# Palladium-Catalyzed Cyclization of 1-Iodo-Substituted 1,4-, 1,5-, and 1,6-Dienes as Well as of 5-Iodo-1,5-dienes in the Presence of Carbon Monoxide

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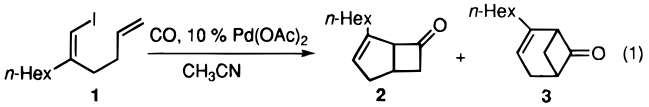
**Abstract:** A series of $\omega$-alkene-containing alkenyl iodides were prepared via (a) various allyl-, homoallyl-, and higher $\omega$-alkenylmetalation reactions of alkynes involving Zn, Al−Zr, Zn−Zr, and Cu, (b) *trans*-hydroalumination and Cu-catalyzed *trans*-carbomagnesiation of propargyl alcohols, and (c) Zr-promoted alkyne−alkene coupling. Various factors affecting three cyclic acylpalladation (Types I−III Ac-Pd) and three cyclic carbopalladation (Types I−III C-Pd) processes of the $\omega$-alkene-containing alkenyl iodides under the influence of CO and Pd−phosphine catalysts have been delineated. In the presence of methanol or other alcohols at relatively high pressures (30−100 atm) of CO (Conditions IV), Type II Ac-Pd products containing five-membered ketones, such as **22**, **26**−**28**, **30**, and **32**, can be obtained generally in high yields. The order of rates of various carbonylative cyclization reactions producing five-membered rings is as follows: lactonization > Type II Ac-Pd reaction > *C*-enolate trapping with malonate anion. The preparation of six-membered ketones via the Type II Ac-Pd process is less satisfactory. Attempts to prepare seven-membered ketones failed, and no attempts were made to obtain small ring ketones. In the absence of an external nucleophile (Conditions I and II), α-alkylidenecyclopentanones can be obtained in high yields via the Type I Ac-Pd process in cases where the $\omega$-alkenyl group is 1,2-disubstituted. Terminal vinyl-containing 1,4-pentadienyl iodides can give Type I Ac-Pd products, *e.g.*, **31**, **33**, **35**, **56**−**58**, and **65**, in moderate to good yields only with the stoichiometric amount of a Pd−phosphine complex. In sharp contrast, 1,5-hexadienyl iodides give predominantly Type III Ac-Pd products, *e.g.*, **5**, **60**, **63**, and **64**, in moderate yields under comparable conditions. The Type III Ac-Pd products can be cleanly converted to the corresponding Type II Ac-Pd products via alcoholysis. At 1 atm of CO in the presence of an alcohol (Conditions III), noncarbonylative cyclic carbopalladation process (Types I−III C-Pd) can be observed along with premature esterification. With terminal vinyl-containing alkenyl iodides, the cyclic Heck reaction (Type I C-Pd) is the dominant path. In cases where the $\omega$-alkenyl group is 1,1-disubstituted, however, the Type II C-Pd process can be observed selectively using either *i*-PrOH as an external nucleophile or a mixture consisting of $H_2O$, MeOH, and DMF (1:10:20). Collectively, the three Ac-Pd processes and the Type II C-Pd process in conjunction with novel and efficient methods for the preparation of the required $\omega$-alkene-containing alkenyl iodides provide a potentially useful methodology for the preparation of five- and six-membered-ring compounds.

In the preceding paper[1,2] we disclosed and discussed various Pd-catalyzed reactions of $\omega$-alkene-containing aryl halides via cyclic acylpalladation under four different conditions shown below: Conditions I, CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, $NEt_3$ (1.5-4 equiv); Conditions II, CO (30−100 atm), 5% $Cl_2Pd(PPh_3)_2$, $NEt_3$ (1.5−4 equiv); Conditions III, CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, $NEt_3$ (1.5−4 equiv), ROH (R = Me, Et, or *i*-Pr); and Conditions IV, CO (30−100 atm), 5% $Cl_2Pd(PPh_3)_2$, $NEt_3$ (1.5−4 equiv), ROH (R = Me, Et, or *i*-Pr).

In short, the use of 30−100 atms of CO (Conditions II and IV) is advantageous to induce cyclic acylpalladation (Ac-Pd). In cases where the cyclic Ac-Pd process is favorable, the Type I Ac-Pd reaction is dominant in the absence of an external nucleophile, such as MeOH (Conditions II), while the use of a suitable alcohol at 30−100 atm of CO (Conditions IV) induces the Type II Ac-Pd reaction. In the absence of an external trapping agent at 30−100 atm of CO (Conditions II), the Type III Ac-Pd process can proceed and compete with the Type I Ac-Pd process. The absence of an external trapping agent (Conditions I and II) can also induce apparently polymeric processes[3] as serious side reactions, especially with terminal alkene-containing substrates, while premature alcoholysis of putative acylpalladium intermediates can be competitive at 30−100 atm of CO in the presence of an alcohol (Conditions IV). Both *exo*-mode and *endo*-mode cyclization processes producing 5- and 6-membered Ac-Pd products have been observed. Neither smaller nor larger rings have been obtained via cyclic Ac-Pd reactions. In fact, attempts to obtain 7-membered Ac-Pd products or, in some cases, even 6-membered Ac-Pd products have led to non-carbonylative cyclic carbopalladation (C-Pd) reactions. Both cyclic Heck reaction (Type I C-Pd process) and Type II C-Pd reaction involving the cyclic carbopalladation−carbonylative esterification tandem have been observed.

In the corresponding reaction of alkenyl halides some additional cyclization processes must be considered in addition to the three Ac-Pd and two C−Pd reactions. Thus, one dienyl iodide **1** gave **2** and **3**[2b] which were thought to arise via [2 + 2] ketene cycloaddition (eq 1). In cases where cyclic C-Pd



(1)

reactions are observed even in the presence of CO, the Type

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

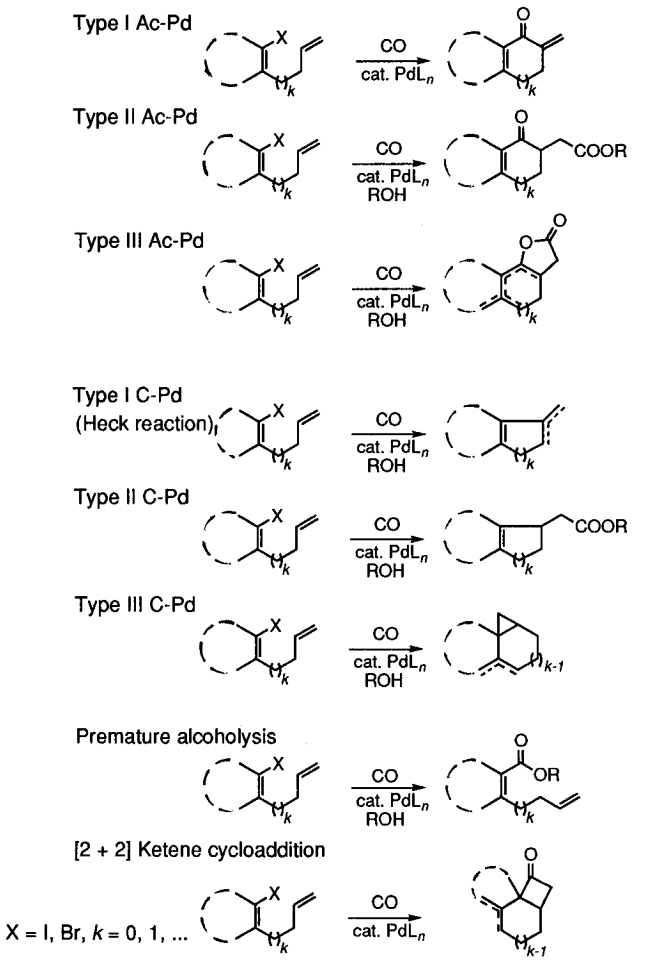
(1) Negishi, E.; Copéret, C.; Ma, S.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* Previous paper in this issue.

(2) For preliminary communications reporting some of the results discussed herein, see: (a) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761. (b) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (c) Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986**, *27*, 4869. (d) Negishi, E.; Sawada, H.; Tour, J. M.; Wei, Y. *J. Org. Chem.* **1988**, *53*, 913. (e) Zhang, Y.; O'Connor, B.; Negishi, E. *J. Org. Chem.* **1988**, *53*, 5588.

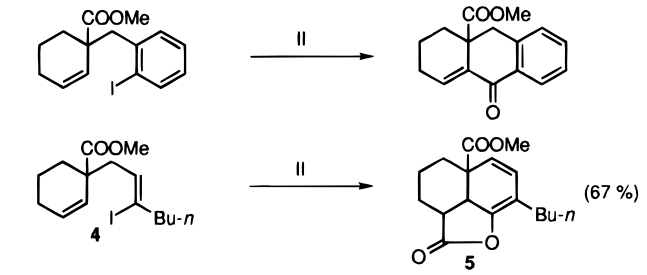
(3) (a) Tsuji, J.; Hosaka, S. *J. Polym. Lett.* **1965**, *3*, 705. (b) Sen, A.; Lai, T. *J. Am. Chem. Soc.* **1982**, *104*, 3520.

S0002-7863(95)03320-8 CCC: $12.00 

**Scheme 1**




**Scheme 2**




II = CO (40 atm), 5 % $Pd(PPh_3)_4$, $NEt_3$ (1.5 equiv), THF-$CH_3CN$, 100°C

III C-Pd process involving cyclopropanation[4] is also available to alkenyl halides. Even within the category of acylpalladation there can be significant differences between aryl and alkenyl halides, as eloquently indicated by the results shown in Scheme 2.[2e,5] It may be anticipated that alkenyl halides are generally more prone to the Type III Ac-Pd reaction. With these preliminary findings[2] in mind we undertook to investigate the Pd-catalyzed cyclization reactions of $\omega$-alkene-containing alkenyl iodides under the influence of 1−100 atm of CO either in the presence or absence of an external alcohol (Conditions I−IV).

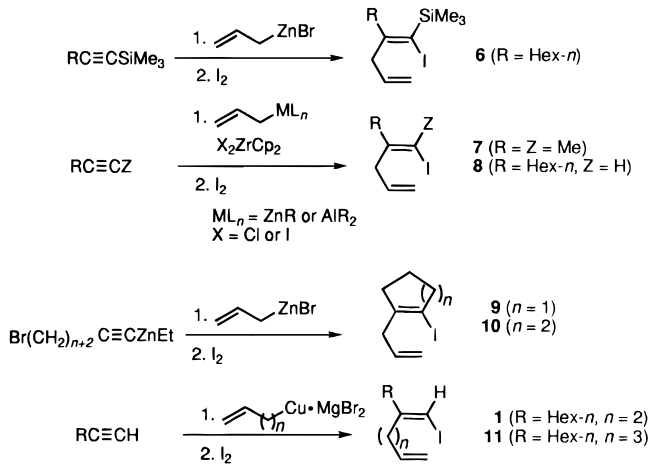
## Results and Discussion

**Preparation of $\omega$-Alkene-Containing Alkenyl Iodides.** *Cis*-carbometalation of alkynes with allyl- and homoallylmetals[6] followed by halogenolysis provides one of the shortest and most straightforward routes to the requisite dienyl halide precursors (Scheme 3). Specifically, allylzincation of 1-octynyltrimethylsilane[2a,d,7] provided **6**. The preparation of **9** and **10** was performed similarly using diallylzinc,[2d] while the Zr-catalyzed allylalumination and allylzincation[8] afforded **7** and **8**. A recently developed Zr-promoted alkyne−allyl coupling reaction[9] also offers an attractive route to dienyl halides although this reaction was not used in this study. Stereo- and regiodefined 1,5-hexadienyl halides, such as **1**, are conveniently synthesized via homoallylcupration of alkynes.[10] Similarly, **11** was prepared through the use of 4-pentenylmagnesium bromide. *Trans*-hydroalumination with $NaAlH_2(OCH_2CH_2OCH_3)_2$ (Red-Al) or $LiAlH_4$[11] and Cu-catalyzed *trans*-carbomagnesiation[12] of propargyl alcohols followed by iodinolysis provide a variety of appropriately stereodefined alkenyl iodides that either are or are convertible into 1,4-pentaidenyl and 1,5-hexadienyl iodides (Scheme 4). Thus, **12** was directly prepared by this process, while 1,5-hexadienyl iodides, such as **4** and **13**−**15**, were prepared via allyl−allyl or allyl−propargyl coupling using either allylmagnesium derivatives or $\beta,\gamma$-unsaturated enolates. Related allylation reactions of enolates were employed to prepare **16a**, **16b**, and **17**. Zirconium-promoted alkene−alkyne coupling[13] followed by iodinolysis provides appropriately stereodefined 1,4-diiodoalkenes convertible to various 1,5-hexadienyl iodides (Scheme 5). For example, **18**−**21** were prepared via this reaction followed by the Wittig reaction.

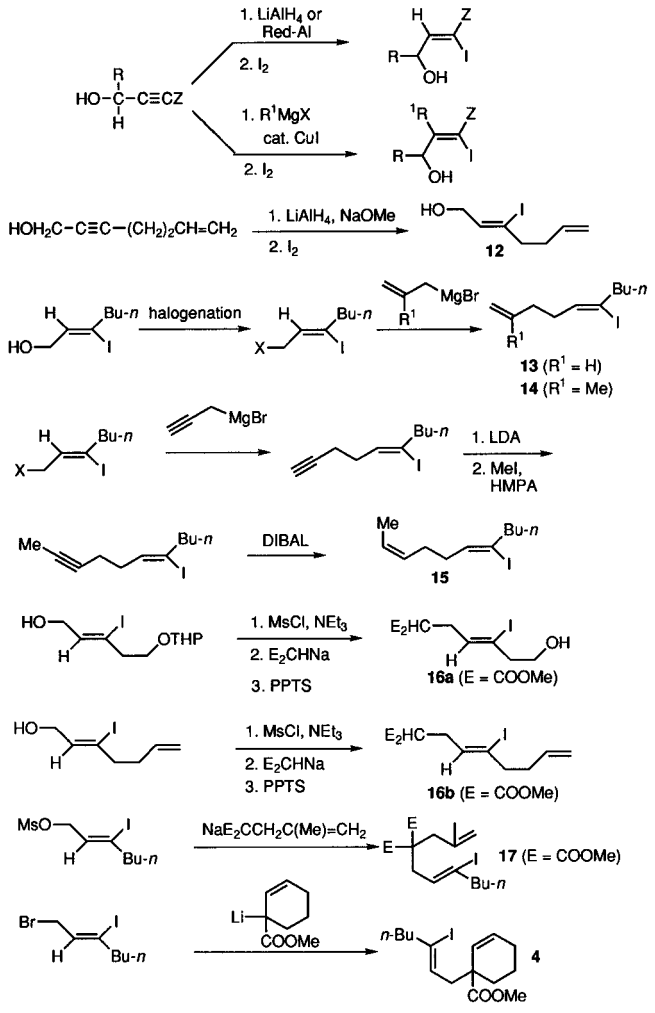
**Pd-Catalyzed Cyclic Acylpalladation of $\omega$-Alkene-Containing Alkenyl Halides in the Presence of Methanol (Type II Ac-Pd Process) (Table 1).** A series of dienyl iodides prepared as described above were treated with CO (30−100 atm) in the presence of 5 mol % of $Cl_2Pd(PPh_3)_2$, $NEt_3$ (1.5−4 equiv) and MeOH (4−100 equiv) at elevated temperatures (Conditions IV) and the experimental results are summarized in Table 1. Although varying amounts of $NEt_3$ were used, any excess of $NEt_3$ beyond 1.5 equiv had relatively insignificant effects. These results lead to the following generalizations. First, as in the corresponding reaction of aryl halides, cyclic acylpalladation may be observed only in those cases where the formation of 5- and 6-membered rings with incorporation of CO is possible. Whereas **8** and **1** were cleanly converted to Type II Ac-Pd products **22** and **23**, respectively, in excellent yields (entries 1-1 and 1-2), **11** did not yield **24** to any detectable extent (entry 1-3), the only major monomeric product being that of premature esterification, *i.e.*, **25**. Second, in cases where the $\omega$-alkenyl group is the parent vinyl group, the desired Type II Ac-Pd products containing a 5- and 6-membered ketone were produced in good yields at 30−100 atm of CO in the presence of MeOH (Conditions IV). Thus, cyclopentenone derivatives **22** and **26**−**28** were produced in 82−100% yields (entries 1-1 and 1-4 to 1-6), while the yields of cyclohexenone derivatives **23** and **29** were 73 and 50%, respectively (entries 1-2 and 1-7). Although the number of examples of cyclohexanones is very small, it does appear that formation of cyclopentanones is generally more favorable than that of cyclohexanones. Third, in cases where the $\omega$-alkenyl group is additionally substituted the Type I Ac-Pd process and premature esterification can be

(4) Owczarczyk, Z.; Lamaty, F.; Vawter, E. J.; Negishi, E. *J. Am. Chem. Soc.* **1992**, *114*, 10091.
(5) Negishi, E.; Copéret, C.; Sugihara, T.; Shimoyama, I.; Zhang, Y.; Wu, G.; Tour, J. M. *Tetrahedron* **1994**, *50*, 425.
(6) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(7) Molander, G. A. *J. Org. Chem.* **1983**, *48*, 5409.
(8) Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863.
(9) Suzuki, N.; Kondakov, D. Y.; Kageyama, M.; Kotora, M.; Hara, R.; Takahashi, T. *Tetrahedron* **1995**, *51*, 4519 and references therein.
(10) (a) Normant, J. F.; Bourgain, M. *Tetrahedron Lett.* **1971**, 2583. (b) Westmijze, H.; Kleijn, H.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1977**, 869.
(11) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245.
(12) Duboudin, J. G.; Jousseaume, B. *J. Organomet. Chem.* **1979**, *168*, 1.
(13) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, *Tetrahedron Lett.* **1993**, *34*, 687.

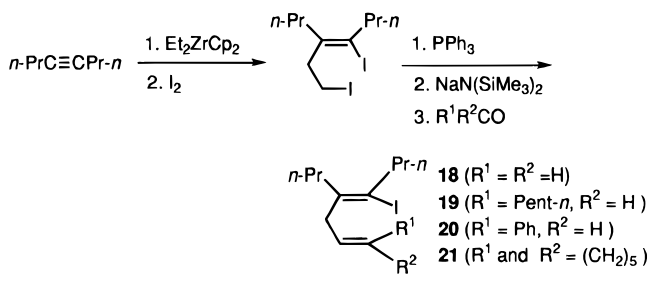
**Scheme 3**




**Scheme 4**




**Scheme 5**



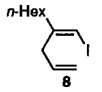
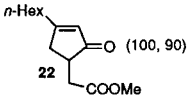
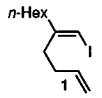
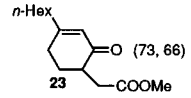
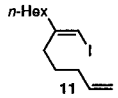
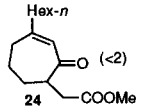
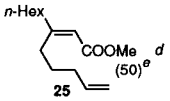
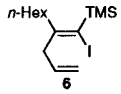
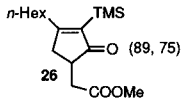
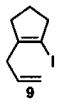
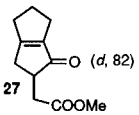
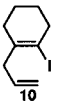
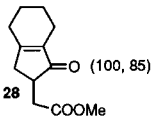
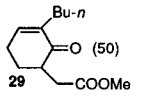
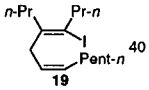
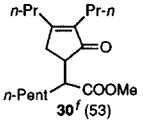
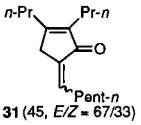
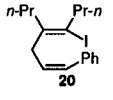
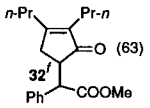
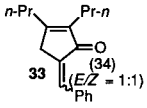
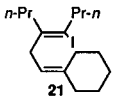
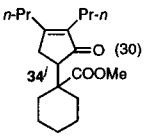
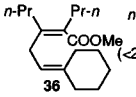
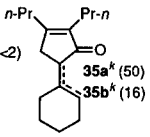
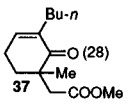
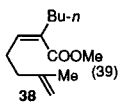
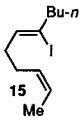
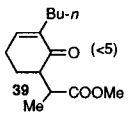
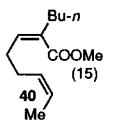
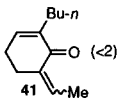
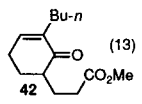

serious side reactions. Furthermore, the Type II Ac-Pd/Type I Ac-Pd ratio is very much dependent on CO pressure, solvents, amount of an external nucleophile, *e.g.*, MeOH, and substitution pattern. Thus, the results obtained with **19** indicate that the ratio of **30** to **31** is 53/45 (entry 1-8) at 40 atm of CO in DMF, but that the yield of **30** can be improved to 93% in DMF−MeOH (1:1) at 100 atm of CO (entry 1-10) at which pressure the amount of **31** was 5%. Similar results were also obtained with **20** (entries 1-11 and 1-12). In the reaction of **21** containing a trisubstituted $\omega$-alkenyl group, however, the yields of **34** and **35** were 30 and 66%, respectively, corresponding to the Type II/Type I Ac-Pd ratio of 0.7 even at 100 atm of CO (entry 1-13). Whereas cyclopentenones can be formed in moderate to high yields even in cases where the $\omega$-alkenyl group is di- and trisubstituted (entries 1-8 to 1-13), related reactions leading to the formation of cyclohexenones are more sluggish and less clean (entries 1-14 to 1-16). In these cases, premature esterification is one of the main side reactions, and some other unidentified byproducts were also formed. The yields of the desired Type II Ac-Pd products, *e.g.*, **37**, **39**, and **42**, are low (<30−35%). However, some such compounds may be obtained in higher yields by an indirect route via Type III Ac-Pd products (*vide infra*).

To further probe the scope of the Type II Ac-Pd reaction, specifically its chemoselectivity aspect, the Pd-catalyzed reaction of **12** and **16b** using 40 atm of CO, 10 equiv of MeOH, and DMF as a solvent (Conditions IV) was examined. For the sake of comparison, the corresponding reaction of **16a** was also investigated. As the results summarized in Scheme 6 indicate, the Type II Ac-Pd reaction of **12** to give **43** cannot compete with premature intramolecular esterification to give a lactone **44** (87% yield). On the other hand, the corresponding reaction of **16b** gave the Type II Ac-Pd product **45** without yielding the product of trapping by the *C*-enolate,[14] *i.e.*, **46**. As expected from the above, lactonization to produce **47** ($E/Z$ = 2) completely overshadowed *C*-enolate trapping to give **48**. Although the position of the iodine-bearing double bond in each of the three test substrates is not totally neutral with respect to the two competing processes, it appears reasonable to tentatively conclude that the order of relative rates of the three processes is the following: lactonization > Type II Ac-Pd reaction > *C*-enolate trapping.

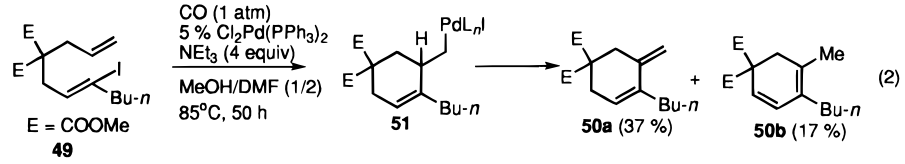
**Type II Cyclic Carbopalladation of 1-Iodo-1,5-hexadienes and 1-Iodo-1,7-heptadienes (Type II C-Pd Process) (Table 2).** As discussed above, our earlier attempts to observe the formation of 7-membered enones via the cyclic Ac-Pd process led only to the formation of premature esterification product, such as **25** (entry 1-3), and other unidentified products. Further investigation with **49** and **17** has indicated, whereas cyclic acylpalladation leading to the formation of cycloheptenones may not be observed, other interesting and potentially useful cyclic processes can be observed at lower pressures of CO. Specifically, treatment of **49** with 1 atm of CO, a 2/1 mixture of DMF, and MeOH at 85 °C for 50 h (Conditions III) merely led to the formation of the cyclic Heck reaction[15] (Type I C-Pd) products **50a** and **50b** in 54% combined yield (**50a**/**50b** = 2-3) without incorporation of either CO or MeOH (eq 2). In fact, very similar results were obtained in the absence of CO and MeOH. Evidently a putative intermediate **51** undergoes $\beta$-dehydropalladation with exclusion of other potentiall competitive processes.

In sharp contrast, the corresponding reaction of **17** presumably gives initial carbopalladation products containing no $\beta$-hydrogen, which can be further converted to **52**, **53**, and/or **54**, as summarized in Table 2. As expected from similar results reported earlier,[4] **17** gives the Type III C-Pd product **53** in 75% yield in the absence of CO and MeOH (entry 2-8). At 1 atm of CO and the heating bath temperature of ca. 65 °C in MeOH,

**Table 1.** Pd-Catalyzed Carbonylation of $\omega$-Alkene-Containing Alkenyl Iodides in the Presence of Methanol at 30−100 atm of CO (Conditions IV[a])

| entry | substrate | CO, atm | MeOH, equiv | solvent | temp, °C | time, h | products (yield,[b] %) Type II Ac-Pd | premature methanolysis | others |
|---|---|---|---|---|---|---|---|---|---|
| 1-1 |  **8** | 40 | 4 | MeCN-$C_6H_6$ (1:1) | 100 | 24 |  **22** (100, 90) | *c* | *c* |
| 1-2 |  **1** | 40 | 4 | MeCN-$C_6H_6$ (1:1) | 100 | 24 |  **23** (73, 66) | *d* | *d* |
| 1-3 |  **11** | 40 | 4 | MeCN-$C_6H_6$ (1:1) | 100 | 24 |  **24** (<2) |  **25** (50)[e] | *d* |
| 1-4 |  **6** | 40 | 4 | MeCN-$C_6H_6$ (1:1) | 100 | 24 |  **26** (89, 75) | *c* | *c* |
| 1-5 |  **9** | 40 | 4 | MeCN-$C_6H_6$ (1:1) | 100 | 24 |  **27** (*d*, 82) | *d* | *d* |
| 1-6 |  **10** | 40 | 4 | MeCN-$C_6H_6$ (1:1) | 100 | 24 |  **28** (100, 85) | *c* | *c* |
| 1-7 |  **13** | 30 | 4 | DMF | 100 | 24 |  **29** (50) | *c* | *d* |
| 1-8 |  **19** | 40 | 4 | DMF | 100 | 40 |  **30**[f] (53) | *c* |  **31** (45, *E*/*Z* = 67/33) |
| 1-9 | **19** | 55 | 100 | MeOH[g] | 100 | 48 | **30**[f] (76) | *c* | **31** (14, *E*/*Z* = 80/20) |
| 1-10 | **19** | 100 | 25 | DMF-MeOH (1:1) | 100 | 69 | **30**[h] (93) | *c* | **31**[i] (5) |
| 1-11 |  **20** | 40 | 4 | DMF | 100 | 4 |  **32**[f] (63) | *c* |  **33** (34) (*E*/*Z* = 1:1) |
| 1-12 | **20** | 100 | 50 | DMF-MeOH (1:1) | 100 | 24 | **32**[f] (94) | *c* | **33** (trace) |
| 1-13 |  **21** | 100 | 50 | DMF-MeOH (1:1) | 100 | 37 |  **34**[j] |  **36** (<2) |  **35a**[k] (50) **35b**[k] (16) |
| 1-14 |  **14** | 40 | 4 | DMF | 100 | 17 |  **37** (28) |  **38** (39) | *d* |
| 1-15 |  **15** | 40 | 8 | DMF | 100 | 24 |  **39** (<5) |  **40** (15) |  **41** (<2) |
| 1-16 | **15** | 70 | 4 | MeCN | 100 | 24 | **39** (21) | **40** (10) |  **42** (13) |

[a] See text. [b] NMR yield. The second number in parentheses is the isolated yield. [c] <2%, if any. [d] Not determined. [e] By GLC. [f] A 60/40 mixture of two diastereomers. [g] $K_2CO_3$ (2 equiv) was used as a base in place of $NEt_3$. [h] A 54/46 mixture of two diastereomers. [i] Only the *E* isomer was detected. [j] An 90/10 mixture of the two diastereomers. [k] **35a**: *exo*, **35b**: *endo*.




**Scheme 6**

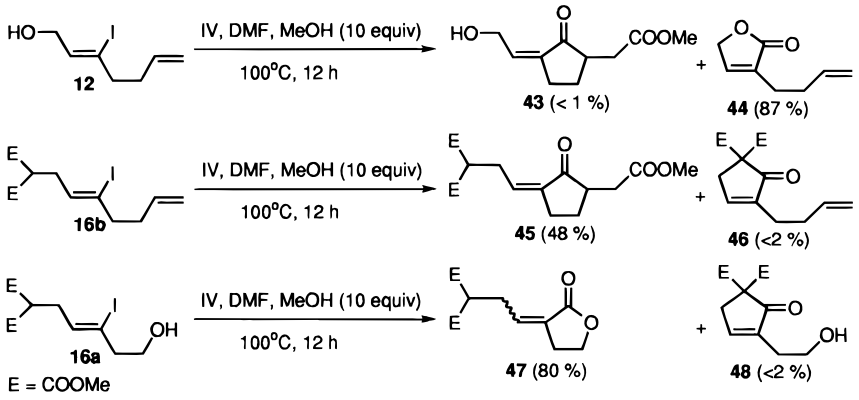
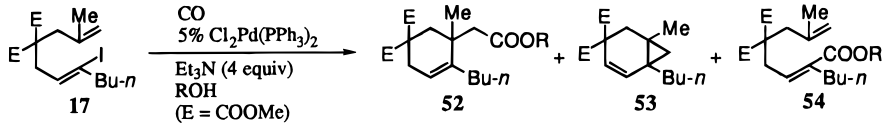



**Table 2.** Pd-Catalyzed Reaction of 2-Methyl-4,4-bis(methoxycarbonyl)-7-iodo-1,6-undecadiene in the Presence of CO and Alcohols.




| entry | ROH and solvent | CO presssure, atm | temp,[a] °C | time, h | product yield,[b] % 52 | 53 | 54 |
|---|---|---|---|---|---|---|---|
| 2-1 | MeOH | 1 | 65 | 40 | 18 | <1 | 82(73) |
| 2-2 | MeOH | 1 | reflux | 30 | 52 | 23 | 22 |
| 2-3 | EtOH | 1 | reflux | 24 | 30(26) | 2 | 59(45) |
| 2-4 | *i*-PrOH | 1 | 85 | 24 | 53 | 3 | 27 |
| 2-5 | *i*-PrOH | 1 | reflux | 24 | 64(55) | 10 | 6 |
| 2-6 | MeOH-DMF (1/2) | 1 | 85 | 1 | 63 | 8 | <3 |
| 2-7 | MeOH-DMF-$H_2O$ (1/2/0.1) | 1 | 85 | 1 | 81(74) | 3 | <3 |
| 2-8 | $CH_3CN$[c] | none | reflux | 48 | - | 75(71) | - |

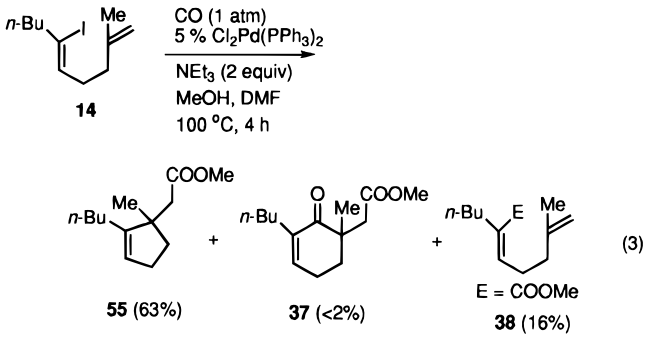
[a] Heating bath temperature. [b] By NMR. The numbers in parentheses are isolated yields. [c] Listed for comparison. For similar results, see ref. 4.

where no vigorous boiling of MeOH was observed, the premature esterification product **54a** was obtained in 82% yield along with an 18% yield of **52a** (entry 2-1). At somewhat higher bath temperature, where vigorous refluxing was observed, the desired **52a** became the major product (52%), but **53** and **54a** were also formed to the extent of 23 and 22% yields, respectively (entry 2-2). In order to suppress premature esterification, MeOH was replaced with EtOH and *i*-PrOH. With the latter as both trapping agent and solvent, the yields of **52c**, **53**, and **54c** were 64, 10, and 6%, respectively (entry 2-5). Similar results were obtained using a DMF−MeOH mixture (2/1 by volume) (entry 2-6). However, by far the most satisfactory results were obtained with a medium consisting of DMF, MeOH, and $H_2O$ in a 20/10/1 ratio. The yield of the Type II C-Pd product[16,17] **52a** was 81%, and those of **53** and **54a** were ≤2−3% (entry 2-7). In summary, it now is possible to produce selectively and in high yield **52**, **53**, or **54** from **17**.

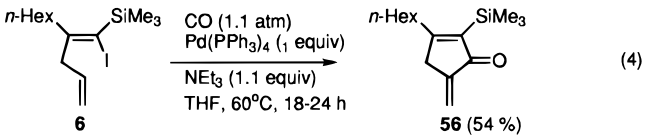
Cyclopropanation of homoallylpalladium derivatives has been identified as one of the major side reactions in the cyclic carbopalladation involving the interaction of alkenylpalladiums with 1,1-disubstituted alkenes, which can lead to the formation of vinylcyclopropanes or ring-expanded "apparent" endo-mode carbopalladation products.[4,18] The results summarized in Table 2 now indicate that, in the presence of CO (1 atm) and a suitable alcohol, *e.g.*, MeOH, cyclic carbopalladation, *i.e.*, the Type II C-Pd process, can be achieved with nearly complete suppression of cyclopropanation and premature esterification. Although somewhat less clean, similar results were also observed with **14** (eq 3).

**Pd-Catalyzed or Pd-Promoted Cyclic Acylpalladation of ω-Alkene-Containing Alkenyl Halides in the Absence of External Nucleophiles (Type I and Type III Ac-Pd Processes) (Table 3).** The first example of the Type I Ac-Pd reaction of

(14) Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018.
(15) For a review, see: Heck, R. F *Org. React.* **1982**, *27*, 345.
(16) (a) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454. (b) Sugihara, T.; Copéret, C.; Owczarczyk, Z.; Harring, L. S.; Negishi, E. *J. Am. Chem. Soc.* **1994**, *116*, 7923.
(17) (a) Grigg, R.; Kennewell, P.; Teasdale, A. *J. Tetrahedron Lett.* **1992**, *33*, 7789. (b) Grigg, R.; Redpath, J.; Sridharan, V.; Wilson, D. *Tetrahedron Lett.* **1994**, *35*, 4429.
(18) Negishi, E. *Pure Appl. Chem.* **1992**, *64*, 323.



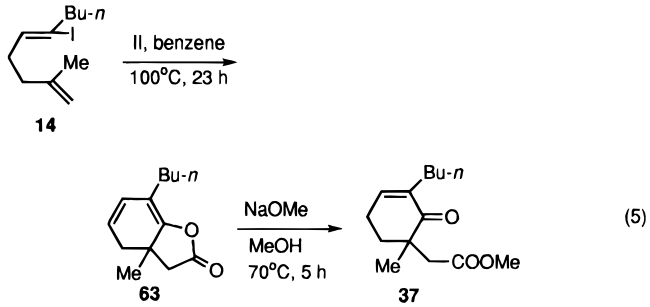

$\omega$-alkene-containing alkenyl halide reported by us in 1983[2a] involved the conversion of **6** into **56** (eq 4). Under the conditions




used, the reaction was only stoichiometric in Pd. Several years later, we obtained another example of the Type I Ac-Pd reaction shown in Scheme 2, which turned out to be catalytic in Pd.[2e,5] Another point of interest is to examine the extent to which the Type III Ac-Pd process competes with the Type I Ac-Pd process. The results shown in Scheme 2 suggest that alkenyl halides are more prone to the Type III Ac-Pd process than the corresponding aryl halides. The third objective of this part of the study is to probe the scope of the [2 + 2] ketene cycloaddition, which was observed with most of the benzylic halides examined to date,[19] as well as with **1**.

A series of $\omega$-alkene-containing alkenyl iodides were carbonylated under Conditions II (40−100 atm of CO in the absence of nucleophiles), and the results are summarized in Table 3. Also included in Table 3 are the results of carbonylation of **6**, **7**, **9**, and **18** with 1 atm of CO in the presence of the stoichiometric amount of $Pd(PPh_3)_4$ (entries 3-1 to 3-4). With 5−20 mol % of a Pd−phosphine catalyst, these substrates were converted to monomeric cyclic products only in low yields. For example, **18** was converted to **65** in ≤21% yields (entries 3-5 to 3-7). On the other hand, di- or trisubstituted alkene-containing substrates **19**−**21** can be converted to the corresponding Type I Ac-Pd products, *i.e.*, **31**, **33**, and **35**, respectively, in moderate to excellent yields (entries 3-10 to 3-12). No other monomeric cyclic products, such as Type III Ac-Pd products, are formed in significant yields. Interestingly, 1,5-hexadienyl iodides, *i.e.*, **4** and **13**−**15**, afforded under similar conditions Type III Ac-Pd products, *i.e.*, **5**, **60**, **63**, and **64**, respectively, in moderate to good yields (entries 3-9, 3-13, and 3-16 to 3-18). In these reactions, the yields of the Type I Ac-Pd products were less than 5%, except that of **41** (34%) (entry 3-18). The contrasting behavior exhibited by 1,4-pentadienyl and 1,5-hexadienyl iodides may be attributable to the greater strain energy associated with $\gamma$-lactones containing a bicyclo[3.3.0]octane framework than that in $\gamma$-lactones containing a bicyclo[4.3.0]nonane framework. In cases where $Pd(PPh_3)_4$ or $Cl_2Pd(PPh_3)_2$ was used as a catalyst, the extent of [2 + 2] ketene cycloaddition was negligible. However, carbonylation of **1** using $Pd(OAc)_2$ as a catalyst did produce **2** in 36% isolated yield along with a minor amount of **3** (entry 3-14).

It is worth noting that treatment of **63** with NaOMe in MeOH cleanly gave **37** in 85% yield (eq 5). The use of aqueous HCl in place of NaOMe in MeOH led to several products. Since the yield of **37** obtained from **14** at 40 atm of CO in the presence of MeOH (4 equiv) (Conditions IV) is limited to 28%, due to competitive premature esterification, the above-mentioned sequence consisting of the Type III Ac-Pd process and methanolysis provides a potentially attractive alternative.




## Conclusions

1. The Pd-catalyzed reaction of $\omega$-alkene-containing alkenyl iodides in the presence of CO can lead to three types of cyclic acylpalladation (Types I−III Ac-Pd) and three types of cyclic carbopalladation (Types I−III C-Pd) processes in addition to previously known noncyclic carbonylative esterification and polymerization processes. Although [2 + 2] ketene cycloaddition has been observed with one alkenyl iodide, *i.e.*, **1**, using $Pd(OAc)_2$ as a catalyst, this process is not competitive in cases where Pd−phosphine complexes are used as catalysts.

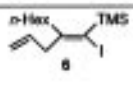
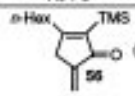
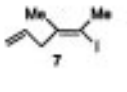
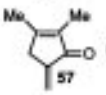
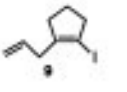
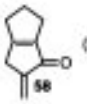
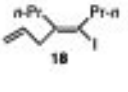
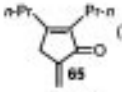
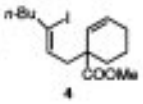
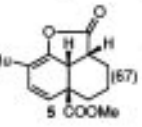
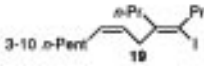
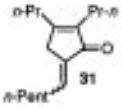
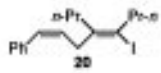
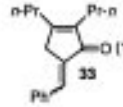
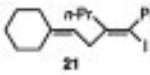
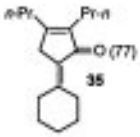
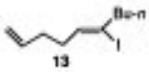
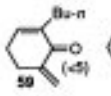
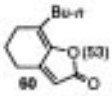
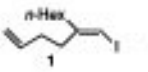
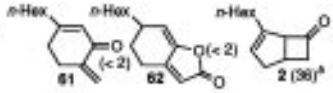
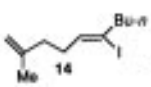
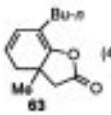
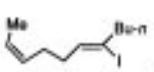
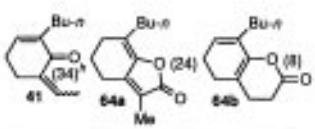
2. In the presence of methanol or other alcohols at relatively higher pressures (30−100 atm) of CO (Conditions IV), Type II Ac-Pd products containing five-membered ketones can be obtained generally in high yields. The order of rates of various carbonylative cyclization reactions producing various types of five-membered rings is the following: lactonization > Type II Ac-Pd reaction > *C*-enolate trapping with malonate anion. Conversion of 1,5-hexadienyl iodides into six-membered-ring ketones is less satisfactory, the observed yields being ≤50%, except for that of **23** which was obtained in 73% yield. Attempts to obtain seven-membered-ring ketones totally failed, and no attempts were made to obtain small-ring ketones.

3. In the absence of an alcohol or any external nucleophile (Conditions I and II), a considerably different reaction profile has emerged. Thus, 1,4-pentadienyl iodides containing the parent vinyl group can be converted to Type I Ac-Pd products in moderate to good yields only with a stoichiometric amount of a Pd−phosphine catalyst. On the other hand, those containing a 1,2-disubstituted alkene can be converted to Type I Ac-Pd products in high yields under catalytic conditions. Interestingly, 1,5-hexadienyl iodides do not give Type I Ac-Pd products in significant yields. Under similar conditions, the predominant course of reaction is the Type III Ac-Pd process, although the observed yields have been generally modest (≤67%).

4. At 1 atm of CO in the presence of an alcohol (Conditions III), three noncarbonylative cyclic carbopalladation processes, as well as the Type II Ac-Pd process and premature esterification, compete. At relatively high temperatures the Type II Ac-Pd process leading to the formation of six-membered-ring ketones can be suppressed. In cases where the $\omega$-alkenyl group is the parent vinyl group, the Type I C-Pd process, *i.e.*, cyclic Heck reaction, along with premature esterification, is the dominant path. On the other hand, in cases where the $\omega$-alkenyl group is a 1,1-disubstituted alkene, the Type II C-Pd process can take place selectively by supressing premature esterification and cyclopropanation (Type III C-Pd process). Although the use of *i*-PrOH in place of MeOH in conjunction with high reaction temperatures is effective in observing the Type II C-Pd process, the most satisfactory conditions observed to date involve the use of a 1:10:20 mixture of $H_2O$, MeOH, and DMF.

(19) Wu, G.; Shimoyama, I.; Negishi, E. *J. Org. Chem.* **1991**, *56*, 6506.

**Table 3.** Pd-Catalyzed or Pd-Promoted Cyclic Acylpalladation of $\omega$-Alkene-Containing Alkenyl Halides in the Absence of External Nucleophiles

| entry | substrate | CO, atm | catalyst (mol %) | solvent | temp, °C | time, h | products (yield,[a] %) Type I Ac-Pd | Type II Ac-Pd | other monomeric products |
|---|---|---|---|---|---|---|---|---|---|
| 3-1 |  6 | 1 | $Pd(PPh_3)_4$ (100) | THF | 60 | 24 |  56 (54)[b] | c | c |
| 3-2 |  7 | 1 | $Pd(PPh_3)_4$ (100) | THF | 60 | 24 |  57 (51)[b] | c | c |
| 3-3 |  9 | 1 | $Pd(PPh_3)_4$ (100) | THF | 60 | 24 |  58 (75)[b] | c | c |
| 3-4 |  18 | 1 | $Pd(PPh_3)_4$ (100) | THF | 60 | 24 |  65 (76) | c | c |
| 3-5 | 18 | 1 | $Pd(PPh_3)_4$ (20) | THF | 60 | 36 | 65 (21) | c | c |
| 3-6 | 18 | 1 | $Pd(PPh_3)_4$ (5) | THF | 60 | 36-48 | 65 (3-10) | c | c |
| 3-7 | 18 | 1 | $Cl_2Pd(PPh_3)_2$ (5) or $Pd(PPh_3)_4$ (5) | DMF | 100 | 36 | 65 (14-17) | c | c |
| 3-8 | 18 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | DMF | 100 | 12 | 65 (18) | c | c |
| 3-9 |  4 | 40 | $Pd(PPh_3)_4$ (5) | THF MeCN (1:1) | 100 | 18 | c |  5 (67) | c |
| 3-10 |  19 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | DMF | 100 | 12 |  31 (82)[d] | e | e |
| 3-11 |  20 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | DMF | 100 | 10 |  33 (100)[f] | e | e |
| 3-12 |  21 | 100 | $Cl_2Pd(PPh_3)_2$ (5) | DMF | 100 | 24 |  35 (77) | e | e |
| 3-13 |  13 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | benzene | 100 | 47 |  59 (<5) |  60 (53) | e |
| 3-14 |  1 | 40 | $Pd(OAc)_2$ (10) | MeCN | 100 | 24 |  61 (< 2) 62 (< 2) 2 (36)[h] | | |
| 3-15 | 1 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | benzene | 100 | 22 | 61 (< 2) | 62 (< 5 %) | 2 (< 2) |
| 3-16 |  14 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | benzene | 100 | 23 | g |  63 (46) | e |
| 3-17 | 14 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | DMF | 100 | 24 | g | 63 (47) | e |
| 3-18 |  15 | 40 | $Cl_2Pd(PPh_3)_2$ (5) | benzene | 100 | 22 |  61 (34)[h] 64a (24) 64b (8) | | |

[a] NMR yield unless otherwise mentioned. [b] Isolated yield. [c] Not determined. [d] $E/Z = 70/30$. [e] Less than 2%, if any. [f] $E/Z = 45/55$. [g] Not a possible product. [h] $E/Z = 40/60$.

5. Various factors affecting several carbonylative and non-carbonylative cyclization reactions of $\omega$-alkene-containing alkenyl iodides under the influence of CO and Pd-phosphine catalysts have been delineated. The generalizations presented

in this work and summarized above may now be used in a predictive manner. Although the scope of each process may be limited, each can take place selectively to give in many cases one predominant product, and the three Ac-Pd processes and the Type II C-Pd process promise to provide synthetically attractive routes to five- or six-membered-ring compounds.

## Experimental Section

**General Procedures.** All reactions were conducted under a dry Ar atmosphere. Gas chromatographic measurements were performed on SE-30 (Chromosorb W) columns with appropriate saturated hydrocarbon standards. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ on Varian Gemini-200, VXR-500, and GE QE-300 NMR spectrometers using $Me_4Si$ as an internal standard unless otherwise noted. All commercially available reagents were used without further purification unless otherwise noted. THF was distilled from sodium benzophenone ketyl. Benzene, $CH_3CN$, DMF, and $NEt_3$ were dried over molecular sieves 4A. The preparation of $PdCl_2(PPh_3)_2$ was performed as reported in the literature.[20] Pd-catalyzed high-pressure carbonylation experiments were carried out in a 22-mL autoclave (Parr Instrument Co.).

**Preparation of $\omega$-Alkene-Containing Alkenyl Iodides (Schemes 3−5). (a) (*Z*)-1-Iodo-2-(*n*-hexyl)-1,5-hexadiene (1).** Following the reported procedure,[6,21] 1-octyne (5.5 g, 7.4 mL, 50 mmol) was treated with a reagent obtained by mixing CuBr (8.6 g, 60 mmol) and 3-butenylmagnesium bromide (1.1 M in ether, 52 mL, 55 mmol) in ether (50 mL). The crude product mixture was cooled to −78 °C, treated with iodine (15 g, 60 mmol) in THF, and warmed to 0 °C over 30 min. The reaction mixture was poured into a mixture of 3 N HCl and pentane, filtered through Celite, extracted with pentane, washed with $NaHCO_3$ and brine, dried over $MgSO_4$, and distilled at 75−80 °C (0.5 mmHg) to afford 9.5 g (65%) of **1**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7 Hz, 3 H), 1.2−1.8 (m, 8 H), 2.0−2.6 (m, 6 H), 4.9−5.2 (m, 2 H), 5.5−6.1 (m, 2 H).

**(b) Methyl 1-(*Z*-3′-Iodo-2′-hepten-1′-yl)-2-cyclohexene-1-carboxylate (4).** The procedure of Schlessinger *et al.*[22] was used for the following alkylation. To a solution of $(i\text{-Pr})_2NH$ (1.1 g, 11 mmol) in 20 mL of THF were added successively *n*-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol, 0 °C, 5 min) and HMPA (2.15 g, 12 mmol, −78 °C, 30 min), methyl 1-cyclohexenylcarboxylate (1.4 g, 10 mmol, −78 °C, 40 min), and 1-bromo-3-iodo-2(*Z*)-heptene (3.94 g, 13 mmol) in 2 mL of THF. The mixture was stirred at −78 °C for 2 h, quenched with 3 N HCl, extracted with ether, and washed with aqueous $NaHCO_3$ and brine. Drying over $MgSO_4$, evaporation of the solvents, and flash column chromatography (1:20, ether−pentane) gave 2.65 g (73%) of **4**: $^1$H NMR 0.89 (t, $J$ = 7 Hz, 3 H), 1.4−1.7 (m, 8 H), 1.9−2.5 (m, 6 H), 3.69 (s, 3 H), 5.37 (5, $J$ = 7 Hz, 1 H), 5.69 (bd, $J$ = 7 Hz, 1 H), 5.83 (dt, $J$ = 3 and 7 Hz, 1 H); $^{13}$C NMR $\delta$ 13.89, 19.69, 21.28, 24.90, 30.60, 31.46, 45.24, 46.34, 46.91, 52.03, 112.59, 129.09, 129.42, 129.92, 175.87.

**(c) (*Z*)-1-Iodo-1-(trimethylsilyl)-2-(*n*-hexyl)-1,4-pentadiene (6).**[7] To a stirred mixture of granular zinc (8.64 g, 144 mmol) in THF (60 mL) was added dropwise allyl bromide (10.44 mL, 100 mmol) at a rate which maintained the temperature below 15 °C. After 30 min at 25 °C, 1-octynyltrimethylsilane (10.9 g, 60.0 mmol) was added, and the mixture was heated at 60 °C for 24 h, cooled to −78 °C, treated with $I_2$ (38.1 g, 150 mmol) in THF (60 mL), and stirred at −78 °C for 1 h. After the usual workup, Kugelrohr distillation (90−95 °C at 0.1 mmHg) gave an 84:16 mixture of the *Z* and *E* isomers of the title compound. ***Z*-6**: $^1$H NMR $\delta$ 0.20 (*s*, 9 H), 0.80 (t, 3 H), 1.2−1.3 (m, 8 H), 2.1−2.3 (m, 2 H), 3.1 (d, $J$ = 7 Hz, 2 H), 4.9−5.2 (m, 2 H), 5.5−5.9 (m, 1 H); $^{13}$C NMR $\delta$ 2.11, 14.02, 22.58, 29.31, 31.67, 35.54, 49.02, 108.88, 116.30, 134.17, 157.07.

**(d) 2-Iodo-3-methyl-2(*Z*)-5-hexadiene (7).** This compound was prepared according to a literature procedure.[8]

**(e) (*Z*)-1-Iodo-2-(*n*-hexyl)-1,4-pentadiene (8).**[8] Allylmagnesium bromide in ether (5.72 mL, 0.77 M, 4.4 mmol) was treated with $(i\text{-Bu})_2AlCl$ (0.88 mL, 4.4 mmol) in ether (2 mL) at 0 °C. The mixture was stirred at 25 °C for 1 h. Ether was removed under reduced pressure (0.1 mmHg, 50 °C, 1 h) and replaced with 1,2-dichloroethane (10 mL). To the resulting gray slurry were successively added at 25 °C $Cp_2ZrCl_2$ (1.16 g, 4.0 mmol) and 1-octyne (0.44 g, 4.0 mmol), and the mixture was stirred at 25 °C for 1 h. The solvent was removed under reduced pressure (0.1 mmHg), and the residue was dissolved in THF (15 mL), cooled to −78 °C, treated with $I_2$ (0.81 g, 3.2 mmol) in THF (3 mL), stirred at −78 °C for 30 min, and warmed slowly to 25 °C. After the usual workup, Kugelrohr distillation (70 °C at 0.1 mmHg) afforded 0.71 g (64%) of **8**: $^1$H NMR $\delta$ 0.85 (t, $J$ = 7 Hz, 3 H), 1.1−1.6 (m, 8 H), 2.18 (m, 2 H), 2.95 (d, $J$ = 7 Hz, 2 H), 5.0−5.2 (m, 2 H), 5.5−6.0 (m, 1 H), 5.95 (s, 1 H); $^{13}$C NMR $\delta$ 14.04, 22.57, 27.68, 28.84, 31.63, 37.25, 41.86, 75.40, 116.54, 133.92, 149.49.

**(f) 1-Iodo-2-(2′-propenyl)-1-cyclopentene (9).**[2d] 5-Iodo-1-pentyne (5.82 g, 30 mmol) in *n*-hexane (100 mL) was treated successively with *n*-BuLi (2.4 M, 12.5 mL, 30 mmol) in *n*-hexane at −90 °C for 1 h then at −78 °C for 1 h and EtZnCl (1.0 M, 33 mL, 33 mmol), prepared from 1 equiv each of $Et_2Zn$ and $ZnCl_2$ in $CH_2Cl_2$ at −78 °C, for 30 min. After warming this mixture to 0 °C over 3 h, the solvents were removed under vacuum and replaced at 0 °C with THF (100 mL). The reaction mixture was treated with allylzinc bromide, prepared from Zn (2.94 g, 45 mmol) in THF (45 mL) and allyl bromide (5.44 g, 3.9 mL, 45 mmol), at 25 °C for 12 h, quenched with $I_2$ (25.4 g, 100 mmol) in THF (50 mL) at −78 °C, and warmed to 25 °C. The reaction mixture was diluted with pentane at 0 °C, quenched with aqueous $NH_4Cl$, washed with aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine, and dried over $MgSO_4$. Distillation afforded 6.25 g (86%, 93% by GLC) of **9**: bp 71−74 °C (5 mmHg); $^1$H NMR $\delta$ 1.8−2.1 (m, 2 H), 2.1−2.5 (m, 2 H), 2.5−2.8 (m, 2 H), 2.8−3.0 (m, 2 H), 4.9−5.2 (m, 2 H), 5.56.0 (m, 1 H); $^{13}$C NMR $\delta$ 23.36, 33.83, 37.68, 44.17, 91.54, 116.10, 134.12, 145.69.

**(g) 1-Iodo-2-(2′-propenyl)-1-cyclohexene (10).** This compound was prepared according to a literature procedure.[2d]

**(h) (*Z*)-1-Iodo-2-(*n*-hexyl)-1,6-heptadiene (11).** This compound was prepared in 56% yield (bp 80−90 °C at 0.5 mmHg, Kugelrohr distillation) following the procedure for **1** using 4-pentenylmagnesium bromide instead of 3-butenylmagnesium bromide: $^1$H NMR $\delta$ 0.89 (t, $J$ = 6 Hz, 3 H), 1.1−1.7 (m, 10 H), 1.9−2.4 (m, 6 H), 4.9−5.2 (m, 2 H), 5.6−5.9 (m, 2 H).

**(i) (*Z*)-3-Iodo-2,6-heptadien-1-ol (12).**[11] A suspension of NaOMe (562 mg, 10.4 mmol) in THF (10 mL) was treated with $LiAlH_4$ in THF (1.0 M, 5.2 mL, 5.2 mmol) at 0 °C for 30 min. To this were added successively 6-hepten-2-yn-1-ol (550 m g, 5.0 mmol) in THF (5 mL) at 0 °C for 6 h, ethyl acetate (0.75 mL) at 0 °C for 15 min, $I_2$ (1.5 g, 6 mmol) in THF (10 mL) at −78 °C, concentrated $NH_4OH$ at 25 °C, aqueous $Na_2S_2O_3$, and $Et_2O$. The reaction mixture was decanted, extracted with $Et_2O$, washed with aqueous HCl and $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (90/10 pentane−$Et_2O$) afforded 303 mg (64%) of **12**: $^1$H NMR $\delta$ 2.2−2.4 (m, 2 H), 2.5−2.7 (m, 2 H), 4.17 (d, $J$ = 5.7 Hz, 2 H), 4.95−5.2 (m, 2 H), 5.6−6.0 (m, 2 H); $^{13}$C NMR $\delta$ 33.35, 44.42, 67.12, 108.90, 115.79, 134.06, 136.29; IR (neat) 3400, 1642 cm$^{-1}$; HRMS calcd for $C_7H_9I$ ($M^+ - H_2O$) 220.9927, found 220.9829.

**(j) (*Z*)-6-Iodo-1,5-decadiene (13). Preparation of (*Z*)-3-Iodo-2-hepten-1-ol.**[11] To a suspension of NaOMe (4.82 g, 89.2 mmol) in THF (89 mL) at 0 °C was added a solution of $LiAlH_4$ in THF (1.0 M, 44.6 mL, 44.6 mmol). After 30 min at 0 °C, 2-heptyn-1-ol (5.0 g, 44.6 mmol) in THF was added at 0 °C. After stirring at 0 °C for 10 h, the mixture was cooled to −5 °C and treated successively with EtOAc (7.8 mL) to destroy unreacted $LiAlH_4$ and $I_2$ (13.24 g, 52.1 mmol) in THF (50 mL) at −78 °C. The reaction mixture was quenched with aqueous $Na_2S_2O_3$ at 0 °C, extracted with ether, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (10/1 *n*-hexane−EtOAc) afforded 8.61 g (80%) of the title compound: $^1$H NMR $\delta$ 0.90 (t, $J$ = 6.5 Hz, 3 H), 1.2−1.45 (m, 2 H), 1.45−1.7 (m, 2 H), 2.50 (t, $J$ = 6.1 Hz, 2 H), 4.20 (d, $J$ = 6.0 Hz, 2 H), 5.85 (t, $J$ = 6.0 Hz, 1 H); $^{13}$C

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NMR $\delta$ 13.95, 21.50, 31.40, 44.50, 67.30, 110.60, 133.70. **Preparation of (*Z*)-1-Bromo-3-iodo-2-heptene.**[22] NBS (9.65 g, 54.2 mmol) in $CH_2Cl_2$ (180 mL) was treated successively with $Me_2S$ (4.74 mL, 54.2 mmol) at 0 °C for 10 min and (*Z*)-3-iodo-2-hepten-1-ol (8.61 g, 35.9 mmol) in $CH_2Cl_2$ (5 mL) at −20 °C. The reaction mixture was warmed to 25 °C over 12 h, quenched with cold brine, extracted with ether, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (*n*-hexane) afforded 8.51 g (78%) of the title compound: $^1$H NMR $\delta$ 0.90 (t, $J$ = 6.3 Hz, 3 H), 1.2−1.45 (m, 2 H), 1.45−1.65 (m, 2 H), 2.52 (t, $J$ = 6.5 Hz, 2 H), 4.00 (d, $J$ = 8.4 Hz, 2 H), 5.82 (t, $J$ = 8.4 Hz, 1 H); $^{13}$C NMR $\delta$ 13.95, 21.50, 31.50, 35.95, 45.00, 116.40, 130.20. **Conversion of (*Z*)-1-Bromo-3-iodo-2-heptene to (*Z*)-6-Iodo-1,5-decadiene (13): Representative Procedure.** (*Z*)-1-Bromo-3-iodo-2-heptene (2.0 g, 6.6 mmol) in THF (20 mL) was added to allylmagnesium bromide in ether (1.0 M, 7.9 mL, 7.9 mmol). After 10 h at 25 °C, the reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (*n*-hexane) afforded 1.26 g (72%) of **13**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 6.6 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.6 (m, 2 H), 2.05−2.3 (m, 4 H), 2.45 (t, $J$ = 6.7 Hz, 2 H), 4.9−5.1 (m, 2 H), 5.47 (t, $J$ = 6.7 Hz, 1 H), 5.7−5.95 (m, 1 H), $^{13}$C NMR $\delta$ 13.86, 21.26, 31.45, 32.47, 35.64, 44.82, 110.26, 115.10, 133.74, 137.69; IR (neat) 1640 cm$^{-1}$; HRMS calcd for $C_{10}H_{17}I$ 264.0375, found 264.0378.

**(k) (*Z*)-6-Iodo-2-methyl-1,5-decadiene (14).** This compound was prepared in 57% yield (0.53 g) according to the procedure for **13** starting with (*Z*)-1-bromo-3-iodo-2-heptene (1.0 g, 3.3 mmol) in THF (5 mL) and 2-methyl-2-propenylmagnesium chloride in THF, prepared by adding 2-methyl-2-propenyl chloride (1.13 g, 12.5 mmol) in THF (18 mL) to a suspension of Mg (0.61 g, 25.4 mmol) in THF (5 mL), instead of allylmagnesium bromide in ether. **14**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.7 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.6 (m, 2 H), 1.72 (s, 3 H), 2.05−2.15 (m, 2 H), 2.15−2.35 (m, 2 H), 2.45 (t, $J$ = 7.6 Hz, 2 H), 4.70 (s, 1 H), 4.72 (s, 1 H), 5.46 (t, $J$ = 7.5 Hz, 1 H); $^{13}$C NMR $\delta$ 13.84, 21.24, 22.40, 31.45, 34.52, 36.27, 44.79, 110.07, 110.45, 133.95, 144.84.

**(l) (2*Z*,6*Z*)-7-Iodo-2,6-undecadiene (15). Preparation of (*Z*)-6-Iododec-5-en-1-yne.** Propargylmagnesium bromide prepared by adding propargyl bromide (80% in toluene, 6.7 mL, 60 mmol) in THF to Mg turning (2.88 g, 120 mmol) and $HgCl_2$ (30 mg) in THF (10 mL) was added to (*Z*)-1-bromo-3-iodo-2-heptene (2.75 g, 9.1 mmol) in THF (10 mL) at 25 °C. After 3 h, the reaction mixture was refluxed overnight, quenched with aqueous $NH_4Cl$, extracted with ether, and dried over $MgSO_4$. Filtration through a short column of silica gel (*n*-hexane) afforded 2.04 g (86%) of (*Z*)-6-iododec-5-en-1-yne: $^1$H NMR $\delta$ 0.92 (t, $J$ = 7.7 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.6 (m, 2 H), 1.95 (t, $J$ = 1.3 Hz, 1 H), 2.2−2.4 (m, 4 H), 2.48 (t, $J$ = 7.5 Hz, 2 H), 5.60 (t, $J$ = 6.3 Hz, 1 H); $^{13}$C NMR $\delta$ 13.85, 17.59, 21.28, 31.43, 35.34, 44.86, 68.79, 83.49, 111.25, 132.45. **Preparation of (*Z*)-7-Iodoundec-6-en-2-yne.** LDA prepared by treating (*i*-Pr)$_2$NH (0.38 mL, 2.7 mmol) in THF (4 mL) with *n*-BuLi (2.5 M in hexane, 1.12 mL, 2.8 mmol) at −50 °C for 30 min was cooled to −90 °C and added to (*Z*)-6-iododec-5-en-1-yne (0.701 g, 2.67 mmol) in THF (5 mL) at −90 °C. After 15 min at −90 °C, the mixture was kept at −70 °C for 13 min and treated with $CH_3I$ (2 mL, 21.56 mmol) in HMPA (1.7 mL) below −65 °C. After the usual workup, chromatography on silica gel (*n*-hexane) afforded 595 mg (81%) of (*Z*)-7-iodoundec-6-en-2-yne: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.7 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.6 (m, 2 H), 1.77 (t, $J$ = 1.2 Hz, 3 H), 2.1−2.4 (m, 4 H), 2.47 (t, $J$ = 7.5 Hz, 2 H), 5.57 (t, $J$ = 6.0 Hz, 1 H); $^{13}$C NMR $\delta$ 3.48, 1385, 17.89, 21.25, 31.43, 35.97, 44.85, 76.10, 78.22, 110.77, 133.07. **Preparation of (2*Z*,6*Z*)-7-Iodo-2,6-undecadiene (15).** To (*Z*)-7-iodoundec-6-en-2-yne (0.595 g, 2.16 mmol) in *n*-hexane was added (*i*-Bu)$_2$AlH (0.58 mL, 3.26 mmol) at 25 °C under Ar. After 27 h at 50−55 °C, the reaction mixture was quenched at −66 °C with aqueous $NH_4Cl$, extracted with ether, and dried over $MgSO_4$. Chromatography on silica gel (*n*-hexane) afforded 0.416 g (69%) of **15**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.7 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.6 (m, 2 H), 1.64 (d, $J$ = 5.8 Hz, 3 H), 2.1−2.2 (m, 4 H), 2.48 (t, $J$ = 7.6 Hz, 2 H), 5.35−5.55 (m, 3 H); $^{13}$C NMR $\delta$ 12.82, 13.86, 21.29, 25.74, 31.49, 36.29, 44.87, 110.10, 124.68, 129.36, 134.01.

**(m) Methyl (*Z*)-2-(Methoxycarbonyl)-5-iodo-7-hydroxy-4-heptenoate (16a).** 3-Iodo-5-(2′-tetrahydropyranyloxy)-2-penten-1-ol was prepared in 92% yield (1.30 g) from 5-(2′-tetrahydropyranyloxy)-2-pentyn-1-ol (920 mg, 5.0 mmol) according to the procedure described for **12** followed by chromatography on silica gel (80/20 pentane−Et$_2$O): $^1$H NMR $\delta$ 1.4−1.9 (m, 6 H), 2.32 (bs, 1 H), 2.80 (t, $J$ = 6.4 Hz, 2 H), 3.4−3.65 (m, 2 H), 3.75−4.0 (m, 2 H), 4.1−4.3 (m, 2 H), 4.55−4.7 (m, 1 H), 5.95 (t, $J$ = 5.8 Hz, 1 H); $^{13}$C NMR $\delta$ 19.41, 25.32, 30.48, 45.23, 62.35, 65.90, 67.20, 98.83, 104.65, 135.82. A solution of this alcohol (624 mg, 2.0 mmol) and $Et_3N$ (0.54 mL, 4.0 mmol) in $CH_2Cl_2$ (10 mL) was treated with methanesulfonyl chloride (0.23 mL, 3 mmol) at 0 °C for 2 h. The reaction mixture was diluted with $Et_2O$, washed successively with 2 N HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel afforded 640 mg (82%) of the corresponding mesylate which was added to dimethyl sodiomalonate in THF (1.0 M, 2 equiv, at 0 °C for 2 h) freshly prepared by addition of dimethyl malonate to a suspension of NaH in THF at 0 °C. The reaction mixture was extracted with $Et_2O$, washed with 1 N HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (90/10 pentane−Et$_2$O) afforded 570 mg (81%) of methyl (*Z*)-2-(methoxycarbonyl)-5-iodo-7-(2′-tetrahydropyranyloxy)-4-heptenoate: $^1$H NMR $\delta$ 1.4−1.9 (m, 6 H), 2.6−2.85 (m, 3 H), 3.4−3.6 (m, 2 H), 3.75 (s, 3 H), 3.75−3.9 (m, 2 H), 4.55−4.65 (m, 1 H), 5.65 (t, $J$ = 6.8 Hz, 1 H); $^{13}$C NMR $\delta$ 19.37, 25.40, 30.51, 35.63, 45.4, 50.41, 52.61, 62.20, 65.98, 98.73, 107.44, 132.16, 168.94. A mixture of this compound (570 mg, 1.32 mmol) and pyridinium *p*-toluenesulfonate (10 mol %) in MeOH (10 mL) was stirred for 12 h, evaporated, and filtered on silica gel to give 395 mg (88%) of **16a**: $^1$H NMR $\delta$ 2.1−2.2 (m, 1 H), 2.7−2.9 (m, 4 H), 3.53 (t, $J$ = 7.2 Hz, 1 H), 3.6−3.8 (m, 7 H), 5.70 (t, $J$ = 6.9 Hz, 1 H); $^{13}$C NMR $\delta$ 35.61, 48.32, 50.19, 52.77, 60.51, 107.77, 134.34, 169.01.

**(n) Methyl (*Z*)-2-(Methoxycarbonyl)-5-iodo-4,8-nonadienoate (16b).** The corresponding mesylate of **12**, prepared following the procedure for **16a**, was added to dimethyl sodiomalonate in THF (1.0 M, 2 equiv, 0 °C, 2 h) freshly prepared by addition of dimethyl malonate to a suspension of NaH in THF. The reaction mixture was extracted with $Et_2O$, washed with 1 N HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel afforded 250 mg (74%) of **16b**: $^1$H NMR $\delta$ 2.2−2.35 (m, 2 H), 2.56 (t, $J$ = 7.2 Hz, 2 H), 2.71 (t, $J$ = 7.1 Hz, 2 H), 3.49 (t, $J$ = 7.5 Hz, 1 H), 3.75 (s, 6 H), 4.9−5.1 (m, 2 H), 5.56 (t, $J$ = 6.8 Hz, 1 H), 5.72 (ddt, $J$ = 17.0, 10.3, 6.7 Hz, 1 H); $^{13}$C NMR $\delta$ 25.11, 29.42, 50.12, 52.89, 65.49, 128.48, 134.90, 168.74, 170.69.

**(o) (*Z*)-4,4-Bis(methoxycarbonyl)-7-iodo-2-methyl-1,6-dodecadiene (17).** The mesylate of (*Z*)-3-iodo-2-hepten-1-ol, prepared similarly as above in 70% yield, was added to dimethyl (2-methyl-2-propenyl)-sodiomalonate in THF (1.0 M, 1 equiv, 0 °C, 2 h) freshly prepared by addition of dimethyl (2-methyl-2-propenyl)malonate to a suspension of NaH in THF. The reaction mixture was extracted with $Et_2O$, washed with 1 N HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (95/5 pentane−Et$_2$O) afforded 1.27 g (76%) of **17**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.3 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.55 (m, 2 H), 1.66 (s, 3 H), 2.46 (t, $J$ = 7.2 Hz, 2 H), 2.65−2.8 (m, 4 H), 3.72 (s, 6 H), 4.73 (bs, 1 H), 4.89 (t, $J$ = 0.5 Hz, 1 H), 5.43 (t, $J$ = 6.55 Hz, 3 H); $^{13}$C NMR $\delta$ 13.81, 21.23, 23.21, 31.44, 39.75, 41.00, 45.24, 52.47, 56.80, 112.90, 116.07, 128.81, 140.08, 171.33; IR (neat) 1736 cm$^{-1}$.

**(p) (*Z*)-4,4-Bis(methoxycarbonyl)-7-iodo-1,6-undecadiene (49).** The mesylate of 3-iodo-2-hepten-1-ol (4.0 mmol) prepared above was treated with dimethyl sodioallylmalonate in THF (1.0 M, 2 equiv, 0 °C, 2 h) freshly prepared by addition of dimethyl allylmalonate to a suspension of NaH in THF. The reaction mixture was extracted with $Et_2O$, washed with 1 N HCl and aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel afforded 1.29 g (82%) of **49**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.3 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.55 (m, 2 H), 2.47 (t, $J$ = 7.2 Hz, 2 H), 2.74 (d, $J$ = 6.8 Hz, 2 H), 2.79 (d, $J$ = 7.6 Hz, 2 H), 3.72 (s, 6 H), 5.0−5.2 (m, 2 H), 5.38 (t, $J$ = 6.8 Hz, 1 H), 5.55−5.8 (m, 1 H); $^{13}$C NMR $\delta$ 13.75, 21.17, 31.34, 37.57, 39.66, 45.20, 52.45, 57.28, 113.13, 119.39, 128.51, 132.11, 170.93; IR (neat) 1736 cm$^{-1}$.

**(q) (*Z*)-5-Iodo-4-(*n*-propyl)-1,4-octadiene (18). Representative Procedure for the Preparation of 1-Iodo-1,3-pentadiene Derivatives 18−21. Preparation of (*Z*)-4-Iodo-3-(*n*-propyl)-3-heptenyltriphenylphosphonium Iodide.** A mixture of (*Z*)-1,4-diiodo-3-(*n*-propyl)-3-heptene (8.9 g, 22.6 mmol)[24] and triphenylphosphine (17.8 g, 68.0 mmol) in $CH_3CN$ (20 mL) was refluxed for 36 h. The solvent was removed, and the resulting light brown precipitate was recrystallized from $CH_2Cl_2$ and $Et_2O$ to give 11.0 g (75%) of (*Z*)-4-iodo-3-(*n*-propyl)-

3-heptenyltriphenylphosphonium iodide: $^1$H NMR $\delta$ 0.8−1.0 (m, 6 H), 1.2−1.65 (m, 4 H), 2.4−2.6 (m, 6 H), 3.5−3.7 (m, 2 H), 7.7−7.8 (m, 15 H); $^{13}$C NMR $\delta$ 12.82, 13.55, 20.74, 21.69, 21.76, 22.74, 33.36, 34.60, 34.65, 42.73, 108.50, 116.37, 118.08, 130.30, 130.55, 133.48, 133.68, 135.08, 135.14, 140.66, 140.98. **Conversion of (*Z*)-4-Iodo-3-(*n*-propyl)-3-heptenyltriphenylphosphonium Iodide to 18.** A suspension of 4-iodo-3-(*n*-propyl)-3-heptenyltriphenylphosphonium iodide (3.3 g, 5.0 mmol) in THF (15 mL) was treated successively at 25 °C with $NaN(SiMe_3)_2$ (1.0 in THF, 5 mL, 5 mmol) for 10 min, HMPA (1.5 mL) at −60 °C, and paraformaldehyde (320 mg, 10 mmol) at −78 °C. After 3 h at 25 °C, the reaction mixture was diluted with hexane, filtered, washing with aqueous NaCl and water, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (*n*-hexane) afforded 1.25 g (90% yield) of **18**: $^1$H NMR $\delta$ 0.85−0.95 (m, 6 H), 1.35−1.65 (m, 4 H), 2.1−2.2 (m, 2 H), 2.5−2.55 (m, 2 H), 3.02 (d, $J$ = 6.2 Hz, 2 H), 5.05−5.15 (m, 2 H), 5.65−5.8 (m, 1 H); $^{13}$C NMR $\delta$ 12.91, 14.00, 21.80, 23.06, 33.62, 42.99, 46.96, 106.31, 115.86, 134.66, 141.57; IR (neat) 1638, 1624 cm$^{-1}$; HRMS calcd for $C_{11}H_{19}I$ ($M^+$) 278.0532, found 278.0532.

**(r) (4*Z*,7*Z*)-4-Iodo-5-(*n*-propyl)-4,7-tridecadiene (19).** Use of *n*-hexanal (0.58 g, 0.70 mL, 5.5 mmol) in place of paraformaldehyde (10 mmol) in the representative procedure for the preparation of **18** provided, after chromatography on silica gel (*n*-hexane), 1.50 g (86%) of **19**: $^1$H NMR $\delta$ 0.85−1.0 (m, 9 H), 1.2−1.65 (m, 10 H), 2.0−2.2 (m, 4 H), 2.4−2.55 (t, $J$ = 7.3 Hz, 2 H), 2.95−3.05 (d, $J$ = 7.0 Hz, 2 H), 5.15−5.35 (m, 1 H), 5.35−5.55 (m, 1 H); $^{13}$C NMR $\delta$ 12.91, 14.07, 21.84, 22.60, 23.05, 27.64, 29.37, 31.60, 33.65, 41.01, 43.03, 105.35, 126.12, 131.43, 142.84; IR (neat) 1670, 1624 cm$^{-1}$; HRMS calcd for $C_{16}H_{29}I$ ($M^+$) 348.1314, found 348.1317.

**(s) (1*Z*,4*Z*)-5-Iodo-1-phenyl-4-(*n*-propyl)-1,4-octadiene (20).** This compound was prepared in 79% yield (1.40 g) following the procedure for **18** and using benzaldehyde (0.63 g, 5.8 mmol) instead of paraformaldehyde: $^1$H NMR $\delta$ 0.81 (t, $J$ = 7.3 Hz, 3 H), 0.91 (t, $J$ = 7.3 Hz, 3 H), 1.2−1.4 (m, 2 H), 1.4−1.7 (m, 2 H), 2.05−2.2 (m, 2 H), 2.52 (t, $J$ = 7.0 Hz, 2 H), 3.32 (d, $J$ = 7.0 Hz, 2 H), 5.55 (dt, $J$ = 7.0 and 11.6 Hz, 1 H), 6.55 (d, $J$ = 11.6 Hz, 1 H), 7.15−7.4 (m, 5 H); $^{13}$C NMR $\delta$ 12.90, 13.90, 21.63, 23.04, 33.95, 42.09, 42.96, 106.05, 126.61, 128.12, 128.72, 129.57, 130.33, 137.38, 142.76; IR (neat) 1622, 1600 cm$^{-1}$; HRMS calcd for $C_{17}H_{23}I$ ($M^+$) 354.0845, found 354.0849.

**(t) (*Z*)-5-Iodo-1,1-pentamethylene-4-(*n*-propyl)-1,4-octadiene (21).** This compound was prepared in 84% yield (1.46 g) following the procedure for **18** and using cyclohexanone (0.54 g, 5.5 mmol) instead of paraformaldehyde: $^1$H NMR $\delta$ 0.85−1.0 (m, 6 H), 1.3−1.65 (m, 10 H), 2.1−2.25 (m, 6 H), 2.50 (t, $J$ = 7.4 Hz, 2 H), 3.00 (d, $J$ = 7.3 Hz, 2 H), 5.01 (t, $J$ = 7.3 Hz, 1 H); $^{13}$C NMR $\delta$ 12.95, 14.11, 21.87, 23.07, 26.93, 27.83, 28.57, 29.11, 33.51, 37.25, 40.90, 43.03, 105.00, 117.73, 140.74, 143.23; IR (neat) 1664, 1624 cm$^{-1}$; HRMS calcd for $C_{16}H_{27}I$ ($M^+$) 346.1158, found 346.1162.

**Pd-Catalyzed Carbonylation of ω-Alkene-Containing Alkenyl Iodides in the Presence of an Alcohol (Table 1). (a) Carbonylation of 1. Representative Procedure (Conditions IV).** A mixture of (*Z*)-1-iodo-2-(*n*-hexyl)-1,5-hexadiene (**1**) (0.44 g, 1.5 mmol), MeOH (0.19 g, 0.24 mL, 6.0 mmol), $NEt_3$ (0.23 g, 0.31 mL, 2.3 mmol), and $Cl_2Pd(PPh_3)_2$ (0.053 g, 0.075 mmol) in benzene (2 mL) and $CH_3CN$ (2 mL) was charged with 40 atm of CO in an autoclave and heated to 100 °C for 24 h with stirring. The autoclave was cooled to 25 °C, and CO was vented. The reaction mixture was poured into a mixture of 10 mL each of ether and water, extracted with ether, dried over $MgSO_4$, and evaporated. Kugelrohr distillation (115−120 °C at 0.4 mmHg) afforded 0.25 g (66%) of 3-(*n*-hexyl)-6-((methoxcarbonyl)methyl)-2-cyclohexenone (**23**): $^1$H NMR $\delta$ 0.89 (t, $J$ = 6 Hz, 3 H), 1.1−3.1 (m, 17 H), 3.70 (s, 3 H), 5.89 (bs, 1 H); $^{13}$C NMR $\delta$ 14.05, 22.59, 27.08, 28.81, 29.00, 29.83, 31.67, 34.42, 37.88, 43.08, 51.48, 125.01, 165.82, 172.91, 198.94; IR (neat) 1740, 1670, 1630 cm$^{-1}$; HRMS calcd for $C_{15}H_{24}O_3$ ($M^+$) 252.1725, found 252.1722.

**(b) Carbonylation of 8.** Under Conditions IV (40 atm of CO, MeCN−$C_6H_6$ (1/1), 100 °C, 24 h), **8** (0.42 g, 1.5 mmol) gave a quantitative yield of **22**. Kugelrohr distillation (105−110 °C at 0.1 mmHg) afforded 0.32 g (90%) of 3-(*n*-hexyl)-5-((methoxycarbonyl)-methyl)-2-cyclopentenone (**22**): $^1$H NMR $\delta$ 0.89 (t, $J$ = 6 Hz, 3 H), 1.1−1.8 (m, 8 H), 2.2−3.5 (m, 7 H), 3.69 (s, 3 H), 5.94 (bs, 1 H); $^{13}$C NMR $\delta$ 14.02, 22.56, 27.07, 29.06, 31.61, 33.54, 35.07, 38.41, 42.54, 51.63, 128.34, 172.51, 181.48, 209.10; IR (neat) 1740, 1705 1616 cm$^{-1}$; HRMS calcd from $C_{14}H_{22}O_3$ ($M^+$) 238.1569, found 238.1570.

**(c) Carbonylation of 11.** Under Conditions IV (40 atm of CO, MeCN−$C_6H_6$ (1/1), 100 °C, 24 h), **11** (0.47 g, 1.5 mmol) afforded methyl (*Z*)-3-(*n*-hexyl)-2,7-octadienoate (**25**) in 50% GLC yield: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7 Hz, 3 H), 1.1−1.8 (m, 8 H), 2.0−2.3 (m, 4 H), 2.66 (bt, $J$ = 10 Hz, 2 H), 3.69 (s, 3 H), 4.9−5.1 (m, 2 H), 5.6−6.1 (m, 2 H); $^{13}$C NMR $\delta$ 14.06, 22.64, 27.77, 28.01, 29.10, 31.77, 34.06, 38.51, 50.71, 114.71, 115.12, 138.59, 138.59, 164.74, 166.74, 166.92; IR (neat) 1720, 1640 cm$^{-1}$; MS ($M^+$ + 1) 239.

**(d) Carbonylation of 6.** Under Conditions IV (40 atm of CO, MeCN−$C_6H_6$ (1/1), 100 °C, 24 h), **6** (0.71 g, 2.0 mmol) afforded 0.47 g (75%) of 3-(*n*-hexyl)-2-(trimethylsilyl)-5-(methoxycarbonyl)cyclopent-2-enone (**26**): $^1$H NMR $\delta$ 0.22 (s, 9 H), 0.89 (t, $J$ = 5 Hz, 3 H), 1.0−1.7 (m, 8 H), 2.1−3.1 (m, 7 H), 3.68 (s, 3 H); $^{13}$C NMR $\delta$ 0.76, 13.59, 22.13, 28.16, 29.07, 31.26, 33.68, 34.84, 39.27, 42.53, 51.14, 137.91, 172.34, 187.53, 212.84; IR (neat) 1742, 1691, 1586 cm$^{-1}$; HRMS calcd for $C_{17}H_{30}O_3Si$ ($M^+$) 310.1964, found 310.1967.

**(e) Carbonylation of 9.** Under Conditions IV (40 atm of CO, MeCN−$C_6H_6$ (1/1), 100 °C, 24 h), **9** (0.71 g, 3.0 mmol) afforded 0.48 g (82%) of 3-((methoxycarbonyl)methyl)bicyclo[3.3.0]oct-1(5)-en-2-one (**27**) via Kugelrohr distillation (100−105 °C at 0.15 mmHg): $^1$H NMR $\delta$ 2.2−3.1 (m, 11 H), 3.70 (s, 3 H); $^{13}$C NMR $\delta$ 24.70, 27.61, 32.00, 32.66, 35.30, 48.50, 51.53, 147.65, 172.39, 185.14, 202.72; IR (neat) 1735, 1695, 1633 cm$^{-1}$; HRMS $C_{11}H_{14}O_3$ ($M^+$) 194.0943, found 194.0937.

**(f) Carbonylation of 10.** Under Conditions IV (40 atm of CO, MeCN−$C_6H_6$ (1/1), 100 °C, 24 h), **10** (0.83 g, 3.0 mmol) afforded 0.59 g (85%) of 8-((methoxycarbonyl)methyl)bicyclo[4.3.0]non-1(6)-en-7-one (**28**) via Kugelrohr distillation (100−105 °C at 0.15 mmHg) (100 GLC % yield): $^1$H NMR $\delta$ 1.6−1.9 (m, 4 H), 2.0−3.0 (m, 9 H), 3.68 (s, 3 H); $^{13}$C NMR $\delta$ 20.22, 21.85, 22.33, 28.42, 35.26, 37.22, 41.74, 51.48, 137.60, 171.67, 172.42, 207.60; IR (neat) 1740, 1698, 1645 cm$^{-1}$; HRMS calcd for $C_{12}H_{16}O_3$ ($M^+$) 208.1100, found 208.1106.

**(g) Carbonylation of 13.** Under Conditions IV (40 atm of CO, MeCN−$C_6H_6$ (1/1), 100 °C, 24 h), **13** (0.14 g, 0.53 mmol) gave 6-((methoxycarbonyl)methyl)-2-(*n*-butyl)cyclohex-2-enone (**29**) in 50% NMR yield. Chromatography on silica gel (10/1 hexane−ethyl acetate) afforded 52 mg (44%) of **29**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.3 Hz, 3 H), 1.2−1.45 (m, 4 H), 1.65−1.9 (m, 1 H), 2.0−2.5 (m, 6 H), 2.75−2.95 (m, 2 H), 3.70 (s, 3 H), 6.6−6.7 (m, 1 H); $^{13}$C NMR $\delta$ 3.84, 22.42, 25.74, 29.03, 29.30, 30.72, 34.64, 43.88, 51.59, 139.28, 144.07, 173.09, 199.51; IR (neat) 1736, 1674 cm$^{-1}$; HRMS calcd for $C_{13}H_{20}O_3$ ($M^+$) 224.1412, found 224.1417.

**(h) Carbonylation of 19.** At 100 atm of CO in a 1:1 mixture of DMF−MeOH at 100 °C for 69 h, **19** (0.35 g, 1.0 mmol) was converted to 2,3-dipropyl-5-(1′-(methoxycarbonyl)hexyl)cyclopent-2-enone (**30**) in 93% NMR yield (diastereomeric ratio = 54:46) along with a 5% yield of the *E* isomer of **31**. Chromatography on silica gel afforded 0.27 g (88%) of **30**: $^1$H NMR $\delta$ 0.85−1.0 (m, 18 H), 1.25−1.55 (m, 16 H), 1.55−1.85 (m, 4 H), 2.15 (t, $J$ = 7.5 Hz, 4 H), 2.35−2.95 (m, 12 H), [3.57 (s), 3.72 (s), 3 H)]; $^{13}$C NMR $\delta$ 13.83, 13.92, 20.64, 20.68, 21.59, 21.64, 22.27, 22.32, 25.00, 27.03, 27.16, 27.86, 30.09, 30.09, 31.49, 32.55, 32.69, 32.81, 45.03, 45.51, 46.01, 46.56, 51.15, 51.45, 139.72, 140.08, 171.97, 172.61, 174.15, 175.49, 208.78, 209.24; IR (neat) 1736, 1700, 1642 cm$^{-1}$; HRMS calcd for $C_{19}H_{33}O_3$ ($M^+$ + 1) 309.2430, found 309.2417. The results of carbonylation of **19** under other condictions were summarized in Table 1, entries 1-8 and 1-9.

**(i) Carbonylation of 20.** Under the conditions for carbonylation of **19** described above, **20** (0.354 g, 1.0 mmol) was converted in 24 h to 2,3-dipropyl-5-(1′-(methoxycarbonyl)-1′-phenylmethyl)cyclopent-2-enone (**32**) in 94% NMR yield (diastereomeric ratio = 60:40) along with a trace, if any, of **33**. Preparative TLC (90/10 hexanes−EtOAc) afforded 0.295 g (94% yield) of **32**: $^1$H NMR $\delta$ 0.8−9.9 (m, 6 H), 1.25−1.65 (m, 4 H), 2.0−3.3 (m, 7 H), [3.64 (s), 3.75 (s), 3 H], 3.85 (d, $J$ = 8.4 Hz, 1 H), 4.31 (d, $J$ = 5.0 Hz, 1 H), 7.25−7.4 (m, 5 H); $^{13}$C NMR $\delta$ 13.86, 1395, 20.57, 20.71, 21.52, 21.68, 24.99, 25.10, 32.75, 32.86, 33.25, 47.25, 48.68, 50.54, 51.80, 52.09, 127.17, 127.47, 128.28, 128.44, 128.51, 128.57, 136.09, 137.62, 139.64, 172.21, 172.21, 172.39, 172.88, 173.65, 208.36, 208.92; IR (neat) 1638, 1696, 1736 cm$^{-1}$; HRMS calcd for $C_{20}H_{27}O_3$ ($M^+$ + 1) 315.1960, found, 315.1941.

**(j) Carbonylation of 21.** Under the conditions for carbonylation of **19** described above, **21** (170 mg, 0.5 mmol) was converted in 37 h

to a 90/10 diastereomeric mixture of 5-(1′-(methoxycarbonyl)cyclohexyl)-2,3-dipropylcyclopent-2-en-1-one (**34**) in 30% NMR yield along with a 50% NMR yield of 5-cyclohexylidene-2,3-dipropylcyclopent-2-en-1-one (**35a**) and a 16% NMR yield of 5-(1′-cyclohexenyl)-2,3-dipropylcyclopent-2-en-1-one (**35b**). Chromatography on silica gel (19/1 hexane−EtOAc) afforded 35 mg (23%) of **34**, 57 mg (46%) of **35a**, and 15 mg (12%) of **35b**. **34**: $^1$H NMR $\delta$ 0.82 (t, $J$ = 8.0 Hz, 3 H), 0.91 (t, $J$ = 8.0 Hz, 3 H), 1.1−1.7 (m, 12 H), 1.95−2.2 (m, 4 H), 2.2−2.5 (m, 4 H), 2.55 (dt, $J$ = 7.5 and 2.4 Hz, 1 H), 3.65 (s, 3 H); $^{13}$C NMR $\delta$ 14.12, 20.83, 21.77, 22.84, 23.08, 25.09, 25.63, 30.68, 31.04, 32.39, 32.87, 49.33, 50.81, 51.60, 140.73, 171.42, 175.92, 208.63; IR (neat) 1646, 1696, 1730 cm$^{-1}$; HRMS calcd for $C_{19}H_3O_3$ ($M^+$) 306.2195, found 306.2198. **35a**: $^1$H NMR $\delta$ 0.87−1.0 (m, 6 H), 1.38−1.63 (m, 10 H), 2.16−2.24 (m, 4 H), 2.36−2.40 (t, $J$ = 7.7 Hz, 2 H), 2.99 (s, 2 H), 3.06−3.08 (m, 2 H); $^{13}$C NMR $\delta$ 14.13, 20.97, 21.81, 25.37, 26.40, 28.00, 32.32, 35.76, 34.34, 125.78, 143.88, 151.66, 163.32, 197.58; IR (neat) 1628, 1654, 1680 cm$^{-1}$; HRMS calcd for $C_{17}H_{26}O$ ($M^+$ + 1) 247.2062, found 247.2062. **35b**: $^1$H NMR $\delta$ 0.86 (t, $J$ = 7.5 Hz, 3 H), 0.96 (t, $J$ = 7.5 Hz, 3 H), 1.3−1.5 (m, 2 H), 1.5−1.7 (m, 6 H), 1.7−1.85 (m, 2 H), 1.95−2.1 (m, 2 H), 2.15 (t, $J$ = 8.3 Hz, 2 H), 2.3−2.5 (m, 3 H), 2.6−2.8 (m, 1 H), 2.9−3.0 (m, 1 H), 5.5 (bs, 1 H); $^{13}$C NMR $\delta$ 14.08, 14.17, 20.83, 21.82, 22.22, 22.70, 25.02, 25.17, 25.26, 32.98, 35.65, 53.10, 124.62, 135.67, 140.41, 172.70, 209.99; IR (neat) 1638, 1648, 1700 cm$^{-1}$; HRMS calcd for $C_{17}H_{26}O$ ($M^+$) 246.1984, found 246.1982.

**(k) Carbonylation of 14.** Under Conditions IV (40 atm of CO, DMF, 100 °C, 17 h), **14** (0.14 g, 0.5 mmol) gave methyl 2-(*n*-butyl)-6-(methoxycarbonyl)-6-methylcyclohex-2-enone (**37**) in 28% NMR yield and (*Z*)-2-(*n*-butyl)-6-methyl-2,6-heptadienoate (**38**) in 39% NMR yield. Chromatography on silica gel (10/1 *n*-hexane−ethyl acetate) afforded 30 mg (25%) of **37** and 40 mg (38%) of **38**. **37**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.0 Hz, 3 H), 1.28 (s, 3 H), 1.2−1.45 (m, 4 H), 1.7−2.45 (m, 6 H), 2.38 (d, $J$ = 15.5 Hz, 1 H), 2.75 (d, $J$ = 15.5 Hz, 1 H), 3.64 (s, 3 H), 6.60 (t, $J$ = 4.0 Hz, 1 H); $^{13}$C NMR $\delta$ 13.92, 21.96, 22.48, 22.68, 29.67, 30.82, 33.04, 41.86, 43.43, 51.38, 138.15, 142.77, 172.03, 201.87; IR (neat) 1736, 1670 cm$^{-1}$; HRMS calcd for $C_{14}H_{22}O_3$ ($M^+$) 238.1569, found 238.1568. **38**: $^1$H NMR 0.89 (t, $J$ = 7.3 Hz, 3 H), 1.2−1.45 (m, 4 H), 1.72 (s, 3 H), 2.12 (t, $J$ = 7.3 Hz, 2 H), 2.25 (t, $J$ = 7.0 Hz, 2 H), 2.55 (q, $J$ = 7.0 Hz, 2 H), 3.73 (s, 3 H), 4.68 (bs, 1 H), 4.72 (bs, 1 H), 5.84 (t, $J$ = 7.0 Hz, 1 H); $^{13}$C NMR 13.91, 22.21, 22.34, 27.61, 31.31, 34.24, 37.38, 51.16, 110.45, 132.19, 141.06, 144.93, 168.62.

**(l) Carbonylation of 15.** Under Conditions IV (70 atm of CO, MeCN, 100 °C, 24 h), **15** (33.5 mg, 0.12 mmol) gave 2.6 mg (10%) of methyl (*Z*)-2-(*n*-butyl)-2,6-octadienoate (**40**) and 9.7 mg (34%) of a mixture of 6-(1′-(methoxycarbonyl)ethyl)-2-(*n*-butyl)cyclohex-2-enone (**39**) (diastereomeric ratio = 89:11) and 6-(2′-(methoxycarbonyl)ethyl)-2-(*n*-butyl)cyclohex-2-enone (**42**) (**39**:**42** = 61:39). **40**: $^1$H NMR $\delta$ 0.90 (m, 3 H), 1.2−1.5 (m, 4 H), 1.6 (s, 3 H), 2.1−2.5 (m, 6 H), 3.75 (s, 3 H), 5.3−5.6 (m, 3 H); IR (neat) 1718, 1620 cm$^{-1}$; HRMS calcd for $C_{13}H_{22}O_2$ ($M^+$) 210.1620, found 210.1627. **39**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 6.9 Hz, 3 H), [1.12 (d, $J$ = 7.6 Hz), 1.28 (d, $J$ = 7.6 Hz), 3 H], 1.2−1.4 (m, 4 H), 1.9−2.05 (m, 2 H), 2.1−2.25 (m, 2 H), 2.35−2.5 (m, 2 H), 2.6−2.75 (dt, $J$ = 5.0 and 11.5 Hz, 1 H), 2.9−3.05 (m, 1 H), 3.68 (s, 3 H), 6.67 (t, $J$ = 3.8 Hz, 1 H); $^{13}$C NMR $\delta$ 13.99, 14.41, 22.98, 25.96, 26.29, 29.84, 31.30, 13.99, 14.41, 22.98, 25.96, 26.29, 29.84, 31.30, 39.36, 50.30, 52.15, 140.30, 144.24, 175.84, 199.55; IR (neat) 1736, 1670 cm$^{-1}$; HRMS calcd for $C_{14}H_{22}O_3$ ($M^+$) 238.1569, found 238.1569. **42**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.0 Hz, 3 H), 1.25−1.45 (m, 4 H), 1.85 (m, 2 H), 2.0−2.5 (m, 7 H), 2.42 (t, $J$ = 7.7 Hz, 2 H), 3.78 (s, 3 H), 6.62 (t, $J$ = 3.8 Hz, 1 H); $^{13}$C NMR $\delta$ 13.93, 22.50, 25.02, 25.13, 28.50, 29.37, 30.83, 31.71, 45.96, 51.56, 139.43, 143.59, 175.00, 200.50; IR (neat) 1736, 1670 cm$^{-1}$; HRMS calcd for $C_{14}H_{22}O_3$ ($M^+$) 238.1569, found 238.1569.

**Study of the Chemoselectivity in the Pd-Catalyzed Acylpalladation Reaction (Scheme 6). (a) Lactonization vs Acylpalladation.** Carbonylation of **12** (119 mg, 0.5 mmol) under Conditions IV (DMF, MeOH (10 equiv), 100 °C, 12 h) gave 2-(3′-butenyl)-2-buten-4-olide (**44**) in 87% NMR yield with no sign (<1%) of the formation of **43**. Chromatography on silica gel (95/5 pentane−$Et_2O$) afforded 60 mg (87%) of **44**: $^1$H NMR $\delta$ 2.3−2.5 (m, 4 H), 4.75−4.85 (m, 2 H), 5.0−5.15 (m, 2 H), 5.7−5.9 (m, 1 H), 7.1−7.2 (m, 1 H); $^{13}$C NMR $\delta$ 24.55, 31.26, 70.17, 115.78, 133.52, 136.91, 144.74, 174.31; IR (neat) 1752 cm$^{-1}$; HRMS calcd for $C_8H_{11}O_2$ ($M^+$ + 1) 139.0759, found 139.0758.

**(b) Acylpalladation vs *C*-Enolate Trapping.** Carbonylation of **16b** (176 mg, 0.5 mmol) under Conditions IV (DMF, MeOH (10 equiv), 100 °C, 12 h) gave (*Z*)-2-(3′,3′-bis(methoxycarbonyl)propylidene)-5-((methoxycarbonyl)methyl)cyclopentanone (**45**) in 48% NMR yield with no trace (<2%) of **46**. **45**: $^1$H NMR $\delta$ 1.4−1.6 (m, 1 H), 2.2−2.55 (m, 3 H), 2.6−2.95 (m, 4 H), 3.53 (t, $J$ = 7.5 Hz, 1 H), 3.69 (s, 3 H), 3.75 (s, 6 H), 6.4−6.55 (m, 1 H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$) $\delta$ 24.88, 26.53, 28.83, 34.15, 45.66, 50.40, 51.78, 52.78, 131.05, 139.10, 168.89, 172.62, 205.44; IR (neat) 1734 cm$^{-1}$; HRMS calcd for $C_{15}H_{21}O_7$ ($M^+$ + 1) 313.1287, found 313.1280.

**(c) *C*-Enolate Trapping vs Lactonization.** Carbonylation of **16a** (170 mg, 0.5 mmol) under Conditions IV (DMF, MeOH (10 equiv), 100 °C, 12 h) gave 2-(3′,3′-bis(methoxycarbonyl)propylidene)butan-4-olide **47** in 80% NMR yield as a 1:2 mixture of the *E* and *Z* isomers with no sign of **48**. ***Z*-47 (major):** $^1$H NMR $\delta$ 2.85−3.0 (m, 2 H), 3.29 (tt, $J$ = 7.3 and 1.9 Hz, 2 H), 3.56 (t, $J$ = 7.1 Hz, 1 H), 3.75 (s, 6 H), 4.33 (t, $J$ = 7.4 Hz, 2 H), 6.26 (tt, $J$ = 7.5 and 2.4 Hz, 1 H); $^{13}$C NMR $\delta$ 26.32, 29.01, 50.81, 52.67, 65.43, 126.37, 137.96, 169.05, 169.62; IR (neat) 1752 cm$^{-1}$; HRMS calcd for $C_{11}H_{15}O_6$ ($M^+$ + 1) 243.0869, found 243.0867. ***E*-47 (minor):** $^1$H NMR $\delta$ 2.79 (tt, $J$ = 7.5 and 1.6 Hz, 2 H), 2.9−3.05 (m, 2 H), 3.56 (t, $J$ = 7.5 Hz, 1 H), 3.76 (s, 6 H), 4.39 (t, $J$ = 7.4 Hz, 2 H), 6.61 (tt, $J$ = 7.5, 3.0 Hz, 1 H); $^{13}$C NMR $\delta$ 25.11, 29.42, 50.12, 52.89, 65.49, 128.48, 134.90, 168.74, 170.69.

**Pd-Catalyzed Carbonylation of $\omega$-Alkene-Containing Alkenyl Iodides in the Presence of an Alcohol (Table 2, Eqs 2 and 3). (a) Carbonylation of 17. Representative Procedure (Conditions III).** (i) A mixture of **17** (204 mg, 0.5 mmol), $Et_3N$ (0.28 mL, 0.20 g, 2.0 mmol), $Cl_2Pd(PPh_3)_2$ (17 mg, 0.025 mmol), and MeOH (2.0 mL, 1.58 g, 49 mmol) was stirred at 65 °C (temperature of the oil bath) at 1 atm of CO for 40 h, treated with $H_2O$, extracted with $Et_2O$, dried over $MgSO_4$, filtered, and evaporated. Analysis of the crude reaction mixture by $^1$H NMR spectroscopy showed the formation of 5,5-bis(methoxycarbonyl)-2-(*n*-butyl)-3-methyl-3-((methoxycarbonyl)methyl)cyclohexene (**52a**) in 18% NMR yield along with less than a 1% NMR yield of 1-(*n*-butyl)-4,4-bis(methoxycarbonyl)-6-methylbicyclo[4.1.0]hept-2-ene (**53**) and an 82% NMR yield of (*Z*)-2-methyl-4,4,7-tris(methoxycarbonyl)-1,6-undecadiene (**54a**). Chromatography on silica gel (93/7 pentane−$Et_2O$) afforded 124 mg (73%) of **54a**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.1 Hz, 3 H), 1.2−1.45 (m, 4 H), 1.64 (s, 3 H), 2.2−2.3 (m, 2 H), 2.71 (s, 2 H), 3.03 (d, $J$ = 7.2 Hz, 2 H), 3.71 (s, 6 H), 3.73 (s, 3 H), 4.70 (s, 1 H), 4.86 (t, $J$ = 1.5 Hz, 1 H), 5.75 (t, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR $\delta$ 13.85, 22.18, 23.17, 31.19, 32.72, 34.46, 41.11, 51.31, 52.43, 57.13, 115.86, 133.93, 135.26, 140.25, 168.28, 171.50; IR (neat) 1736 cm$^{-1}$; HRMS calcd for $C_{18}H_{29}O_6$ ($M^+$ + 1) 341.1964, found 341.1955.

(ii) Carbonylation of **17** (0.5 mmol) under Conditions III (refluxing MeOH, 30 h) gave **52a** in 52% NMR yield along with a 23% NMR yield of **53** and a 22% NMR yield of **54a**. Chromatography on silica gel (93/7 pentane−$Et_2O$) afforded 77 mg (45%) of **52a**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.1 Hz, 3 H), 1.08 (s, 3 H), 1.2−1.5 (m, 4 H), 1.8−2.0 (m, 2 H), 2.1−2.7 (m, 6 H), 3.65 (s, 3 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 5.4−5.5 (m, 1 H); $^{13}$C NMR $\delta$ 14.09, 22.81, 26.32, 29.70, 30.61, 30.92, 36.70, 39.03, 44.16, 51.25, 51.62, 52.33, 52.58, 118.20, 141.53, 171.80, 172.17, 172.46; IR (neat) 1736 cm$^{-1}$; HRMS calcd for $C_{18}H_{29}O_4$ ($M^+$ + 1) 341.1964, found 341.1947.

(iii) Carbonylation of **17** (0.5 mmol) under Conditions III (refluxing EtOH (70 equiv), 24 h) gave 5,5-bis(methoxycarbonyl)-2-(*n*-butyl)-3-methyl-3-((ethoxycarbonyl)methyl)cyclohexene (**52b**) in 30% NMR yield along with a 2% NMR yield of **53** and a 59% NMR yield of (*Z*)-4,4-bis(methoxycarbonyl)-2-methyl-7-(ethoxycarbonyl)-1,6-undecadiene (**54b**). Chromatography on silica gel (90/10 pentane/$Et_2O$) afforded 46 mg (26%) of **52b** and 80 mg (45%) of **54b**. **52b**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.1 Hz, 3 H), 1.07 (s, 3 H), 1.2−1.5 (m, 7 H), 1.85−2.0 (m, 2 H), 2.1−2.7 (m, 6 H), 3.69 (s, 3 H), 3.70 (s, 3 H), 4.11 (q, $J$ = 7.1 Hz, 2 H), 5.4−5.5 (m, 1 H); $^{13}$C NMR $\delta$ 14.09, 14.26, 22.83, 26.40, 29.72, 30.64, 30.91, 36.80, 39.08, 44.54, 51.57, 52.30, 52.59, 60.08, 118.15, 141.59, 171.35, 172.18, 172.50; IR (neat) 1736 cm$^{-1}$; HRMS calcd for $C_{19}H_{30}O_6$ ($M^+$) 354.2042, found 354.2035. **54b**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.1 Hz, 3 H), 1.2−1.45 (m, 7 H), 1.64 (s, 3 H), 2.2−2.3 (m, 2 H), 2.71 (s, 2 H), 3.03 (d, $J$ = 7.2 Hz, 2 H), 3.71 (s, 6 H), 4.20 (q, $J$ = 7.1, 2 H), 4.71 (s, 1 H), 4.8−4.9 (m, 1 H),

5.73 (t, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR $\delta$ 13.77, 14.18, 22.09, 23.07, 31.10, 32.64, 34.38, 41.09, 52.33, 57.07, 60.16, 115.81, 133.35, 135.48, 140.17, 167.79, 171.43; IR (neat) 1736 cm$^{-1}$; HRMS calcd for $C_{19}H_{30}O_6$ ($M^+$) 354.2042, found 354.2035.

(iv) Carbonylation of **17** (0.5 mmol) under Conditions III (*i*-PrOH (50 equiv), 85 °C, 24 h) gave **52c** (R = *i*-Pr) in 53% NMR yield along with a 3% NMR yield of **53** and a 27% NMR yield of **54c** (R = *i*-Pr).

(v) Carbonylation of **17** (0.5 mmol) under Conditions III (refluxing *i*-PrOH (50 equiv), 24 h) gave a 64% NMR yield of 5,5-bis-(methoxycarbonyl)-2-(*n*-butyl)-3-methyl-3-((isopropoxycarbonyl)methyl)cyclohexene (**52c**) along with a 10% yield of **53** and a 6% yield of (*Z*)-4,4-bis(methoxycarbonyl)-2-methyl-7-(isopropoxycarbonyl)-1,6-undecadiene (**54c**). Chromatography on silica gel afforded 111 mg (55%) of **52c** and 5 mg (3%) of **54c**. **52c**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.1 Hz, 3 H), 1.05 (s, 3 H), 1.2−1.5 (m, 10 H), 1.85−2.0 (m, 2 H), 2.1−2.4 (m, 4 H), 2.55−2.8 (m, 2 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 5.00 (sept, $J$ = 6.2 Hz, 1 H), 5.4−5.5 (m, 1 H); $^{13}$C NMR $\delta$ 14.10, 21.86, 22.85, 326.47, 29.72, 30.66, 30.85, 36.90, 39.08, 44.99, 51.56, 52.26, 52.61, 67.44, 118.06, 141.58, 170.85, 172.16, 172.51; IR (neat) 1736 cm$^{-1}$; HRMS calcd for $C_{20}H_{32}O_6$ ($M^+$) 368.2199, found 368.2191. The following signals are discernible for **54c**: $^1$H NMR $\delta$ 0.88 (t, $J$ = 7.0 Hz, 3 H), 1.1−1.4 (m, 10 H), 1.64 (s, 3 H), 2.1−2.3 (m, 2 H), 2.71 (s, 2 H), 3.02 (d, $J$ = 7.1 Hz, 2 H), 3.71 (s, 6 H), 4.6−4.9 (m, 2 H), 5.0−5.2 (m, 1 H), 5.69 (t, $J$ = 7.1 Hz, 1 H).

(vi) Carbonylation of **17** (0.5 mmol) under Conditions III (2/1 mixture of DMF and MeOH (50 equiv), 85 °C, 1 h) gave **52a** in 63% NMR yield along with an 8% NMR yield of **53**, and a less than 3% NMR yield of **54a**.

(vii) Carbonylation of **17** (0.5 mmol) under Conditions III (2/1/0.1 mixture of DMF, MeOH (50 equiv), and $H_2O$ (10 equiv), 85 °C, 1 h) afforded **52a** in 81% NMR yield along with a 3% NMR yield of **53** and a less than 3% NMR yield of **54a**. Chromatography on silica gel afforded 126 mg (74%) of **52a**.

(viii) Pd-Catalyzed cyclization of **17** (0.5 mmol) in the absence of CO using 5 mol % of $Cl_2Pd(PPh_3)_2$ and $NEt_3$ (4 equiv) in refluxing MeCN for 48 h gave **53** in 75% NMR yield along with the starting material (5% of the initial amount). Chromatography on silica gel (97/3 pentane−$Et_2O$) afforded 99 mg (71%) of **53**: $^1$H NMR $\delta$ 0.4−0.5 (m, 2 H), 0.8−0.95 (m, 3 H), 1.2−1.4 (m, 9 H), 1.98 (d, $J$ = 4.0 Hz, 1 H), 2.60 (d, $J$ = 4.0 Hz, 1 H), 3.71 (s, 3 H), 3.72 (s, 3 H), 5.66 (d, $J$ = 10.0 Hz, 1 H), 6.14 (d, $J$ = 10.0 Hz, 1 H); $^{13}$C NMR $\delta$ 14.10, 21.47, 21.97, 23.01, 24.48, 29.66, 30.32, 33.23, 34.62, 52.85, 54.27, 119.55, 137.36, 171.58, 172.26; IR (neat) 1738 cm$^{-1}$; HRMS calcd for $C_{16}H_{24}O_4$ ($M^+$ 280.1675, found 280.1674.

**(b) Carbonylation of 14.** Under Conditions III (2/1 mixture of DMF and MeOH, 85 °C, 1 h), **14** (0.5 mmol) afforded 2-(*n*-butyl)-3-methyl-3-((methoxycarbonyl)methyl)-1-cyclopentene (**55**) in 63% NMR yield along with a 16% yield of **38** and a trace (<2%), if any, of **37**. Chromatography on silica gel (97/3 pentane−$Et_2O$) afforded 58 mg (56% yield) of **55**: $^1$H NMR $\delta$ 0.84 (t, $J$ = 7.3 Hz, 3 H), 1.09 (s, 3 H), 1.15−2.3 (m, 12 H), 3.56 (s, 3 H), 5.24 (s, 1 H); $^{13}$C NMR $\delta$ 14.02, 22.81, 24.99, 26.11, 29.24, 30.10, 37.27, 43.34, 48.71, 51.12, 110.35, 122.45, 172.76; IR (neat) 1734 cm$^{-1}$; HRMS calcd for $C_{13}H_{22}O_2$ ($M^+$) 210.1620, found 210.1622. In the NMR spectra of the crude product, the following signals for **38** were discernible: $^1$H NMR $\delta$ 2.48 (q, $J$ = 7.4 Hz, 2 H), 3.66 (s, 3 H), 4.62 (bs, 1 H), 4.65 (bs, 1 H), 5.78 (t, $J$ = 7.2 Hz, 1 H); $^{13}$C NMR $\delta$ 13.84, 22.14, 22.26, 27.57, 31.26, 34.17, 37.33, 132.15, 141.00, 144.90, 149.90, 168.95.

**(c) Carbonylation of 49.** Under Conditions III (2/1 mixture of DMF and MeOH (50 equiv), 85 °C, 50 h), **49** (197 mg, 0.5 mmol) gave a 37% NMR yield of 5,5-bis(methoxycarbonyl)-2-(*n*-butyl)-3-methylenecyclohexene (**50a**) along with a 17% yield of 5,5-bis(methoxycarbonyl)-2-(*n*-butyl)-1-methyl-1,3-cyclohexadiene (**50b**). Chromatography on silica gel afforded 50 mg (45%) of a 2:1 mixture of **50a** and **50b**. **50a**: $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.1 Hz, 3 H), 1.2−1.45 (m, 4 H), 2.16 (t, $J$ = 7.2 Hz, 2 H), 2.65−2.75 (m, 2 H), 2.87 (s, 2 H), 3.70 (s, 6 H), 4.9 (bs, 1 H), 5.03 (bs, 1 H), 5.55−6.05 (m, 1 H); $^{13}$C NMR $\delta$ 13.92, 22.51, 30.61, 31.73, 32.07, 37.59, 52.60, 54.20, 110.67, 123.07, 136.74, 138.99, 171.39. The following signals were discernible for **50b**: $^1$H NMR $\delta$ 1.77 (s, 3 H), 2.0−2.1 (m, 2 H), 2.72 (s, 2 H), 3.71 (s, 3 H), 5.80 (d, $J$ = 9.5 Hz, 1 H), 5.97 (d, $J$ = 9.5 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.92, 18.76, 22.10, 30.52, 30.93, 35.94, 52.74, 54.64, 119.76, 126.66, 127.82, 130.73, 171.28; IR (neat) 1736 cm$^{-1}$; HRMS calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1515.

**Pd-Catalyzed Carbonylation of $\omega$-Alkene-Containing Alkenyl Iodides in the Absence of an Alcohol (Table 3). (a) Carbonylation of 6. Representative Procedure (Conditions I).** A mixture of Pd($PPh_3$)$_4$ (1.16 g, 1.0 mmol), $NEt_3$ (0.16 mL, 1.1 mmol), and (*Z*)-1-(trimethylsilyl)-1-iodo-2-(*n*-hexyl)-1,4-pentadiene (**6**) (0.35 g, 1.0 mmol) in THF (5 mL) was heated at 60 °C for 24 h at 1 atm of CO. The reaction mixture was quenched with aqueous $NH_4Cl$, extracted with ether, washed with aqueous NaCl, dried over $MgSO_4$, and evaporated. Column chromatography (Florisil, $CH_2Cl_2$) afforded 0.135 g (54%) of 2-(trimethylsilyl)-3-(*n*-hexyl)-5-methylenecyclopent-2-en-1-one (**56**): [2a] $^1$H NMR 0.15 (s, 9 H), 0.80 (t, 3 H), 1.2−1.4 (m, 8 H), 2.4 (t, 2 H), 3.05 (s, 2 H), 5.15 (d, $J$ = 1 Hz, 1 H), 5.85 (d, $J$ = 1 Hz, 1 H); IR (neat) 1750, 1690, 1650 cm$^{-1}$.

**(b) Carbonylation of 7.** Under the same conditions as above (1 atm of CO, THF, 1 equiv of Pd($PPh_3$)$_4$, $NEt_3$ (1.1 equiv) 60 °C, 24 h), **7** (1.11 g, 5.0 mmol) gave 0.31 g (51%) of methylenomycin B (**57**)[24] after Kugelrohr distillation (60 °C at 0.1 mmHg): $^1$H NMR 1.75 (s, 3 H), 2.05 (s, 3 H), 3.05 (br s, 2 H), 5.3 (d, $J$ = 1 Hz, 1 H), 6.0 (d, $J$ = 1 Hz, 1 H); $^{13}$C NMR 8.23, 16.64, 36.97, 114.85, 138.23, 141.78, 164.02, 196.04; IR (neat) 1690, 1665, 1630 cm$^{-1}$.

**(c) Carbonylation of 18.** Under similar conditions as above (1 atm of CO, THF, 1 equiv of Pd($PPh_3$)$_4$, 4 equiv of $Et_3N$, 60 °C, 24 h), **18** (140 mg, 0.5 mmol) gave, after purification by preparative TLC ($SiO_2$, 19/1 hexanes−EtOAc), 62 mg (70% yield, 76% by NMR) of **65**: $^1$H NMR $\delta$ 0.9−1.0 (m, 6 H), 1.4−1.65 (m, 4 H), 2.28 (t, $J$ = 7.6 Hz, 2 H), 2.48 (t, $J$ = 7.7 Hz, 2 H), 3.12 (s, 2 H), 3.12 (s, 2 H), 5.37 (s, 1 H), 6.07 (s, 1 H); $^{13}$C NMR $\delta$ 14.16 (2 C), 20.82,21.75, 25.43, 32.56, 34.40, 115.08, 141.75, 142.39, 168.06, 196.31; HRMS calcd for $C_{12}H_{18}O$ ($M^+$) 178.1358, found 178.1360.

The results of the carbonylation reaction of **18** run under other conditions were summarized in Table 3 (entries 3-5 to 3-8).

**(d) Carbonylation of 4 To Give 5.** The details of this experiment have been previously described.[5]

**(e) Carbonylation of 19.** Under Conditions II (40 atm of CO, DMF, $Cl_2Pd(PPh_3)_2$ (5 mol %), 100 °C, 12 h), **19** (0.35 g, 1.0 mmol) gave 2,3-dipropyl-5-hexylidenecyclopent-2-enone (**31**) in 82% NMR yield (*E*/*Z* = 70/30). Chromatography on silica gel afforded 0.04 g (16%) of the *Z* isomer and 0.14 g (56%) of the *E* isomer. (*Z*)-**31**: $^1$H NMR $\delta$ 0.8−1.0 (m, 9 H), 1.2−1.65 (m, 10 H), 2.18 (t, $J$ = 7.7 Hz, 2 H), 2.38 (t, $J$ = 7.7 Hz, 2 H), 2.7−2.9 (m, 2 H), 3.00 (s, 2 H), 5.96 (t, $J$ = 7.6 Hz, 1 H); $^{13}$C NMR $\delta$ 14.04, 14.20, 20.99, 21.85, 22.53, 25.33, 27.36, 29.14, 31.59, 32.41, 35.72, 132.80, 139.84, 143.86, 165.83, 197.65. *E*-**31**: $^1$H NMR $\delta$ 0.8−1.05 (m, 9 H), 1.25−1.75 (m, 10 H), 2.1−2.5 (m, 6 H), 3.03 (s, 2 H), 6.57 (t, $J$ = 7.2 Hz, 1 H); IR (neat) 1628, 1654, 1688 cm$^{-1}$; HRMS calcd for $C_{17}H_{29}O$ ($M^+$) 249.2218, found 249.2200.

**(f) Carbonylation of 20.** Under Conditions II (40 atm of CO, DMF, $Cl_2Pd(PPh_3)_2$ (5 mol %), 100 °C, 24 h), **20** (0.354 g, 1.0 mmol) gave 2,3-dipropyl-5-benzylidenecyclopent-2-enone (**33**) in 100% NMR yield (*E*/*Z* = 45:55). Chromatography on silica gel (95/5 hexane−$Et_2O$) afforded 0.13 g (52%) of the *Z* isomer and 0.12 g (48%) of the *E* isomer. (*Z*)-**33**: isomer: $^1$H NMR $\delta$ 0.92 (t, $J$ = 7.3 Hz, 3 H), 1.0 (t, $J$ = 7.3 Hz, 3 H), 1.35−1.7 (m, 4 H), 2.25 (t, $J$ = 7.7 Hz, 2 H), 2.45 (t, $J$ = 7.7 Hz, 2 H), 3.25 (s, 2 H), 6.74 (s, 1 H), 7.3−7.45 (m, 3 H), 8.0−8.1 (m, 2 H); $^{13}$C NMR $\delta$ 14.15, 14.19, 20.92, 21.78, 25.57, 32.36, 37.72, 127.85, 129.07, 130.69, 133.66, 34.67, 135.02, 144.33, 165.56, 194.8; IR (neat) 1612, 1644, 1678 cm$^{-1}$. (*E*)-**33**: $^1$H NMR $\delta$ 0.83 (t, $J$ = 7.0 Hz, 3 H), 1.0 (t, $J$ = 7.0 Hz, 3 H), 1.4−1.75 (m, 4 H), 2.28 (t, $J$ = 7.6 Hz, 2 H), 2.5 (t, $J$ = 7.7 Hz, 2 H), 3.41 (s, 2 H), 7.35−7.5 (m, 4 H), 7.55−7.6 (m, 2 H); $^{13}$C NMR $\delta$ 14.14, 14.19, 20.99, 21.83, 25.45, 32.56, 34.93, 128.73, 128.96, 129.78, 130.21, 133.34, 135.70, 141.80, 166.82, 197.39; IR (neat) 1690, 1652, 1622 cm$^{-1}$; HRMS calcd for $C_{18}H_{23}O$ ($M^+$ + 1) 255.1749, found 255.1711.

**(g) Carbonylation 21.** Under Conditions II (100 atm of CO, DMF, $Cl_2Pd(PPh_3)_2$ (5 mol %), $Et_3N$ (2 equiv), 100 °C, 24 h), **21** (170 mg, 0.5 mmol) gave 2,3-dipropyl-5-cyclohexylidenecyclopent-2-enone (**35**) in 77% NMR yield. Chromatography on silica gel (95/5 hexane−$Et_2O$) afforded 0.057 g (48%) of **35**: $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.7 Hz, 3 H), 0.95 (t, $J$ = 7.7 Hz, 3 H), 1.3−1.7 (m, 10 H), 2.1−2.3 (m, 4 H), 2.4 0 (t, $J$ = 7.7 Hz, 2 H), 2.99 (s, 2 H), 3.0−3.15 (m, 2 H); $^{13}$C NMR $\delta$ 14.13, 20.97, 21.81, 25.37, 26.40, 28.00, 32.32, 33.76, 34.34, 125.78,

143.88, 151.66, 163.32, 197.58; IR (neat) 1628, 1654, 1680 $cm^{-1}$; HRMS calcd for $C_{17}H_{27}O$ ($M^+ + 1$) 247.2062, found 247.2062.

**(h) Carbonylation of 13.** Under Conditions II (40 atm of CO, benzene, $Cl_2Pd(PPh_3)_2$ (5 mol %), 100 °C, 47 h), **13** (50 mg, 0.189 mmol) gave **60** in 53% NMR yield. Chromatography on silica gel (10/1 hexane−EtOAc) afforded 15.4 mg (42%) of 2-(*n*-butyl)-9-oxabicyclo[4.3.0]nona-1,6-dien-8-one (**60**): $^1$H NMR $\delta$ 0.92 (t, $J$ = 7.2 Hz, 3 H), 1.2−1.6 (m, 4 H), 1.75−1.95 (m, 2 H), 2.25−2.4 (m, 4 H), 2.66 (t, $J$ = 7.0 Hz, 2 H), 5.70 (s, 1 H); $^{13}$C NMR $\delta$ 13.79, 22.53, 22.75, 24.16, 27.86, 29.36, 30.46, 109.28, 127.44, 145.95, 155.59, 170.50; IR (neat) 1716 $cm^{-1}$; HRMS calcd for $C_{12}H_{16}O_2$ ($M^+$) 192.1150, found 192.1153.

**(i) Carbonylation of 1.** At 40 atm of CO in the presence of Pd(OAc)$_2$ (10 mol %) and $Et_3N$ (3 equiv) in MeCN at 100 °C for 24 h, **1** (54.6 mg, 0.187 mmol) gave 13 mg (36%) of 2-(*n*-hexyl)bicyclo[3.2.0]hept-2-en-7-one (**2**) by chromatography on silica gel (20/1 hexane−EtOAc): $^1$H NMR $\delta$ 0.89 (t, $J$ = 7.0 Hz, 3 H), 1.1−1.7 (m, 8 H), 2.0−3.5 (m, 7 H), 4.15 (bs, 1 H), 5.55 (bs, 1 H); $^{13}$C NMR $\delta$ 14.08, 22.68, 26.52, 27.51, 29.61, 29.96, 31.74, 40.21, 53.46, 75.29, 125.29, 139.94, 206.71; IR (neat) 1775, 1637 $cm^{-1}$; HRMS calcd for $C_{13}H_{21}O$ ($M^+ + 1$) 193.1592, found 193.1592. The results of another experiment run under Conditions II are summarized in Table 3 (entry 3-15).

**(j) Carbonylation of 14.** Under Conditions II (40 atm of CO, benzene, $Cl_2Pd(PPh_3)_2$ (5 mol %), 100 C, 23 h), **14** (35 mg, 0.126 mmol) gave 2-(*n*-butyl)-6-methyl-9-oxabicyclo[4.3.0]nona-1,6-dien-8-one (**63**) in 46% NMR yield. Chromatography on silica gel (10/1 hexane−EtOAc) afforded 12 mg (46%) of **63**: $^1$H NMR $\delta$ 0.88 (t, $J$ = 7.7 Hz, 3 H), 1.08 (s, 3 H), 1.2−1.5 (m, 4 H), 2.3−2.35 (m, 2 H), 2.32 (d, $J$ = 4.1 Hz, 2 H), 2.52 (d, $J$ = 4.3 Hz, 1 H), 5.63 (dt, $J$ = 4.3 and 9.4 Hz, 1 H), 5.90 (dt, $J$ = 1.2 and 9.4 Hz, 1 H); $^{13}$C NMR $\delta$ 13.89, 21.63, 22.17, 27.26, 30.36, 36.78, 36.89, 44.10, 109.76, 120.51, 126.90, 150.84, 174.20; IR (neat) 1736, 1678 $cm^{-1}$; HRMS calcd for $C_{13}H_{18}O_2$ ($M^+$) 206.1307, found 206.1307. Another experiment run in DMF in place of benzene led to a 47% NMR yield of **63** (entry 3-17).

**(k) Carbonylation of 15.** Under Conditions II (40 atm of CO, benzene, $Cl_2Pd(PPh_3)_2$ (5 mol %), 100 °C, 22 h), **15** (34.5 mg, 0.124 mmol) gave 2-(*n*-butyl)-6-ethylidenecyclohex-2-enone (**41**) (*E*/*Z* = 40/60) in 34% NMR yield and 2-(*n*-butyl)-7-methyl-9-oxabicyclo[4.3.0]-nona-1,6-dien-8-one (**64a**) and 2-(*n*-butyl)-10-oxabicyclo[4.4.0]deca-1(6),2-dien-9-one (**64b**) in 33% NMR yield. Chromatography on silica gel (20/1 hexane−EtOAc) afforded 5.9 mg (27%) of **41** and 8.2 mg (32%) of **64a** (contaminated with **64b** to the extent of 8%). **41**: $^1$H NMR $\delta$ 0.91 (t, $J$ = 7.0 Hz, 3 H), 1.25−1.3 (m, 4 H), 1.70 (d, $J$ = 6.8 Hz, 3 H, *E* isomer), 2.00 (d, $J$ = 6.8 Hz, *Z* isomer), 2.1−2.45 (m, 4 H), 2.5−2.7 (m, 2 H), 5.90 (q, $J$ = 6.8 Hz, 1 H, *Z* isomer), 6.85 (q, $J$ = 6.8 Hz, 1 H, *E* isomer); IR (neat) 1638 $cm^{-1}$; HRMS calcd for $C_{12}H_{18}O$ ($M^+$) 178.1358, found 178.1362, **64a**: $^1$H NMR $\delta$ 0.90 (m, 3 H), 1.25−1.5 (m, 4 H), 1.5−1.8 (m, 2 H), 2.1−2.25 (m, 2 H), 2.2 (s, 3 H), 2.26 (t, $J$ = 6.50 Hz, 2 H), 2.65 (t, $J$ = 6.50 Hz, 2 H); IR (neat) 1718, 1630 $cm^{-1}$; HRMS calcd for $C_{13}H_{18}O_2$ ($M^+$) 206.1307, found 206.1303.

**Methanolysis of 63.** A mixture of **63** (10.5 mg, 0.051 mmol) and NaOMe (14 mg, 0.26 mmol) in MeOH (1 mL) was heated at 70 °C for 5 h. Filtration through a short column of silica gel (10/1 hexane−ethyl acetate) afforded 9.2 mg (85%) of **37**.

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