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Palladium-Catalyzed Carbonylative Cyclization of 1-Iodo-2-alkenylbenzenes

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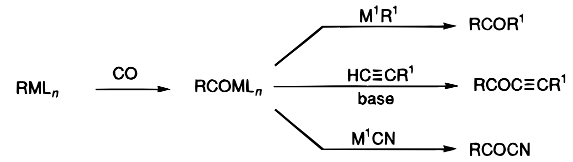
Abstract: The Pd-catalyzed carbonylation of ω-vinyl-substituted *o*-iodoalkenylbenzenes **1**−**4** can provide up to modest yields (50−60%) of 5- and 6-membered Type I cyclic acylpalladation products, *i.e.*, α,β-unsaturated cyclic ketones, in the absence of an external nucleophile and high yields of 5- and 6-membered Type II cyclic acylpalladation products, *i.e.*, α- or β-((alkoxycarbonyl)methyl)substituted cyclic ketones in the presence of an alcohol, *e.g.*, MeOH. In cases where no such processes are available, other side reactions, such as cyclic carbopalladation, polymeric acylpalladation, and trapping of acylpalladiums via esterification and other processes may become predominant. Neither smaller, *i.e.*, 3- or 4-membered, nor 7-membered or larger cyclic ketones appear to be accessible by the reaction. In most cases, the exo-mode cyclic acylpalladation takes place exclusively. However, the cyclic acylpalladation of **3** proceeds exclusively via endo-mode cyclization to give 5-membered ketones. Substitution of one or more hydrogens in the ω-vinyl group with carbon groups has significant effects on the reaction course. Those substrates containing a 1,2-disubstituted alkenyl group in place of a vinyl group, *i.e.*, **19**−**22** and **24** excluding **25**, can give monomeric cyclic acylpalladation products in high yields. These results represent a major deviation from those obtained with **1** and **2**. In the absence of an external nucleophile, formation of Type I cyclic acylpalladation products is, in some cases, accompanied by Type III cyclic acylpalladation involving trapping of acylpalladiums by internal enolates. In the presence of MeOH or other alcohols, Type II acylpalladation products have been obtained in respectable yields from **19**−**20**, **23**, and **24**. In the presence of an alcohol, premature esterification can be a serious side reaction. However, this problem can be alleviated using *i*-PrOH or *t*-BuOH in place of MeOH in combination with appropriate solvents, typically those of lower polarity. Heteroatom-containing substituents on the ω-vinyl groups also exert significant effects on cyclic acylpalladation. Electron-donating substituents tend to lead to high yields of cyclic acylpalladation products, while electron-withdrawing alkoxycarbonyl groups conjugated with the ω-alkenyl group tend to give lower yields of cyclic acylpalladation products. With Me_3Si and alkoxycarbonyl groups products of apparent endo-mode cyclic acylpalladation, *i.e.*, naphthols, have been obtained in significant yields (25−50%). Free OH and other nucleophilic heteroatom groups can seriously interfere with cyclic acylpalladation, and they must be appropriately protected in most cases, although there are indications that acylpalladation−lactonization tandem processes similar to Type II cyclic acylpalladation might be developed.

Until recently, carbon−carbon bond formation via transition metal-catalyzed carbonylation had been dominated by the transformations shown in Scheme 1. Specifically, formation of carbon−carbon bonds is achieved predominantly via migratory insertion of CO. Acylmetal derivatives thus formed can react further with various nucleophiles including carbon nucleophiles, such as organometals, alkynes, and metal cyanides, for the formation of the second carbon−carbon bond.[1]

In principle, acylmetal derivatives can add to π-bonds[2] via carbometalation[3] (acylpalladation hereafter), but little was known about synthetic methods and procedures for the preparation of cyclic ketones based on this process. We have therefore explored such synthetic methods involving the addition of acylpalladation derivatives to alkenes and developed a series of carbonylative cyclization reactions promoted or catalyzed by Pd complexes, of which Type I−III cyclic acylpalladation (Ac-Pd hereafter) processes shown in Scheme 2 appear to be of considerable synthetic significance.[4,5] Although the initial examples of the Type I Ac-Pd reaction were stoichiometric in Pd,[4a] we have subsequently demonstrated that this process can be catalytic.[4b] The Type I and Type II Ac-Pd processes appear to be mechanistically related to a carbonylative diene cyclization reaction[6] and a carbonylative polymerization of alkenes produc-

Scheme 1



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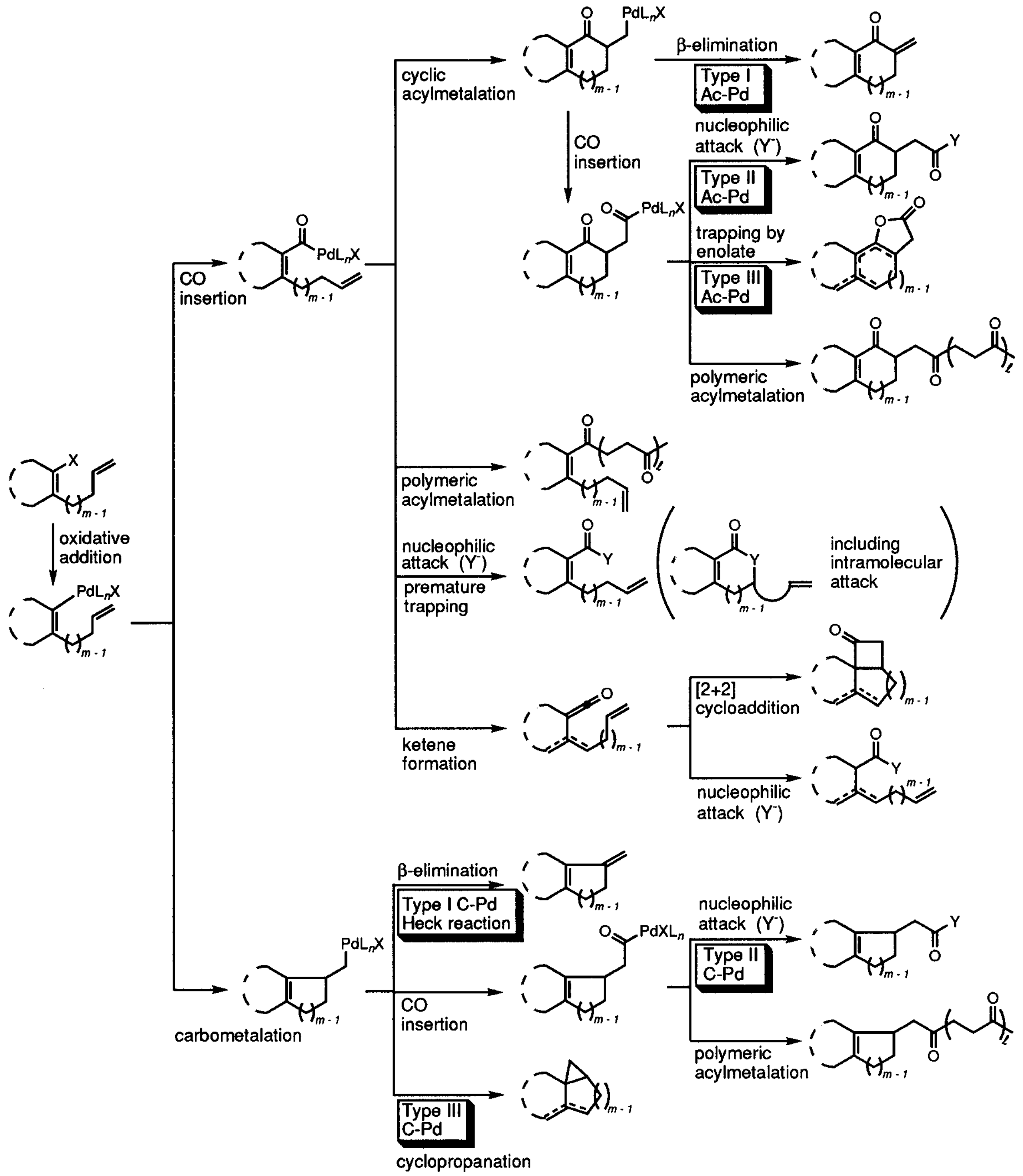
Scheme 2



X = I, Br, OTf, etc. Y^- = nucleophiles centered at H,C, N, O, etc. *l*, *m*, *n* = integers

ing polyketones.[7] However, neither involves the use of organic halides. Also related are a Pd-catalyzed carbonylative cyclization reaction of norbornene and allylic halides[8] and a Ni-promoted reaction of alkynes and allylic halides to give cyclopentanones.[9] Noteworthy extensions of cyclic acylpalladation and the corresponding Ni-catalyzed reactions of alkenes include those cases where organopalladiums generated via Pd and Ni ene reactions are involved.[10] Although different, alkoxycarbonylpalladation of alkenes and alkynes must also involve addition of a carbonyl—palladium bond to alkenes[11] and alkynes.[12]

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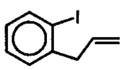
In an attempt to extend the scope of the cyclic acylpalladation reaction, we unexpectedly found in 1989[13] that, even in the presence of CO, cyclic carbopalladation of alkynes to give five- and six-membered rings proceeded without incorporation of CO and that the organopalladium cyclization product could then be trapped by carbonylative esterification. This has been further developed into a cyclization methodology involving cascade carbopalladation and termination via carbonylative esterification.[14] It has also been extended to those cases where alkenes are used in place of alkynes.[15] Despite the failure to incorporate CO in the cyclization mentioned above we have found that acylpalladation of alkynes *per se* is not an intrinsically unfavorable process and that both intermolecular[16] and intramolecular versions[14] producing five-membered ketones and their derivatives are feasible.

Additionally, we have also found that acylpalladium derivatives can serve as sources of ketenes which can undergo [2 + 2] cycloaddition with alkenes.[5c] Various possible courses of the Pd-catalyzed reactions of alkene-containing aryl and alkenyl halides in the presence of CO and a base, such as Et_3N, may be summarized as shown in Scheme 2. Only the exo-mode cyclization proceeses are shown in Scheme 2 for the sake of simplicity. However, the corresponding endo-mode cyclization processes can proceed and have in fact been observed in some cases (*vide infra*). Despite all of these findings reported mainly since 1983 surprisingly little is known about (a) the scope of cyclic acylpalladation and (b) factors governing the selection among the various paths shown in Scheme 2. The major objective of this study is to systematically investigate these aspects of Pd-catalyzed cyclic acylmetalation of alkenes[17] and related reactions.

Results and Discussion

Scope of Cyclic Acylpalladation with Respect to the Product Ring Size. To probe the scope of the cyclic acylpalladation reaction with respect to the product ring size, **1**−**4** were prepared and subjected to four representative reaction conditions (Conditions I−IV): I, CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (1.5−4 equiv); II, CO (30−50 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (1.5−4 equiv); III, CO (1 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (1.5−4 equiv), ROH (R = Me, *i*-Pr, or *t*-Bu); and IV, CO (30−50 atm), 5% $Cl_2Pd(PPh_3)_2$, NEt_3 (1.5−4 equiv), ROH (R = Me, *i*-Pr, or *t*-Bu).



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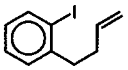

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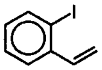

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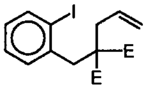

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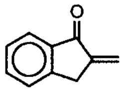

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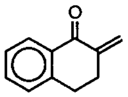

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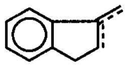

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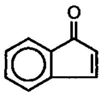

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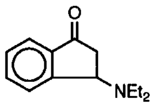

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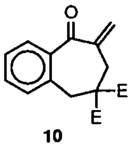

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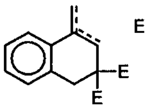

11

E = COOMe

o-Iodoallylbenzene (**1**) was prepared by treatment of iodobenzene diacetate with propargyltrimethylsilane (2 equiv) in the presence of $BF_3{\cdot}OEt_2$ and $MgSO_4$ in CH_2Cl_2, which, after hydrolysis, produced *o*-iodopropargylbenzene in 60% yield,[18] followed by reduction with *i*-Bu_2AlH in hexane at 25 °C. *o*-Iodohomoallylbenzene (**2**) was prepared by the reaction of *o*-iodobenzyl bromide with allylmagnesium bromide, while alkylation of dimethyl allylmalonate with *o*-iodobenzyl bromide provided **4**. The preparation of **3** was achieved in 73% yield by the reaction of *o*-iodobenzaldehyde with $H_2C{=}PPh_3$. In most of the carbonylation experiments, 5 mol % of $Cl_2Pd(PPh_3)_2$ was used as a catalyst, and NEt_3 (1.5−4 equiv) was used as a base to scavenge HI. In most cases, the use of 1.5−2.0 equiv of NEt_3 is satisfactory. Under Conditions I and II, no external nucleophiles, such as alcohols and amines, were employed with the expectation that, under such conditions, Type I cyclic Ac-Pd process might be promoted. It is, however, conceivable to observe other competitive processes, especially Type III cyclic Ac-Pd processes. Under Conditions III and IV an alcohol, *e.g.*, MeOH, *i*-PrOH, or *t*-BuOH, was used to promote the Type II cyclic Ac-Pd process. In these cases, however, premature trapping of the initially formed acylpalladium derivatives before cyclic acylpalladation and other competing processes might also be observed. The CO pressure under Conditions I and III was essentially 1 atm, whereas 30−50 atm of CO was employed under Conditions II and IV. Some other parameters, such as solvents, times, and temperatures, were varied as deemed appropriate. The experimental results with **1**−**4** are summarized in Table 1.

The Pd-catalyzed carbonylation of *o*-iodo-ω-alkenylbenzenes containing a terminal vinyl group (**1**−**4**) in the absence of an external nucleophile can produce up to a modest yield of the expected Type I cyclic Ac-Pd product, *e.g.*, **5** (58%, entry 1-3) and **8** (50%, entry 1-7). However, the Heck reaction[19,20] can be a significant side reaction in cases where the Heck reaction can yield common (5- to 7-membered) rings (entries 1-4, 1-9, and 1-10). In addition, some apparently polymeric processes must also competitively take place, as judged by NMR spectroscopy, GLC analysis, and the viscosity of some isolated products. Those polymeric acylpalladation processes that are shown in Scheme 2 appear to be likely candidates for the latter, although this aspect remains to be further clarified.

With the hope of suppressing the putative polymerization processes via intermolecular acylpalladation, we attempted to trap acylpalladium derivatives with external nucleophiles and chose MeOH, *i*-PrOH, and *t*-BuOH for this purpose. Any external nucleophile can, *a priori*, trap acylpalladium derivatives[1c] formed before or after cyclic acylpalladation, and both of these processes may even competitively and simultaneously take place (Scheme 3). For successful trapping of acylpalladium derivatives after cyclic acylpalladation, it is therefore mandatory that the relative rates of the pertinent processes be as follows: cyclic Ac-Pd process > alcoholysis of acylpalladium derivatives > intermolecular (polymeric) Ac-Pd process.

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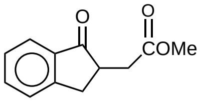
Table 1. Pd-Catalyzed Carbonylation of *o*-Iodo-*ω*-alkenylbenzenes in the Absence of an Alcohol or an External Nucleophile

						products (yield,[a] %)			
entry	substrate	cond.	solvent	temp, °C	time, h	Type I[b] Ac-Pd	Type III[c] Ac-Pd	Heck[d]	others
1-1	**1**	I[e]	DMF	60	24	**5** (25)	*f*	*f*	*g*
1-2	**1**	II[h]	DMF	100	15	**5** (20)	*f*	*f*	*g*
1-3	**1**	II	MeCN-THF	80	18	**5** (58)	*f*	*f*	*g*
1-4	**2**	I	DMF	100	24	**6** (trace)	*f*	**7** (16)	*g*
1-5	**2**	II	DMF	100	24	**6** (trace)	*f*	**7** (trace)	*g*
1-6	**3**	I	DMF	80	1	**8** (9)	*f*	*f*	*j*
1-7	**3**	I	MeCN-PhH	80	6	**8** (50)	*f*	*f*	**9** (11)
1-8	**3**	II	MeCN-THF	100	12	**8** (20)	*f*	*f*	*j*
1-9	**4**	I	MeCN-THF	100	12	**10** (*f*)	*f*	**11** (92)[k]	
1-10	**4**	II	MeCN-THF	100	12	**10** (*f*)	*f*	**11** (54)[k]	

[a] By NMR spectroscopy or GLC. [b] Type I cyclic acylpalladation product. See text for its definition. [c] Type III cyclic acylpalladation product. See text for its defintion. [d] Type I cyclic carbopalladation product or cyclic Heck reaction product. [e] I: 1 atm of CO, 5 mol % of $Cl_2Pd(PPh_3)_2$, NEt_3 (1.5−4 equiv) unless otherwise mentioned. [f] Not detected. [g] Apparently polymeric. [h] II: 30−50 atm of CO, 5 mol % of $Cl_2Pd(PPh_3)_2$, NEt_3 (1.5−4 equiv) unless otherwise mentioned. [i] Exo/endo = 63/37. [j] At least several other products are present. [k] Exo/endo = 45/55.

Table 2. Pd-Catalyzed Carbonylation of *o*-Iodo-*ω*-alkenylbenzenes in the Presence of an Alcohol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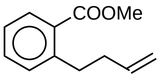
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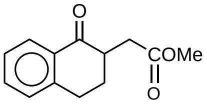
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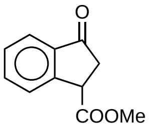
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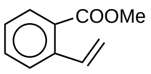
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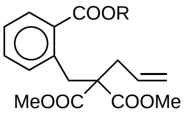
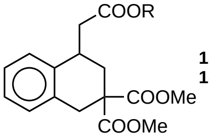
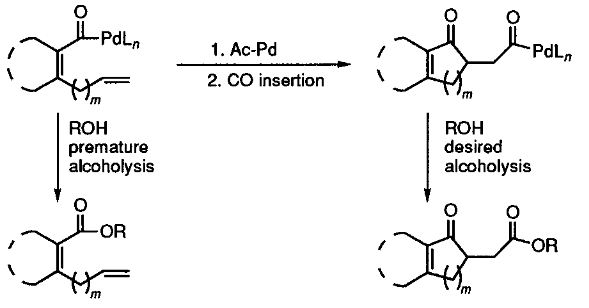

17a (R = Me)


18a (R = Me)
18b (R = *t*-Bu)
18

						products (yield,[a] %)			
entry	substrate	cond (alcohol, equiv)	solvent	temp, °C	time, h	Type I[b] Ac-Pd	Type II[c] Ac-Pd	premature alcoholysis	others
2-1	**1**	III (MeOH, 4)	MeCN-THF	80	20	**5** (18)	**12** (16)	*d*	*d*
2-2	**1**	IV (MeOH, 4)	DMF	100	20	*e*	**12** (90)	*d*	*d*
2-3	**2**	III (MeOH, 100)	MeOH	65	24	*e*	*e*	**13** (37)	**7** (48)
2-4	**2**	III (MeOH, 100)	MeOH	reflux	6	*e*	*e*	**13** (5)	**7** (72)[f]
2-5	**2**	IV (MeOH, 4)	MeCN-PhH	100	11	*d*	**14** (85)	*d*	*d*
2-6	**3**	III (MeOH, 4)	MeCN-PhH	80	6	**8** (26)	**15** (≤3)	**16** (14)	**9** (28)
2-7	**3**	IV (MeOH, 4)	PhH	100	6	**8** (≤2)	**15** (74)	**16**[f] (≤2)	*e*
2-8	**4**	IV (MeOH, 4)	MeCN-PhH	100	12	**10** (*e*)	*e*	**17a** (26)	**11**[f] (33)[h] and **18a** (21)
2-9	**4**	IV[g] (*t*-BuOH, 4)	PhH	100	24	**10** (*e*)	*e*	*e*	**11** (68)[h] and **18b** (5)
2-10	**4**	IV[i] (*t*-BuOH, 4)	PhH	100	24	**10** (*e*)	*e*	*e*	**11** (30)[h] and **18b** (26)

[a] By NMR spectroscopy or GLC. [b] Type I cyclic acylpalladation product. See text for its definition. [c] Type II cyclic acylpalladation product. See text for its definition. [d] Not analyzed. [e] Not detected. [f] Exo/endo = 50/50. [g] 15 atm of CO used. [h] Exo/endo = 45/55. [i] 80 atm of CO used.

Scheme 3



The experimental results obtained with **1**−**4** under Conditions III and IV are summarized in Table 2, which reveal the following. Under Conditions IV using 30−50 atm of CO and MeOH (4 equiv) as an alcohol **1**−**3** are converted in high yields (70−90%) into the Type II Ac-Pd products, *i.e.*, **12** (entry 2-2), **14** (entry 2-5), and **15** (entry 2-7), respectively, even though **4** has failed to produce the desired product **10** in a detectable yield (entries 2-8 through 2-10). At lower pressures of CO, *e.g.*, 1 atm, the yields of Type II Ac-Pd products are low, and the Type I Ac-Pd reaction, the cyclic Heck reaction, and premature esterification can be serious side reactions (entries 2-1, 2-3, 2-4, and 2-6). In the reaction of **3** at 1 atm of CO in the presence of MeOH (Conditions III, entry 2-6), an amino derivative **9** was obtained as a byproduct, which must have arisen via conjugate addition of Et_2NH to **8**, which indeed occurs readily on mixing the two reagents. Oxidation of Et_3N catalyzed by Pd complexes to give Et_2NH and acetaldehyde upon hydrolysis is a known process.[21]

In contrast with the reactions of **1**−**3**, that of **4** does not undergo cyclic acylpalladation to give 7-membered-ring ketones (entry 2-8). Throughout this study no 7-membered-ring or larger cyclic ketones have been obtained via cyclic acylpalladation. Instead, **4** cyclizes via carbopalladation to give 6-membered rings (entries 2-8 through 2-10). At low pressures of CO (15 atm), the cyclic Heck reaction, *i.e.*, the Type I cyclic carbopalladation (C-Pd hereafter) process, which does not incorporate CO into the product at all, is dominant (entry 2-9), while the Type II cyclic C-Pd process involving a cyclic carbopalladation−

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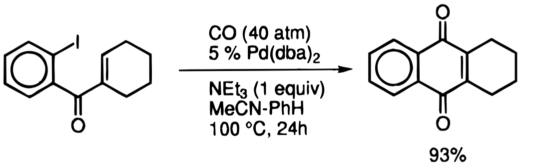
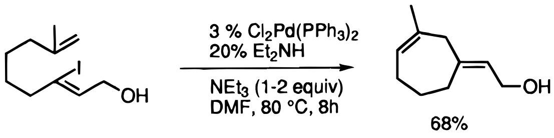
[21] Murahashi, S.; Hirao, T.; Yano, T. *J. Am. Chem. Soc.* **1978**, *100*, 348.

carbonylative esterification tandem competes with the Heck reaction at higher pressures of CO, *e.g.*, 80 atm (entry 2-10).

In summary, the Pd-catalyzed carbonylation of *o*-iodoalkenylbenzenes containing a terminal vinyl group can provide up to modest yields of 5-membered Type I cyclic Ac-Pd products at 1 atm of CO in the absence of a nucleophile (Conditions I) and high yields of 5- and 6-membered Type II cyclic Ac-Pd products at 30−50 atm of CO in the presence of an alcohol, *e.g.*, MeOH (Conditions IV). In cases where no such processes are available, other processes, such as cyclic carbopalladation, polymeric acylpalladation, and trapping of acylpalladiums via esterification, may become dominant. Neither smaller, *i.e.*, 3- or 4-membered, nor 7-membered or larger cyclic ketones appear to be accessible by the reaction. In most cases, the exo-mode cyclic acylpalladation takes place exclusively. However, the cyclic acylpalladation of **3** proceeds exclusively via endo-mode cyclization to give 5-membered rings (entries 1-7, 2-6, and 2-7). Endo-mode cyclization via either carbopalladation or acylpalladation is relatively rare. We earlier reported examples of endo-mode acylpalladation to produce quinones[5a] (eq 1). We also demonstrated a few years ago that some "apparent" endo-mode carbopalladation reactions producing 6- and 7-membered compounds actually proceed via exo-mode carbopalladation−cyclopropanation−cyclopropylcarbinyl-to-homoallyl rearrangement with concomitant ring expansion[22] (eq 2). The endo-mode acylpalladation reaction of **3** to give 5-membered ketones appears to be unprecedented. Although no further mechanistic insights are available at this time, it appears likely that the reaction proceeds via a direct endo-mode cyclization process. Although cyclopropanation via carbopalladation has been shown to be very favorable,[22] the corresponding cyclopropenation appears to be much less favorable and has never been observed.[13,14,22] There have also been ample indications[13,14,22] that formation of 4-membered rings via either carbopalladation or acylpalladation must be generally unfavorable.[23]

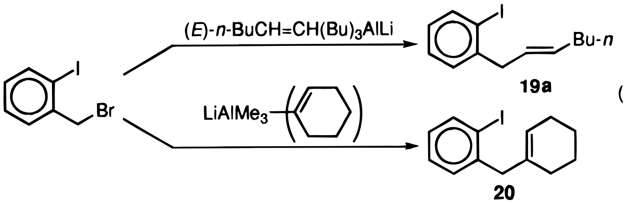


(1)



(2)

Effects of Carbon Substituents in the ω-Vinyl Group. The substrates **1**−**4** all contain the parent vinyl group. Substitution of one or more of the three vinylic hydrogens was anticipated to exert some profound effects on the reaction courses. To probe this matter we chose **19**−**25** as simple and representative *o*-iodo-ω-alkenylbenzenes containing variously di- and tricarbosubstituted alkenyl groups. The reaction of *o*-iodobenzyl bromide with (*E*)-*n*-HexCH=CH(*n*-Bu)(*i*-Bu)$_2$AlLi and lithium 1-cyclohexenyltrimethylaluminate[24] provided **19a** and **20**, respectively (eq 3), while the *Z* isomer of **19a**, *i.e.*, **19b**, was prepared by a sequence shown in eq 4. Successive treatment of *o*-iodobenzyl bromide with HC≡CCH$_2$MgBr, LDA and MeI, and DIBAH provided **21a**, while replacement of the methylation in the above sequence with Pd-catalyzed phenylation gave **21b**. The reactions of *o*-iodobenzyl bromide with the lithio derivative of methyl 1-cyclohexenecarboxylate and methallylmagnesium chloride provided **22** and **23**, respectively. The Wittig reaction of *o*-iodobenzaldehyde with CH$_3$CH=PPh$_3$ gave **24** as a 60:40 mixture of the *cis* and *trans* isomers, while that of *o*-iodoacetophenone with CH$_2$=PPh$_3$ afforded **25**.



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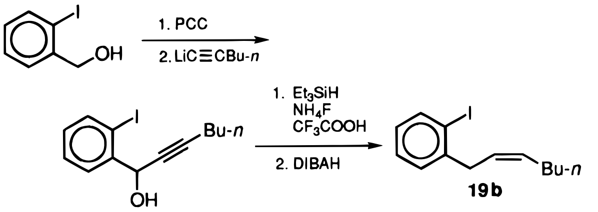

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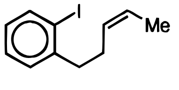
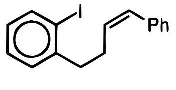


21a



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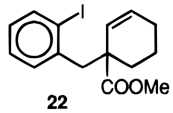

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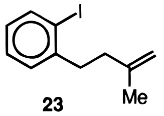

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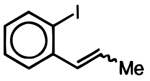

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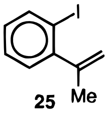

25

The experimental results obtained under Conditions I−IV are summarized in Table 3. Those substrates containing a 1,2-disubstituted alkene, *i.e.*, **19** and **21a**−**22**, all underwent the Pd-catalyzed carbonylation in the absence of an alcohol to give monomeric cyclic Ac-Pd products in high yields (entries 3-1 to 3-3, 3-9, 3-11, and 3-12). Specifically, conversion of **19**, **21b**, and **22** into the corresponding Type I Ac-Pd products **26**, **35**, and **36**, respectively, proceeded cleanly in high yields (entries 3-1 to 3-3, 3-11, and 3-12), even though these products consisted of both *E* and *Z* isomers. These results indeed represent a major deviation from those obtained with **1** and **2** at 30−40 atm of CO under Conditions II (cf. Table 1). The reaction of **21a** under the same conditions yielded a mixture of **29**−**31** in 84% combined yield (entry 3-9). The use of a chelating ligand dppe, *i.e.*, (Ph$_2$PCH$_2$)$_2$, in place of PPh$_3$ led to a nearly exclusive formation of **30** albeit only in 52% yield (Scheme 4). It should be recalled that the parent *o*-iodohomoallylbenzene (**2**) failed to produce **7** or any monomeric cyclization products in detectable yields at 30−50 atm of CO in the absence of a nucleophile (Condition II, entry 1-5). On the other hand, conversion of **24** into **39** at 1 atm of CO under Conditions I (entry 3-14) was lower-yielding than that of **3** into **8** (entry 1-7). Both *E* and *Z* isomers of **19** gave a roughly 93:7 mixture of the *E* and *Z* isomers of **26** (entries 3-1 to 3-3), indicating that the products are thermodynamically equilibrated. In view of the widely observed, strict requirement for β-*cis* hydrogens in the β-elimination step,[1c,22] the initial Ac-Pd product from **22** must be a β,γ-unsaturated enone which then isomerizes to give **36** (entry 3-12).

The reactions of these substrates in the presence of an alcohol yielded similarly favorable results. Thus, **19b**, **20**, **23**, and **24** afforded Type II Ac-Pd products in good yields at 30−50 atm

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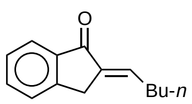
[22] Owczarczyk, Z.; Lamaty, F.; Vawter, E. J.; Negishi, E. *J. Am. Chem. Soc.* **1992**, *114*, 10091. See also: Terakado, M.; Miyazawa, M.; Yamamoto, K. *Synlett* **1994**, 134.

[23] For the formation of 4-membered rings, see: (a) Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5846. (b) Grigg, R.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1991**, *32*, 3855.

[24] Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927.

Table 3. Pd-Catalyzed Carbonylation of *o*-Iodo-ω-alkenylbenzenes Containing Di- and Tricarbosubstituted Alkenes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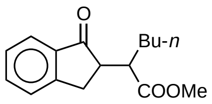
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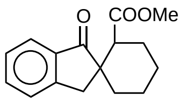
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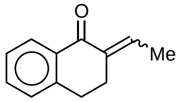
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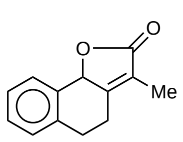
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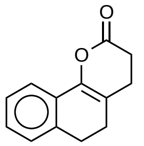
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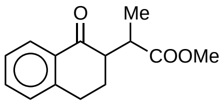
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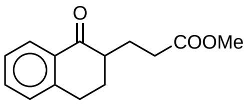
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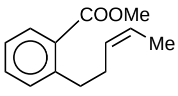
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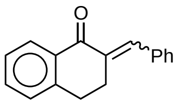
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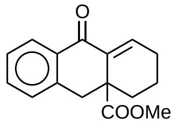
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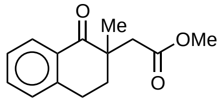
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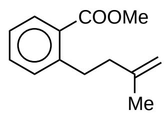
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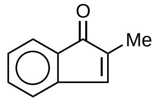
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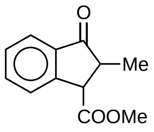
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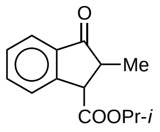
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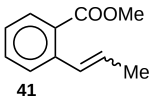
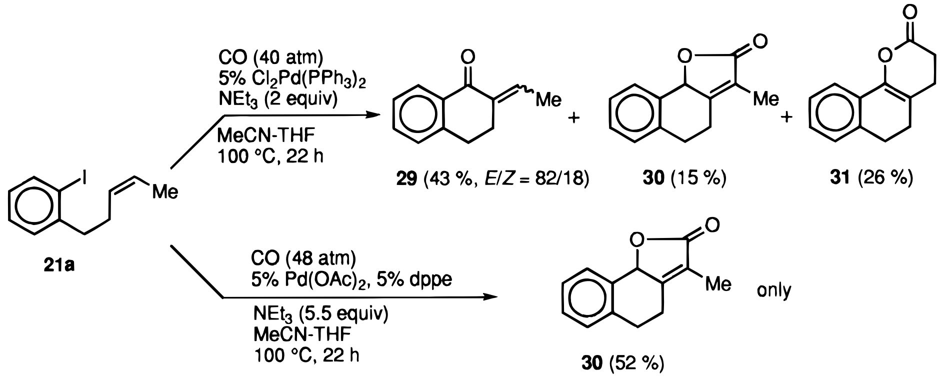

41

						products (yield,[a] %)			
entry	substrate	conditions (solv, equiv)	solvent	temp, °C	time, h	Type I[b] Ac-Pd	Type II[c] Ac-Pd	premature esterification	others
3-1	**19a**	II	DMF	100	18	**26** (82)[d]	*e*	*e*	*f*
3-2	**19b**	I	DMF	60	15	**26** (87)[d]	*e*	*e*	*f*
3-3	**19b**	II	DMF	100	17	**26** (91)[d]	*e*	*e*	*f*
3-4	**19b**	III (CO, 1 atm MeOH, 37)	DMF MeOH	60	18	**26** (50)[d]	**27** (37)[g]	*f*	*f*
3-5	**19b**	III (CO, 14 atm MeOH, 37)	DMF MeOH	100	16	**26** (31)[d]	**27** (63)[g]	*f*	*f*
3-6	**19b**	IV (CO, 42 atm MeOH, 37)	DMF MeOH	100	22	**26** (15)[d]	**27** (80)[g]	*f*	*f*
3-7	**19b**	IV (CO, 84 atm MeOH, 37)	DMF MeOH	100	16	**26** (8)[d]	**27** (90)[g]	*f*	*f*
3-8	**20**	IV (MeOH, 4)	MeCN PhH	100	24	*f*	**28** (84)	*f*	*f*
3-9	**21a**	II	MeCN THF	100	22	**29** (43)[h]	*e*	*e*	**30** (15) and **31** (26)
3-10	**21a**	IV (MeOH, 4)	DMF	100	20	**29** (24)	**32** (45)[i]	**34** (31)	*f*
3-11	**21b**	II	DMF	100	28	**35** (96)[j]	*e*	*e*	*f*
3-12	**22**	II	MeCN THF	100	18	**36** (67)	*e*	*e*	*f*
3-13	**23**	IV (MeOH, 4)	CH_3CN PhH	100	16	*e*	**37** (53)	**38** (17)	*f*
3-14	**24**	I	MeCN PhH	80	12	**39** (22)	*e*	*e*	*f*
3-15	**24**	IV (MeOH, 4)	MeCN PhH	100	6	**39** ($\leq$3)	**40a** (9)	**41** (77)	*f*
3-16	**24**	IV (MeOH, 4)	PhH	100	6	*f*	**40a** (34)[k]	**41a** (57)[l]	*f*
3-17	**24**	IV (*i*-PrOH-4)	PhH	100	24	**39** (13)	**40b** (63)[m]	**41b** (15)[n]	*f*
3-18	**25**	IV (MeOH or *i*-PrOH, 4)	PhH	100	16-24	messy reaction with no products formed in significant yields			

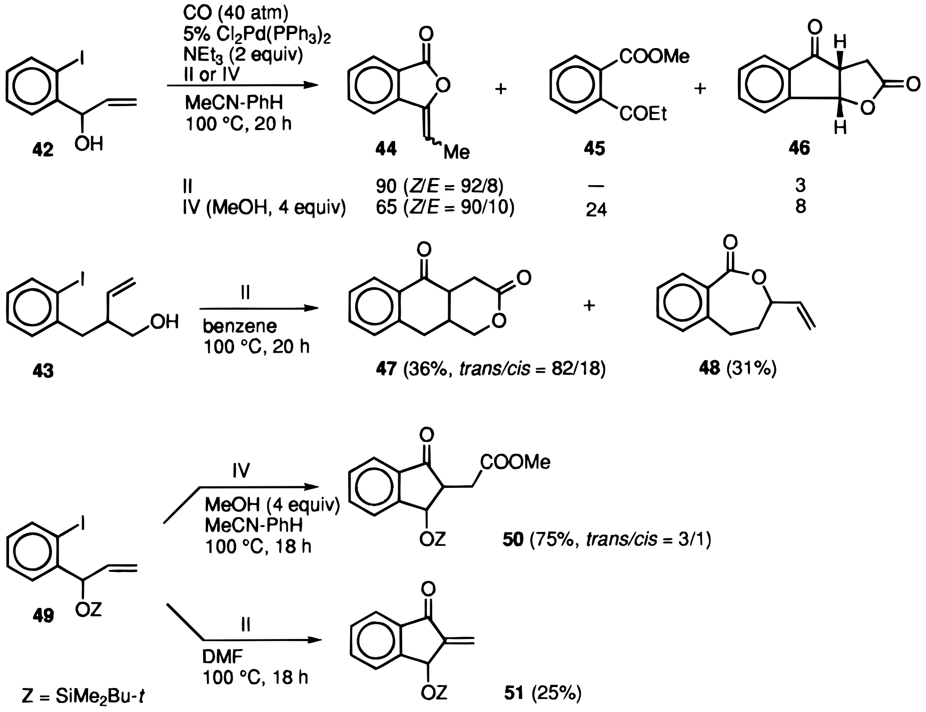
[a] By NMR spectroscopy or GLC. [b] Type I cyclic acylpalladation product. See text for its definition. [c] Type II cyclic acylpalladation product. See text for its definition. [d] *E*/*Z* ≃ 93/7. [e] Not applicable. [f] Not detected or analyzed. [g] 1:1 Diastereomeric mixture. [h] *E*/*Z* = 82/18. [i] Contains a 10% yield of **33**. [j] *E*/*Z* = 58/42. [k] *Trans*/*cis* = 85/15. [l] *Cis*/*trans* = 72/28. [m] *Trans*/*cis* = 90/10. [n] *Cis*/*trans* = 88/12.

of CO in the presence of MeOH or *i*-PrOH (Conditions IV) (entries 3-4 to 3-8, 3-13, and 3-17), although **25** failed to give significant yields of monocyclic products (entry 3-18). Since the numbers of CO molecules incorporated in the Type I and II Ac-Pd products are 1 and 2, respectively, the Type II/Type I ratio was expected to increase by elevating the CO pressure. A series of experiments with **19b** where the CO pressure was varied from 1 to 84 atm under otherwise the same conditions showed that the Type II/Type I ratio indeed changed from 37/50 to 90/8 (entries 3-4 to 3-7). Here again, premature esterification can be a serious side reaction in cases where the desired Ac-Pd step is slow. Thus, the extents of premature esterification observed with **21a**, **23**, and **24** (entries 3-10, 3-13, 3-15, and 3-16) were 31, 17, and 57−77%, respectively, even though it was negligible in the reaction of **19** and **20** producing 5-membered ketones (entries 3-4 to 3-18). As indicated in Scheme 3, one simple solution to this problem was to slow down alcoholysis relative to cyclic acylpalladation. Indeed the use of *i*-PrOH in place of MeOH in the reaction of **24** provided the desired Type II Ac-Pd product **40b** (*trans*/*cis* = 90/10) in 63% yield along with a 13% yield of **39** and only a 15% yield of the premature esterification product **41** (entry 3-17). In cases where more than one diastereomer can be formed, the products were generally diastereomeric mixtures. We believe, however, that the formation of diastereomeric mixtures is due to epimerization after cyclization. Thus, **28** lacking hydrogens α to the ketonic carbonyl group was diastereomerically >95% pure as judged by NMR spectroscopy (entry 3-8). It must be the isomer in which the two carbonyl groups are *cis* to each other, but this point remains to be established.

Scheme 4



Scheme 5



Effects of Heteroatom Substituents. Heteroatom substituents can exert influences on the chemoselectivity, rate, and other aspects of the cyclic acylpalladation reaction. Since acylpalladium derivatives are known to react readily with a variety of nucleophiles,[1] such as alcohols, amines, and enolates,[5,25] such groups present in the substrates can compete with alkenes for the acylpalladium bonds. To probe the chemoselectivity aspect, we chose to compare the relative reactivity of alkenes and alcohols toward acylpalladium derivatives and prepared **42** and **43**. The reaction of *o*-iodobenzaldehyde with vinylmagnesium bromide provided **42**, while the LDA-mediated alkylation of ethyl crotonate with *o*-iodobenzyl bromide followed by DIBAH reduction gave **43**. The Pd-catalyzed carbonylation reaction of **42** at 40 atm of CO either in the absence of MeOH (Conditions II) or in its presence (Conditions IV) gave the premature lactonization product **44** in 90 and 65% yields, respectively, as a roughly 90:10 mixture of the *Z* and *E* isomers. In the latter reaction, **45** was also obtained in 24% yield. It is likely that methanolysis of **44** partially converted it into **45**. In addition to these premature esterification products, however, the above obtained reaction mixtures also contained **46** albeit only in 3 and 8% yields, respectively (Scheme 5). In the reaction of **43** in benzene at 40 atm of CO in the absence of an alcohol (Conditions II), the Type II Ac-Pd product **47** (*trans*/*cis* = 82/18) and the premature lactonization product **48** were obtained in 36 and 31% yields, respectively (Scheme 5). It should be possible to observe cases where the Type II Ac-Pd process is even more strongly favored over premature lactonization. In general, however, hydroxyl groups must be protected to avoid premature lactonization. Indeed, the TBDMS (*t*-BuMe$_2$Si) derivative (**49**) of **42** under Conditions IV (MeOH, 4 equiv) produced **50** as a 3:1 *trans* and *cis* stereoisomeric mixture in 75% yield, even though the yield of the Type I Ac-Pd product **51** obtained under Conditions II was only 25% (Scheme 5). Treatment of **50** (*trans*/*cis* = 3/1) with pyridinium *p*-toluenesulfonate (PPTS) in benzene at 50−60 °C provided a 4/1 mixture of the *trans* isomer of the hydroxy ester and **46** in 73% overall yield.

The effects of ester, protected hydroxymethyl, *e.g.*, CH$_2$OSiMe$_2$Bu-*t*, and silyl groups directly bonded to the ω-alkenyl C=C group were also probed and summarized in Scheme 6. Alkylation of the lithio derivative of **52** with *o*-iodobenzyl bromide gave a 1:1 mixture of **53a** and **53b**. Successive treatment of *o*-iodopropargylbenzene and *o*-iodohomopropargylbenzene with DIBAH in hexanes and ClCOOMe or ClCOOEt provided **54** and **55**, respectively, while hydroalumination

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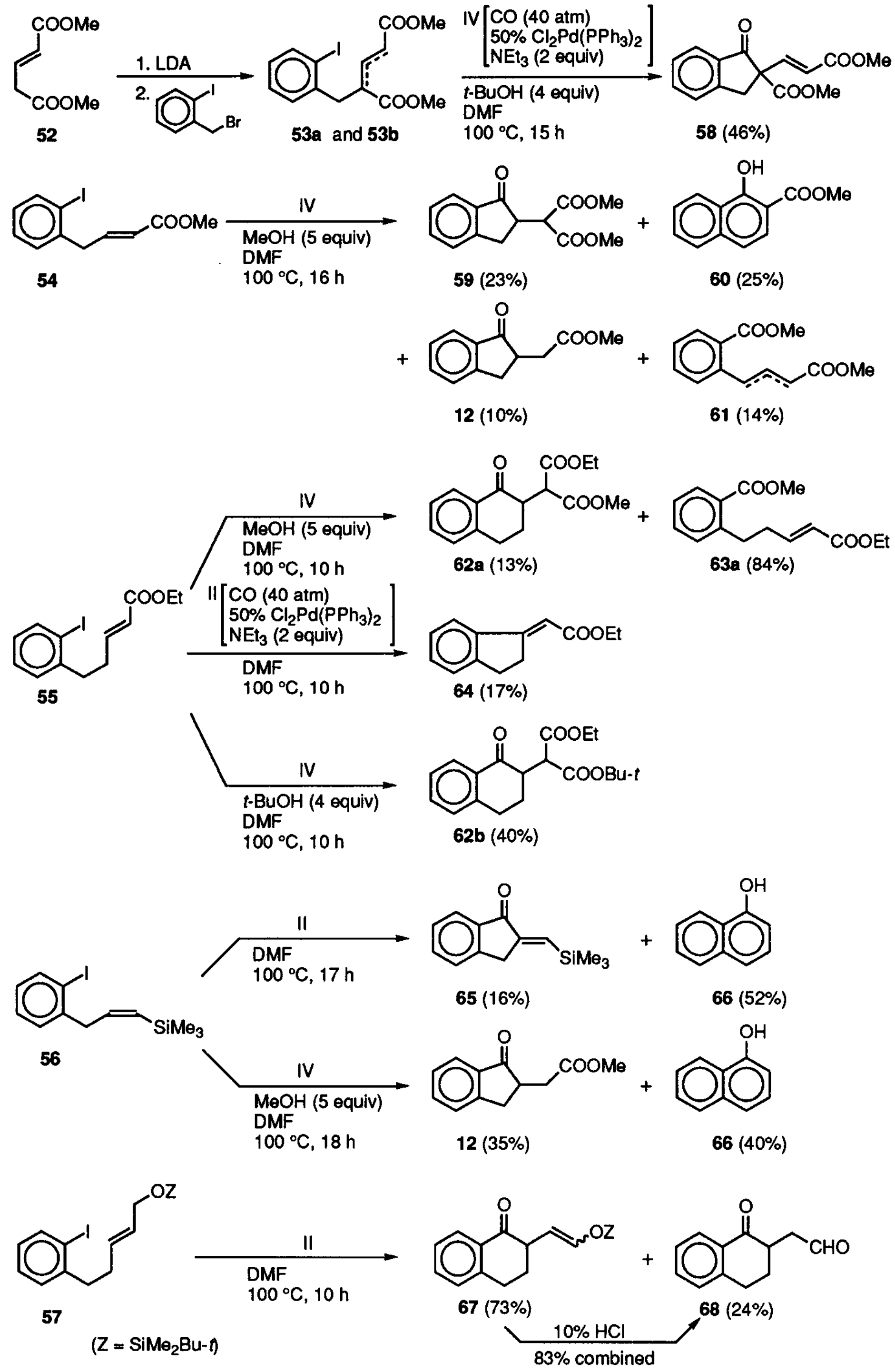
[25] Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018.

Scheme 6



of the Me_3Si derivative of *o*-iodopropargylbenzene with DIBAH in Et_2O yielded **56** upon hydrolysis. Reduction of **55** with DIBAH (2.3 equiv) followed by OH protection with t-$BuMe_2SiCl$ gave **57**.

As indicated earlier by the results with **22** (entry 3-12), unconjugated ester groups appear to exert only minor effects on cyclic acylpalladation. On the other hand, those ester groups that are in conjugation with the ω-alkenyl group tend to retard or hinder cyclic acylpalladation. Thus, for example, **55** gives under Conditions IV using MeOH (5 equiv) as a trapping agent gave only a 13% yield of the Type II Ac-Pd product **62a** along with an 84% yield of the premature esterification product **63a**. Surprisingly, omission of MeOH from the conditions used above led to the formation of the cyclic Heck reaction product **64** in 17% yield without incorporation of CO even at 40 atm along with some unidentified products which appeared to be dimeric. The use of *t*-BuOH in place of MeOH as a trapping agent boosted the yield of the Type II Ac-Pd product, *i.e.*, **62b**, to 40%. The corresponding reaction of **54** using MeOH as a trapping agent provided three cyclic Ac-Pd products (**12**, **59**, and **60**) in 58% combined yield, but none was dominant. The naphthalene derivative **60** must represent yet another example of the endo-mode Ac-Pd reaction. A related endo-mode Ac-Pd reaction must take place in the conversion of **56** into **66**. Since the combined yields of the cyclic Ac-Pd products derived from **56** are 68−75%, the presence of a Me_3Si group on the alkenyl carbon distal to the iodobenzene moiety does not appear to hinder cyclic acylpalladation. In the reaction of **57** at 40 atm of CO in the absence of an alcohol (Conditions II), the combined yield of the cyclic Ac-Pd products **67** and **68** was 97%. Furthermore, when the crude product was treated with 10% HCl, **68** was obtained in 83% overall yield without contamination with **67**.

Conclusions

1. The Pd-catalyzed carbonylation reaction of *o*-iodo-ω-alkenylbenzenes containing a terminal vinyl group (**1**−**3**) in the absence of an external nucleophile (Conditions I and II) can produce up to modest yields of five- and six-membered ring Type I cyclic Ac-Pd products, *e.g.*, **5** and **8**. However, the Heck reaction can be a significant side reaction in cases where it can yield common rings. In addition, some apparently polymeric processes must also competitively take place. Seven-membered-ring ketones do not appear to be formed by this reaction.

2. In the presence of an external nucleophile, *e.g.*, MeOH, *i*-PrOH, and *t*-BuOH, **1**−**3** containing a terminal vinyl group can be converted to five- and six-membered-ring Type II Ac-Pd products in high yields, typically 70−90%, using 30−50 atm of CO (Conditions IV). Here again, seven-membered-ring ketones are not obtainable in significant yields. In general, the scope of the cyclic Ac-Pd reaction appears to be limited to the formation of five- and six-membered-ring ketones. The use of 1 atm of CO (Conditions III) leads to significantly lower yields of the Type II Ac-Pd products. The Type I Ac-Pd reaction, the Heck reaction, and premature esterification tend to be significant side reactions in cases where the yields of the desired Type II Ac-Pd products are low.

3. The effects of carbon substituents in the ω-vinyl group are profound. First, the Type I Ac-Pd products, *e.g.*, **26**, **35**, and **36**, can be obtained in high yields from those substrates containing a 1,2-disubstituted alkene even in the absence of an external nucleophile (Conditions I or II). This reaction is *Z*-stereoselective but not stereospecific, indicating that the products are of thermodynamic control. In some cases, however, the Type III Ac-Pd process involving trapping of putative acylpalladium intermediates with internal enolates can be a significant side reaction under Conditions II. Third, the Type II Ac-Pd products can also be obtainable in high yields at 30−50 atm of CO in the presence of an alcohol, *e.g.*, MeOH (Conditions IV). It should be noted that this process can proceed well even in cases where the substrates cannot undergo the Type I Ac-Pd process due to the absence of an appropriately positioned hydrogen. Here again, the Type I Ac-Pd reaction and premature esterification can be significant side reactions, although the Heck reaction does not appear to be significant with these substrates.

4. The effects of heteroatom substituents are diverse, and the overall picture is not yet clear. Even so, the following observations are noteworthy. First, those OH groups that can participate in the formation of common ring (5- through 7-membered) lactones must be protected to avoid competitive lactonization. The use of a suitable protecting group, *e.g.*, TBDMS, can avoid lactonization. Second, ester groups conjugated with the ω-alkenyl groups can lead to the formation of a variety of products, limiting the yields of the desired Type I and II products. In such cases, the Heck reaction and premature esterification can be significant side reactions depending on the reaction conditions. In addition, formation of phenols presumably via "endo-mode" Ac-Pd processes has also been observed. However, the exact course of the reaction remains to be further clarified. Unconjugated ester groups appear to exert relatively minor influences.

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.[26] Pd-catalyzed high-pressure carbonylation experiments were carried out in a 22-mL autoclave (Parr Instrument Co.).

Preparation of ω-Alkene-Containing Aryl Iodides 1−4. (a) 2-Allyl-1-iodobenzene (1). A solution of 1-(2′-iodophenyl)-2-propyne[18] (2.0 g, 8.25 mmol) in *n*-hexane (8.0 mL) was successively treated with *i*-Bu_2AlH (1.75 mL, 1.41 g, 9.9 mmol, 25 °C then 50 °C, 20 h) and H_2O (2.0 mL, −78 °C). The reaction mixture was warmed to 25 °C, filtered through Celite, washed with brine, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (*n*-hexane) afforded 1.37 g (68%) of **1:** ^{1}H NMR δ 3.47 (d, J = 6.4 Hz, 2 H), 4.95−5.2 (m, 2 H), 5.8−6.1 (m, 1 H), 6.86 (dt, J = 7.5, 2.0 Hz, 1 H), 7.1−7.3 (m, 2 H), 7.80 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 45.53, 101.47, 117.32, 128.55, 128.95, 130.20, 136.28, 140.01, 143.22.

(b) 2-(3′-Butenyl)-1-iodobenzene (2). A solution of 2-iodobenzyl bromide (3.05 g, 10 mmol) in THF (20 mL) was treated with a 1.0 M solution of allylmagnesium bromide in Et_2O (20 mL, 20 mmol, 25 °C). After being heated at reflux for 12 h, the reaction mixture was quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (*n*-pentane) afforded 1.82 g (69%) of **2**: ^{1}H NMR δ 2.25−2.45 (m, 2 H), 2.80 (t, J = 8.0 Hz, 2 H), 4.95−5.15 (m, 2 H), 5.75−6.0 (m, 1 H), 6.80−6.95 (m, 1 H), 7.15−7.35 (m, 2 H), 7.80 (d, J = 7.5 Hz, 1 H); ^{13}C NMR δ 34.13, 40.20, 100.55, 115.23, 127.71, 128.21, 129.41, 137.47, 139.42, 144.24; IR (neat) 3076 (s), 1640 (s) cm^{-1}; high-resolution MS calcd for $C_{10}H_{11}I$ 257.9906, found 257.9909.

(c) 2-Vinyl-1-iodobenzene (3). This compound was prepared according to the literature procedure.[27]

(d) 4,4-Bis(dimethoxycarbonyl)-5-(2′-iodophenyl)-1-pentene (4). To a suspension of NaH (240 mg, 6.0 mmol, 60% dispersion of NaH in mineral oil, 0 °C, 1 h) were successively added methyl 2-(methoxycarbonyl)-4-pentenoate (860 mg, 5 mmol, 0 °C then 25 °C, 30 min) dissolved in THF (25 mL) and 2-iodobenzyl bromide (1.51 g, 5.1 mmol, 25 °C, 3 h) dissolved in THF (5.0 mL). The reaction mixture was diluted, washed with H_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (97/3 *n*-pentane/Et_2O) afforded 1.70 g (88%) of **4:** ^{1}H NMR δ 2.68 (d, J = 7.2 Hz, 2 H), 3.50 (s, 2 H), 3.69 (s, 6 H), 5.0−5.2 (m, 2 H), 5.7−5.95 (m, 1 H), 6.8−6.95 (m, 1 H), 7.15−7.3 (m, 2 H), 7.83 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 38.17, 42.66, 52.43, 59.24, 102.76, 118.99, 128.11, 128.57, 130.07, 132.92, 139.62, 139.92, 171.01; IR (neat) 1736 cm^{-1}; high-resolution MS calcd for $C_{15}H_{17}IO_4$ (M + 1) 389.0250, found 389.0242.

Pd-Catalyzed Carbonylation of *o*-Iodo-ω-alkenylbenzenes in the Absence of an External Nucleophile (Table 1). (a) Carbonylation of 1 at 1 atm of CO. Representative Procedure under Conditions I. Compound **1** (244 mg, 1.0 mmol), Et_3N (0.28 mL, 0.20 g, 2.0 mmol), $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol), and DMF (2 mL) were placed at 25 °C in a flask equipped with a reflux condenser previously flushed with CO and connected to a balloon containing CO (1 atm). The reaction mixture was stirred for 24 h at 65 °C (bath temperature), treated with

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H_2O, extracted with Et_2O, dried over $MgSO_4$, filtered, and evaporated. Analysis of the crude mixture by ^{1}H NMR spectroscopy showed the formation of 2-methylene-2,3-dihydro-1*H*-inden-1-one (**5**) in 25% yield. Chromatography on silica gel (80/20 pentane/Et_2O) afforded 25 mg (18%) of **5:**[33] ^{1}H NMR δ 3.76 (bs, 2 H), 5.63 (dt, J = 1.8, 1.0 Hz, 1 H), 6.36 (dt, J = 2.2, 1.0 Hz, 1 H), 7.41 (dt, J = 7.8, 1.0 Hz, 1 H), 7.50 (dd, J = 7.8, 1.0 Hz, 1 H), 7.60 (dt, J = 7.8, 1.2 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 32.28, 119.76, 125.08, 126.87, 128.09, 135.37, 138.71, 143.79, 150.37, 193.92; IR (neat) 1700 cm^{-1}.

Representative Procedure under Conditions II. The above reaction was performed at 100 °C at 40 atm of CO for 15 h in a 22 mL autoclave. Analysis of the crude mixture by ^{1}H NMR spectroscopy showed the formation of **5** in 20% yield. Chromatography on silica gel (80/20 *n*-pentane/Et_2O) afforded 26 mg (18%) of **5**. Using a 1:1 mixture of THF/benzene in place of DMF at 80 °C for 18 h under otherwise the same conditions as above, **5** was obtained in 58% NMR yield. Chromatography on silica gel (80/20 *n*-pentane/Et_2O) afforded 66 mg (46%) of **5**.

(b) Carbonylation of 2. Under Conditions I (1 atm of CO, 100 °C, 24 h, DMF), **2** (258 mg, 1.0 mmol) gave a 1:1 mixture of 1-methyleneindane and 3-methyl-1*H*-indene (**7**) in 16% NMR yield along with traces of 2-methylene-3,4-dihydronaphthalen-1-one (**6**). **7**:[20e] $_1$H NMR δ 2.1−2.2 (m, 2 H), 2.7−2.85 (m, 2 H), 2.9−3.05 (m, 2 H), 3.29 (bs), 5.0−5.1 (m, 1 H), 5.4−5.5 (m, 1H), 6.15−6.25 (bs, 1 H), 7.0−7.6 (m, 4 H); ^{13}C NMR δ 12.93, 30.12, 31.26, 37.25, 102.34, 118.84, 120.65, 123.58, 124.50, 125.33, 126.07, 126.43, 128.27, 128.61, 139.98, 141.16, 144.33, 146.14, 145.67, 150.88. Under Conditions II (40 atm of CO, 100 °C, 24 h, DMF) **2** gave **6** and **7** only in trace amounts, if any.

(c) Carbonylation of 3. Under Conditions I (1 atm of CO, 80 °C, 6 h, a 1:1 mixture of CH_3CN/benzene), **3** (230 mg, 1.0 mmol) gave 1*H*-indenone (**8**) in 46% NMR yield along with an 11% yield of 3-(diethylamino)-2,3-dihydro-1*H*-inden-1-one (**9**). Chromatography on silica gel (95/5 *n*-pentane/Et_2O) afforded 65 mg (50%) of **8**:[34] ^{1}H NMR δ 5.89 (d, J = 7.1 Hz, 1 H), 7.2−7.3 (m, 1 H), 7.3−7.4 (m, 1 H), 7.43 (d, J = 7.2 Hz, 1 H), 7.57 (dd, J = 6.0, 0.7 Hz, 1 H); ^{13}C NMR δ 122.24, 122.64, 127.18, 129.25, 130.36, 133.67, 144.61, 149.81, 198.44. **9**: ^{1}H NMR δ 1.07 (d, J = 7.1 Hz, 6 H), 2.25−2.55 (m, 4 H), 2.6−2.75 (m, 2 H), 4.71 (t, J = 5.4 Hz, 1 H), 7.3−7.8 (m, 4 H); ^{13}C NMR δ 13.98, 37.11, 44.15, 58.98, 122.95, 126.37, 128.32, 134.68, 137.42, 156.35, 205.02; high-resolution MS calcd for $C_{11}H_{17}NO$ 203.1310, found 203.1312. Under Conditions I (1 atm of CO, 80 °C, 1 h, DMF), **3** gave **8** in 9% NMR yield along with unidentified polymeric products. Under Conditions II (40 atm of CO, 100 °C, 12 h, DMF), **3** gave **8** in 20% NMR yield.

(d) Carbonylation of 4. Under Conditions I (1 atm of CO, 100 °C, 12 h, DMF), **4** (388 mg, 1.0 mmol) gave a 1:1 mixture of 2,2-bis(methoxycarbonyl)-4-methyl-1,2-dihydronaphthalene and 2,2-bis(methoxycarbonyl)-4-methylene-1,2,3-trihydronaphthalene (**11**) in 94% NMR yield with no sign of the formation of the carbonylated product **10**. **11**: ^{1}H NMR δ 2.12 (s, 3 H), 3.04 (s, 2 H, exo), 3.32 (s, 2 H, exo), 3.36 (s, 2 H, endo), 3.67 (s, 6 H), 3.68 (s, 6 H), 5.06 (s, 1 H, exo), 5.55 (s, 1 H, exo), 5.96 (s, 1 H, endo), 7.0−7.6 (m, 4 H); ^{13}C NMR δ 19.35, 34.53, 35.46, 37.86, 52.71, 52.83, 54.36, 54.68, 111.01, 121.01, 123.37, 123.84, 126.40, 126.88, 127.65, 127.86, 128.17, 128.49, 128.87, 132.54, 133.24, 134.90, 138.82, 170.84, 171.02; high-resolution MS calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1052. Under Conditions II (100 °C, 12 h, DMF), **4** gave **11** in 54% NMR yield with no sign of the formation of the other monomeric products (<3%).

Pd-Catalyzed Carbonylation of *o*-Iodo-*ω*-alkenylbenzenes in the Presence of an Alcohol (Table 2). (a) Carbonylation of 1. (1) Representative Procedure under Conditions III. A mixture of **1** (244 mg, 1.0 mmol), Et_3N (0.28 mL, 0.20 g, 2.0 mmol), MeOH (0.16 mL, 0.13 g, 4.0 mmol), $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol), and a 1:1 mixture of acetonitrile/benzene (4.0 mL) was stirred at 80 °C under 1 atm of CO (*vide supra*, see Conditions I for more details) for 20 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** in 18% yield along with 2-(methoxycarbonyl)methyl-1-indanone (**12**) produced in 16% yield. Chromatography on silica gel (80/20 *n*-hexane/Et_2O) afforded 25 mg (17%) of **5** and 26 mg (13%) of **12**:[35] ^{1}H NMR δ 2.62 (dd, J = 17.1, 9.4 Hz, 1 H), 2.8−3.1 (m, 3 H), 3.43 (dd, J = 17.1, 7.4 Hz, 1 H), 3.68 (s, 3 H), 7.37 (t, J = 7.4 Hz, 1 H), 7.46 (d, J = 7.8 Hz, 1 H), 7.59 (dt, J = 7.4, 1.2 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ 33.44, 35.37, 44.02, 52.30, 124.40, 127.00, 127.96, 135.36, 136.74, 153.72, 172.91, 207.10; IR (neat) 1735, 1718 cm^{-1}.

(2) Representative Procedure under Conditions IV. A mixture of **1** (244 mg, 1.0 mmol), Et_3N (0.28 mL, 0.20 g, 2.0 mmol), MeOH (0.16 mL, 0.13 g, 4.0 mmol), $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol), and DMF was stirred at 100 °C under 40 atm of CO. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed the formation of **12** in 90% yield. Chromatography on silica gel (67/33 *n*-hexane/Et_2O) afforded 168 mg (82%) of **12**.

(b) Carbonylation of 2. Under Conditions III (1 atm of CO, 65 °C, 24 h, MeOH as a solvent), **2** (258 mg, 1.0 mmol) was converted to **7** in 48% NMR yield along with a 37% yield of methyl 2-(3′-butenyl)benzoate (**13**): ^{1}H NMR δ 2.2−2.4 (m, 2 H), 2.9−3.05 (m, 2 H), 3.82 (s, 3 H), 4.85−5.05 (m, 2 H), 5.81 (ddt, J = 17.0, 10.3, 6.6 Hz, 1 H), 7.1−7.25 (m, 2 H), 7.3−7.4 (m, 1 H), 7.75−7.85 (m, 1 H); IR (neat) 1750 cm^{-1}. Under the conditions described above (MeOH reflux, 6 h), **2** gave **7** in 72% NMR yield along with a 5% yield of **13**. The product **14** was not detected. Under Conditions IV (100 °C, 11 h, 1:1 mixture of acetonitrile/benzene), **2** (258 mg, 1.0 mmol) gave 2-((methoxycarbonyl)methyl)-1-tetralone (**14**) in 85% NMR yield. Kugelrohr distillation afforded 130 mg (58%) of **14**: ^{1}H NMR δ 1.6−3.2 (m, 7 H), 3.70 (s, 3 H), 7.2−7.6 (m, 6 H), 8.0−8.1 (m, 1 H); ^{13}C NMR δ 29.24, 34.85, 44.78, 51.60, 126.52, 127.38, 128.78, 132.19, 133.37, 144.03, 172.85, 198.11; IR (neat) 1740 cm^{-1}; high-resolution MS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0943.

(c) Carbonylation of 3. Under Conditions III (1 atm of CO, 70 °C, 24 h, MeOH), **3** (230 mg, 1.0 mmol) gave methyl 2-vinylbenzoate (**16**) in 14% NMR yield along with **8** and **9** obtained in 26 and 28% yields, respectively. The compound **15** was not detected (<3%). **16**: ^{1}H NMR δ 3.90 (s, 3 H), 5.36 (dd, J = 11.0, 1.3 Hz, 1 H), 5.65 (dd, J = 17.5, 1.3 Hz, 1 H), 7.25−7.4 (m, 1 H), 7.4−7.6 (m, 3 H), 7.88 (d, J = 7.9, 1.3 Hz, 1 H); ^{13}C NMR δ 52.08, 116.46, 127.19, 127.37, 128.55, 130.29, 132.09, 135.84, 139.54, 167.83; IR (neat) 1722 cm^{-1}; high-resolution MS calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0678. Under Conditions IV (40 atm of CO, 100 °C, 11 h, benzene), **3** gave 3-(methoxycarbonyl)-2,3-dihydro-1*H*-indenone (**15**) in 74% yield as the sole product. Chromatography on silica gel (90/10 *n*-pentane/Et_2O) afforded 139 mg (73%) of **15**:[36] ^{1}H NMR δ 2.88 (dd, J = 19.1, 8.1 Hz, 1 H), 3.15 (dd, J = 19.1, 3.6 Hz, 1 H), 3.78 (s, 3 H), 4.31 (dd, J = 8.1, 3.6 Hz, 1 H), 7.4−7.5 (m, 1 H), 7.6−7.7 (m, 2 H), 7.76 (d, J = 7.7 Hz, 1 H); ^{13}C NMR δ 39.48, 43.59, 52.68, 123.88, 126.52, 128.79, 134.99, 136.32, 151.06, 172.21, 204.03.

(d) Carbonylation of 4. Under Conditions IV (40 atm of CO, 100 °C, 10 h, MeOH (4 equiv), 1/1 acetonitrile−benzene), **4** (306 mg, 0.78 mmol) gave **11** in 33% NMR yield along with a 26% yield of methyl 2-(2′,2′-bis(methoxycarbonyl)-4′-pentyl)benzoate (**17a**) and a 21% yield of **18a:** ^{1}H NMR δ 1.99 (dd, J = 13.6, 10.0 Hz, 1 H), 2.52 (dd, J = 15.9, 10.9 Hz, 1 H), 2.68 (ddd, J = 13.6, 6.3, 1.9 Hz, 1 H), 2.89 (dd, J = 15.9, 4.8 Hz, 1 H), 3.1−3.5 (m, 5 H), 3.66 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 7.05−7.2 (m, 4 H); ^{13}C NMR δ 32.37, 34.51, 35.21, 40.69, 51.69, 52.69, 52.81, 53.63, 126.34, 126.44, 126.68, 128.99, 133.78, 136.99, 171.07, 172.03, 172.55; IR (neat) 1734 (bs) cm^{-1}. **17a:** ^{1}H NMR δ 2.59 (dd, J = 7.2, 0.8 Hz, 2 H), 3.62 (s, 6 H), 3.75 (s, 2 H), 3.88 (s, 3 H), 5.0−5.2 (m, 2 H), 5.65−5.8 (m, 1 H), 7.2−7.55 (m, 3 H), 7.75−7.85 (m, 1 H); ^{13}C NMR δ 35.29, 38.43, 52.03, 52.21, 59.44, 118.91, 126.81, 130.44, 131.29, 131.55, 131.99, 132.79, 137.42, 171.15; IR (neat) 1736 (s) cm^{-1}. Under Conditions IV (15 atm of CO, 100 °C, 24 h, *t*-BuOH (4 equiv), benzene), **4** (388 mg, 1.0 mmol) gave **11** in 68% NMR yield along with a 5% yield of **18b**. Under Conditions IV (100 °C, 24 h, 80 atm, *t*-BuOH (4 equiv), benzene), **4** (388 mg, 1.0 mmol) gave **11** in 30% NMR yield along with a 26% yield of **18b**: ^{1}H NMR δ 1.43 (s, 9 H), 2.02 (dd, J = 13.5, 10.5 Hz, 1 H), 2.43 (dd, J

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= 15.4, 8.7 Hz, 1 H), 2.6−2.75 (m, 1 H), 2.79 (dd, J = 15.4, 4.6 Hz, 1 H), 3.20 (d, J = 16.0 Hz, 1 H), 3.25−3.45 (m, 2 H), 3.67 (s, 3 H), 3.75 (s, 3 H), 7.05−7.20 (m, 4 H); ^{13}C NMR δ 28.02, 29.69, 32.55, 34.42, 35.27, 41.99, 52.68, 52.82, 53.69, 80.64, 126.31, 126.45, 126.55, 128.90, 133.77, 137.23, 171.13, 171.41, 172.13; IR (neat) 1736 (s) cm^{-1}; high-resolution MS calcd for $C_{20}H_{26}O_6$ 362.1729, found 362.1725.

Preparation of ω-Alkene-Containing Aryl Iodides 19−25. (a) (*E*)-2-(2′-Heptenyl)-1-iodobenzene (19a). A solution of 1-hexyne (4.1 g, 50 mmol) in hexane (50 mL) was successively treated with i-Bu$_2$AlH (8.5 g, 11.1 mL, 60 mmol, 50 °C, 4 h), a 1.6 M solution of n-BuLi in hexane (38 mL, 60 mmol, 25 °C, 30 min), 2-iodobenzyl bromide (11.9 g, 40 mmol, 18 h, 50 °C) in hexane, and HMPA (10 mL, 10.7 g, 60 mmol) in THF (30 mL). The reaction mixture was quenched with aqueous NH_4Cl, extracted with Et_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (n-hexane) afforded 4.8 g (37%) of **19a**: ^{1}H NMR δ 0.8−1.0 (m, 3 H), 1.15−1.5 (m, 4 H), 1.9−2.1 (m, 2 H), 3.3−3.5 (m, 2 H), 5.45−5.6 (m, 2 H), 6.9−7.1 (m, 1 H), 7.3−7.5 (m, 2 H), 7.7−7.9 (m, 1 H); ^{13}C NMR δ 14.52, 22.79, 32.09, 32.84, 44.47, 100.37, 126.93, 127.56, 128.10, 129.35, 133.01, 139.27, 143.52; high-resolution MS calcd for $C_{13}H_{17}I$ 300.0375, found 300.0372.

(b) (*Z*)-2-(2′-Heptenyl)-1-iodobenzene (19b). A solution of 1-hexyne (2.51 g, 30.6 mmol) in THF (30 mL) was treated with a 2.5 M solution of n-BuLi (11.2 mL, 28 mmol, 0 °C, 1 h). The resultant mixture was added to a solution of 2-iodobenzaldehyde (5.0 g, 21.5 mmol) in THF (20 mL) at −78 °C. After 3 h, the reaction mixture was treated with NH_4Cl, extracted with Et_2O, washed with brine, dried over $MgSO_4$, and evaporated to give 6.68 g (99%) of crude 1-(2′-iodophenyl)-2-heptyn-1-ol. A mixture of the crude alcohol (5.93 g, 18.9 mmol), triethylsilane (3.9 mL, 2.84 g, 24.4 mmol), NH_4F (0.91 g, 24.6 mmol), and CH_2Cl_2 (30 mL) was treated with a solution of CF_3COOH (7.3 mL, 10.80 g, 94.7 mmol, 0 °C, addition over 30 min)[28] in CH_2Cl_2 (10 mL) and stirred for 2 h at 0 °C. The reaction mixture was poured into ice-water, extracted with Et_2O, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated to yield 5.57 g (99%) of crude 1-(2′-iodophenyl)-2-heptyne. Reduction of 1-(2′-iodophenyl)-2-heptyne (1.40 g, 4.7 mmol) by i-Bu$_2$AlH (1.2 equiv, 50 °C, 20 h) as described in the preparation of **1** gave 1.12 g (79%) of **19b** after chromatography on silica gel (n-hexane): ^{1}H NMR δ 0.8−1.0 (m, 3 H), 1.2−1.5 (m, 4 H), 2.15 (q, J = 6.8 Hz, 2 H), 3.46 (d, J = 6.2 Hz, 2 H), 5.4−5.65 (m, 2 H), 6.86 (dt, J = 7.3, 2.2 Hz, 1 H), 7.15−7.35 (m, 2 H), 7.81 (dd, J = 7.8, 1.0 Hz, 1 H); ^{13}C NMR δ 14.46, 22.76, 31.66, 32.50, 78.32, 98.85, 128.03, 129.09, 129.67, 130.77, 134.33, 139.89, 145.52; IR (neat) 1462 (s), 1432 (s), 1010 (s), 746 (s) cm^{-1}.

(c) 2-((1′-Cyclohexenyl)methyl)-1-iodobenzene (20). A solution of Me_3Al (2.3 g, 3.2 mL, 32 mmol) in THF (15 mL) was successively treated with a 1.5 M solution of 1-cyclohexenyllithium in Et_2O (20 mL, 29 mmol, 0 °C then 25 °C, 15 min) prepared according to the literature procedure,[29] HMPA (7.0 mL, 7.2 g, 40 mol), and 2-iodobenzyl bromide (7.40 g, 33 mmol, 25 °C, 2 h) dissolved in THF (5 mL).[30] The reaction mixture was slowly poured into water, extracted with n-hexane, acidified with HCl, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Purification of the crude oil by Kugelrohr distillation afforded 3.30 g (55%) of **20**: ^{1}H NMR δ 1.5−2.2 (m, 8 H), 3.37 (s, 2 H), 5.31 (bs, 1 H), 6.8−7.0 (m, 1 H), 7.2−7.4 (m, 2 H), 7.8−7.9 (m, 1 H); ^{13}C NMR δ 22.43, 23.00, 25.39, 28.62, 48.76, 101.74, 123.94, 127.66, 128.01, 129.94, 135.73, 139.41, 143.00.

(d) (*Z*)-2-(3′-Pentenyl)-1-iodobenzene (21a). To a mixture of I_2 (5 mg), $HgCl_2$ (64 mg, 0.235 mmol), Mg turnings (6.0 g, 250 mmol), and THF (35 mL) was added a solution of propargyl bromide (80% in toluene, 14 mL, 125 mmol) in THF (90 mL) at a rate that kept the reaction mixture refluxing. After refluxing for an additional 15 min, it was transferred to a solution of 2-iodobenzyl bromide (7.38 g, 24.8 mmol) in THF (25 mL). After refluxing for 12 h, the reaction mixture was quenched with aqueous NH_4Cl at 0 °C, extracted with Et_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (n-pentane) afforded 5.80 g (91%) of 2-(3′-heptynyl)-1-iodobenzene: ^{1}H NMR δ 2.00 (bs, 1H), 1.4−1.6 (m, 2 H), 2.85−3.05 (m, 2 H), 6.8−7.0 (m, 1 H), 7.2−7.4 (m, 2 H), 7.80 (d, J = 6.4 Hz, 1 H); ^{13}C NMR δ 19.08, 39.59, 69.30, 83.13, 100.32, 128.25, 129.77, 139.45, 142.61. To (i-Pr)$_2$NH (1.80 mL, 12.96 mmol) in THF (18 mL) were successively added a 2.1 M solution of n-BuLi in n-hexane (5.9 mL, 2.39 mmol, −50 °C, 20 min), a solution of 2-(3′-butynyl)-1-iodobenzene (2.50 g, 9.76 mmol, −65 °C, 25 min) in THF (4 mL), and CH_3I (4.3 mL, 68.75 mmol, −70 °C) in HMPA (2.5 mL). The reaction mixture was warmed to 25 °C, quenched with aqueous NH_4Cl, extracted with Et_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (n-pentane) afforded 2.26 g (86%) of 2-(3′-pentynyl)-1-iodobenzene: ^{1}H NMR δ 1.78 (t, J = 2.0 Hz, 3 H), 2.35−2.5 (m, 2 H), 2.90 (t, J = 6.8 Hz, 2 H), 6.8−7.0 (m, 1 H), 7.2−7.35 (m, 2 H), 7.80 (d, J = 6.9 Hz, 1 H). Reduction of 2-(3′-pentynyl)-1-iodobenzene (2.0 g, 7.4 mmol) with i-Bu$_2$AlH (1.5 equiv, 50 °C, 20 h) as described in the preparation of **1** gave 1.69 g (84%) of **21a** after chromatography on silica gel (n-pentane): ^{1}H NMR δ 1.55 (d, J = 4.6 Hz, 3 H), 2.25−2.45 (m, 2 H), 2.75 (t, J = 8.0 Hz, 2 H), 5.3−5.6 (m, 2 H), 6.8−6.95 (m, 1 H), 7.1−7.35 (m, 2 H), 7.80 (d, J = 7.7 Hz, 1 H); ^{13}C NMR δ 12.80, 27.52, 40.64, 100.55, 125.02, 127.64, 128.17, 128.91, 129.52, 139.40, 144.50; high-resolution MS calcd for $C_{11}H_{13}I$ 272.5063, found 272.5060.

(e) (*Z*)-2-(4′-Phenyl-3′-butenyl)-1-iodobenzene (21b). A mixture of 2-(3′-butynyl)-1-iodobenzene (1.0 g, 3.9 mmol), iodobenzene (15.9 g, 77.9 mmol), CuI (7.4 mg, 0.039 mmol), and $Cl_2Pd(PPh_3)_2$ (13.7 mg, 0.031 mmol) in Et_2NH (24 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (n-hexane) afforded 388 mg (30%) of 2-(4′-phenyl-3′-butynyl)-1-iodobenzene: ^{1}H NMR δ 2.72 (t, J = 6.3 Hz, 2 H), 3.05 (t, J = 6.3 Hz, 2 H), 6.85−7.0 (m, 1 H), 7.2−7.45 (m, 7 H), 7.85 (d, J = 8.2 Hz, 1 H). This compound was reduced with i-Bu$_2$A1H (1.5 equiv, 50 °C, 20 h) as described in the preparation of **1**. The compound **21b** was isolated in 50% yield after chromatography on silica gel (n-pentane): ^{1}H NMR δ 2.5−3.0 (m, 4 H), 5.72 (dt, J = 7.1 Hz, 10.8 Hz, 1 H), 6.48 (d, J = 10.8 Hz, 1 H), 6.75−6.9 (m, 1 H), 7.05−7.4 (m, 7 H), 7.80 (d, J = 8.3 Hz, 1 H).

(f) 3-Carbomethoxy-3-(2′-iodobenzyl)cyclohexene (22). To i-Pr$_2$NH (0.36 mL, 2.6 mmol) in THF (4.0 mL) were successively added a 2.5 M solution of n-BuLi in n-hexane (1.05 mL, 2.6 mmol, 0 °C, 15 min), HMPA (0.61 mL, 3.50 mmol, −78 °C, 5 min), 1-carbomethoxycyclohexene (322 mg, 2.3 mmol, −78 °C, 30 min), and 2-iodobenzyl bromide (820 mg, 2.8 mmol, −78 °C, 2 h) dissolved in THF.[30] The reaction mixture was diluted with Et_2O, washed with 2.5 N HCl solution and aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (95/5 n-hexane−Et_2O) afforded 663 mg (81%) of **22:** ^{1}H NMR δ 1.5−2.2 (m, 6 H), 3.18 (d, J = 5.0 Hz, 2 H), 3.67 (s, 3 H), 5.7−5.8 (m, 2 H), 6.8−7.8 (m, 4 H); ^{13}C NMR δ 19.49, 24.62, 30.96, 48.34, 51.76, 102.86, 127.68, 128.05, 128.61, 129.05, 129.95, 139.57, 140.22, 175.66; IR (neat) 1740 cm^{-1}.

(g) 2-(3′-Methyl-3′-butenyl)-1-iodobenzene (23). Compound **23** was prepared in 63% yield following the procedure described for **2** using 2-methyl-2-propenylmagnesium chloride in THF in place of allylmagnesium bromide: ^{1}H NMR δ 1.8 (s, 3 H), 2.25 (t, J = 7.0 Hz, 2 H), 2.85 (t, J = 7.0 Hz, 2 H), 4.75 (s, 2 H), 6.8−6.95 (m, 1 H), 7.15−7.35 (m, 2 H), 7.83 (d, J = 6.4 Hz, 1 H); ^{13}C NMR δ 22.59, 38.25, 39.41, 100.60, 110.46, 127.69, 128.30, 129.27, 139.44, 149.50, 145.00.

(h) (*E*)- and (*Z*)-2-(1′-Propenyl)-1-iodobenzene (24). This compound was prepared in 84% yield according the reported procedure described for the preparation of **3**,[27] except that ethyltriphenylphosphonium bromide was used in place of methyltriphenylphosphonium bromide. Compound **24** thus obtained was a 60/40 mixture of the *Z*/*E* isomers: ***Z*-24**: ^{1}H NMR δ 1.74 (dd, J = 7.0, 0.65 Hz, 3 H), 5.7−5.9 (m, 1 H), 6.36 (d, J = 11.4 Hz, 1 H), 6.8−7.0 (m, 1 H), 7.2−7.35 (m, 2 H), 7.85 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 14.19, 100.19, 127.56, 127.66, 128.15, 128.24, 129.77, 133.67, 140.78. The following signals were discernible for ***E*-24**: ^{1}H NMR δ 1.91 (dd, J = 6.5, 0.5 Hz, 1 H), 6.0−6.2 (m, 1 H), 6.57 (d, J = 15.5 Hz, 1 H), 6.8−7.0 (m, 1 H), 7.2−7.35 (m, 1 H), 7.41 (d, J = 7.7 Hz, 1 H), 7.79 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 18.54, 99.21, 126.26, 128.91, 134.68, 138.91, 139.25, 140.84; IR (neat) 1462 (m), 1432 (m), 1266 (c), 1012 (s) cm^{-1}; high-resolution MS calcd for 243.9749, found 243.9752.

(i) 2-(1′-Methylethenyl)-1-iodobenzene (25). A solution of 2-iodobenzaldehyde (1.16 g, 5.0 mmol, 0 °C, 10 min) in THF (10 mL) was treated with a 2.7 M solution of MeMgBr in THF (1.8 mL, 5.0 mmol). The reaction mixture was quenched with H_2O, extracted with Et_2O, dried over $MgSO_4$, and evaporated. A mixture of the crude compound, Celite (2.1 g), and pyridinium chlorochromate (2.15 g, 10 mmol) in CH_2Cl_2 was stirred for 2 h, diluted with pentane, and filtered through a short column of silica gel (9/1 *n*-pentane-Et_2O) to give 1.10 g (94%) of 2-iodoacetophenone. This compound was converted to **25** in 42% yield according to the reported procedure described for the preparation of **3**[27] using 2-iodoacetophenone in place of 2-iodobenzaldehyde. The starting material was recovered to the extent of 50%. **25**: ^{1}H NMR δ 2.06 (s, 3 H), 4.8−4.95 (m, 1 H), 5.15−5.25 (m, 1 H), 7.1−7.2 (m, 1 H), 7.2−7.35 (m, 2 H), 7.82 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 23.86, 96.91, 115.99, 127.94, 128.29, 128.40, 139.08, 148.25, 148.69; IR (neat) 1642 (m), 1584 (w), 1563 (w), 1012 (s), 904 (s) cm^{-1}; high-resolution MS calcd for C_9H_9I 243.9749, found 243.9752.

Pd-Catalyzed Carbonylation of *o*-Iodo-*ω*-alkenylbenzenes Containing Di- and Trisubstituted Alkenes (Table 3). (a) Carbonylation of 19a or 19b. Under Conditions II (40 atm of CO, 100 °C, 15 h, DMF), **19a** (300 mg, 1.0 mmol) gave 2-pentylidene-2,3-dihydro-1*H*-inden-1-one (**26**) in 82% NMR yield as a 93/7 mixture of the *E* and *Z* isomers. Chromatography on silica gel (83/17 *n*-hexane/Et_2O) afforded 166 mg (83%) of (***E***)-**26** and 12 mg (6%) of (***Z***)-**26**, which slowly isomerized to an equilibrium mixture of the *E* and *Z* isomers (*E*/*Z* = 94/6). (***E***)-**26**: ^{1}H NMR δ 0.93 (t, J = 7.2 Hz, 3 H), 1.3−1.6 (m, 4 H), 2.30 (q, J = 7.3 Hz, 2 H), 3.63 (bs, 2 H), 6.88 (tt, J = 7.7, 2.1 Hz, 1 H), 7.37 (dt, J = 7.4, 1.0 Hz, 1 H), 7.48 (d, J = 7.4 Hz, 1 H), 7.56 (dt, J = 7.3, 1.2 Hz, 1 H), 7.84 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 14.37, 22.98, 30.06, 30.41, 31.05, 124.72, 126.79, 127.87, 134.84, 136.84, 138.78, 139.37, 149.85, 193.82; IR (neat) 1702 cm^{-1}; high-resolution MS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1199. The following signals were discernible for (***Z***)-**26**: ^{1}H NMR δ 0.94 (t, J = 7.1 Hz, 3 H), 1.3−1.6 (m, 4 H), 2.94 (q, J = 7.3 Hz, 2 H), 3.68 (bs, 2 H), 6.30 (tt, J = 7.7, 1.6 Hz, 1 H), 7.38 (t, J = 7.6 Hz, 1 H), 7.46 (d, J = 7.6 Hz, 1 H), 7.56 (dt, J = 7.3, 1.2 Hz, 1 H), 7.81 (d, J = 7.4 Hz, 1 H); ^{13}C NMR δ 14.40, 22.98, 28.16, 31.97, 33.52, 124.36, 126.57, 127.70, 134.51, 134.68, 140.08, 144.29, 149.72, 195.09. Under Conditions I (1 atm of CO, 60 °C, 15 h, DMF), **19b** (300 mg, 1.0 mmol) gave **26** in 87% NMR yield as an 84/16 mixture of the *E* and *Z* isomers. Under Conditions II (40 atm of CO, 100 °C, 15 h, DMF), **19b** (300 mg, 1.0 mmol) gave **26** in 91% NMR yield as a 94/6 mixture of the *E* and *Z* isomers. Chromatography on silica gel (83/17 *n*-hexane/Et_2O) afforded 166 mg (83%) of (***E***)-**26** and 12 mg (6%) of (*Z*)-**26**. Under Conditions III (1 atm of CO, 60 °C, 18 h, a 1:1 mixture of MeOH (37 equiv)/DMF), **19b** (300 mg, 1.0 mmol) gave **26** in 50% NMR yield along with a 37% yield of 2-(1′-(methoxycarbonyl)pentyl)-1-indanone (**27**) as a 1:1 mixture of its two diastereomers. At 14 atm of CO in a 1:1 mixture of MeOH (37 equiv)/DMF), **19b** (300 mg, 1.0 mmol) gave, after 16 h at 100 °C, **26** in 31% NMR yield along with a 63% yield of **27** as a 1:1 mixture of two diastereomers. Chromatography on silica gel (83/17 pentane/Et_2O) afforded 45 mg (23%) of **26** and 170 mg (65%) of **27**: 1:1 mixture of diastereomers, ^{1}H NMR δ 0.8−1.0 (m, 6 H), 1.2−2.05 (m, 12 H), 2.8−3.4 (m, 8 H), 3.50 (s, 3 H), 3.74 (s, 3 H), 7.35 (t, J = 7.8 Hz, 2 H), 7.4−7.5 (m, 2 H), 7.45−7.55 (m, 2 H), 7.7−7.8 (m, 2 H); ^{13}C NMR δ 14.10, 14.33, 22.96, 23.02, 28.85, 30.22, 30.31, 30.38, 45.60, 46.20, 48.68, 49.57, 51.92, 52.17, 124.21, 124.30, 126.92, 127.76, 127.93, 135.02, 135.32, 137.15, 137.26, 153.66, 153.86, 174.66, 175.82, 206.55, 207.22; IR (neat) 1738, 1718 cm^{-1}; high-resolution MS calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1410. Under Conditions IV (40 atm of CO, 100 °C, 22 h, 1:1 mixture of MeOH (37 equiv)/DMF), **19b** gave **26** in 15% NMR yield along with an 80% yield of **27** as a 1:1 mixture of its diastereomers. Under Conditions IV (80 atm of CO, 100 °C, 16 h, DMF), **19b** gave **26** in 8% NMR yield along with a 90% yield of **27** as a 1:1 mixture of two diastereomers.

(b) Carbonylation of 20. Under Conditions IV (40 atm of CO, 100 °C, 24 h, 1:1 mixture acetonitrile/benzene), **20** (298 mg, 1.0 mmol) gave 173 mg (67% yield) of 2-methoxycarbonylspiro(cyclohexane-1′,2′-indan-1-one) (**28**) after Kugelrohr distillation. **28**: bp 105−110 °C (0.15 mm Hg); ^{1}H NMR δ 1.2−3.3 (m, 11 H), 3.48 (s, 3 H), 7.2−7.8 (m, 4 H); ^{13}C NMR δ 20.73, 25.18, 25.69, 35.58, 43.15, 48.77, 50.97, 51.50, 123.91, 126.08, 134.10, 136.90, 151.16, 174.26, 208.02; IR (neat) 1725, 1700 cm^{-1}; high-resolution MS calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1259.

(c) Carbonylation of 21a. Under Conditions II (40 atm of CO, 100 °C, 22 h, a 1:1 mixture of THF/CH_3CN), **21a** (272 mg, 1.0 mmol) gave a 43% NMR yield of 1,2,3,4-tetrahydro-2-ethylidene-1-oxonaphthalene (**29**) as an 81/19 mixture of two diastereomers along with a 15% yield of **30** and a 26% yield of **31**. Chromatography on silica gel (10/1 *n*-hexane/ethyl acetate) afforded 24 mg (37%) of **29** and 28 mg (37%) of a mixture of **30** and **31**. **29**:[37] ^{1}H NMR δ 1.88 (d, J = 7.9 Hz, 3 H, *E*), 2.15 (d, J = 7.9 Hz, 3 H, *Z*), 2.7−2.85 (m, 2 H), 2.9−3.05 (m, 2 H), 7.02 (q, J = 7.9 Hz, 1 H), 7.2−7.55 (m, 3 H), 8.10 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 14.00, 25.00, 28.50, 112.30, 126.50, 128.00, 133.00, 133.50, 134.50, 136.00, 144.00, 187.70; IR (neat) 1736, 1684 cm^{-1}. **30**:[38] ^{1}H NMR δ 1.85 (s, 3 H), 2.7−2.9 (m, 2 H), 2.95−3.1 (m, 2 H), 5.70 (s, 1 H), 7.15−7.4 (m, 3 H), 7.45−7.6 (m, 1 H); ^{13}C NMR δ 8.50, 22.20, 28.10, 78.80, 121.00, 124.80, 137.20, 128.00, 128.40, 134.00, 135.80, 161.00, 175.00; IR (neat) 1712 cm^{-1}. The following signals were assignable to **31**: ^{1}H NMR δ 2.42 (t, J = 8.6 Hz, 2 H), 2.50 (t, J = 8.6 Hz, 2 H), 2.76 (t, J = 8.6 Hz, 2 H), 2.88 (t, J = 8.6 Hz, 2 H), 7.1−7.6 (m, 4 H); ^{13}C NMR δ 24.00, 26.40, 27.40, 29.00, 111.90, 121.00, 126.40, 126.60, 126.70, 129.00, 135.00, 168.60. Under Conditions II (40 atm of CO, 100 °C, 48 atm, 22 h, $Pd(OAc)_2$ (5 mol %), dppe (5 mol %), 1:1 mixture of acetonitrile/THF), **21a** (272 mg, 1.0 mmol) gave **30** in 51% NMR yield as the only monomeric product. Chromatography on silica gel (10/1 *n*-hexane/ethyl acetate) afforded 40 mg (52%) of **30**. Under Conditions IV (40 atm of CO, 100 °C, 20 h, a 1:1 mixture of benzene/acetonitrile), **21a** (272 mg, 1.0 mmol) gave 100 mg (44%) of a mixture of 1,2,3,4-tetrahydro-2-((methoxycarbonyl)methyl)-1-oxonaphthalene (**32**) (77/23 mixture of diastereomers) and **33**, 40 mg (24%) of 1,2,3,4-tetrahedro-2-ethylidene-1-oxonaphthalene (**29**), and 60 mg (31%) of methyl (*Z*)-2-(3′-pentenyl)benzoate (**34**) after chromatography on silica gel (10/1 *n*-hexne/ethyl acetate). Data for **32**:[39] ^{1}H NMR δ 1.18 (d, J = 6.8 Hz, 3 H), 1.30 (d, J = 6.8 Hz, 3 H), 2.0−2.3 (m, 2 H), 2.8−3.3 (m, 4 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 7.2−8.15 (m, 4 H); ^{13}C NMR δ 13.50, 26.00, 29.00, 39.00, 50.20, 51.60, 126.60, 127.60, 128.40, 132.40, 133.60, 143.80, 175.00, 198.00; IR (neat) 1736, 1684, 1600 cm^{-1}. The following signals were discernible for **33**:[40] ^{1}H NMR δ 1.75−2.05 (m, 2 H), 2.1−2.4 (m, 2 H), 2.45−2.65 (m, 3 H), 2.95−3.15 (m, 2 H), 3.70 (s, 3 H), 7.2−7.4 (m, 2 H), 7.4−7.6 (m, 1 H), 8.05 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 25.20, 28.40, 28.80, 31.60, 46.40, 51.60, 126.20, 127.00, 128.40, 132.20, 133.60, 144.00, 174.00, 199.40; IR (neat) 1736, 1684, 1600 cm^{-1}. **34**: ^{1}H NMR δ 1.55 (d, J = 4.7 Hz, 3 H), 2.3−2.45 (m, 2 H), 3.00 (d, J = 7.0 Hz, 2 H), 3.90 (s, 3 H), 5.4−5.55 (m, 2 H), 7.2−7.9 (m, 4 H).

(d) Carbonylation of 21b. Under Conditions II (40 atm of CO, 100 °C, 28 h, DMF), **21b** (334 mg, 1.0 mmol) gave 226 mg (96%) of **35** as a 1:1 mixture of the *E* and *Z* isomers after chromatography on silica gel (10:1 *n*-hexane/ethyl acetate):[39] ^{1}H NMR δ 2.85−3.0 (m, 2 H), 3.05−3.2 (m, 2H), 6.84 (s, 1 H, *Z*), 6.89 (s, 1 H, *E*), 7.2−7.55 (m, 8 H), 8.12 (t, J = 6.9 Hz, 1 H); ^{13}C NMR δ 27.20, 28.80, 31.00, 36.00, 126.80, 127.00, 127.80, 127.90, 128.10, 128.20, 128.40, 128.50, 129.40, 129.80, 133.20, 133.30, 133.40, 134.20, 135.40, 135.70, 135.80, 136.40, 136.60, 143.20, 143.50, 188.00, 189.00; IR (neat) 1664, 1602 cm^{-1}.

(e) Carbonylation of 22. Under Conditions II (40 atm of CO, 100 °C, 16 h, $Pd(PPh_3)_4$ (0.05 equiv), a 1:1 mixture of acetonitrile/benzene), **22** (356 mg, 1.0 mmol) gave 170 mg (67%) of **36** after purification by chromatography on silica gel (63/27 hexane/Et_2O): ^{1}H NMR δ 1.6−1.8 (m, 3 H), 2.3−2.4 (m, 3 H), 2.96 (d, J = 15.0 Hz, 1 H), 3.37 (d, J = 15.0 Hz, 1 H), 3.45 (s, 3 H), 7.2−8.1 (m, 5 H); ^{13}C NMR δ 18.78, 26.04, 34.26, 40.38, 48.39, 52.26, 127.30, 127.78, 128.15, 132.66, 133.24, 135.87, 139.15, 139.77, 175.62, 185.80; high-resolution MS calcd for $C_{16}H_{16}O_3$ 256.1100, found 256.1097.

(f) Carbonylation of 23. Under Conditions IV (40 atm of CO, 100 °C, 15.5 h), a 1/1 mixture of acetonitrile/benzene), **23** (272 mg, 1.0 mmol) gave 122 mg (53%) of 1,2,3,4-tetrahydro-2-((methoxycarbonyl)-methyl)-2-methyl-1-oxonaphthalene (**37**) along with 35 mg (17%) of methyl 2-(3′-butenyl)benzoate (**38**) after chromatography on silica gel (10/1 *n*-hexane/ethyl acetate). **37**:[41] ^{1}H NMR δ 1.12 (s, 3 H), 1.98 (dt, J = 2.3, 6.8 Hz, 1 H), 2.15−2.25 (m, 1 H), 2.25 (d, J = 7.5 Hz, 1 H),

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2.47 (d, $J = 7.5$ Hz, 1 H), 2.4−2.6 (m, 2 H), 3.82 (s, 3 H), 7.2−7.4 (m, 2 H), 7.44 (t, $J = 3.8$ Hz, 1 H), 8.04 (d, $J = 3.8$ Hz, 1 H); ^{13}C NMR δ 21.90, 25.30, 33.13, 42.15, 43.63, 51.45, 126.70, 128.08, 128.63, 131.19, 133.23, 142.89, 171.88, 200.68; IR (neat) 1734 cm^{-1}. **38**: ^{1}H NMR δ 1.80 (s, 3 H), 2.30 (t, $J = 8.8$ Hz, 2 H), 3.10 (t, $J = 8.8$ Hz, 2 H), 3.90 (s, 3 H), 4.72 (bs, 2 H), 7.2−7.35 (m, 2 H), 7.35−7.5 (m, 1 H), 7.85−7.95 (m, 1 H); ^{13}C NMR δ 22.52, 33.06, 39.82, 51.90, 110.14, 125.85, 129.43, 130.63, 130.90, 131.89, 143.99, 145.53, 168.08; IR (neat) 1724 cm^{-1}; high-resolution MS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1149.

(g) Carbonylation of 24. Under Conditions I (1 atm of CO, 80 °C, 12 h, a 1:1 mixture of acetonitrile/benzene), **24** (244 mg, 1.0 mmol) gave **39** in 22% NMR yield:[42] ^{1}H NMR δ 1.87 (d, $J = 1.7$ Hz, 3 H), 6.93 (d, $J = 7.1$ Hz, 1 H), 7.0−7.2 (m, 2 H), 7.2−7.35 (m, 1 H), 7.36 (d, $J = 7.0$ Hz, 1 H). Under Conditions IV (40 atm of CO, 100 °C, 6 h, a 1:1 mixture of acetonitrile/benzene), **24** (244 mg, 1.0 mmol) gave 3-(methoxycarbonyl)-2-methyl-2,3-dihydro-1-*H*-indenone (**40a**) in 9% yield along with methyl 2-(1′-propenyl)benzoate (**41a**) (70%). Chromatography on silica gel (90/10 *n*-pentane/Et$_2$O) afforded 120 mg (67%) of **41a** as a 3/2 mixture of the (*E*) and (*Z*) isomers. ***trans*-40a**: ^{1}H NMR δ 1.39 (d, $J = 7.4$ Hz, 3 H), 3.12 (dq, $J = 7.4$, 4.6 Hz, 1 H), 3.82 (s, 3 H), 3.87 (d, $J = 4.6$ Hz, 1 H), 7.4−7.5 (m, 1 H), 7.6−7.7 (m, 2 H), 7.78 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR δ 15.17, 45.92, 52.13, 52.56, 124.08, 126.28, 128.76, 134.99, 135.64, 149.42, 172.23, 206.16; IR (neat) 1722 cm^{-1}; high-resolution MS calcd for $C_{12}H_{12}O_3$ 204.0786, found 204.0790. The following signals were discernible for ***cis*-40a**: ^{1}H NMR δ 1.28 (d, $J = 7.4$ Hz, 3 H), 3.01 (p, $J = 7.7$ Hz, 1 H), 3.71 (s, 3 H), 4.41 (d, $J = 4.6$ Hz, 1 H), 7.81 (d, $J = 7.7$ Hz, 1 H). **(*Z*)-41a**: ^{1}H NMR δ 1.73 (dd, $J = 7.05$, 1.8 Hz, 3 H), 3.87 (s, 3 H), 5.84 (dq, $J = 11.6$, 7.05 Hz, 1 H), 6.8−7.0 (m, 1 H), 7.2−7.6 (m, 3 H), 7.9−8.0 (m, 1 H); ^{13}C NMR δ 14.27, 51.92, 126.22, 126.54, 129.26, 129.61, 130.41, 130.85, 131.46, 138.79, 167.73; IR (neat) 1722 cm^{-1}; high-resolution MS calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0839. The following signals were discernible for **(*E*)-41a**: ^{1}H NMR δ 1.92 (dd, $J = 6.6$, 1.7 Hz, 3 H), 3.89 (s, 3 H), 6.15 (dq, $J = 15.6$, 6.6 Hz, 1 H), 7.1−7.2 (m, 1 H), 7.2−7.6 (m, 3 H), 7.83 (dd, $J = 7.8$, 1.3, 1 H). Under Conditions IV (40 atm of CO, 100 °C, 6 h, benzene), **24** (244 mg, 1.0 mmol) gave **40a** in 34% yield along with a 57% yield of **41a**. Under Conditions IV (40 atm of CO, 100 °C, 24 h, *i*-PrOH (4 equiv), benzene), **24** (244 mg, 1.0 mmol) gave 3-(isopropoxycarbonyl)-2-methyl-2,3-dihydro-1*H*-indenone (**40b**) in 63% NMR yield along with a 15% yield of isopropyl 2-(1′-propenyl)benzoate (**41b**) and a 13% yield of **39**. Chromatography on silica gel (90/10 *n*-pentane/Et$_2$O) afforded 128 mg (55%) of **40b** as a single isomer. ***trans*-40b**: ^{1}H NMR δ 1.31 (d, $J = 6.3$ Hz, 6 H), 1.39 (d, $J = 7.3$ Hz, 3 H), 3.12 (dq, $J = 7.3$, 4.5 Hz, 1 H), 3.81 (d, $J = 4.5$ Hz, 1 H), 5.12 (sept, $J = 6.25$ Hz, 1 H), 7.4−7.5 (m, 1 H), 7.6−7.75 (m, 2 H), 7.78 (d, $J = 7.7$, 1 H); ^{13}C NMR δ 15.08, 21.76, 21.80, 45.79, 52.41, 69.06, 124.04, 126.06, 128.63, 134.89, 135.65, 149.75, 171.18, 206.41; IR (neat) 1722 cm^{-1}; high-resolution MS calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1104.

(h) Carbonylation of 25. Under Conditions IV (40 atm of CO, 100 °C, 24 h, *i*-PrOH (4 equiv), benzene), **25** (244 mg, 1.0 mmol) did not yield monomeric cyclization products.

Preparation of ω-Alkene-Containing Aryl Iodides 42, 43, 49, and 53−57. (a) 2-(1′-Hydroxy-2′-propenyl)-1-iodobenzene (42). Compound **42** was prepared according to a reported procedure.[31]

(b) 2-(2′-(Hydroxymethyl)-3′-butenyl)-1-iodobenzene (43). Using the procedure described for the preparation of **22**,[30] except that ethyl crotonate was used in place of 1-carbomethoxycyclohexene, ethyl α-(*o*-iodobenyl)vinylacetate was obtained. Its reduction with *i*-Bu$_2$AlH (3 equiv, −78 °C, 10 min) gave **43** in 46% yield after chromatography on silica gel (90/10 pentane/Et$_2$O): ^{1}H NMR δ 1.64 (bs, 1 H), 2.55−2.8 (m, 2 H), 2.89 (dd, $J = 13.3$, 6.55 Hz, 1 H), 3.4−3.8 (m, 2 H), 5.0−5.2 (m, 2 H), 5.65−5.85 (m, 1 H), 6.8−6.95 (m, 1 H), 7.1−7.3 (m, 2 H), 7.81 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR δ 41.64, 46.69, 64.60, 101.00, 117.71, 127.94, 127.98, 130.60, 138.51, 139.51, 142.33; IR (neat) 3346 (bs), 1030 (s) cm^{-1}; high-resolution MS calcd for $C_{11}H_{13}IO$ 289.0089, found 289.0080.

(c) 2-(1′-(*tert*-Butyldimethylsilyloxy)-2′-propenyl)-1-iodobenzene (49). Compound **49** was prepared according to a reported procedure.[31]

(d) 5-(2′-Iodophenyl)-4-(methoxycarbonyl)-2-pentenoate (53a) and 5-(2′-Iodophenyl)-4-(methoxycarbonyl)-3-pentenoate (53b). To *i*-Pr$_2$NH (2.6 mL, 1.87 g, 18.5 mmol, −78 °C, 0.5 h) in THF (20 mL) were successively added a 2.0 M solution of *n*-BuLi in hexane (10.1 mL, 20.2 mmol), dimethyl pentenedioate (2.8 g, 17.7 mmol, −78 °C, 1 h) in THF (10 mL), and 2-iodobenzyl bromide (5.0 g, 16.8 mmol, −78 °C) in THF (20 mL). The reaction mixture was warmed and stirred at 25 °C for 2 h, quenched with aqueous NH$_4$Cl, extracted with Et$_2$O, washed with aqueous NaHCO$_3$, dried over MgSO$_4$, and evaporated. Chromatography on silica gel (3/1 *n*-hexane/pentane) afforded 5.24 g (83%) of a 1:1 mixture of **53a** and **53b**: ^{1}H NMR δ 2.8−3.8 (m, 19 H), 6.6−7.4 (m, 9 H), 7.7−7.9 (m, 2 H).

(e) Methyl (*E*)-4-(2′-Iodophenyl)-2-butenoate (54). Reduction of 1-(2′-iodophenyl)-2-propyne (1.96 g, 8.1 mmol) with *i*-Bu$_2$AlH (1.05 equiv, 25 °C, 16 h) followed by treatment with methyl chloroformate (2.30 g, 24.3 mmol, 0 to 25 °C, 3 h) afforded, upon quenching with H$_2$O (2 mL), 1.50 g (61%) of **54** after chromatography on silica gel (83/17 hexane/Et$_2$O): ^{1}H NMR δ 3.63 (dd, $J = 6.5$, 1.5 Hz, 2 H), 3.70 (s, 3 H), 5.79 (dt, $J = 15.6$, 1.6 Hz, 1 H), 6.92 (dt, $J = 7.6$, 1.8 Hz, 1 H), 7.05 (dt, $J = 15.6$, 6.5 Hz, 1 H), 7.17 (dd, $J = 7.6$, 1.8 Hz, 1 H), 7.29 (dt, $J = 7.4$, 1.2 Hz, 1 H), 7.82 (d, $J = 8.0$ Hz, 1 H); ^{13}C NMR δ 43.75, 52.04, 101.20, 123.11, 129.11, 130.43, 140.17, 141.14, 146.37, 167.22; IR (neat) 1718 cm^{-1}.

(f) Ethyl (*E*)-5-(2′-Iodophenyl)-2-pentenoate (55). This compound was prepared in 69% yield as described in the preparation of **54** using 4-(2′-iodophenyl)-1-butyne (*vide supra*, preparation of **21a**) in place of 3-(2′-iodophenyl)-1-propyne: ^{1}H NMR δ 1.28 (t, $J = 7.3$ Hz, 3 H), 2.4−2.6 (m, 2 H), 2.8−2.95 (m, 2 H), 4.19 (q, $J = 7.3$ Hz, 2 H), 5.8−5.95 (m, 1 H), 6.8−6.95 (m, 1 H), 6.95−7.1 (m, 1 H), 7.1−7.35 (m, 2 H), 7.75−7.85 (m, 1 H); ^{13}C NMR δ 14.42, 32.70, 39.41, 60.34, 122.19, 128.21, 128.57, 129.48, 139.71, 143.40, 147.49, 166.57.

(g) (*Z*)-2-(3′-(Trimethylsilyl)-2′-propenyl)-1-iodobenzene (56). Reduction of 1-(2′-iodophenyl)-3-(trimethylsilyl)-2-propyne[32] (0.90 g, 2.90 mmol) with *i*-Bu$_2$AlH (1.5 equiv, 40 °C, 18 h) gave **56** after chromatography on silica gel (*n*-hexane): ^{1}H NMR δ 0.18 (s, 9 H), 3.57 (d, $J = 7.0$ Hz, 2 H), 5.73 (dt, $J = 14.0$, 1.4 Hz, 1 H), 6.38 (dt, $J = 14.0$, 7.0 Hz, 1 H), 6.89 (dt, $J = 7.2$, 1.6 Hz, 1 H), 7.15−7.35 (m, 2 H), 7.82 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR δ 0.78, 44.82, 101.52, 128.49, 128.90, 129.69, 132.00, 139.92, 143.59, 145.63; IR (neat) 1606 (s), 1464 (s), 1436 (s), 1248 (s), 1012 (s), 838 (s), 746 (s) cm^{-1}; high-resolution MS calcd for $C_{12}H_{17}ISi$ 316.0144, found 316.0141.

(h) (*E*)-1-(*tert*-Butyldimethylsilyl)oxy)-5-(2′-iodophenyl)-2-pentene (57). A solution of 2-iodobenzyl bromide (5.94 g, 20 mmol) in THF (20 mL) was treated with a solution of allenylmagnesium bromide (*vide supra*, preparation of **21a**) and heated at reflux for 10 h. The reaction mixture was quenched with aqueous NH$_4$Cl, extracted with Et$_2$O, washed with aqueous NaHCO$_3$, dried over MgSO$_4$, and evaporated. Chromatography on silica gel (99/1 *n*-pentane/Et$_2$O) afforded 5.10 g (99%) of 4-(2′-iodophenyl)-1-butyne: ^{1}H NMR δ 1.97 (t, $J = 2.6$ Hz, 1 H), 2.46 (dt, $J = 7.5$, 2.6 Hz, 2 H), 2.92 (t, $J = 7.5$ Hz, 2 H), 6.8−6.95 (m, 1 H), 7.2−7.3 (m, 2 H), 7.78 (d, $J = 8.3$ Hz, 1 H); ^{13}C NMR δ 19.01, 39.51, 69.27, 83.04, 100.25, 129.16, 129.67, 139.35, 142.49. Reduction of 4-(2′-iodophenyl)-1-butyne (5.10 g, 19.9 mmol) with *i*-Bu$_2$AlH (1.05 equiv, 25 °C, 10 h) followed by treatment with ethyl chloroformate (5.71 mL, 59.7 mmol, 0 °C then 25 °C, 2 h) gave 5.65 g (86%) of ethyl (*E*)-4-(2′-iodophenyl)-2-butenoate. A portion of this crude product (651 mg, 1.97 mmol) in CH$_2$Cl$_2$ was treated with *i*-Bu$_2$AlH (0.81 mL, 4.55 mmol, 0 °C, 1 h). The reaction mixture was quenched with NH$_4$Cl, extracted with Et$_2$O, washed with NaHCO$_3$, dried over MgSO$_4$, and evaporated to give 567 mg (100%) of (*E*)-4-(2′-iodophenyl)-2-buten-1-ol. A mixture of (*E*)-4-(2′-iodophenyl)-2-buten-1-ol (394 mg, 1.37 mmol), *tert*-butylchlorodimethylsilane (248 mg, 1.65 mmol), and imidazole (100 mg, 2.06 mmol) in DMF (2 mL) was stirred at 25 °C for 1 h. The reaction mixture was diluted with *n*-pentane, extracted with H$_2$O, dried over MgSO$_4$, and evaporated. Chromatography on silica gel (8/1 *n*-pentane/Et$_2$O) afforded 535 mg (97%) of **57**: ^{1}H NMR δ 0.52 (s, 6 H), 0.90 (s, 9 H), 2.25−2.4 (m, 2 H), 2.7−2.85 (m, 2 H), 4.05−4.2 (m, 2 H), 5.5−5.8 (m, 2 H), 6.8−6.9 (m, 1 H), 7.1−7.3 (m, 2 H), 7.76 (d, $J = 7.7$ Hz, 1 H); ^{13}C NMR δ −5.11, 18.39, 25.98, 32.60, 40.44, 63.82, 100.54, 127.65, 128.18, 129.30, 129.53, 130.08, 139.38, 144.26; IR (neat) 1462 (s), 1262 (s) cm^{-1}; high-resolution MS calcd for $C_{12}H_{17}ISi$ 316.0114, found 316.0141.

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[42] Floyd, M. B.; Allen, G. R. *J. Org. Chem.* **1970**, *35*, 2847.

Pd-Catalyzed Carbonylation of *o*-Iodo-*ω*-alkenylbenzenes Containing Heteroatom Substituents (Schemes 5 and 6). (a) Carbonylation of 42. Under Conditions II (40 atm of CO, 100 °C, 20 h), where a 1:1 mixture of acetonitrile/benzene was used in place of DMF, **42** (260 mg, 1.0 mmol) gave 3-ethylidene-1-isobenzofuranone (**44**) in 90% yield along with a 3% yield of 3,3a,8b-trihydro-2,4-2*H*-indeno-[1,2-*b*]furandione (**46**). **44-(*E*)**:[31] ^{1}H NMR δ 2.01 (d, J = 7.2 Hz, 3 H), 5.67 (q, J = 7.2 Hz, 1 H), 7.4−7.55 (m, 1 H), 7.55−7.75 (m, 2 H), 7.86 (d, J = 7.7 Hz, 1 H); ^{13}C NMR δ 11.29, 104.23, 119.58, 124.33, 125.14, 129.32, 134.29, 139.48, 146.36, 167.13. The following signals were discernible for **44-(*Z*)**: ^{1}H NMR δ 2.15 (d, J = 7.9 Hz, 3 H), 5.92 (q, J = 7.2 Hz, 1 H), 7.56 (t, J = 7.5 Hz, 3 H), 7.7−7.8 (m, 2 H), 7.86 (m, 1 H), 7.86 (d, J = 7.9 Hz, 1 H), 7.94 (d, J = 7.7 Hz, 1 H). An authentic sample of **46** was prepared by heating at 50 °C a mixture of **50** (50 mg, 0.15 mmol, *vide infra* for preparation) and pyridinium *p*-toluenesulfonate (0.3 equiv) in CH_3OH for 24 h. The reaction mixture was evaporated, diluted with Et_2O, washed with H_2O, dried over $MgSO_4$, and evaporated. Chromatography on silica gel (90/10 pentane/Et_2O) gave 23 mg (71%) of a 1/4 mixture of **46** and 2-*trans*-((methoxycarbonyl)methyl)-3-hydroxy-1-indanone: ^{1}H NMR δ 2.67 (dd, J = 18.0, 10 Hz, 1 H), 2.75−2.9 (m, 1 H), 3.20 (dd, J = 18.0, 4.0 Hz, 1 H), 3.73 (s, 3 H), 4.15 (bs, 1 H), 5.11 (d, J = 6.0 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 1 H), 7.6−7.8 (m, 3 H); ^{13}C NMR δ 32.70, 52.17, 54.24, 74.39, 123.09, 125.44, 129.07, 135.22, 135.29, 153.17, 173.96, 201.81. The following signals were discernible for **46**: ^{1}H NMR δ 3.06 (dd, J = 19.0, 12.5 Hz, 1 H), 3.55−3.65 (m, 2 H), 6.00 (d, J = 6.7 Hz, 1 H); ^{13}C NMR δ 31.03, 45.69, 79.06, 124.34, 127.48, 131.06, 135.98, 136.07, 149.57, 174.78, 202.42. Under Conditions IV (40 atm of CO, 100 °C, 20 h, a 1:1 mixture of acetonitrile/benzene), **42** (260 mg, 1.0 mmol) gave **44** in 65% NMR yield along with a 24% yield of **45** and a 3% yield of **46**. **45**:[39] ^{1}H NMR δ 1.23 (t, J = 7.2 Hz, 3 H), 2.81 (q, J = 7.2 Hz, 2 H), 3.89 (s, 3 H), 7.3−7.4 (m, 1 H), 7.4−7.6 (m, 2 H), 7.85−7.95 (m, 1 H).

(b) Carbonylation of 43. Under Conditions II (40 atm of CO, 100 °C, 20 h, benzene), **43** (288 mg, 1.0 mmol) gave 3-vinyl-3,4,5-trihydro-2-benzoxepin-1-one (**48**) in 31% NMR yield along with a 36% yield of 4,4a,10,10a-tetrahydro-3,4-1*H*-naphtho[2,3-*c*]pyrandione (**48**). Chromatography on silica gel (90/10 *n*-pentane/Et_2O) afforded 58 mg (31%) of **47**, and further elution (80/20 CH_2Cl_2/Et_2O) afforded 75 mg (35%) of **48**. ***trans*-47**: ^{1}H NMR δ 2.4−2.6 (m, 1 H), 2.7−3.3 (m, 5 H), 4.19 (t, J = 11.15 Hz, 1 H), 4.52 (dd, J = 11.15, 4.5 Hz, 1 H), 7.2−7.45 (m, 2 H), 7.5−7.6 (m, 1 H), 7.95−8.05 (m, 1 H); ^{13}C NMR δ 29.69, 30.62, 35.33, 45.06, 72.60, 127.44, 127.56, 128.99, 131.30, 134.25, 140.88, 169.49, 195.63; IR (neat) 1743, 1690 cm^{-1}; high-resolution MS calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0781. The following signals were discernible for the *cis* isomer: ^{13}C NMR δ 28.72, 28.88, 32.33, 35.33, 45.06, 72.60, 127.44, 127.56, 128.99, 131.30, 134.47, 140.89, 195.85. **48**: ^{1}H NMR δ 2.77 (dd, J = 13.15, 5.15 Hz, 1 H), 2.9−3.15 (m, 2 H), 3.91 (dd, J = 12.2, 6.65 Hz, 1 H), 4.18 (dd, J = 12.2, 5.55 Hz, 1 H), 5.05−5.15 (m, 2 H), 5.7−5.85 (m, 1 H), 7.22 (d, J = 7.4 Hz, 1 H), 7.38 (t, J = 7.5 Hz, 1 H), 7.45−7.55 (m, 1 H), 7.74 (d, J = 7.5, 1 H); ^{13}C NMR δ 35.75, 43.08, 70.02, 116.75, 127.53, 129.25, 130.30, 131.39, 132.57, 136.27, 136.75, 171.99; IR (neat) 1726 cm^{-1}; high-resolution MS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0841.

(c) Carbonylation of 49. Under Conditions II (40 atm of CO, 100 °C, 18 h, DMF), **49** (374 mg, 1.0 mmol) gave 3-((*tert*-butyldimethylsilyl)oxy)-2-methylene-2,3-dihydro-1*H*-inden-one (**51**) in 25% NMR yield. Chromatography on silica gel (86/14 *n*-hexane/Et_2O) afforded 57 mg (20%) of **51**:[31] ^{1}H NMR δ 0.19 (s, 3 H), 0.25 (s, 3 H), 0.96 (s, 9 H), 5.67 (bs, 1 H), 6.43 (d, J = 2.2 Hz, 1 H), 7.48 (dt, J = 7.2, 1.0 Hz, 1 H), 7.63 (d, J = 6.8 Hz, 1 H), 7.69 (dt, J = 7.2, 1.2 Hz, 1 H), 7.85 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ −3.36, 18.58, 26.26, 70.58, 121.14, 124.32, 126.32, 129.80, 135.87, 137.84, 149.07, 152.45, 191.83; IR (neat) 1718 cm^{-1}. Under Conditions IV (40 atm of CO, 100 °C, 18 h, a 1:1 mixture of acetonitrile/benzene), **49** (374 mg, 1.0 mmol) gave 2-((methoxycarbonyl)methyl)-3-((dimethyl-*tert*-butylsilyl)oxy)-1-indanone (**50**) in 75% NMR yield as a 3/1 mixture of the *trans* and *cis* isomers. Chromatography on silica gel (83/17 *n*-hexane/Et_2O) afforded 231 mg (69%) of **50**[31] as a 74/26 mixture of the *trans* and *cis* isomers. Data for the *trans* isomer: ^{1}H NMR δ 0.18 (s, 3 H), 0.26 (s, 3 H), 0.46 (s, 9 H), 2.7−3.2 (m, 3 H), 3.65 (s, 3 H), 5.23 (d, J = 4 Hz, 1 H), 7.4−7.7 (m, 3 H), 7.7−7.9 (m, 1 H); ^{13}C NMR δ −4.24, −4.08, 17.89, 25.67, 30.11, 49.79, 54.49, 73.87, 122.94, 125.14, 128.78, 134.86, 135.50, 153.97, 154.14, 171.98, 202.09; IR (neat) 1718 cm^{-1}. The following signals were discernible for the *cis* isomer: ^{1}H NMR δ 0.14 (s, 3 H), 0.17 (s, 3 H), 0.84 (s, 9 H), 3.1−3.3 (m, 1 H), 3.60 (s, 3 H), 5.51 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (17.88, 25.61, 29.71, 49.52, 49.64, 70.27, 123.44, 126.24, 129.26, 134.78, 135.44, 153.97, 172.91, 204.72.

(d) Carbonylation of 53a and 53b. Under Conditions IV (40 atm of CO, 100 °C, 15 h, 4 equiv of *t*-BuOH DMF), a 1:1 mixture of **53a** and **53b** (374 mg, 1.0 mmol) gave 125 mg (46%) of 2-((methoxycarbonyl)methyl)-2-(2′-methoxycarbonylvinyl)-1-indanone (**58**) after chromatography on silica gel (1/1 *n*-pentane/Et_2O): ^{1}H NMR δ 3.37 (d, J = 17.3 Hz, 1 H), 3.72 (s, 3 H), 3.76 (s, 3 H), 3.91 (d, J = 17.3 Hz, 1 H), 5.97 (d, J = 16 Hz, 1 H), 7.3−7.85 (m, 5 H); ^{13}C NMR δ 37.93, 52.28, 53.89, 63.12, 122.72, 125.91, 126.88, 128.76, 134.26, 136.44, 144.49, 152.61, 166.59, 169.89, 198.66.

(e) Carbonylation of 54. Under Conditions IV (40 atm of CO, 100 °C, 10 h, DMF), **54** (302 mg, 1.0 mmol) gave methyl 2-(2-(2,3-dihydro-1-oxo-1*H*-indenyl))malonate (**59**) in 23% NMR yield along with methyl 1-hydroxy-2-naphthoate (**60**) (25%), **12** (10%), 4-(2′-(methoxycarbonyl)phenyl)-3-butenoate (**61a**) (12%), and 4-(2′-(methoxycarbonyl)phenyl)-2-butenoate (**61b**) (3%) obtained in the yields indicated in parentheses. Chromatography on silica gel (83/17 *n*-hexane/Et_2O) afforded 57 mg (22%) of **59**, 50 mg (25%) of **60**,[43] 11 mg (5%) of **12**, and 37 mg of a mixture of **61a** (12%) and **61b** (3%). **59**: ^{1}H NMR δ 3.1−3.5 (m, 3 H), 3.66 (s, 3 H), 3.82 (s, 3 H), 4.16 (d, J = 5.0 Hz, 1 H), 7.38 (dt, J = 7.4, 1.0 Hz, 1 H), 7.47 (d, J = 7.8 Hz, 1 H), 7.61 (dt, J = 7.4, 1.2 Hz, 1 H), 7.77 (d, J = 7.6, 1.0 Hz, 1 H); ^{13}C NMR δ 31.14, 46.91, 51.86, 53.13, 53.30, 124.52, 126.94, 128.01, 135.44, 136.59, 153.64, 168.63, 169.57, 205.02; high-resolution MS calcd for $C_{14}H_{14}O_5$ 203.0708, found 203.0697. **60**:[43] ^{1}H NMR δ 3.96 (s, 3 H), 6.55−6.7 (m, 2 H), 6.7−6.85 (m, 2 H), 6.85−6.9 (m, 2 H), 8.15−8.25 (m, 1 H), 11.98 (s, 1 H); ^{13}C NMR δ 52.23, 105.53, 118.55, 123.82, 124.17, 124.70, 125.70, 127.41, 129.44, 137.14, 160.87, 171.38. **61a**: ^{1}H NMR δ 3.32 (dd, J = 7.0, 1.6 Hz, 1 H), 3.73 (s, 3 H), 3.90 (s, 3 H), 6.22 (dt, J = 15.8, 7.1 Hz, 1 H), 7.25−7.4 (m, 2 H), 7.47 (dt, J = 7.4, 1.6 Hz, 1 H), 7.57 (dd, J = 7.8, 1.4 Hz, 1 H), 7.87 (d, J = 7.8, 1.4 Hz, 1 H); ^{13}C NMR δ 38.76, 52.42, 52.57, 124.95, 127.70, 127.99, 130.87, 132.61, 139.17, 148.34, 168.27, 172.49. The following signals were discernible for **61b**: ^{1}H NMR δ 3.7 (s, 3 H), 3.88 (s, 3 H), 5.74 (dt, J = 15.6, 1.7 Hz, 1 H), 7.15 (dt, J = 15.8, 6.6 Hz, 1 H), 7.47 (d, J = 7.8 Hz, 1 H), 7.61 (dt, J = 7.4, 1.2 Hz, 1 H), 7.77 (dd, J = 7.96, 1.5 Hz, 1 H).

(f) Carbonylation of 55. Under Conditions II (40 atm of CO, 100 °C, 10 h, DMF), **55** (402 mg, 1.0 mmol) gave a 17% NMR yield of 1-(ethoxycarbonyl)methyleneindane (**64**):[43] a 1/1 mixture of the *E* and *Z* isomers: ^{1}H NMR δ 1.25 (t, J = 7.2 Hz, 3 H), 1.32 (t, J = 7.2 Hz, 3 H), 2.9−3.15 (m, 2 H), 3.2−3.35 (m, 2 H), 3.36 (s, 2 H), 3.57 (s, 2 H), 4.1−4.3 (m, 4 H), 6.30 (t, J = 2.5 Hz, 1 H), 6.42 (s, 1 H), 7.1−7.6 (m, 8 H); ^{13}C NMR δ 14.33, 14.58, 30.73, 31.28, 34.28, 38.06, 59.82, 60.99, 107.80, 119.27, 121.74, 123.89, 124.96, 125.76, 126.25, 126.89, 130.96, 131.77, 140.09, 144.17, 144.59, 149.59, 163.09, 167.68, 171.11. Under Conditions IV (40 atm of CO, 100 °C, 10 h, DMF), **55** (402 mg, 1.0 mmol) gave an 84% NMR yield of ethyl (*E*)-5-(2′-(methoxycarbonyl)phenyl)-2-pentanoate (**63**) along with a 13% yield of ethyl methyl 2-(1-tetralone)malonate (**62**), obtained as a 1:1 mixture of two diastereomers. Chromatography on silica gel (6/1 pentane/Et_2O) afforded 194 mg (78%) of **63** and 27.6 mg (13%) of **62a**: ^{1}H NMR δ 1.27 (t, J = 7.2 Hz, 3 H), 1.31 (t, J = 7.2 Hz, 3 H), 2.1−2.3 (m, 4 H), 2.9−3.2 (m, 4 H), 3.3−3.45 (m, 2 H), 3.76 (s, 3 H), 3.81 (s, 3 H), 3.95−4.1 (m, 2 H), 4.23 (q, J = 7.2 Hz, 2 H), 4.26 (q, J = 7.2 Hz, 2 H), 7.2−7.4 (m, 2 H), 7.4−7.55 (m, 1 H), 7.65−7.75 (m, 2 H), 8.10 (d, J = 7.9 Hz, 1 H); IR (neat) 1734, 1684 cm^{-1}; high-resolution MS calcd for $C_{16}H_{18}O_5$ 290.1154, found 290.1150. **63a**: ^{1}H NMR δ 1.28 (t, J = 7.0 Hz, 3 H), 2.4−2.6 (m, 2 H), 3.05−3.2 (m, 2 H), 3.88 (s, 3 H), 4.18 (q, J = 7.0 Hz, 2 H), 5.84 (d, J = 16.4 Hz, 1 H), 6.95−7.1 (m, 1 H), 7.15−7.35 (m, 2 H), 7.35−7.5 (m, 1 H), 7.90 (d, J = 8.1 Hz, 1 H); ^{13}C NMR δ 14.13, 32.97, 33.93, 51.82, 59.98, 121.56, 126.16, 129.13, 130.78, 130.86, 132.02, 142.69, 148.09, 166.42, 167.55; IR (neat) 1718 cm^{-1}; high-resolution MS calcd for $C_{15}H_{18}O_4$ 262.1205,

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[43] Broom, N. J. P.; Sammes, P. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 465.

found 262.1208. Using *t*-BuOH (4 equiv) in place of MeOH in the procedure described above, **62b** was obtained in 40% NMR yield.

(g) Carbonylation of 56. Under Conditions II (40 atm of CO, 100 °C, 17 h, DMF), **56** (316 mg, 1.0 mmol) gave 2-((trimethylsilyl)-methylene)-2,3-dihydro-1*H*-inden-1-one (**65**) in 15% NMR yield along with a 52% yield of 1-naphthol (**66**). Chromatography on silica gel (80/20 *n*-hexane/Et_2O) afforded 36 mg (17%) of **65** and 75 mg (52%) of **66**. **65**: *E*/*Z* = 97/3, ^{1}H NMR δ 0.26 (s, 9 H), 3.76 (bs, 2 H), 7.09 (t, *J* = 1.8 Hz, 1 H), 7.35−7.65 (m, 3 H), 7.89 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR δ −0.44, 32.77, 125.39, 126.83, 128.07, 135.28, 136.71, 138.29, 149.97, 150.47, 192.80; high-resolution MS calcd for $C_{13}H_{16}$-OSi 217.1049, found 217.1042. Under Conditions IV (40 atm of CO, 100 °C, 18 h, DMF), **56** (316 mg, 1.0 mmol) gave **12** in 35% NMR yield along with a 40% yield of 1-naphthol (**66**). Chromatography on silica gel (75/25 *n*-hexane/Et_2O) afforded 70 mg (34%) of **12** and 54 mg (38%) of **66**.

(h) Carbonylation of 57. Under Conditions II (40 atm of CO, 100 °C, 10 h, DMF), **57** (402 mg, 1.0 mmol) gave a 73% NMR yield of **67** as a 1:1 mixture of two diastereomers along with a 24% yield of 2-(formylmethyl)-1-tetralone (**68**). The following signals were assignable to *E*-**67**: ^{1}H NMR δ 0.14 (s, 6 H), 0.91 (s, 9H), 1.9−2.3 (m, 2 H), 2.9−3.2 (m, 3 H), 5.21 (dd, *J* = 12.0, 8.1 Hz, 1 H), 6.37 (d, *J* = 12.0 Hz, 1 H), 7.1−7.6 (m, 3 H), 7.95−8.2 (m, 1 H); ^{13}C NMR δ −5.2, 25.64, 27.95, 30.48, 46.84, 108.50, 126.58, 127.60, 128.63, 133.18, 142.75. The following signals are discernible for *Z*-**67**: ^{1}H NMR δ 3.6−3.9 (m, 2 H), 3.95−4.05 (m, 1 H), 4.45 (d, *J* = 5.8 Hz, 1 H), 4.78 (dd, *J* = 8.0, 5.8 Hz, 1 H). A mixture of the crude products, 1 M HCl (0.6 mL), and THF (1.2 mL) was stirred at 25 °C for 1 h, diluted with Et_2O, washed with $NaHCO_3$, dried over $MgSO_4$, and evaporated. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy indicated the formation of **68** in 83% yield. Chromatography on silica gel (6:1 *n*-pentane/Et_2O) afforded 150 mg (80%) of **68**: ^{1}H NMR δ 1.9−2.1 (m, 1 H), 2.15−2.35 (m, 1 H), 2.45−2.65 (m, 1 H), 2.9−3.1 (m, 1 H), 3.1−3.3 (m, 3 H), 7.2−7.4 (m, 2 H), 7.4−7.55 (m, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 9.92 (d, *J* = 1.1 Hz, 1 H); ^{13}C NMR δ 29.29, 29.41, 43.24, 126.68, 127.45, 128.74, 131.91, 133.52, 143.98, 198.36, 200.61; high-resolution MS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0835.

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