield of **8** in these reactions. By contrast, we have previously found that the reaction of $Pd(CO)(PPh_3)_3$ with cinnamyl bromide under 20 atm of CO gives a similar acyl complex ($PhCH{=}CHCH_2CO$)$PdBr(PPh_3)_2$ while the reaction under 1 atm of CO results in the formation of π-allylpalladium complex Pd(η^3-C_3H_5)$Br(PPh_3)_2$.[5] Treatment of complex **8** with Ac_2O and NEt_3 under the catalytic reaction conditions (CO 50 atm, 160 °C, 1 h, in benzene) afforded **2a** in 41–51% yield (Scheme II). These results strongly indicates that 3,5-

(8) Negishi, E.; Wu, G.; Tour, J. M. *Tetrahedron Lett.* **1988**, *29*, 6745.

Scheme III



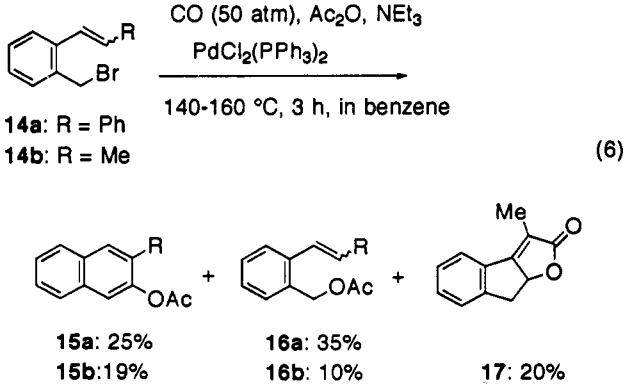
hexadienoyl complexes similar to 8 also behave as key intermediates in the catalytic reaction.

Scheme III depicts a plausible mechanism for the palladium-catalyzed cyclocarbonylation of **1a**. Oxidative addition of **1a** to a Pd(0) species followed by CO insertion forms a 3,5-hexadienoyl complex **9**. After trans–cis isomerization of the internal C=C double bond in **9** to give complex **10**, intramolecular acylpalladation in **10** affords complex **11**. A related acylmetalation mechanism is proposed in $Ni(CO)_4$-catalyzed synthesis of phenols from allylic chlorides, acetylene, and CO.[9,10] Isomerization of **11** to **12** via a π-allylpalladium complex and subsequent β-hydrogen elimination gives a cyclohexadienone,[11] which tautomerizes to the corresponding phenol and is finally acetylated by Ac_2O to yield **2a**.

In the presence of MeOH, acyl complex **9** is quickly trapped to yield ester **7** (eq 5). However, in the present cyclocarbonylation there is added no nucleophile which effectively reacts with complex **9**, and complex **10** with cis configuration can be formed by the isomerization of **9**. This is the reason why trans substrates can be used in the present cyclocarbonylation (eq 1) but not in eq 4. On the other hand, the fact that eq 1 gave only the six-membered ring product **2a** clearly indicates that complex **10** selectively gives rise to **11** but not to **13** by the acylpalladation, while a complex analogous to **13** is a possible intermediate in eq 4. Although it is not clear how the selectivity is controlled, this point is obviously critical to design a new reaction which involves acylpalladation or related reactions.

Cyclocarbonylation of *o*-(Bromomethyl)(1-alkenyl)benzenes. With the intention of obtaining further information on the detailed reaction mechanism of the cyclocarbonylation, we investigated carbonylation of *o*-(bromomethyl)(1-alkenyl)benzenes **14** which can undergo cyclization without the trans–cis isomerization of the C=C double bond.

Catalytic carbonylation of (*E*)-2-(bromomethyl)stilbene (**14a**) at 160 °C in the presence of Ac_2O, NEt_3, and $PdCl_2(PPh_3)_2$ catalyst gave 3-phenyl-2-naphthyl acetate (**15a**) as a six-membered ring product in 25% yield concurrent with a byproduct **16a** (35%) (eq 6). Similarly 3-methyl-



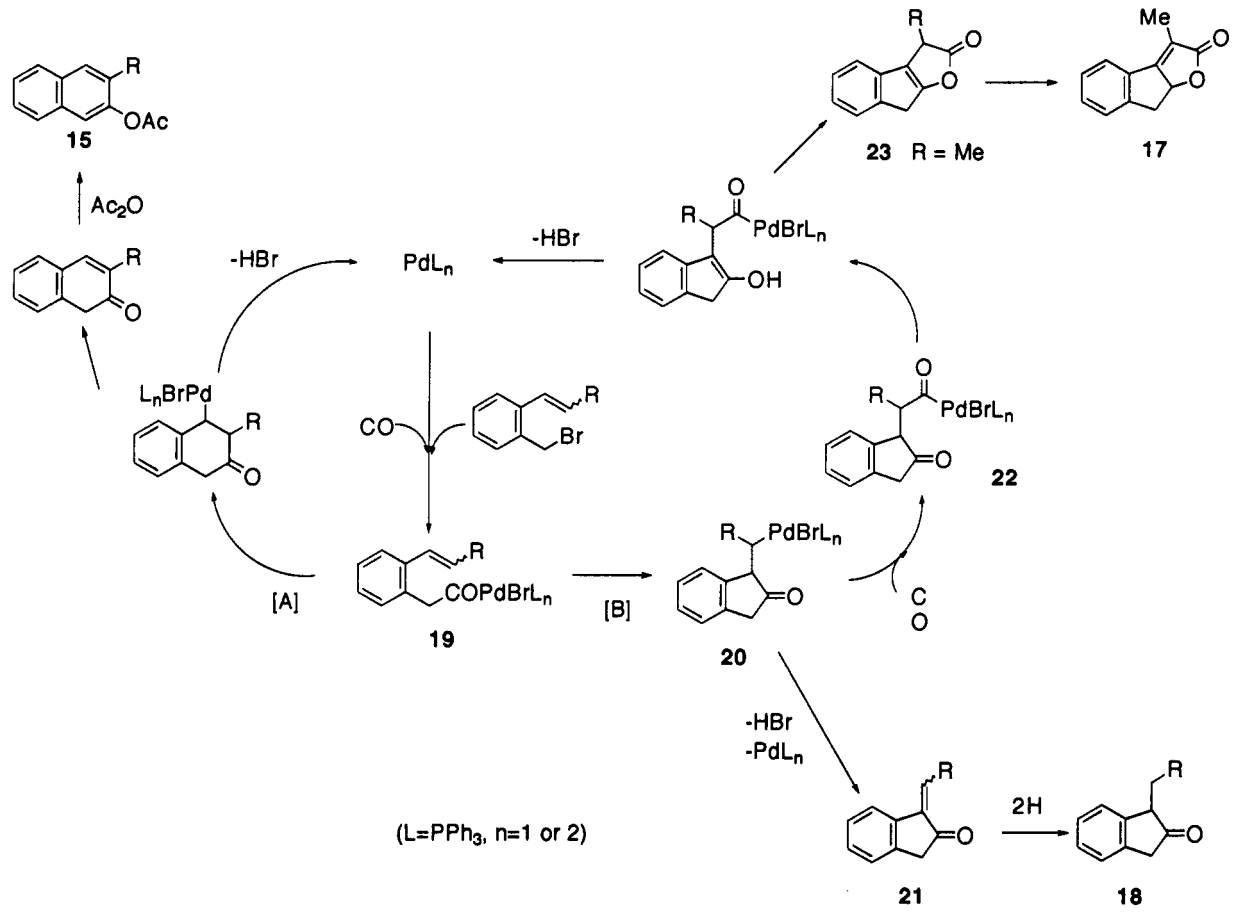
2-naphthyl acetate (**15b**) was obtained from **14b** in 19% at 140 °C, but in this reaction a tricyclic lactone **17** was

(9) Pagès, L.; Llebaria, A.; Camps, F.; Molins, E.; Miravitlles, C.; Moretó, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10449.

(10) (a) Mullen, A. *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer: Berlin, 1980; p 433. (b) Tkatchenko, I. *Comprehensive Organometallic Chemistry*; Wilkinson, J., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 172. (c) Casser, L.; Foa, M.; Chiusoli, G. P. *Organomet. Chem. Synth.* **1971**, *1*, 302.

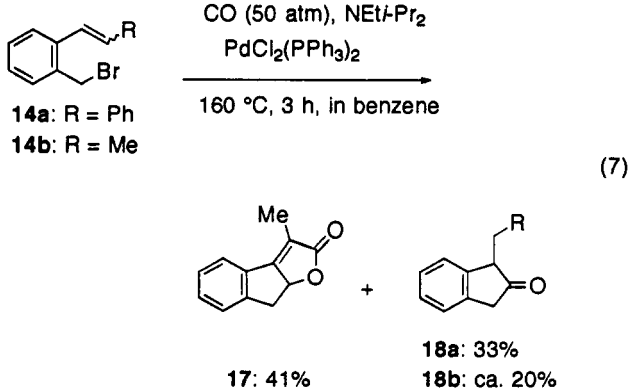
(11) The mechanism involving syn acylpalladation to the C=C double bond followed by syn β-hydrogen elimination requires a change of the position of palladium. See: Larock, R.; Baker, B. E. *Tetrahedron Lett.* **1988**, *29*, 905.

Scheme IV



also formed in 20% yield. Interestingly, **17** is a product via five-membered ring forming acylpalladation and is produced through incorporation of two molecules of CO and two cyclization reactions.

In contrast, carbonylation of **14a** under similar reaction conditions (160 °C) but in the absence of Ac_2O gave no six-membered ring product such as **15a** or 3-phenyl-2-naphthol, but 1-benzyl-2-indanone (**18a**) in 7% yield. Use of $NEt\text{-}i\text{-}Pr_2$ instead of NEt_3 improved the yield of **18a** up to 33% (eq 7). An analogous reaction of **14b** afforded two



(7)

types of five-membered cyclization products, **17** and **18b**, in 41% and ca. 20% yield, respectively.

A reaction mechanism depicted in Scheme IV can account for the formation of **15**, **17**, and **18**. An acylpalladium complex **19** produced by the oxidative addition of **14** to a Pd(0) species and CO insertion acts as a common intermediate. In the presence of Ac_2O, the acylpalladation forming a six-membered ring (path A) mainly occurs and gives a 2-naphthyl acetate **15** as the catalytic cyclocarbonylation product. Contrastingly, in the absence of Ac_2O, the acylpalladation forming a five-membered ring (path B) predominates to give complex **20**. β-Hydrogen elimination in **20** liberates an 1-alkylidene-2-indanone (**21**), which is further converted to the indanone **18** under the catalytic conditions probably by a hydrogen-transfer[12] reaction with NEt_3. In case R is Me, the second CO insertion to the Pd–C bond in **20** also occurs to give complex **22**, and the succeeding intramolecular reaction of the acylpalladium with the enolizable carbonyl group in **22** yields a lactone **23**,[13,14] which isomerizes to **17** under the reaction conditions.

Although some mechanistic details remain unclear, the results shown above suggest that acetate anion delivered from Ac_2O plays an important role in controlling the products; the presence of acetate anion seems to promote path A over path B. We believe that a similar effect of acetate anion also contributes, at least to some extent, to the selective formation of **2** in the cyclocarbonylation of **1**.

Experimental Section

Melting point determinations are uncorrected. ^1H NMR spectra were recorded at 400 or 270 MHz using $CDCl_3$ as solvent and TMS as internal standard. ^{13}C NMR spectra were recorded at 100 MHz using $CDCl_3$ as solvent and as internal standard (δ

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= 77.05 ppm). GLC analyses were performed with a HiCap CBP1-M25–0.25 capillary column and a flame ionization detector. $PdCl_2(PPh_3)_2$,[15] $Pd(CO)(PPh_3)_3$,[16] $Pd(PPh_3)_4$,[17] $PdCl_2(PMe_2Ph)_2$,[18] $PdCl_2$(dpe),[19] $PtCl_2(PPh_3)_2$,[20] $Pt(CO)(PPh_3)_3$,[21] $NiBr_2(PPh_3)_2$,[22] $RhCl(PPh_3)_3$,[23] and $RuCl_2(PPh_3)_3$[24] were prepared by literature procedures.

Substrates (1, 4, 5, 14) and products (2a-i, 2l-o, 6, 7, 15, 16, 17, 18a) of the catalytic reactions were fully characterized by spectroscopic means (IR, NMR, MS). Compounds 2j, 2k, and 3 were identified by comparing their IR, ^1H NMR, and ^{13}C NMR with those of commercial samples. Compound 18b was not stable under the workup conditions described below, and was tentatively characterized by GC–MS.

(2*E*,4*E*)-5-Phenyl-2,4-pentadienyl Acetate (1a). To a THF (300 mL) solution of distilled cinnamaldehyde (26.4 g, 0.20 mol) and triethyl phosphonoacetate (44.8 g, 0.20 mol), an ethanol (80 mL) solution of sodium ethoxide (prepared from 0.22 mol of Na) was added slowly at −30 °C with stirring. The reaction mixture was further stirred for 4 h at room temperature. Water was added and the mixture was extracted repeatedly with ether. The ether solution was dried over $MgSO_4$ and evaporated to dryness. Distillation of the residue (108–112 °C, 1 mmHg) gave ethyl 5-phenyl-2,4-pentadienoate (32.7 g, 81%) as a pale yellow oil, which solidifies on cooling. An ether (300 mL) solution of the ester (32.7 g, 0.16 mol) was added dropwise to an ether suspension of $LiAlH_4$ (3.88 g, 0.10 mol) at −30 °C with stirring. The reaction mixture was kept at this temperature until all the ester was consumed (2 h), and then it was quenched with excess ethyl acetate and then aqueous Na_2SO_4. The organic layer was separated and the inorganic solid was further extracted with ether. The combined ether solution was dried over $MgSO_4$ and evaporated to give a yellow crystalline solid. Recrystallization from ether gave 5-phenyl-2,4-pentadienol (20.6 g, 80%) as pale yellow crystals. The alcohol (10.6 g, 0.066 mol), Ac_2O (13.4 g, 0.13 mol), and NEt_3 (20.3 g, 0.20 mol) were dissolved in ether (100 mL) at room temperature and stirred for 3 h. The reaction mixture was poured into ice–water and extracted with ether. The organic layer was dried over $MgSO_4$, evaporated, and further purified by recrystallization from hexane or distillation (126–129 °C, 3 mmHg) to give 1a (10.8 g, 81%) as colorless crystals: mp 34–35 °C; ^1H NMR δ 2.09 (s, 3 H), 4.65 (d, J = 6.6 Hz, 2 H), 5.87 (dt, J = 15.2, 6.6 Hz, 1 H), 6.45 (dd, J = 15.2, 10.5 Hz, 1 H), 6.59 (d, J = 15.5 Hz, 1 H), 6.77 (dd, J = 15.5, 10.5 Hz, 1 H), 7.21–7.44 (m, 5 H); ^{13}C NMR δ 20.9, 64.7, 126.5, 126.9, 127.7, 127.8, 128.6, 133.8, 134.5, 136.9, 170.7; IR (KBr) 1740 cm^{-1} (C=O); HREIMS calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.1011.

(2*E*,4*E*)-5-(4-Methoxyphenyl)-2,4-pentadienyl acetate (1b) was prepared by Claisen condensation of 4-methoxycinnamaldehyde with ethyl acetate,[25] followed by $LiAlH_4$ reduction at −30 °C and acetylation with Ac_2O/NEt_3. Colorless crystals: mp 63–64 °C; ^1H NMR δ 2.08 (s, 3 H), 3.81 (s, 3 H), 4.64 (d, J = 6.7 Hz, 2 H), 5.82 (dt, J = 15.1, 6.7 Hz, 1 H), 6.43 (dd, J = 15.1, 10.3 Hz, 1 H), 6.54 (d, J = 15.6 Hz, 1 H), 6.65 (dd, J = 15.6, 10.3 Hz, 1 H), 6.86 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H); ^{13}C NMR δ 21.0, 55.3, 64.9, 114.1, 125.66, 125.70, 127.7, 129.8, 133.4, 135.0, 159.5, 170.8; IR (KBr) 1738 cm^{-1} (C=O); HREIMS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1095.

(2*E*,4*E*)-5-(2-Chlorophenyl)-2,4-pentadienyl acetate (1c) was prepared similarly to 1a from 2-chlorobenzaldehyde and triethyl phosphonocrotonate. Colorless oil: ^1H NMR δ 2.10 (s, 3 H), 4.67 (d, J = 6.4 Hz, 2 H), 5.93 (dt, J = 15.3, 6.4 Hz, 1 H), 6.52 (dd, J = 15.3, 10.7 Hz, 1 H), 6.75 (dd, J = 15.6, 10.7 Hz, 1 H), 6.99 (d, J = 15.6 Hz, 1 H), 7.17 (td, J = 7.6, 1.5 Hz, 1 H), 7.23 (td, J = 7.6, 1.5 Hz, 1 H), 7.36 (dd, J = 7.6, 1.5 Hz, 1 H), 7.56 (dd, J = 7.6, 1.5 Hz, 1 H); ^{13}C NMR δ 20.9, 64.5, 126.3, 126.8, 128.1, 128.7, 129.4, 129.8, 130.1, 133.3, 134.1, 134.9, 170.7; IR (neat) 1740 cm^{-1} (C=O); HREIMS calcd for $C_{13}H_{13}O_2Cl$ 236.0605, found 236.0581.

(2*E*,4*E*)-4-Methyl-5-phenyl-2,4-pentadienyl acetate (1d) was prepared similarly to 1b from 2-methyl-3-phenylpropenal and ethyl acetate. Colorless oil: ^1H NMR δ 2.00 (d, J = 1.2 Hz, 3 H), 2.10 (s, 3 H), 4.69 (d, J = 6.7 Hz, 2 H), 5.85 (dt, J = 15.3, 6.7 Hz, 1 H), 6.49 (d, J = 15.3 Hz, 1 H), 6.56 (br s, 1 H), 7.21–7.36 (m, 5 H); ^{13}C NMR δ 13.8, 21.0, 65.2, 122.3, 126.8, 128.2, 129.2, 132.7, 134.7, 137.5, 139.6, 170.9; IR (neat) 1745 cm^{-1} (C=O); HREIMS calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1161.

(2*E*,4*E*)-2-Methyl-5-phenyl-2,4-pentadienyl acetate (1e) was prepared similarly to 1b from cinnamaldehyde and ethyl propionate. Colorless crystals: mp 35–36 °C; ^1H NMR δ 1.89 (s, 3 H), 2.10 (s, 3 H), 4.58 (s, 2 H), 6.24 (d, J = 11.0 Hz, 1 H), 6.58 (d, J = 15.6 Hz, 1 H), 6.99 (dd, J = 15.6, 11.0 Hz, 1 H), 7.22 (t, J = 7.3 Hz, 1 H), 7.32 (t, J = 7.3 Hz, 2 H), 7.42 (d, J = 7.3 Hz, 2 H); ^{13}C NMR δ 14.7, 21.0, 69.7, 124.2, 126.4, 127.6, 128.3, 128.6, 132.7, 133.3, 137.4, 170.9; IR (KBr) 1737 cm^{-1} (C=O); HREIMS calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1150.

(2*E*,4*E*)-5-(1-Naphthyl)-2,4-pentadienyl acetate (1f) was prepared similarly to 1a from 1-naphthaldehyde and triethyl phosphonocrotonate. Colorless crystals: mp 45–47 °C; ^1H NMR δ 2.11 (s, 3 H), 4.70 (d, J = 6.6 Hz, 2 H), 5.94 (dt, J = 15.3, 6.6 Hz, 1 H), 6.61 (dd, J = 15.3, 10.7 Hz, 1 H), 6.83 (dd, J = 15.3, 10.7 Hz, 1 H), 7.37 (d, J = 15.3 Hz, 1 H), 7.45 (t, J = 7.8 Hz, 1 H), 7.47–7.54 (m, 2 H), 7.65 (d, J = 7.8 Hz, 1 H), 7.78 (d, J = 7.8 Hz, 1 H), 7.85 (d, J = 7.3 Hz, 1 H), 8.12 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 21.0, 64.7, 123.47, 123.51, 125.6, 125.8, 126.1, 127.2, 128.2, 128.6, 130.5 (2 C), 131.1, 133.7, 134.3, 134.7, 170.7; IR (KBr) 1735 cm^{-1} (C=O); HREIMS calcd for $C_{17}H_{16}O_2$ 252.1150, found 252.1148.

(2*E*,4*E*)-5-(2-Furyl)-2,4-pentadienyl acetate (1g) was prepared similarly to 1a from 3-(2-furyl)acrolein and triethyl phosphonoacetate. Colorless crystals: mp 40-41 °C; ^1H NMR δ 2.02 (s, 3 H), 4.57 (d, J = 6.4 Hz, 2 H), 5.79 (dt, J = 15.4, 6.4 Hz, 1 H), 6.22 (d, J = 3.4 Hz, 1 H), 6.28–6.34 (m, 3 H), 6.61 (dd, J = 15.6, 11.0 Hz, 1 H), 7.30 (d, J = 1.5 Hz, 1 H); ^{13}C NMR δ 20.9, 64.7, 109.0, 111.6, 121.2, 126.3, 127.0, 134.1, 142.4, 152.8, 170.7; IR (neat) 1737 (C=O), 1642 cm^{-1} (C=C); HREIMS calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0783.

(2*E*,4*E*)-5-(2-Furyl)-2-methyl-2,4-pentadienyl acetate (1h) was prepared similarly to 1b from 3-(2-furyl)acrolein and ethyl propionate. Yellow oil: ^1H NMR δ 1.87 (d, J = 0.9 Hz, 3 H), 2.10 (s, 3 H), 4.56 (s, 2 H), 6.17 (br d, J = 11.3 Hz, 1 H), 6.27 (d, J = 3.4 Hz, 1 H), 6.36 (d, J = 15.6 Hz, 1 H), 6.39 (dd, J = 3.4, 1.8 Hz, 1 H), 6.89 (dd, J = 15.6, 11.3 Hz, 1 H), 7.37 (d, J = 1.8 Hz, 1 H); ^{13}C NMR δ 14.7, 20.9, 69.7, 108.6, 111.7, 120.7, 122.9, 127.9, 133.0, 142.2, 153.2, 170.8; IR (neat) 1725 cm^{-1} (C=O); HREIMS calcd for $C_{12}H_{14}O_3$ 206.0942, found 206.0936.

(2*E*,4*E*)-5-(2-Thienyl)-2,4-pentadienyl acetate (1i) was prepared similarly to 1a from 2-thiophenecarbaldehyde and triethyl phosphonocrotonate. Colorless crystals: mp 40–41°C; ^1H NMR δ 2.09 (s, 3 H), 4.64 (d, J = 6.6 Hz, 2 H), 5.84 (dt, J = 15.3, 6.6 Hz, 1 H), 6.39 (dd, J = 15.3, 10.4 Hz, 1 H), 6.58 (dd, J = 15.4, 10.4 Hz, 1 H), 6.72 (d, J = 15.4 Hz, 1 H), 6.96–6.99 (m, 2 H), 7.18 (d, J = 4.6 Hz, 1 H); ^{13}C NMR δ 20.9, 64.7, 124.7, 126.3, 126.5, 126.7, 127.4, 127.6, 134.0, 142.2, 170.7; IR (neat) 1730 cm^{-1} (C=O); HREIMS calcd for $C_{11}H_{12}O_2S$ 208.0570, found 208.0558.

(*E*)-2,4-Pentadienyl acetate (1j)[26] was prepared similarly to 1a from acrolein and triethyl phosphonoacetate. Colorless oil: ^1H NMR δ 2.08 (s, 3 H), 4.60 (d, J = 6.4 Hz, 2 H), 5.16 (dd, J = 10.1, 1.8 Hz, 1 H), 5.26 (dd, J = 16.3, 1.8 Hz, 1 H), 5.78 (dt, J = 14.3, 6.4 Hz, 1 H), 6.25–6.39 (m, 2 H); ^{13}C NMR 20.9, 64.5, 118.6, 127.2, 134.7, 136.0, 170.6; IR (neat) 1742 (C=O), 1605 cm^{-1} (C=C).

(2*E*,4*E*)-2,4-Hexadienyl acetate (1k)[27] was prepared by acetylation of (2*E*,4*E*)-2,4-hexadien-1-ol. Colorless oil: ^1H NMR δ 1.77 (d, J = 6.7 Hz, 3 H), 2.06 (s, 3 H), 4.57 (d, J = 6.7 Hz, 2 H), 5.63 (dt, J = 15.3, 6.7 Hz, 1 H), 5.76 (dq, J = 15.0, 6.7 Hz, 1 H), 6.05 (dd, J = 15.0, 10.7 Hz, 1 H), 6.25 (dd, J = 15.3, 10.7 Hz, 1 H); ^{13}C NMR 18.1, 21.0, 65.0, 123.7, 130.5, 131.3, 134.9,

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170.8; IR (neat) 1738 (C=O), 1660 cm^{-1} (C=C); HREIMS calcd for $C_8H_{12}O_2$ 140.0838, found 140.0837.

(2*E*,4*E*)-2,4-Nonadienyl acetate (1l) was prepared by $LiAlH_4$ reduction of (2*E*,4*E*)-2,4-nonadienal and acetylation. Colorless oil: ^{1}H NMR δ 0.89 (t, J = 7.2 Hz, 3 H), 1.28–1.40 (m, 4 H), 2.05–2.11 (m, 2 H), 2.06 (s, 3 H), 4.56 (d, J = 6.7 Hz, 2 H), 5.63 (dt, J = 15.3, 6.7 Hz, 1 H), 5.74 (dq, J = 15.1, 6.7 Hz, 1 H), 6.03 (dd, J = 15.1, 10.7 Hz, 1 H), 6.25 (dd, J = 15.3, 10.7 Hz, 1 H); ^{13}C NMR 13.9, 21.0, 22.2, 31.3, 32.3, 65.0, 123.9, 129.1, 135.1, 136.8, 170.8; IR (neat) 1738 (C=O), 1657 cm^{-1} (C=C); HREIMS calcd for $C_{11}H_{18}O_2$ 182.1312, found 182.1306.

(*E*)-2,4-Dimethyl-2,4-pentadienyl acetate (1m) was prepared similarly to **1b** from methacrolein and ethyl propionate. Colorless oil: ^{1}H NMR δ 1.84 (s, 3 H), 1.87 (s, 3 H), 2.10 (s, 3 H), 4.50 (s, 2 H), 4.87 (s, 1 H), 5.03 (s, 1 H), 5.92 (s, 1 H); ^{13}C NMR δ 15.5, 21.0, 23.3, 70.4, 115.9, 130.3, 131.4, 141.1, 170.9; IR (neat) 1745 cm^{-1} (C=O); HREIMS calcd for $C_9H_{14}O_2$ 154.0994, found 154.0988.

(2*E*,4*E*,6*E*)-2,4,6-Undecatrienyl acetate (1n) was prepared similarly to **1a** from (2*E*,4*E*)-2,4-nonadienal and triethyl phosphonoacetate. Colorless oil: ^{1}H NMR δ 0.89 (t, J = 7.0 Hz, 3 H), 1.24–1.42 (m, 4 H), 2.07 (s, 3 H), 2.10 (q, J = 7.3 Hz, 2 H), 4.59 (d, J = 6.7 Hz, 2 H), 5.71 (dt, J = 15.0, 6.7 Hz, 1 H), 5.75 (dt, J = 15.0, 7.3 Hz, 1 H), 6.06 (dd, J = 15.0, 10.4 Hz, 1 H), 6.10 (dd, J = 15.0, 10.4 Hz, 1 H), 6.23 (dd, J = 15.0, 10.4 Hz, 1 H), 6.29 (dd, J = 15.0, 10.4 Hz, 1 H); ^{13}C NMR δ 13.9, 21.0, 22.2, 31.4, 32.5, 64.9, 125.4, 129.0, 130.0, 134.7, 134.9, 136.7, 170.8; IR (neat) 1742 (C=O), 1638 cm^{-1} (C=C); HREIMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1488.

(2*E*,4*E*)-3,5-Di(*p*-tolyl)-2,4-pentadienyl acetate (1o) was prepared similarly to **1a** from *E*-1,3-di(*p*-tolyl)propen-1-one and triethyl phosphonoacetate. Colorless oil: ^{1}H NMR δ 2.10 (s, 3 H), 2.34 (s, 3 H), 2.39 (s, 3 H), 4.95 (d, J = 7.2 Hz, 2 H), 5.67 (t, J = 7.2 Hz, 1 H), 6.46 (d, J = 15.9 Hz, 1 H), 7.13 (d, J = 7.9 Hz, 2 H), 7.18 (d, J = 15.9 Hz, 1 H), 7.18 (d, J = 7.9 Hz, 2 H), 7.24 (d, J = 7.9 Hz, 2 H), 7.30 (d, J = 7.9 Hz, 2 H); ^{13}C NMR δ 21.0, 21.2, 21.3, 61.0, 123.6, 123.8, 126.6, 128.7, 128.9, 129.4, 134.2, 134.6, 137.4, 137.9, 138.0, 143.8, 171.0; IR (neat) 1740 cm^{-1} (C=O); HREIMS calcd for $C_{21}H_{22}O_2$ 306.1620, found 306.1607.

(1*E*,3*E*)-5-Chloro-1-phenyl-1,3-pentadiene (4) was prepared by chlorination of (2*E*,4*E*)-5-phenyl-2,4-pentadienol with CCl_4/PPh_3.[28] Colorless crystals: mp 47-49 °C (lit.[29] mp 50–51 °C); ^{1}H NMR δ 4.18 (d, J = 7.3 Hz, 2 H), 5.92 (dt, J = 15.0, 7.3 Hz, 1 H), 6.46 (dd, J = 15.0, 10.1 Hz, 1 H), 6.60 (d, J = 15.5 Hz, 1 H), 6.77 (dd, J = 15.5, 10.1 Hz, 1 H), 7.22–7.45 (m, 5 H); ^{13}C NMR δ 45.2, 126.6, 127.3, 128.0, 128.5, 128.7, 134.3, 134.6, 136.8; HREIMS calcd for $C_{11}H_{11}Cl$ 178.0550, found 178.0565.

Ethyl (2*E*,4*E*)-5-phenyl-2,4-pentadienyl carbonate (5) was prepared by ethoxycarbonylation of (2*E*,4*E*)-5-phenyl-2,4-pentadienol with ethyl chloroformate. Colorless oil: ^{1}H NMR δ 1.32 (t, J = 7.2 Hz, 3 H), 4.22 (q, J = 7.2 Hz, 2 H), 4.71 (d, J = 6.7 Hz, 2 H), 5.89 (dt, J = 14.9, 6.7 Hz, 1 H), 6.49 (dd, J = 14.9, 10.5 Hz, 1 H), 6.60 (d, J = 15.6 Hz, 1 H), 6.77 (dd, J = 15.6, 10.5 Hz, 1 H), 7.22–7.41 (m, 5 H); ^{13}C NMR δ 14.3, 64.0, 67.9, 126.2, 126.5, 127.6, 127.9, 128.6, 134.1, 135.0, 136.8, 155.0; IR (neat) 1745 (C=O), 1645 cm^{-1} (C=C); HREIMS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1107.

(*E*)-2-(Bromomethyl)stilbene (14a) was prepared according to a literature procedure[30] from *o*-bromobenzyl methyl ether and β-bromostyrene. Colorless crystals: mp 48–49 °C; ^{1}H NMR δ 4.64 (s, 2 H), 7.09 (d, J = 16.0 Hz, 1 H), 7.22-7.41 (m, 6 H), 7.48 (d, J = 16.0 Hz, 1 H), 7.57 (dd, J = 7.0, 1.0 Hz, 2 H), 7.65 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ 32.0, 124.9, 126.4, 126.8, 127.9, 128.0, 128.8, 129.2, 130.4, 131.6, 134.8, 136.9, 137.2; HREIMS calcd for $C_{15}H_{13}Br$ 272.0201, found 272.0193.

***o*-(Bromomethyl)(1-propenyl)benzene (14b)** was prepared according to a literature procedure[30] from *o*-bromobenzyl methyl ether and 1-bromo-1-propene. Characterized and used as a 1:1.3 mixture of *E*- and *Z*-isomers. *E*-Isomer: ^{1}H NMR δ 1.94 (dd, J = 6.7, 1.8 Hz, 3 H), 4.56 (s, 2 H), 6.22 (dq, J = 15.5, 6.7 Hz, 1 H), 6.74 (br d, J = 15.5 Hz, 1 H), 7.16–7.30 (m, 3 H), 7.44 (d, J = 7.6 Hz, 1 H). *Z*-Isomer: ^{1}H NMR δ 1.73 (dd, J = 7.0, 1.7 Hz, 3 H), 4.49 (s, 2 H), 5.95 (dq, J = 11.4, 7.0 Hz, 1 H), 6.61 (br d, J = 11.4 Hz, 1 H), 7.16–7.30 (m, 3 H), 7.38 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 14.4, 18.9, 32.1, 32.2, 126.5, 127.1, 127.2, 127.3 (2 C), 128.4, 128.8, 129.0, 129.1, 129.99, 130.02, 130.2, 133.9, 135.5, 137.0, 137.5; HREIMS calcd for $C_{10}H_{11}Br$ 210.0044, found 210.0025.

Catalytic Cyclocarbonylation of 2,4-Pentadienyl Acetates or *o*-(Bromomethyl)(1-alkenyl)benzenes. The following procedure is representative. A mixture of 5-phenyl-2,4-pentadienyl acetate (**1a**) (0.606 g, 3 mmol), $PdCl_2(PPh_3)_2$ (63.2 mg, 0.09 mmol), Ac_2O (0.613 g, 6 mmol), NEt_3 (0.668 g, 6.6 mmol), and benzene (10 mL) in a stainless steel autoclave was pressurized with CO (50 atm) and was heated at 140 °C for 3 h with stirring. Then the autoclave was cooled and CO was discharged. GLC analysis of the reaction mixture (octadecane as the internal standard) revealed that 2-acetoxybiphenyl **2a** was formed in 74%. The reaction mixture was diluted with ether, washed with water, and dried over $MgSO_4$. Solvent was evaporated and the crude product was purified by silica gel column chromatography (hexane/ether, 6:1) and bulb-to-bulb distillation to give pure **2a** (69%) as colorless crystals: mp 60–62 °C (lit.[31] 63–64 °C); ^{1}H NMR δ 2.08 (s, 3 H), 7.13 (dd, J = 7.9, 1.2 Hz, 1 H), 7.29–7.42 (m, 8 H); ^{13}C NMR δ 20.8, 122.8, 126.4, 127.4, 128.3, 128.5, 128.9, 130.9, 134.9, 137.7, 147.8, 169.3; IR (KBr) 1760 cm^{-1} (C=O); HREIMS calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0833.

2-Acetoxy-4′-methoxybiphenyl (2b). Colorless crystals: mp 84–85 °C; ^{1}H NMR δ 2.10 (s, 3 H), 3.84 (s, 3 H), 6.94 (d, J = 8.9 Hz, 2 H), 7.11 (dd, J = 7.8, 1.4 Hz, 1 H), 7.27–7.40 (m, 3 H), 7.35 (d, J = 8.9 Hz, 2 H); ^{13}C NMR δ 20.9, 55.2, 113.8, 122.8, 126.4, 128.1, 130.0 (2 C), 130.8, 134.5, 147.8, 159.1, 169.4; IR (KBr) 1755 cm^{-1} (C=O); HREIMS calcd for $C_{15}H_{14}O_3$ 242.0943, found 242.0942.

2-Acetoxy-2′-chlorobiphenyl (2c). Colorless crystals: mp 70–71 °C (lit.[32] 73 °C); ^{1}H NMR δ 2.00 (s, 3 H), 7.20 (d, J = 7.9 Hz, 1 H), 7.24–7.34 (m, 5 H), 7.42-7.48 (m, 2 H); ^{13}C NMR δ 20.6, 122.4, 125.8, 126.4, 129.0, 129.2, 129.4, 131.1, 131.4, 132.4, 133.5, 136.3, 148.1, 169.0; IR (KBr) 1760 cm^{-1} (C=O); HREIMS calcd for $C_{14}H_{11}O_2Cl$ 246.0448, found 246.0439.

2-Acetoxy-6-methylbiphenyl (2d). Colorless oil: ^{1}H NMR δ 1.87 (s, 3 H), 2.12 (s, 3 H), 6.95 (d, J = 7.6 Hz, 1 H), 7.16–7.19 (m, 3 H), 7.25–7.41 (m, 4 H); ^{13}C NMR δ 20.4, 20.5, 119.7, 127.2, 127.8, 128.0, 128.1, 129.4, 135.0, 136.5, 138.2, 148.5, 169.7; IR (neat) 1765 cm^{-1} (C=O); HREIMS calcd for $C_{15}H_{14}O_2$ 226.0993, found 226.0999.

2-Acetoxy-4-methylbiphenyl (2e). Colorless oil: ^{1}H NMR δ 2.08 (s, 3 H), 2.39 (s, 3 H), 6.95 (br s, 1 H), 7.12 (br d, J = 7.6 Hz, 1 H), 7.30 (d, J = 7.6 Hz, 1 H), 7.30-7.40 (m, 5 H); ^{13}C NMR δ 20.8, 21.0, 123.3, 127.2 (2 C), 128.2, 128.8, 130.6, 131.9, 137.7, 138.8, 147.6, 169.5; IR (neat) 1762 cm^{-1} (C=O); HREIMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0981.

2-(1-Naphthyl)phenyl Acetate (2f). Pale yellow oil: ^{1}H NMR δ 1.72 (s, 3 H), 7.24 (dd, J = 7.9, 1.2 Hz, 1 H), 7.35–7.44 (m, 4 H), 7.46–7.52 (m, 3 H), 7.60 (br d, J = 8.9 Hz, 1 H), 7.86–7.90 (m, 2 H); ^{13}C NMR δ 20.4, 122.7, 125.1, 125.6, 125.8, 125.99, 126.04, 127.3, 128.05, 128.08, 128.14, 128.8, 131.7, 132.0, 133.41, 133.44, 148.7, 169.3; IR (neat) 1767 cm^{-1} (C=O); HREIMS calcd for $C_{18}H_{14}O_2$ 262.0993, found 262.1003.

2-(2-Furyl)phenyl Acetate (2g). Colorless oil: ^{1}H NMR δ 2.37 (s, 3 H), 6.48 (dd, J = 3.4, 1.8 Hz, 1 H), 6.68 (dd, J = 3.4, 0.8 Hz, 1 H), 7.11–7.14 (m, 1 H), 7.27-7.31 (m, 2 H), 7.48 (dd, J = 1.8, 0.8 Hz, 1 H), 7.81–7.83 (m, 1 H); ^{13}C NMR δ 21.2, 108.9, 111.7, 123.4, 123.8, 126.3, 127.0, 128.1, 142.2, 146.3, 149.7, 169.0; IR (neat) 1768 cm^{-1} (C=O); HREIMS calcd for $C_{12}H_{10}O_3$ 202.0630, found 202.0653.

2-(2-Furyl)-5-methylphenyl Acetate (2h). Yellow oil: ^{1}H NMR δ 2.36 (s, 3 H), 2.37 (s, 3 H), 6.47 (dd, J = 3.4, 1.8 Hz, 1 H), 6.60 (dd, J = 3.4, 0.6 Hz, 1 H), 6.93 (br s, 1 H), 7.10 (br d, J = 7.9 Hz, 1 H), 7.46 (dd, J = 1.8, 0.6 Hz, 1 H), 7.69 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 21.1, 21.3, 108.0, 111.5, 121.0, 123.8, 126.8, 127.2, 138.6, 141.8, 146.1, 149.9, 169.3; IR (neat) 1760 cm^{-1} (C=O); HREIMS calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0792.

2-(2-Thienyl)phenyl Acetate (2i). Yellow oil: ^{1}H NMR δ 2.31 (s, 3 H), 7.09 (dd, J = 5.0, 3.7 Hz, 1 H), 7.14 (dd, J = 7.5, 1.6 Hz, 1 H), 7.27 (td, J = 7.5, 1.6 Hz, 1 H), 7.32 (td, J = 7.5, 2.0

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Hz, 1 H), 7.32 (dd, J = 3.7, 1.2 Hz, 1 H), 7.35 (dd, J = 5.0, 1.2 Hz, 1 H), 7.64 (dd, J = 7.5, 2.0 Hz, 1 H); ^{13}C NMR δ 21.3, 123.4, 126.0, 126.1, 126.4, 127.2, 127.3, 128.4, 129.5, 138.3, 146.9, 169.2; IR (neat) 1768 cm^{-1} (C=O); HREIMS calcd for $C_{12}H_{10}O_2S$ 218.0413, found 218.0402.

2-Butylphenyl Acetate (2l). Colorless oil: ^{1}H NMR δ 0.93 (t, J = 7.3 Hz, 3 H), 1.35 (sextet, J = 7.3 Hz, 2 H), 1.52–1.59 (m, 2 H), 2.32 (s, 3 H), 2.52 (pseudo t, J = 7.8 Hz, 2 H), 7.01 (dd, J = 7.8, 1.4 Hz, 1 H), 7.14–7.25 (m, 3 H); ^{13}C NMR δ 13.9, 20.9, 22.5, 29.8, 32.1, 122.2, 126.0, 126.8, 130.2, 134.5, 148.9, 169.5; IR (neat) 1765 cm^{-1} (C=O); HREIMS calcd for $C_{12}H_{16}O_2$ 192.1159, found 192.1151.

3,5-Dimethylphenyl Acetate (2m). Colorless oil: ^{1}H NMR δ 2.28 (s, 3 H), 2.31 (s, 6 H), 6.69 (s, 2 H), 6.86 (s, 1 H); ^{13}C NMR δ 21.1, 21.2, 119.2, 127.6, 139.3, 150.6, 169.7; IR (neat) 1765 cm^{-1} (C=O); HREIMS calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0853.

2-(1-Hexenyl)phenyl Acetate (2n). E-Isomer, colorless oil: ^{1}H NMR δ 0.92 (t, J = 7.2 Hz, 3 H), 1.32–1.57 (m, 4 H), 2.21 (q, J = 7.0 Hz, 2 H), 2.33 (s, 3 H), 6.22 (dt, J = 15.9, 7.0 Hz, 1 H), 6.37 (d, J = 15.9 Hz, 1 H), 7.00 (dd, J = 7.4, 1.8 Hz, 1 H), 7.18 (td, J = 7.4, 1.8 Hz, 1 H), 7.22 (td, J = 7.4, 1.8 Hz, 1 H), 7.51 (dd, J = 7.4, 1.8 Hz, 1 H); ^{13}C NMR δ 13.9, 20.9, 22.2, 31.4, 33.0, 122.5, 123.0, 126.1, 126.6, 127.6, 130.5, 133.9, 147.6, 169.3; IR (neat) 1760 (C=O), 1650 cm^{-1} (C=C); HREIMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1291. Z-Isomer, obtained as a mixture with E-**2n**: ^{1}H NMR δ 0.85 (t, J = 7.2 Hz, 3 H), 1.28–1.57 (m, 4 H), 2.15–2.21 (m, 2 H), 2.27 (s, 3 H), 5.74 (dt, J = 11.8, 7.3 Hz, 1 H), 6.27 (d, J = 11.8 Hz, 1 H), 7.04 (dd, J = 7.9, 1.5 Hz, 1 H), 7.17–7.31 (m, 3 H).

2,4-Di(*p*-tolyl)phenyl Acetate (2o). Colorless crystals: mp 101–102 °C; ^{1}H NMR δ 2.12 (s, 3 H), 2.39 (s, 3 H), 2.40 (s, 3 H), 7.17 (d, J = 8.2 Hz, 1 H), 7.22–7.26 (m, 4 H), 7.36 (m, 2 H), 7.49 (m, 2 H), 7.54 (dd, J = 8.2, 2.2 Hz, 1 H), 7.59 (d, J = 2.2 Hz, 1 H); ^{13}C NMR δ 20.9, 21.1, 21.2, 123.0, 126.8, 127.0, 128.7, 129.1, 129.46, 129.52, 134.7, 135.0, 137.2, 137.3, 137.5, 139.5, 147.0, 169.6; IR (KBr) 1764 cm^{-1} (C=O); HREIMS calcd for $C_{22}H_{20}O_2$ 316.1463, found 316.1478.

(*E*)-7-Methyl-4-(2-*p*-tolylethenyl)-1-naphthyl Acetate (6). Colorless crystals: mp 137–139 °C; ^{1}H NMR δ 2.38 (s, 3 H), 2.48 (s, 3 H), 2.53 (s, 3 H), 7.08 (d, J = 16.1 Hz, 1 H), 7.21 (d, J = 8.1 Hz, 2 H), 7.22 (d, 7.9 Hz, 1 H), 7.39 (dd, J = 8.8, 1.7 Hz, 1 H), 7.49 (d, J = 8.1 Hz, 2 H), 7.64 (br s, 1 H), 7.64 (d, J = 7.9 Hz, 1 H), 7.76 (d, J = 16.1 Hz, 1 H), 8.12 (d, J = 8.8 Hz, 1 H); ^{13}C NMR δ 21.1, 21.3, 21.8, 118.1, 120.4, 122.1, 124.1, 124.3, 126.6, 126.9, 128.8, 129.4, 130.7, 131.7, 133.4, 134.7, 136.1, 137.7, 145.7, 169.6; IR (KBr) 1762 cm^{-1} (C=O); HREIMS calcd for $C_{22}H_{20}O_2$ 316.1463, found 316.1445.

Methyl (3*E*,5*E*)-6-Phenyl-3,5-hexadienoate (7). Colorless crystals: mp 46–47 °C; ^{1}H NMR δ 3.19 (d, 7.3 Hz, 2 H), 3.70 (s, 3 H), 5.89 (dt, J = 15.3, 7.3 Hz, 1 H), 6.30 (dd, J = 15.3, 10.4 Hz, 1 H), 6.50 (d, J = 15.7 Hz, 1 H), 6.77 (dd, J = 15.7, 10.4 Hz, 1 H), 7.21 (t, J = 7.6 Hz, 1 H), 7.30 (t, J = 7.6 Hz, 2 H), 7.38 (d, J = 7.6 Hz, 2 H); ^{13}C NMR δ 38.0, 51.9, 125.5, 126.3, 127.5, 128.3, 128.6, 132.2, 134.0, 137.1, 171.9; IR (KBr) 1732 cm^{-1} (C=O); HREIMS calcd for $C_{13}H_{14}O_2$ 202.0993, found 202.1011.

3-Phenyl-2-naphthyl Acetate (15a). Yellow oil: ^{1}H NMR δ 2.10 (s, 3 H), 7.30-7.53 (m, 7 H), 7.60 (s, 1 H), 7.81–7.87 (m, 2 H), 7.87 (s, 1 H); ^{13}C NMR δ 20.8, 120.0, 126.1, 126.5, 127.3, 127.5, 127.8, 128.3, 129.1, 130.0, 131.8, 133.1, 134.3, 137.7, 146.2, 169.5; IR (neat) 1765 cm^{-1} (C=O); HREIMS calcd for $C_{18}H_{14}O_2$ 262.0993, found 262.0985.

3-Methyl-2-naphthyl Acetate (15b). Pale yellow crystals: mp 63–65 °C, ^{1}H NMR δ 2.35 (s, 3 H), 2.38 (s, 3 H), 7.41–7.43 (m, 2 H), 7.49 (s, 1 H), 7.69 (s, 1 H), 7.74–7.77 (m, 2 H); ^{13}C NMR δ 16.8, 20.9, 119.0, 125.7 (2 C), 127.0, 127.3, 129.47, 129.52, 131.9, 132.5, 148.0, 169.5; IR (KBr) 1752 cm^{-1} (C=O); HREIMS calcd for $C_{13}H_{12}O_2$ 200.0838, found 200.0809.

(*E*)-2-(Acetoxymethyl)stilbene (16a). Yellow oil: ^{1}H NMR δ 2.09 (s, 3 H), 5.27 (s, 2 H), 7.04 (d, J = 15.9 Hz, 1 H), 7.26–7.39 (m, 7 H), 7.52 (d, J = 7.6 Hz, 2 H), 7.67 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ 21.0, 64.4, 125.0, 125.9, 126.7, 127.6, 127.9, 128.7, 128.9, 130.1, 131.4, 133.0, 137.0, 137.2, 170.8; IR (neat) 1740 cm^{-1} (C=O); HREIMS calcd for $C_{17}H_{16}O_2$ 252.1150, found 252.1144.

o-(Acetoxymethyl)(1-propenyl)benzene (16b). Characterized as a 1:1.3 mixture of E- and Z-isomers. E-Isomer: ^{1}H NMR δ 1.94 (dd, J = 6.7, 1.8 Hz, 3 H), 2.10 (s, 3 H), 5.16 (s, 2 H), 6.15 (dq, J = 15.6, 6.7 Hz, 1 H), 6.61 (dd, J = 15.6, 1.8 Hz, 1 H), 7.19–7.33 (m, 3 H), 7.46 (d, J = 7.9 Hz, 1 H). Z-Isomer: ^{1}H NMR δ 1.71 (dd, J = 7.0, 1.8 Hz, 3 H), 2.09 (s, 3 H), 5.09 (s, 2 H), 5.88 (dq, J = 11.6, 7.0 Hz, 1 H), 6.51 (dd, J = 11.6, 1.8 Hz, 1 H), 7.19–7.33 (m, 3 H), 7.38 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 14.3, 18.8, 20.9, 21.0, 64.4 (2 C), 126.1, 126.88, 126.92, 127.3, 127.5, 127.9, 128.4, 128.7, 128.8, 128.9, 129.6 (2 C), 132.1, 133.7, 136.8, 137.6, 170.9 (2 C); IR 1740 cm^{-1} (C=O); HREIMS calcd for $C_{12}H_{14}O_2$ 190.0993, found 190.0997.

7,8-Benzo-2-methyl-4-oxabicyclo[3.3.0]oct-1-en-3-one (17). Colorless crystals: mp 136–137 °C, ^{1}H NMR δ 2.07 (d, J = 2.1 Hz, 3 H), 2.81 (dd, J = 14.7, 7.3 Hz, 1 H), 3.41 (dd, J = 14.7, 7.3 Hz, 1 H), 5.39 (tq, J = 7.3, 2.1 Hz, 1 H), 7.36-7.44 (m, 3 H), 7.60 (m, 1 H); ^{13}C NMR δ 9.3, 36.5, 84.0, 118.5, 124.0, 126.6, 128.1, 131.0, 132.6, 145.3, 165.3, 176.3; IR (KBr) 1738 (C=O), 1686 cm^{-1} (C=C); HREIMS calcd for $C_{12}H_{10}O_2$ 186.0681, found 186.0705.

1-Benzyl-2-indanone (18a).[33] Yellow oil: ^{1}H NMR δ 2.99 (dd, J = 13.7, 8.2 Hz, 1 H), 3.26 (d, J = 22.6 Hz, 1 H), 3.33 (dd, J = 13.7, 4.7 Hz, 1 H), 3.47 (d, J = 22.6 Hz, 1 H), 3.78 (dd, J = 8.2, 4.7 Hz, 1 H), 6.95 (d, J = 7.3 Hz, 1 H), 7.07 (d, J = 7.8 Hz, 2 H), 7.16–7.24 (m, 6 H); ^{13}C NMR δ 37.9, 43.2, 54.5, 124.7, 125.2, 126.5, 127.2, 127.5, 128.3, 129.4, 136.9, 138.1, 141.3, 217.1; IR (neat) 1752 cm^{-1} (C=O); HREIMS calcd for $C_{16}H_{14}O$ 222.1045, found 222.1039.

1-Ethyl-2-indanone (18b).[34] GC-MS m/e (rel inten) 160 (30, M$^+$), 159 (26), 132 (57), 131 (51), 117 (100), 116 (75), 115 (35), 91 (21), 77 (16).

Preparation and Cyclization of (PhCH=CHCH=CHCH$_2$CO)MCl(PPh$_3$)$_2$ (8; M = Pd, Pt). 4 (0.447 g, 2.5 mmol) was added to a toluene (15 mL) solution of Pd(CO)(PPh$_3$)$_3$ (0.766 g, 0.83 mmol) under a CO atmosphere at room temperature. After stirring for 30 min, hexane was added to the solution, and yellow powder precipitated was collected, washed with hexane, and dried to give (PhCH=CHCH=CHCH$_2$CO)PdCl(PPh$_3$)$_2$ (**8a**) (0.659 g, 94%). Analytically pure sample was obtained by recrystallization from benzene–hexane under CO: ^{1}H NMR δ 2.87 (d, J = 7.3 Hz, 2 H), 5.73 (dd, J = 15.2, 10.3 Hz, 1 H), 5.85 (dt, J = 15.2, 7.3 Hz, 1 H), 6.54 (d, J = 15.6 Hz, 1 H), 6.87 (dd, J = 15.6, 10.3 Hz, 1 H), 7.1–7.5, 7.7-8.3 (m, 35 H); IR (KBr) 1674 cm^{-1} (C=O). Anal. Calcd for $C_{48}H_{41}OClP_2Pd$: C, 68.83; H, 4.93; Cl, 4.23. Found: C, 69.09; H, 5.12; Cl, 4.20. **8a** was also obtained in a quantitative yield from a reaction conducted under 20 atm of CO. (PhCH=CHCH=CHCH$_2$CO)PtCl(PPh$_3$)$_2$ (**8b**) was prepared by a similar procedure in a quantitative yield. White powder: ^{1}H NMR δ 2.64 (d, J = 7.3 Hz, 2 H), 5.73 (dd, J = 15.1, 10.4 Hz, 1 H), 5.88 (dt, J = 15.1, 7.3 Hz, 1 H), 6.53 (d, J = 15.6 Hz, 1 H), 6.90 (dd, J = 15.6, 10.4 Hz, 1 H), 7.1–7.5, 8.1–8.2 (m, 35 H); IR (KBr) 1653 cm^{-1} (C=O). Anal. Calcd for $C_{48}H_{41}OClP_2Pt$: C, 62.24; H, 4.46; Cl, 3.83. Found: C, 63.32; H, 4.79; Cl, 3.94.

A benzene (10 mL) solution containing **8a** (0.1003 g, 0.12 mmol), Ac_2O (2 mL), and NEt_3 (3 mL) was heated in a stainless autoclave pressurized with CO (50 atm) at 160 °C for 1 h with stirring. GC analysis of the reaction mixture indicated that **2a** was formed in 41% yield. Similar reaction of **8b** gave **2a** in 51%.

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Supplementary Material Available: ^{1}H NMR spectra of **1a-i, 1l-o, 2b, 2d-i, 2n-o, 5, 6, 7, 14a,b, 15a,b, 16a,b,** and **17** (32 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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