Pd-Catalyzed Reactions of Donor−Acceptor-Substituted Cyclopropanes and Their Ring-Opened Derivatives: Attempted Heck Cyclization and Novel One-Pot Enolate Arylations

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Dedicated to Professor Axel Kleemann on the occasion of his 60th birthday

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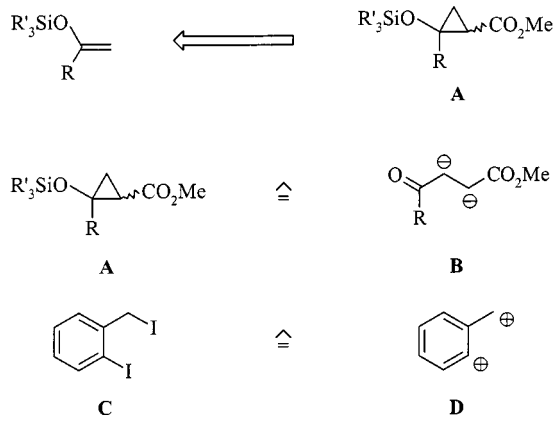
Donor–acceptor substituted cyclopropane derivatives **4a**–**g** were synthesized in good yields from ketones, via the corresponding silyl enol ethers **2a**–**g**, by cyclopropanation with methyl diazoacetate followed by alkylation using *o*-iodobenzyl iodide. The γ-oxo esters **5a**–**g** were prepared in high yield, employing $NEt_3 \cdot 3\,HF$. A novel Pd-catalyzed one-pot transformation of **4a**–**f** into 1,2-disubstituted indanes **6a**–**f** was accomplished using either CsF (Method A or B) or Bu_4NF (Method C) as the fluoride source to achieve the in situ ring-opening of **4a**–**f**. The two reagents CsF and Bu_4NF function in a complementary manner. For example, CsF works better with enones **4b** and **4c**, while Bu_4NF functions well with aryl/alkyl ketones **4d**–**f**. Pd-catalyzed Heck cyclization of vinyl ketone **5a** furnished mainly the 7-*exo*-trig cyclization product **7** but isopropenyl ketone **5b** gave a moderate yield of indane derivative **6b**, arising from enolate arylation. When the carbonyl group in **5b** was protected, a novel tricyclic compound **13** was obtained in low yield.

Introduction

Pd-catalysis is perhaps among the most fertile areas of contemporary research, both from the academic and the industrial standpoint. In the recent past, there has been tremendous growth in this field, resulting in amazingly large numbers of new applications of palladium-catalyzed processes.[1] The utility of Pd-catalysis for C−C bond forming processes, which continue to be the fundamental theme of organic synthesis, is particularly remarkable. We became interested in applying Pd-catalysis to donor−acceptor substituted cyclopropanes[2] and the corresponding ring-opened γ-oxo ester derivatives that could readily be obtained by methods developed in our laboratory, starting from ketones via the corresponding silyl enol ethers (Scheme 1). Siloxycyclopropane derivatives **A** possess a masked carbonyl group, which can be unveiled at an appropriate stage during synthesis to furnish the corresponding γ-oxo ester derivatives. Thus, substituted siloxycyclopropanes serve as important three-carbon building blocks in the synthesis of numerous target molecules.[3] Our aim was to make use of the easily available cyclopropanes **A** as bisnucleophilic synthon **B**, and to combine this with an appropriate partner such as *o*-iodobenzyl iodide **C**, which can be viewed formally as a bis-electrophile synthon **D** (Scheme 1). The task of the initial



Scheme 1

installation of an electrophile on C-1 of **A** could easily be achieved by the deprotonation and alkylation strategy developed earlier.[2] In the second step, Pd-catalysis should play a crucial role by providing the means to ring-closure by intramolecular α-arylation of the ketone moiety, leading to substituted indane derivatives.[4] Pd-catalyzed inter-[5] and intramolecular[6] α-arylations of ketones have been the subject of recent investigations. Alternatively, for R = an alkenyl group, this substituent could participate in a Heck type ring-closure to furnish a seven- or eight-membered carbocycle.[7] Since cleavage of siloxycyclopropanes **A** is feasible under basic conditions, a one-pot procedure is ideally suited to accomplish this goal. In our preliminary report,[8] we have already demonstrated the one-pot conversion of siloxycyclopropane derivatives into substituted indanes. Here, we present a full account of our results.

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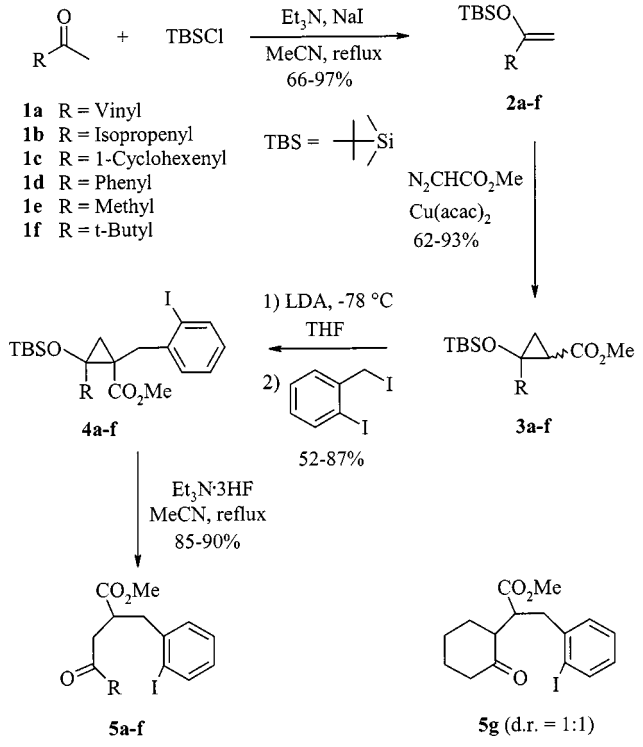
Results and Discussion

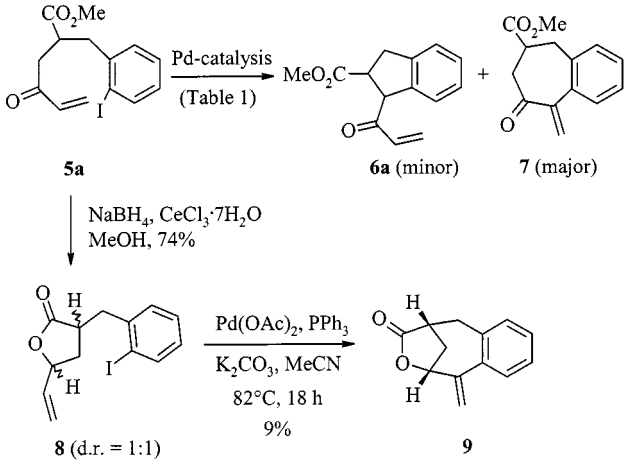
The silyl enol ethers **2a**,**b**,**d**−**f** were synthesized in 66−97% yield from the corresponding ketones, under thermodynamic control conditions, using NEt_3 as the base, 1.2 equivalents of tBuMe$_2$SiCl, and NaI in refluxing acetonitrile.[9] The silyl enol ether **2c** was prepared according to the literature procedure. The Cu(acac)$_2$-catalyzed [2+1] cycloadditions between silyl enol ethers **2a**−**f** and methyl diazoacetate furnished a mixture of *cis* and *trans* methyl 2-siloxycyclopropanecarboxylates **3a**−**f** in good yield.[10] For the introduction of a substituent at C-1 of **3a**−**f**, the deprotonation and alkylation of the resulting enolate is a feasible route. The enolate generated in THF at −78 °C with 1.2 equivalents of LDA, upon treatment with *o*-iodobenzyl iodide, furnished alkylated siloxycyclopropane derivatives **4a**−**f**. The geometry of the alkylated products was exclusively *trans* in all cases except **4e**; this is attributed, among other factors, to a stereoelectronic effect.[11] In the case of **4e**, a *trans*/*cis* mixture of isomers was obtained in a ratio of 81:19 (Scheme 2; only *trans*-**4** is shown). The ring cleavage of the substituted siloxycyclopropanes **4a**−**f** was accomplished in high yield using $NEt_3 \cdot 3$ HF and acetonitrile as solvent at reflux temperature to afford the γ-oxo esters **5a**−**f**.[12] The γ-oxo ester derivative **5g**[13] was also obtained as a 1:1 mixture of diastereomers when starting from cyclohexanone and following the same sequence as for **5a**−**f**.



Scheme 2

Palladium(0)-Catalyzed Cyclization of 5a and 8

Originally, palladium(0)-catalyzed reactions of **5a** had been pursued with the intention of synthesizing cyclooctanoid derivatives; these constitute the main structural motif of taxane diterpenes, as well as other natural products.[14] Our efforts in this direction revealed that Heck-cyclization of **5a**, contrary to our expectation, proceeds via the 7-*exo*-trig mode to furnish mainly **7** (along with a small amount (≈10%) of indane derivative **6a**) in 68% yield after optimization (Scheme 3). The reaction conditions employed to optimize the yield are summarized in Table 1. Increasing the amount of catalyst from 1% to 17% helped in cutting down the reaction time (entries 1 and 2), but without any significant consequences for the yield. When K_2CO_3 was used as the base, keeping other things the same, the optimum yield was obtained (entry 3). Changing the solvent to DMF and using Bu_4NCl (1 equiv.) as an additive resulted in a diminished yield (entry 4). The sensitive enone moiety appears to be the main culprit in restricting further improvement in the isolated yield of the product from an apparently clean reaction. Conversion of the enone moiety to the corresponding allyl alcohols using Luche's reagent ($NaBH_4/CeCl_3 \cdot 7\ H_2O$)[15] furnished the γ-lactones **8** after the crude allyl alcohols had been passed through an alumina column. However, subjecting **8** to the optimized conditions (e.g., entry 3, Table 1) gave only 9% of the cyclized tricyclic lactone **9**, with 13% of the starting lactone **8** (m.d. ≈1:1) being recovered (Scheme 3).



Scheme 3

Palladium(0)-Catalyzed Reactions of 5b,d,e,g and 12

The above cyclization reaction was also performed on **5b** under a variety of conditions, and a few are shown in Table 2. The methyl substituent in the α-position of enone **5b** dramatically altered the course of the reaction. In this case, the 7-*exo*-trig cyclization was rather difficult and an indane derivative **6b** was formed; sometimes minor amounts of **10** and **11** (entry 1) were observed (Scheme 4). Even with longer reaction times and higher temperatures the yield could not be improved beyond a mere 23%, using 10 mol-% $Pd(PPh_3)_4$ and 2 equivalents of K_2CO_3 in DMF (entry 3).

The mechanism of formation of indane derivatives is depicted in Scheme 5 (path A). Intramolecular attack, by the

Table 1. Palladium(0)-catalyzed cyclization of **5a**

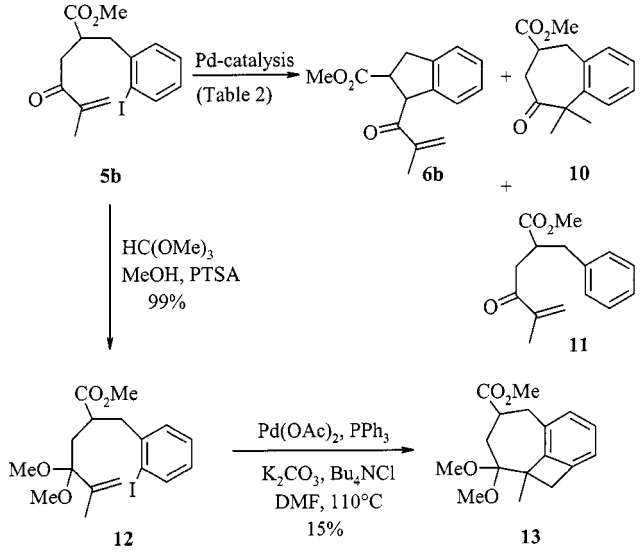
Entry	Catalyst/ Additive	Base (1.2 equiv.)	Solvent	*T* [°C]	Reaction Time [h]	Product	Yield (%)
1	1% $Pd(OAc)_2$ 2% PPh_3	NEt_3	MeCN	82	4	**7**	22
2	17% $Pd(OAc)_2$ 34% PPh_3	NEt_3	MeCN	82	0.8	**7**	24
3	15% $Pd(OAc)_2$ 30% PPh_3	K_2CO_3	MeCN	82	0.5	**7** + **6a**[a] (9:1)	68[b]
4	15% $Pd(OAc)_2$ 30% PPh_3 Bu_4NCl (1 equiv.)	K_2CO_3	DMF	57	3	**7** + **6a**[a] (9:1)	23[b]

[a] **6a** could not be isolated for characterization but its presence was inferred from characteristic 1-H signal in the ^1H NMR spectrum of the mixture. – [b] An inseparable mixture of **7** + **6a** containing *ca* 90% of **7**.

Table 2. Palladium(0)-catalyzed Reactions of **5b**,**d**–**e**

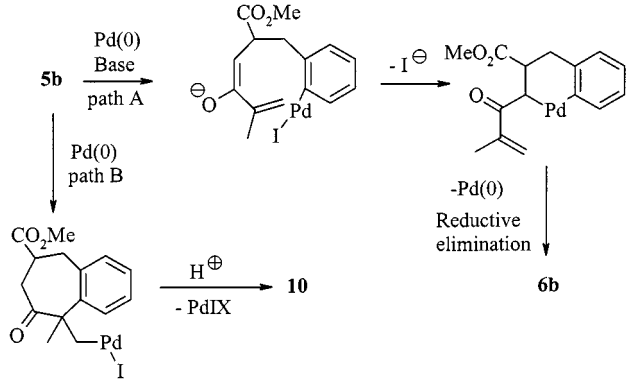
Entry	Starting Material	Catalyst/ Base (1.2 equiv.)	Solvent	*T* [°C]	Reaction Time [h]	Products	Yield (%)
1	**5b**	10% $Pd(OAc)_2$, 20% PPh_3/NEt_3	MeCN	82	65	**6b** + **10** + **11** (≈4:1:1)	≈10[a]
2	**5b**	12% $Pd(PPh_3)_4$/ NEt_3	DMF	120	13	**6b**	6
3	**5b**	10% $Pd(PPh_3)_4$/ K_2CO_3[b]	DMF	110	4.5	**6b**	23
4	**5d**	20% $Pd(PPh_3)_4$/ *t*BuOK[c]	THF	rt	5	**6d**	42
5	**5e**	20% $Pd(PPh_3)_4$/ *t*BuOK[c]	THF	rt	5	**6e**	6[d]

[a] All the components from the inseparable mixture were confirmed by GCMS analysis. – [b] 2 equivalents of K_2CO_3. – [c] 1.35 M solution in *t*BuOH. – [d] 10% of unchanged **5e** was recovered.



Scheme 4

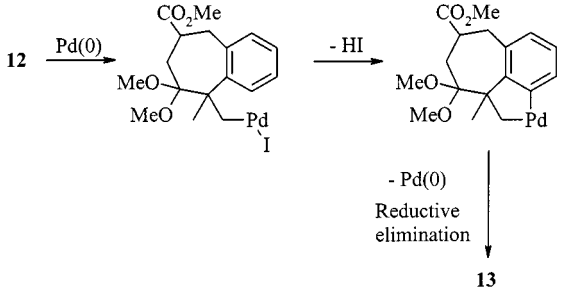
enolate generated under the reaction conditions, onto the organopalladium(II) species, formed by the initial oxidative addition of palladium(0) at the carbon-iodine bond of **5b**, leads to a 6-membered palladacycle. Reductive elimination yields **6b** and palladium(0), to continue the catalytic cycle. On the other hand, 7-*exo*-trig Heck cyclization of **5b** produces an organopalladium(II) species that lacks the β-hydrogen necessary for β-elimination and is eventually responsible for trace amounts of **10** after protonation and reductive elimination (Scheme 5, path B). Apparently, neither path (A and B) is efficient enough, and hence some quantities of reduced product **11** are also observed.



Scheme 5

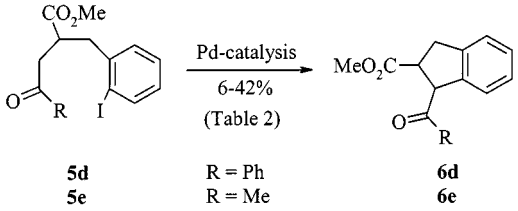
Path A could be inhibited if the carbonyl group were transformed into the acetal. Hence, **5b** was converted into the corresponding acetal **12**, using an excess of trimethyl orthoformate and catalytic amount of PTSA in MeOH. Interestingly, Heck cyclization of **12** employing 15 mol-% $Pd(OAc)_2$, 30 mol-% PPh_3, 1.2 equivalents of K_2CO_3, and 2 equivalents of Bu_4NCl furnished a novel tricyclic compound **13** in 15% yield (Scheme 4). In this case, the Pd^{II} species initially formed by 7-*exo*-trig cyclization undergoes intramolecular electrophilic aromatic substitution, ultimately leading to **13** via a 5-membered palladacycle

(Scheme 6). The low yield of **13** could perhaps result from oligomeric products originating from intermolecular reactions. In the literature there are a few related examples of this type of cyclization leading to a polycyclic system possessing a benzocyclobutane moiety.[16] The structure of **13** was unambiguously determined from careful NMR studies. The NOESY experiments showed that the relative geometry of the methyl and ester group is *cis*.



Scheme 6

We also applied the arylation methodology to alkyl ketones **5d** and **5e**, with no α,β-double bond (Scheme 7). The cyclization conditions reported by Piers[17] were used (entry 4, 5, Table 2); under these, **5d** gave moderate, and **5e** poor, yields of **6d** and **6e**. In the case of **5g**, we anticipated that this might lead to spiro compounds. Our efforts in this direction were not successful and probably demonstrate one limitation of this method.

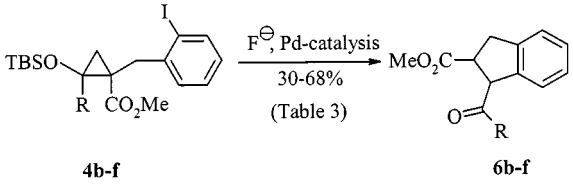


Scheme 7

Our results clearly established that, in the case of vinyl ketone **5a**, there exists a high preference for intramolecular 7-*exo*-trig cyclization over the alternative 8-*endo*-trig cyclization. The α-methyl substituted isopropenyl ketone **5b**, as a 1,1-disubstituted alkene, is not a particularly good candidate for Heck cyclization because of its lower binding affinity to Pd^{II}, and therefore formation of **6b** dominates, albeit in low yield.

One-Pot Indane Formation

Recently, one-pot procedures have been developed for converting methyl 2-trimethylsiloxy-2-vinylcyclopropanecarboxylates and their C-1 substituted derivatives into polyfunctionalized compounds by ring-opening followed by inter-[18] or intramolecular[19] Michael addition. In the first step, cesium fluoride in the presence of a phase transfer catalyst (benzyltriethylammonium chloride) in DMF was employed as the fluoride source for effecting the siloxycyclopropane ring cleavage to generate a Michael acceptor; this then accepted the nucleophile generated under the reaction conditions, thus constituting a one-pot procedure.[20] Encouraged by these results, we attempted to transform cyclopropane derivatives **4b**−**f** directly into indane derivatives by incorporating a suitable fluoride source for the in situ ring-opening of **4b**−**f** (Scheme 8).



Scheme 8

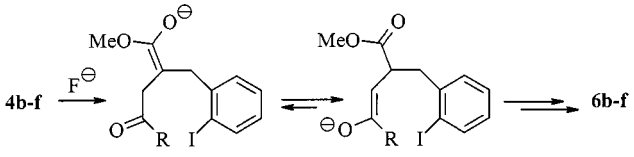
Our results are summarized in Table 3. A few trial experiments were needed in order to arrive at reaction conditions that gave 30−47% yields of indane derivatives **6b**−**d**, starting from **4b**−**d** (entries 1−3, Table 3). For **4b**, we were guided by results summarized in Table 2 for the corresponding ring-opened derivative **5b**, and conditions similar to entry 3 together with CsF and $BnEt_3NCl$ were used. The cyclohexenyl and phenyl derivatives **4c** and **4d** gave better results with $Pd(OAc)_2/PPh_3$ (entries 2 and 3). On the other hand, **4e** and **4f** reacted sluggishly under these conditions (entries 4 and 5), possibly due to the very slow rate of ring-opening by CsF reagent of these derivatives under the conditions employed. This was substantiated by the presence, even after prolonged reflux, of unchanged compounds **4e** and **4f**; ^1H NMR spectra of the reaction mixture also showed the presence of small amounts of ring-opened products **5e** and **5f**. At this stage, it was desired to modify the reaction conditions so as to facilitate a smooth ring-opening of the siloxycyclopropane derivatives **4e** and **4f**. This was conveniently accomplished by changing the fluoride source from CsF to Bu_4NF. Under these modified conditions, 20 mol-% $Pd(PPh_3)_4$ in THF and 3 equivalents of Bu_4NF in THF were slowly added to a solution of substrate (**4b**−**f**) in THF at room temperature. The results obtained are shown in Table 3 (entries 6−10). The derivative **4b** furnished only 24% of the ring-opened product **5b** with no indication of **6b**, while the derivative **4c** yielded 17% of **5c** and 33% of **6c**. On the other hand, **4d**−**f** gave better results. It is interesting to note that, while **4e** and **4f** reacted sluggishly with CsF, good yields of **6d**−**f** were obtained when Bu_4NF was used (compare entries 4 and 5 with 8−10). The presence of the sensitive enone moiety, prone to polymerization, may be responsible for this behavior.

In all the cases, the major diastereomer formed was *trans*, with only minor amounts (11 to ≤5%) of the *cis* isomer. This was anticipated, as the reactions had been carried out under thermodynamic control conditions. The relative configuration was unambiguously assigned on the basis of comparison of ^1H and ^{13}C NMR spectroscopic data with those of related compounds.[21] A plausible mechanism for the one-pot transformation of **4b**−**f** into indane derivatives requires equilibration of the initially formed ester enolate to a more stable ketone enolate as depicted in Scheme 9. Subsequent steps follow path A in Scheme 4 to give **6b**−**f**.

Table 3. Palladium(0)-catalyzed transformation of **4b−f** into indan derivatives **6b−f**

Entry	Starting Material	R	Method[a]	Yield (%)	Product
1	**4b**	Isopropenyl	A	30	**6b**
2	**4c**	1-Cyclohexenyl	B	37	**6c**
3	**4d**	Ph	B	47	**6d**
4	**4e**	Me	B	≈5[b]	**6e**
5	**4f**	*t*Bu	B	−[c]	**4f** + **5f** + **6f**
6	**4b**	Isopropenyl	C	24	**5b**
				0	**6b**
7	**4c**	1-Cyclohexenyl	C	17	**5c**
				33	**6c**
8	**4d**	Ph	C	61	**6d**
9	**4e**	Me	C	51	**6e**
10	**4f**	*t*Bu	C	68	**6f**

[a] Method A: CsF (2 equiv.), $BnEt_3NCl$ (0.4 equiv.), K_2CO_3 (2 equiv.), $Pd(PPh_3)_4$ (10 mol-%), DMF, 110 °C, 4.5 h. Method B: CsF (1.2 equiv.), Bu_4NCl (2 equiv.), K_2CO_3 (2 equiv.), $Pd(OAc)_2$ (10 mol-%), PPh_3 (20 mol-%), MeCN, 92 °C, 9 h. Method C: $Pd(PPh_3)_4$ (20 mol-%) in THF and Bu_4NF (3 equiv.) in THF were slowly added to a solution of substrate (**4b−f**) in THF at room temp. over a period of ≈15 h. − [b] Present in a complex mixture. − [c] The crude mixture was analyzed by ^1H NMR; **4f**, **5f** and **6f** were present in a ratio of 3.7:3.5:1.



Scheme 9

Conclusion

We have developed a novel one-pot procedure for the preparation of functionalized indane derivatives by palladium(0)-catalyzed reactions of **4b−f**. The two reagent systems CsF and Bu_4NF function in a complementary manner. For substrates possessing α,β-unsaturated double bond (**4b** and **4c**), CsF is the reagent of choice for effecting in situ ring opening, while Bu_4NF is efficient for other derivatives. The moderate or even low yield in a number of examples may be due to competing enone polymerization. In this new approach to functionalized indane derivatives, our concept of employing two bisfunctionalized synthons, one acting as bisnucleophile (**3b−f**) and the other as biselectrophile (*o*-iodobenzyl iodide) has again been demonstrated.

Experimental Section

General: All reactions were carried out under an atmosphere of dry argon, using glassware that had been thoroughly dried by flame or oven. − Thin layer chromatography (TLC) was carried out on commercial Polygram Sil G/UV_{254} or Polygram Alox N/UV_{254} (Macherey-Nagel). Conventional chromatography was performed using 70−230 mesh silica gel (E. Merck) or neutral aluminium oxide with activity grade-III (E. Merck). − Unless stated otherwise, ^1H NMR and ^{13}C NMR spectra were determined on Bruker AC-200, AC-300, or DRX-500 machines in $CDCl_3$ solution. − IR spectra were measured on Nicolet 205 FT-IR spectrometer. − Melting points are uncorrected. − A Büchi B-580 Kugelrohr oven was used for distillation. − The GC-MS spectra were recorded with a Hewlett Packard HP 5890 (series II) instrument and an HP 5972 MS-selective detector: Operating conditions were as follows: start temperature 70 °C, programmed to 310 °C at 10 °C/min. − Compounds **2a**, **2b**,[22] **2c**,[23] **2d**,[10] **2e**,[24] **2f**,[25] and **3a**, **3b**,[22] and **3d**[10] were prepared using known procedures.

General Procedure for the Preparation[10] of Methyl 2-*tert*-Butyldimethylsiloxycyclopropanecarboxylates (3c,e,f): To a vigorously stirred suspension of 2 mol-% copper(II)-acetylacetonate in silyl enol ether at ca. 100 °C was added, drop by drop, 1.1 equivalents of methyl diazoacetate in dry ethyl acetate (1 mL per mmol methyl diazoacetate). The temperature of the reaction mixture was slowly reduced to ca. 80 °C and a steady rate of nitrogen evolution was maintained. After completion of methyl diazoacetate addition, the solvent was removed under reduced pressure. The residue was diluted with pentane and filtered through a small, neutral alumina column. The filtrate was concentrated and the residue was fractionally distilled under vacuum.

Methyl *cis*/*trans*-2-(*tert*-Butyldimethylsiloxy)-2-(1-cyclohexenyl)cyclopropanecarboxylate (3c): The reaction was performed as described in the general procedure. Thus, **2c** (4.67 g, 19.6 mmol), $Cu(acac)_2$ (0.157 g, 0.60 mmol), and methyl diazoacetate (3.93 g, 39.3 mmol) in ethyl acetate (40 mL) gave crude product (5.50 g), which was distilled under vacuum (88−89 °C/0.029 mbar) to furnish **3c** (4.66 g, 77%), *cis*/*trans* = 42:58. − ^1H NMR (200 MHz): from *trans* and *cis* mixture: δ = 5.74 (m_c, 1 H, 2′-H, *trans*), 5.66 (m_c, 1 H, 2′-H, *cis*), 3.62 (s, 3 H, CO_2Me, *trans*), 3.67 (s, 3 H, CO_2Me, *cis*), 2.33−1.39 (series of m, 9 H, 3-H, 3′-H to 6′-H, *trans* and 11 H, 1-H, 3-H, 3-H, 3′-H to 6′-H, *cis*), 1.94 (dd, J_1 = 9.1 Hz, J_2 = 7.0 Hz, 1 H, 1-H, *trans*), 1.24 (dd, J_1 = 9.1 Hz, J_2 = 5.6 Hz, 1 H, 3-H, *trans*), 0.83 (s, 9 H, *t*BuSi, *trans*), 0.84 (s, 9 H, *t*BuSi, *cis*), 0.069, 0.073 (2s, 6 H, Me_2Si, *trans*), 0.10, −0.04 (2s, 6 H, Me_2Si, *cis*). − ^{13}C NMR (50.3 MHz): from *trans and cis* mixture: δ = 171.3, 51.4 (s, q, CO_2Me, *trans*), 170.1, 51.5 (s, q, CO_2Me, *cis*), 133.9, 126.6 (s, d, C-1′, C-2′, *trans*), 138.3, 123.4 (s, d, C-1′, C-2′, *cis*), 67.5 (s, C-2, *trans*), 65.6 (s, C-2, *cis*), 28.4 (d, C-1, *trans*), 27.7 (d, C-1, *cis*), 25.5, 17.7 (q, s, *t*BuSi, *trans*), 25.5, 17.9 (q, s, *t*BuSi, *cis*), 26.0, 25.1, 22.6, 22.3* (4t, C-3′ to C-6′, *trans*), 25.5, 24.9, 22.5, 22.3* (4t, C-3, C-3′ to C-6′, *cis*), −3.9, −4.2 (2q, Me_2Si, *trans*), −4.0, −4.2 (2q, Me_2Si, *cis*) *signal has double intensity. − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1735 (C=O), 1440, 1240, 1160, 835, 775. − $C_{17}H_{30}O_3Si$ (310.5): calcd. C 65.76, H 9.73; found C 65.14, H 10.07.

Methyl *cis*/*trans*-2-(*tert*-Butyldimethylsiloxy)-2-methylcyclopropanecarboxylate (3e): The reaction was performed as described in the general procedure. Thus, **2e** (2.51 g, 14.6 mmol), $Cu(acac)_2$ (0.076 g, 0.3 mmol), and methyl diazoacetate (2.12 g, 91% w/w in CH_2Cl_2, 19.3 mmol) in ethyl acetate (21 mL) gave crude product (3.34 g), which was distilled under vacuum (65−69 °C/0.25 mbar) to furnish **3e** (3.12 g, 87%), *cis*/*trans* = 68:32. − ^1H NMR (200 MHz): δ = 3.68 (s, 3 H, CO_2Me, *cis*), 3.66 (s, 3 H, CO_2Me, *trans*), 1.85 (dd, J_1 = 9.2 Hz, J_2 = 7.1 Hz, 1 H, *cis*), 1.65−1.56, 1.28−1.15, 0.98−0.88 (3m, 2 H, *trans*, 3 H, *cis*), 1.50 (s, 3 H, 2-Me, *cis*), 1.46 (s, 3 H, 2-Me, *trans*), 0.85 (s, 9 H, *t*BuSi, *cis*), 0.86 (s, 9 H, *t*BuSi, *trans*), 0.14, 0.12 (2s, 6 H, Me_2Si, *cis* and *trans*). − IR (neat): $\tilde{\nu}$ = 3050−2860 cm^{-1} (C-H), 1730 (C=O), 1255, 1165, 835.

Methyl *cis*/*trans*-2-*tert*-Butyl-2-(*tert*-butyldimethylsiloxy)cyclopropanecarboxylate (3f): The reaction was performed as described in the general procedure. Thus, **2f** (5.35 g, 25 mmol), $Cu(acac)_2$ (0.131

g, 0.5 mmol), and methyl diazoacetate (4.5 g, 91% w/w in CH_2Cl_2, 41 mmol) in ethyl acetate (45 mL) gave crude product (5.76 g), which was distilled under vacuum (80−85 °C/0.25 mbar) to furnish **3f** (4.72 g, 66%), *cis*/*trans* = 56:44. ^{1}H NMR (200 MHz): δ = 3.68 (s, 3 H, CO_2Me, *cis*), 3.65 (s, 3 H, CO_2Me, *trans*), 1.87−1.76, 1.54−1.43, 1.09−0.99 (3m, 3 H, *trans*, 3 H, *cis*), 0.95, 0.88 (2s, each 9 H, *t*BuSi, *t*Bu, *cis*), 0.94, 0.86 (2s, each 9 H, *t*BuSi, *t*Bu, *trans*), 0.10, 0.11 (2s, each 3 H, Me_2Si, *cis*), 0.16, 0.13 (2s, each 3 H, Me_2Si, *trans*).

General Procedure for the Alkylation[11] of 2-Substituted Methyl 2-(*tert*-Butyldimethylsiloxy)cyclopropanecarboxylates 3a−f: To a solution of 1.2 equivalents of LDA (generated in situ from diisopropylamine and *n*-butyllithium in THF at −78 °C, 20 min) at −78 °C was added the corresponding cyclopropane derivative. The reaction mixture was stirred for 2 h and then *o*-iodobenzyl iodide (1.2 equivalents) in THF was introduced into the reaction mixture and the contents were stirred for 36 h at −78 °C. The reaction mixture was quenched with saturated NH_4Cl solution and allowed to warm to room temperature. The two phases were separated and the aqueous phase was repeatedly extracted with ether. The combined organic phase was washed with brine and dried.

Methyl *trans*-2-(*tert*-Butyldimethylsiloxy)-1-(*o*-iodobenzyl)-2-vinylcyclopropanecarboxylate (4a): The reaction was performed as described in the general procedure. Thus, LDA (9.36 mmol) in THF (6 mL), **3a** (2.00 g, 7.81 mmol), and *o*-iodobenzyl iodide (3.22 g, 9.36 mmol) in THF (10 mL) were used. The crude product was purified by column chromatography using silica gel and elution with 1% ethyl acetate/hexane to give **4a** (2.40 g, 65%), as a colorless oil. − ^{1}H NMR (200 MHz): δ = 7.83, 7.26, 6.88 ($3m_c$, 1 H, 2 H, 1 H, C_6H_4), 5.94, 5.36, 5.19 (ABX-system: J_{AX} = 17.2 Hz, J_{BX} = 10.6 Hz, J_{AB} = 1.4 Hz, each 1 H, 1′-H, 2′-H), 3.56 (s, 3 H, CO_2Me), 3.50, 3.05 (2d, *J* = 18.4 Hz, each 1 H, 1′′-H), 2.11, 1.19 (2d, *J* = 6.4 Hz, each 1 H, 3-H), 0.90 (s, 9 H, *t*BuSi), 0.13, 0.07 (2s, each 3 H, Me_2Si). − ^{13}C NMR (50.3 MHz): δ = 172.1, 52.0 (s, q, CO_2Me), 142.5, 139.2, 128.1, 127.9, 127.5, 101.5 (s, 4d, s, Ar), 136.5, 115.9 (d, t, C-1′, C-2′), 65.3 (s, C-2), 40.2 (t, C-1′′), 36.7 (s, C-1), 25.9, 18.1 (q, s, *t*BuSi), 24.8 (t, C-3), − 3.3, 3.4 (2q, Me_2Si). − IR (neat): $\tilde{\nu}$ = 3050−2860 cm^{-1} (C-H), 1725 (C=O), 1475, 1465, 1255, 1210, 835, 780. − $C_{20}H_{29}IO_3Si$ (472.4): calcd. C 50.85, H 6.19; found C 50.92, H 6.18.

Methyl *trans*-2-(*tert*-Butyldimethylsiloxy)-1-(*o*-iodobenzyl)-2-(isopropenyl)cyclopropanecarboxylate (4b): The reaction was performed as described in the general procedure. Thus, LDA (11.1 mmol) in THF (10 mL), **3b** (2.50 g, 9.26 mmol), and *o*-iodobenzyl iodide (3.82 g, 11.1 mmol) in THF (15 mL) were used. The crude product (4.64 g) was purified by column chromatography using neutral alumina and elution with 1% ethyl acetate/hexane to give 1,2-bis(*o*-iodophenyl)ethane (0.283 g), m.p. 101−102 °C (ref.[26]: 101.5−102 °C) first, followed by **4b** (2.60 g, 58%), as a low-melting solid, m.p. 42−45 °C. − Compound **4b:** ^{1}H NMR (200 MHz): δ = 7.84, 7.31−7.21, 6.88 ($3m_c$, 1 H, 2 H, 1 H, C_6H_4), 5.01−4.98 (m, 2 H, 2′-H), 3.54 (s, 3 H, CO_2Me), 3.59, 3.03 (2d, *J* = 17.8 Hz, each 1 H, 1′′-H), 2.22, 1.01 (2d, *J* = 6.2 Hz, each 1 H, 3-H), 1.80 (m, 3 H, 1′-Me), 0.91 (s, 9 H, *t*BuSi), 0.12, 0.09 (2s, each 3 H, Me_2Si). − ^{13}C NMR (50.3 MHz): δ = 172.0, 51.9 (s, q, CO_2Me), 142.7, 139.2, 128.1, 127.7, 127.5, 101.7 (s, 4d, s, Ar), 142.0, 114.7 (s, t, C-1′, C-2′), 68.7 (s, C-2), 39.6 (t, C-1′′), 35.5 (s, C-1), 25.8, 18.1 (q, s, *t*BuSi), 23.2 (t, C-3), 19.2 (q, 1′-Me), −4.1 (q, Me_2Si). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1730 (C=O), 1435, 1200, 835, 780. − $C_{21}H_{31}IO_3Si$ (486.5): calcd. C 51.85, H 6.42; found C 51.70, H 6.49.

1,2-Bis(*o*-iodophenyl)ethane: ^{1}H NMR (200 MHz): δ = 7.82, 7.24, 6.89 ($3m_c$, 1 H, 2 H, 1 H, C_6H_4), 2.98 (s, 4 H, 1-H, 2-H). − ^{13}C NMR (50.3 MHz): δ = 143.7, 139.5, 129.7, 128.4, 128.0, 100.6 (s, 4d, s, Ar), 41.2 (t, C-1, C-2). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1465, 1005, 755. − $C_{14}H_{12}I_2$ (434.1): calcd. C 38.74, H 2.79; found C 38.85, H 2.79.

Methyl *trans*-2-(*tert*-Butyldimethylsiloxy)-2-(cyclohexen-1-yl)-1-(*o*-iodobenzyl)cyclopropanecarboxylate (4c): The reaction was performed as described in the general procedure. Thus, LDA (12 mmol) in THF (10 mL), **3c** (3.10 g, 10.0 mmol), and *o*-iodobenzyl iodide (4.13 g, 12.0 mmol) in THF (15 mL) were used. The crude product (6.64 g) was purified by column chromatography using neutral alumina and elution with 1% ethyl acetate/hexane to furnish **4c** (3.20g, 65%), as a colorless solid, m.p. 84−86 °C. − ^{1}H NMR (200 MHz): δ = 7.83, 7.31−7.22, 6.87 ($2m_c$, m, 1 H, 2 H, 1 H, C_6H_4), 5.74 (m_c, 1 H, 2′-H), 3.52 (s, 3 H, CO_2Me), 3.57, 3.02 (2d, *J* = 17.7 Hz, each 1 H, 1′′-H), 2.18, 0.94 (2d, *J* = 6.1 Hz, each 1 H, 3-H), 2.35−2.27, 2.04−1.42 (series of m, 1 H, 7 H, 3′ to 6′-H), 0.90 (s, 9 H, *t*BuSi), 0.10, 0.07 (2s, each 3 H, Me_2Si). − ^{13}C NMR (75.5 MHz): δ = 172.2, 51.7 (s, q, CO_2Me), 143.0, 139.3, 128.1, 127.8, 127.4, 101.8 (s, 4d, s, Ar), 134.7, 126.5 (s, d, C-1′, C-2′), 69.2 (s, C-2), 39.8 (t, C-1′′), 35.1 (s, C-1), 25.8, 18.1 (q, s, *t*BuSi), 25.6, 25.1, 22.9, 22.7, 22.3 (5t, C-3, C-3′ to C-6′), −3.8, −4.1 (2q, Me_2Si). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1725 (C=O), 1210, 1095, 830, 775. − $C_{24}H_{35}IO_3Si$ (526.5): calcd. C 54.75, H 6.70; found C 54.92, H 6.80.

Methyl *trans*-2-(*tert*-Butyldimethylsiloxy)-1-(*o*-iodobenzyl)-2-phenylcyclopropanecarboxylate (4d): The reaction was performed as described in the general procedure. Thus, LDA (12.0 mmol) in THF (10 mL), **3d** (3.06 g, 10.0 mmol), and *o*-iodobenzyl iodide (5.16 g, 15.0 mmol) in THF (25 mL) were used. The crude product (5.90 g) was purified first by passing it through a neutral alumina column (elution with 1% ethyl acetate/hexane) and then by further chromatography of the resulting material (4.2 g) using silica gel (elution with 1% ethyl acetate/hexane) to yield **4d** (4.00 g, 77%), as a colorless solid, which was then recrystallized (hexane), m.p. 74−75 °C. − ^{1}H NMR (200 MHz): δ = 7.85, 7.45−7.21, 6.89 (3m, 1 H, 7 H, 1 H, Ar), 3.75, 3.19 (2d, *J* = 17.6 Hz, each 1 H, 1′′-H), 3.12 (s, 3 H, CO_2Me), 2.50, 1.21 (2d, *J* = 6.3 Hz, each 1 H, 3-H), 0.86 (s, 9 H, *t*BuSi), 0.01, −0.36 (2s, each 3 H, Me_2Si). − ^{13}C NMR (50.3 MHz): δ = 171.7, 51.6 (s, q, CO_2Me), 142.8, 138.9, 101.7 (3s, *ipso*-C, Ar), 139.4, 128.8*, 128.2, 127.9*, 127.8*, 127.6 (6d, Ar), 67.2 (s, C-2), 39.7 (t, C-1′′), 36.6 (s, C-1), 25.8, 18.0 (q, s, *t*BuSi), 22.9 (t, C-3), −4.0, −4.1 (2q, Me_2Si), *signal has double intensity. − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1725 (C=O), 1440, 1215, 1100, 832, 780. − $C_{24}H_{31}IO_3Si$ (522.5): calcd. C 55.17, H 5.98; found C 55.68, H 6.11.

Methyl *cis*/*trans*-2-(*tert*-Butyldimethylsiloxy)-1-(*o*-iodobenzyl)-2-methylcyclopropanecarboxylate (4e): The reaction was performed as described in the general procedure. Thus, LDA (14.7 mmol) in THF (10 mL), **3e** (2.96 g, 12.1 mmol), and *o*-iodobenzyl iodide (5.16 g, 15.0 mmol) in THF (20 mL) were used. The crude product (6.50 g) was purified by column chromatography using neutral alumina and elution with 0.4% ethyl acetate/hexane to furnish **4e** (4.87 g, 87%), as a colorless oil (*trans*/*cis* = 81:19). − ^{1}H NMR (200 MHz): δ = 7.82, 7.25, 6.86 ($3m_c$, 1 H, 2 H, 1 H, C_6H_4, *trans*), 7.80, 7.33−7.23, 6.86 ($2m_c$, m, 1 H, 2 H, 1 H, C_6H_4, *cis*), 3.59 (s, 3 H, CO_2Me, *trans*), 3.60 (s, 3 H, CO_2Me, *cis*), 3.47, 2.93 (2d, *J* = 17.7 Hz, each 1 H, 1′′-H, *trans*), 3.68, 2.50 (2d, *J* = 16.4 Hz, each 1 H, 1′′-H, *cis*), 1.71, 0.96 (2d, *J* = 6.1 Hz, each 1 H, 3-H, *trans*), 1.93 [d, *J* = 6.1 Hz, 1 H, 3-H (one more 3-H signal could not be located in the ^{1}H NMR spectrum of the *cis*-*trans* mixture because

of the overlapping peaks), *cis*], 1.51 (s, 3 H, 2-Me, *trans*), 1.58 (s, 3 H, 2-Me, *cis*), 0.88 (s, 9 H, *t*BuSi, *trans*), 0.84 (s, 9 H, *t*BuSi, *cis*), 0.20, 0.11 (2s, each 3 H, Me_2Si, *trans*), 0.15, 0.11 (2s, each 3 H, Me_2Si, *cis*). − ^{13}C NMR (50.3 MHz): δ = 173.4, 52.0 (s, q, CO_2Me, *trans*), 171.3, 51.8 (s, q, CO_2Me, *cis*), 142.9, 139.3, 128.1, 127.6, 127.4, 101.7 (s, 4d, s, Ar, *trans*), 142.3, 139.5, 128.4, 128.3, 127.9, 101.3 (s, 4d, s, Ar, *cis*), 62.4 (s, C-2, *trans*), 61.1 (s, C-2, *cis*), 40.4 (t, C-1′′, *trans*), 40.7 (t, C-1′′, *cis*), 34.4 (s, C-1, *trans*), 35.7 (s, C-1, *cis*), 25.8, 17.9 (q, s, *t*BuSi, *trans*), 25.5, 17.7 (q, s, *t*BuSi, *cis*), 26.1 (t, C-3, *trans*), 24.6 (t, C-3, *cis*), 21.2 (q, 2-Me, *trans*), 22.1 (q, 2-Me, *cis*), −3.3, −3.6 (2q, Me_2Si, *trans*), −3.3, −4.0 (2q, Me_2Si, *cis*). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1725 (C=O), 1435, 1250, 1080, 1025, 840, 775. − $C_{19}H_{29}IO_3Si$ (460.4): calcd. C 49.57, H 6.35; found C 49.83, H 6.41.

Methyl *trans*-2-*tert*-Butyl-2-(*tert*-butyldimethylsiloxy)-1-(*o*-iodobenzyl)cyclopropanecarboxylate (4f): The reaction was performed as described in the general procedure. Thus, LDA (12.0 mmol) in THF (10 mL), **3f** (2.86 g, 10.0 mmol), and *o*-iodobenzyl iodide (5.16 g, 15.0 mmol) in THF (22 mL) were used. The crude product (5.69 g) was purified by column chromatography using neutral alumina and elution with 0.5% ethyl acetate/hexane to furnish **4f** (2.13 g, 43%; 52%, based on starting material recovery), which was recrystallized (hexane), m.p. 89−90 °C. − ^1H NMR (200 MHz): δ = 7.81, 7.43, 7.28, 6.87 ($4m_c$, each 1 H, C_6H_4), 3.53 (s, 3 H, CO_2Me), 3.47, 3.03 (2d, J = 18.0 Hz, each 1 H, 1′′-H), 1.93, 1.04 (2d, J = 7.3 Hz, each 1 H, 3-H), 0.99 (s, 9 H, *t*Bu), 0.98 (s, 9 H, *t*Bu), 0.14, −0.07 (2s, each 3 H, Me_2Si). − ^{13}C NMR (50.3 MHz): δ = 173.5, 51.8 (s, q, CO_2Me), 142.0, 139.6, 128.3, 128.0, 127.5, 101.7 (s, 4d, s, Ar), 71.0 (s, C-2), 41.2 (t, C-1′′), 36.8 (s, C-1), 33.5, 27.5 (s, q, *t*Bu), 26.3, 18.8 (q, s, *t*BuSi), 19.7 (t, C-3), −1.2, −2.8 (2q, Me_2Si). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1715 (C=O), 1435, 1205, 1125, 835, 775. − $C_{22}H_{35}IO_3Si$ (502.5): calcd. C 52.59, H 7.02; found C 52.74, H 7.14.

General Procedure for the Ring-Opening[12] of 2-Substituted Methyl 2-(*tert*-Butyldimethylsiloxy)cyclopropanecarboxylates 4a−f: A mixture of siloxycyclopropane derivative in dry acetonitrile and $NEt_3 \cdot 3$ HF under an argon atmosphere was refluxed for 3 h. The progress of the reaction was continuously monitored by TLC. The reaction mixture was diluted with dichloromethane and washed with water. The aqueous layer was extracted twice with dichloromethane. The combined organic phase was washed with brine and dried. The solvent was removed under reduced pressure and the residue was purified using a short column if necessary.

Methyl 2-(*o*-Iodobenzyl)-4-oxo-hex-5-enoate (5a): The reaction was performed as described in the general procedure. Thus, a mixture of **4a** (0.472 g, 1.00 mmol) and $NEt_3 \cdot 3$ HF (0.465 g, 2.90 mmol) in dry acetonitrile (8 mL) gave the product (0.345 g), which was purified by column chromatography using neutral alumina and elution with 10% ethyl acetate/hexane to furnish **5a** (0.304 g, 85%). − ^1H NMR (200 MHz): δ = 7.83, 7.27, 7.16, 6.92 ($4m_c$, each 1 H, C_6H_4), 6.31, 6.21, 5.84 (ABX-system: J_{AB} = 17.7 Hz, J_{AX} = 9.6 Hz, J_{BX} = 2.0 Hz, each 1 H, 5-H, 6-H), 3.64 (s, 3 H, CO_2Me), 3.32 (m_c, 1 H, 2-H), 3.17 (dd, J_1 = 13.6 Hz, J_2 = 7.0 Hz, 1 H, 3-H), 2.92 (dd, J_1 = 13.6 Hz, J_2 = 8.2 Hz, 1 H, 3-H), 3.10 (dd, J_1 = 17.6 Hz, J_2 = 9.0 Hz, 1 H, 1′-H), 2.70 (dd, J_1 = 17.6 Hz, J_2 = 4.0 Hz, 1 H, 1′-H). − ^{13}C NMR (50.3 MHz): δ = 198.1 (s, C=O), 174.7, 51.8 (s, q, CO_2Me), 141.3, 139.8, 130.2, 128.4, 128.3, 100.8 (s, 4d, s, Ar), 136.2, 128.5 (d, t, C-5, C-6), 42.1 (t, C-3), 40.7 (d, C-2), 40.4 (t, C-1′). − IR (neat): $\tilde{\nu}$ = 3050−2860 cm^{-1} (C-H), 1735 (C=O), 1685 (C=O), 1475, 1170. − $C_{14}H_{15}IO_3$ (358.2): calcd. C 46.95, H 4.22; found C 47.00, H 4.37.

Methyl 2-(*o*-Iodobenzyl)-5-methyl-4-oxohex-5-enoate (5b): The reaction was performed as described in the general procedure. Thus, a mixture of **4b** (2.60 g, 5.35 mmol) and $NEt_3 \cdot 3$ HF (2.67 g, 16.6 mmol) in dry acetonitrile (40 mL) gave the crude product (2.30 g), which was purified by column chromatography using neutral alumina and elution with 15% ethyl acetate/hexane to furnish **5b** (1.78 g, 89%) as a colorless oil. − ^1H NMR (200 MHz): δ = 7.83, 7.27, 7.17, 6.91 ($4m_c$, each 1 H, C_6H_4), 5.96, 5.77 (s, m_c, each 1 H, 6-H), 3.63 (s, 3 H, CO_2Me), 3.31−3.10 (series of m, 3 H), 2.97−2.75 (series of m, 2 H), 1.84 (m_c, 3 H, 5-Me). − ^{13}C NMR (50.3 MHz): δ = 199.3 (s, C=O), 174.9, 51.7 (s, q, CO_2Me), 141.4, 139.7, 130.2, 128.4, 128.2, 100.8 (s, 4d, s, Ar), 144.1, 124.8 (s, t, C-5, C-6), 42.2 (t, C-3), 41.1 (d, C-2), 38.7 (t, C-1′), 17.4 (q, 5-Me). − IR (neat): $\tilde{\nu}$ = 3050−2860 cm^{-1} (C-H), 1735 (C=O), 1680 (C=O), 1435, 1300, 1170. − $C_{15}H_{17}IO_3$ (372.2): calcd. C 48.41, H 4.60; found C 48.69, H 4.68.

Methyl 4-Cyclohex-1-enyl-2-(*o*-iodobenzyl)-4-oxobutanoate (5c): The reaction was performed as described in the general procedure. Thus, a mixture of **4c** (1.00 g, 1.90 mmol) and $NEt_3 \cdot 3$ HF (0.92 g, 5.70 mmol) in dry acetonitrile (15 mL) gave the crude product (0.81 g), which was purified by column chromatography using neutral alumina and elution with 10% ethyl acetate/hexane to furnish **5c** (0.69 g, 88%). − ^1H NMR (200 MHz): δ = 7.82, 7.26, 7.17, 6.90 ($4m_c$, 1 H, 1 H, 1 H, 2 H, C_6H_4, 2′-H), 3.63 (s, 3 H, CO_2Me), 3.35−3.07 (series of m, 3 H, 2-H, 3-H, 1′-H), 2.91 (dd, J_1 = 13.5 Hz, J_2 = 7.8 Hz, 1 H, 3-H), 2.76 (dd, J_1 = 16.5 Hz, J_2 = 3.3 Hz, 1 H, 1′-H), 2.21, 1.59 ($2m_c$, 4 H and 3′′-H to 6′′-H). − ^{13}C NMR (50.3 MHz): δ = 198.5 (s, C=O), 175.1, 51.7 (s, q, CO_2Me), 141.5, 139.7, 130.2, 128.3, 128.2, 100.8 (s, 4d, s, Ar), 140.1, 138.9 (d, s, C-2′′, C-1′′), 42.3 (t, C-3), 41.1 (d, C-2), 38.3 (t, C-1′), 26.0, 23.0, 21.9, 21.5 (4t, C-3′′ to C-6′′). − IR (neat): $\tilde{\nu}$ = 3050−2860 cm^{-1} (C-H), 1735 (C=O), 1665 (C=O), 1435, 1200, 1170, 1010, 755. − $C_{18}H_{21}IO_3$ (412.3): calcd. C 52.44, H 5.13; found C 52.72, H 5.31.

Methyl 2-(*o*-Iodobenzyl)-4-oxo-4-phenylbutanoate (5d): The reaction was performed as described in the general procedure. Thus, a mixture of **4d** (1.00 g, 1.92 mmol) and $NEt_3 \cdot 3HF$ (0.92 g, 5.70 mmol) in dry acetonitrile (15 mL) gave the crude product (0.81 g), which was purified by column chromatography using neutral alumina and elution with 10% ethyl acetate/hexane to furnish **5d** (0.77 g, 99%) as a colorless solid, m.p. 61−62 °C. − ^1H NMR (200 MHz): δ = 7.94, 7.83, 7.59−7.39, 7.30−7.17, 6.90 ($3m_c$, 2m, 2 H, 1 H, 3 H, 2 H, 1 H, Ar), 3.65 (s, 3 H, CO_2Me), 3.64−2.95 (series of m, 5 H, 2-H, 3-H, 1′-H). − ^{13}C NMR (50.3 MHz): δ = 197.7 (s, C=O), 174.8, 51.8 (s, q, CO_2Me), 141.4, 136.5, 100.8 (3s, Ar), 139.8, 133.1, 130.2, 128.5*, 128.5, 128.3, 128.0* (7d, Ar), 42.2 (t, C-3), 41.0 (d, C-2), 39.6 (t, C-1′), *signal has double intensity. − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1725 (C=O), 1695 (C=O), 1470, 1445, 1430, 1360, 1235, 1170, 1015. − $C_{18}H_{17}IO_3$ (408.2): calcd. C 52.96, H 4.20; found C 53.05, H 4.21.

Methyl 2-(*o*-Iodobenzyl)-4-oxopentanoate (5e): The reaction was performed as described in the general procedure. Thus, a mixture of **4e** (0.82 g, 1.78 mmol) and $NEt_3 \cdot 3HF$ (0.86 g, 5.35 mmol) in dry acetonitrile (10 mL) gave the crude product (0.57 g, 93%), which was further purified by recrystallization (dichloromethane/hexane), m.p. 71−72 °C. − ^1H NMR (200 MHz): δ = 7.83, 7.28, 7.15, 6.92 ($4m_c$, each 1 H, C_6H_4), 3.64 (s, 3 H, CO_2Me), 3.25 (m_c, 1 H, 2-H), 3.14 (dd, J_1 = 13.2 Hz, J_2 = 6.9 Hz, 1 H, 3-H), 2.92 (dd, J_1 = 18.0 Hz, J_2 = 9.3 Hz, 1 H, 1′-H), 2.87 (dd, J_1 = 13.2 Hz, J_2 = 8.3 Hz, 1 H, 3-H), 2.52 (dd, J_1 = 18.0 Hz, J_2 = 4.0 Hz, 1 H, 1′-H), 2.13 (s, 3 H, 5-H). − ^{13}C NMR (50.3 MHz): δ = 206.2 (s, C=O), 174.7, 51.8 (s, q, CO_2Me), 141.3, 139.8, 130.2, 128.5, 128.3,

100.7 (s, 4d, s, Ar), 44.1 (t, C-3), 42.0 (t, C-1′), 40.6 (d, C-2), 29.9 (q, C-5). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1730 (C=O), 1700 (C=O), 1400, 1225, 1165, 1010, 745. − $C_{13}H_{15}IO_3$ (346.2): calcd. C 45.11, H 4.37; found C 45.09, H 4.41.

Methyl 2-(*o*-Iodobenzyl)-5,5-dimethyl-4-oxohexanoate (5f): The reaction was performed as described in the general procedure. Thus, a mixture of **4f** (0.40 g, 0.80 mmol) and $NEt_3 \cdot 3\,HF$ (0.40 g, 2.48 mmol) in dry acetonitrile (10 mL) gave the crude product (0.32 g), which was purified by column chromatography using neutral alumina and elution with 10% ethyl acetate/hexane to furnish **5f** (0.28 g, 92%). − ^{1}H NMR (300 MHz): δ = 7.83, 7.27, 7.16, 6.91 (4m_c, each 1 H, C_6H_4), 3.62 (s, 3 H, CO_2Me), 3.27−2.96 (series of m, 3 H, 2-H, 3-H, 1′-H), 2.89 (dd, J_1 = 13.3 Hz, J_2 = 7.8 Hz, 1 H, 3-H), 2.60 (dd, J_1 = 17.8 Hz, J_2 = 3.8 Hz, 1 H, 1′-H), 1.12 (s, 9 H, *t*Bu). − ^{13}C NMR (75.5 MHz): δ = 213.8 (s, C=O), 175.0, 51.7 (s, q, CO_2Me), 141.5, 139.8, 130.1, 128.4, 128.2, 100.8 (s, 4d, s, Ar), 43.9 (s, C-5), 42.2 (t, C-3), 40.8 (d, C-2), 38.0 (t, C-1′), 26.4 (q, 5-Me_3). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1735 (C=O), 1705 (C=O), 1450, 1230, 1170, 1010, 755. − $C_{16}H_{21}IO_3$ (388.2): calcd. C 49.50, H 5.45; found C 49.68, H 5.60.

Methyl 9-Methylene-8-oxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-6-carboxylate (7): A mixture of **5a** and catalyst in a solvent under argon atmosphere was heated as indicated in Table 1.

Detailed Procedure for Entry 3 (Table 1): To a solution of **5a** (110 mg, 0.31 mmol) in MeCN (10 mL) under an argon atmosphere were added K_2CO_3 (51 mg, 0.37 mmol), $Pd(OAc)_2$ (10 mg, 0.046 mmol), and PPh_3 (24 mg, 0.092 mmol). The contents were heated to 82 °C (bath temperature) with vigorous stirring for 35 min. The mixture was cooled, and water (10 mL) and ether (20 mL) were added. The phases were separated and the aqueous phase was extracted with ether (2 × 10 mL). The combined organic phase was washed with water and brine. The solvent was removed and the residue was filtered through a small, neutral alumina pad and eluted with 10% ethyl acetate/hexane, to furnish **7**+**6a** (ca. 9:1, 48 mg, 68%). − Compound **7**: ^{1}H NMR (200 MHz): δ = 7.43−7.15 (m, 4 H, C_6H_4), 6.44, 5.65 (2d, J = 1.6 Hz, each 1 H, 9-CH_2), 3.72 (s, 3 H, CO_2Me), 3.27−2.64 (series of m, 5 H, 5-H, 6-H, 7-H). − ^{13}C NMR (50.3 MHz): δ = 197.9 (s, C=O), 173.4, 52.1 (s, q, CO_2Me), 147.4, 124.8 (s, t, C-9, 9-CH_2), 137.7, 135.4, 129.7, 129.1, 128.3, 127.7 (2s, 4d, Ar), 42.0 (d, C-6), 40.5, 33.4 (2t, C-7, C-5). − MS (EI, 70 eV): *m*/*z* (relative intensity) = 230 [M^+] (2), 200 (3), 170 (6), 144 (100), 128 (48), 115 (57), 89 (9). − IR (gas-phase): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1755 (C=O), 1715 (C=O), 1260, 1170, 755.

The presence of **6a** could be inferred from the characteristic signal at δ = 4.85 (J = 7.2 Hz, 1 H, 1-H); see **6b−f** for comparison.

3-(2-Iodobenzyl)-5-vinyldihydrofuran-2-one (8): To a cooled solution (ice-bath) of **5a** (230 mg, 0.64 mmol) in MeOH (6 mL) was added $CeCl_3 \cdot 7\,H_2O$ (288 mg, 0.77 mmol). After stirring the mixture for 5 min, $NaBH_4$ (12 mg, 0.32 mmol) was added, and stirring was continued for an additional 25 min. MeOH was removed under reduced pressure. The residue was diluted with ethyl acetate and water. The phases were separated and the aqueous layer was extracted twice with ethyl acetate. The combined organic layer was washed with brine and dried. The crude product (205 mg) was purified by column chromatography using neutral alumina and elution with 30% ethyl acetate/hexane to furnish **8** (155 mg, 74%) as a 1:1 mixture of *cis* and *trans* isomers. − ^{1}H NMR (300 MHz): *cis* and *trans*: δ = 7.83 (d, J = 7.8 Hz, 1 H, Ar), 7.34−7.17, 6.97−6.90 (2m, 3 H, Ar), 5.94−5.77, 5.40−5.19 (2m, 3 H, CH=CH_2), 4.96, 4.75 (m_c, dt, J_1 = 5.9 Hz, J_2 = 11.3 Hz, 1 H, 5-H, *cis* and *trans*), 3.48−3.31 (m, 1 H), 3.11−2.78 (m, 2 H), 2.42−1.69 (m, 2 H). − ^{13}C NMR (75.5 MHz): *cis* and *trans*: δ = 177.7, 177.2 (2s, C=O), 141.2, 141.0 (s, Ar), 139.7, 139.7, 135.3, 130.1, 130.1, 128.6, 128.5, 128.5 (8d, Ar, CH=CH_2), 118.1, 116.8 (2t, CH=CH_2), 100.7, 100.4 (2s, Ar), 78.8, 77.8 (2d, C-5), 41.3, 39.0 (2d, C-3), 40.5, 40.3 (2t, C-1′), 35.0, 32.9 (2t, C-4). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1775 (C=O), 1450, 1420, 1170, 1010, 765.

9-Methylene-11-oxatricyclo[8.2.1.0^{3,8}]trideca-3(8),4,6-trien-12-one (9): To a solution of **8** (90 mg, 0.27 mmol) in MeCN (8 mL) under an argon atmosphere were added K_2CO_3 (41 mg, 0.30 mmol), $Pd(OAc)_2$ (8.4 mg, 0.038 mmol), and PPh_3 (20 mg, 0.075 mmol). The contents were heated to 82 °C (bath temperature), with stirring, for 18 h. The mixture was cooled, and water (10 mL) and ether (20 mL) were added. The phases were separated and the aqueous phase was extracted with ether (2x10 mL). The combined organic phase was washed with water and brine. The solvent was removed and the residue was purified by column chromatography using neutral alumina and elution with 40% ethyl acetate/hexane to furnish **8** (mixture of diastereomers, *d.r.* = 1:1, 12 mg, 13%), followed by **9** (5 mg, 9%; 11% based on starting material recovery). − ^{1}H NMR (300 MHz): δ = 7.42−7.36, 7.28−7.13 (2m, 1 H, 3 H, Ar), 5.38−5.26 (m, 3 H, 10-H, C=CH_2), 3.43−3.30 (m, 1 H), 3.13−2.88 (series of m, 3 H), 2.19−2.09 (m, 1 H). − ^{13}C NMR (75.5 MHz): δ = 178.1 (C=O), 151.4, 136.2, 134.3 (3s, C=CH_2, Ar), 131.1, 130.5, 128.5, 127.7 (4d, Ar), 115.5 (t, C=CH_2), 80.6 (d, C-10), 40.1, 39.7 (2t, C-2, C-13), 37.5 (d, C-1). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1780 (C=O), 1460, 1330, 1150, 980. − MS: *m*/*z* (relative intensity): 290 [M^+] (100), 182 (2), 171(6), 155 (33), 141 (58), 128 (26), 115 (47). − $C_{13}H_{12}O_2$ (200.2): calcd. C 77.98, H 6.04; found C 77.23, H 5.95.

Methyl 2-(*o*-Iodobenzyl)-4,4-dimethoxy-5-methylhex-5-enoate (12): To a solution of **5b** (783 mg, 2.1 mmol) in dry MeOH (10 mL) were added ca. 20 equivalents (4.46 g, 4.6 mL, 42 mmol) of $HC(OMe)_3$ and a catalytic amount (ca. 5 mg) of *p*-toluenesulfonic acid. The reaction mixture was stirred vigorously at room temperature under an argon atmosphere for 7d. The reaction mixture was then quenched with half-saturated $NaHCO_3$ solution and extracted thrice with ether. The combined organic phase was washed with brine. Removal of solvent furnished 879 mg (near quantitative) of crude **12**. − ^{1}H NMR (300 MHz): δ = 7.80, 7.23, 7.11, 6.88 (4m_c, each 1 H, C_6H_4), 5.25, 5.08 (2m_c, each 1 H, 6-H), 3.48 (s, 3 H, CO_2Me), 3.06, 3.01 (2s, each 3 H, 4-OMe), 2.97−2.65, 2.39−2.26 (2m, 3 H, 1 H), 1.73 (dd, J_1 = 14.7 Hz, J_2 = 2.1 Hz, 1 H), 1.59 (m, 3 H, 5-Me). − ^{13}C NMR (75.5 MHz): δ = 175.3, 51.0 (s, q, CO_2Me), 141.3, 139.6, 130.3, 128.3, 128.1, 100.7 (s, 4d, s, Ar), 141.9, 116.8 (s, t, C-5, C-6), 102.5 (s, C-4), 48.5, 48.3 (2q, 4-OMe), 44.1, 34.0 (2t, C-1′, C-3), 41.4 (d, C-2), 18.5 (q, 5-Me). − IR (neat): $\tilde{\nu}$ = 3050−2860 cm^{-1} (C-H), 1735 (C=O), 1425, 1050. − $C_{17}H_{23}IO_4$ (418.3): calcd. C 48.82, H 5.54; found C 49.07, H 5.61.

Methyl 11,11-Dimethoxy-1-methyltricyclo[5.4.1.0^{3,12}]dodeca-3,5,7-(12)-triene-9-carboxylate (13): To a solution of **12** (66 mg, 0.16 mmol) in DMF (10 mL) under an argon atmosphere were added K_2CO_3 (26 mg, 0.19 mmol), $Pd(OAc)_2$ (5 mg, 0.024 mmol), PPh_3 (13 mg, 0.048 mmol), and Bu_4NCl (93 mg, 0.32 mmol). The contents were heated to 110 °C (bath temperature), with stirring, for 22 h. The mixture was cooled, and water (10 mL) and ether (20 mL) were added. The phases were separated and the aqueous phase was extracted with ether (2 × 10 mL). The combined organic phase was washed with water and brine. The solvent was removed and the residue was purified by column chromatography using silica gel and elution with 3% ethyl acetate/hexane to furnish **13** (7 mg, 15%). − ^{1}H NMR (500 MHz): δ = 7.08 (m_c, 1 H, Ar), 6.91−6.87 (m, 2 H, Ar), 3.90 (d, J = 13.2 Hz, 1 H, 2-H), 3.70 (s, 3 H, CO_2Me),

3.23, 3.16 (2s, each 3 H, 11-OMe), 2.97 (dd, J_1 = 14.5 Hz, J_2 = 11.5 Hz, 1 H, 8-H)*, 2.83 (d, J = 13.2 Hz, 1 H, 2-H), 2.79 (dt, J_1 = 14.5 Hz, J_2 = 1.6 Hz, 1 H, 8-H)*, 2.54 (dt, J_1 = 11.6 Hz, J_2 = 1.6 Hz, 1 H, 9-H)*, 2.39 (dt, J_1 = 14.9 Hz, J_2 = 1.5 Hz, 1 H, 10-H)*, 2.30 (d, J = 14.9 Hz, 1 H, 10-H)*, 1.52 (s, 3 H, Me); *some inconsistencies in the magnitudes of the coupling constants of these protons are due to higher order coupling. − ^{13}C NMR (125.8 MHz): δ = 175.7, 51.9 (s, q, CO_2Me), 148.4, 141.9, 133.2, 127.5, 125.4, 121.1 (3s, 3d, Ar), 101.3 (s, C-11), 51.7 (s, C-1), 49.3, 48.2 (2q, 11-OMe), 42.0 (d, C-9), 41.1, 37.4, 34.9 (3t, C-2, C-10, C-8), 21.4 (q, 1-Me). − IR (gas phase): $\tilde{\nu}$ = 3060−2840 cm^{-1} (C-H), 1755 (C=O), 1440, 1270, 1155, 1120, 1055. − MS (EI, 70 eV): *m*/*z* (relative intensity): 290 [M^+] (14), 275 (1), 259 (1), 243 (1), 227 (2), 211 (6), 183 (9), 167 (12), 159 (100), 141 (9), 128 (9).

Methyl 1-(2-Methyl-1-oxoprop-2-enyl)indan-2-carboxylate (6b) Starting from γ-Oxo Ester Derivative 5b: To an argon-purged suspension of K_2CO_3 (61 mg, 0.44 mmol) in DMF (10 mL) under an argon atmosphere was added $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) and the mixture was heated to 110 °C (bath temperature). The enone **5b** (82 mg, 0.22 mmol) was dissolved in argon-purged DMF (10 mL) and added to the hot reaction mixture (110 °C) over a period of 4.5 h, using a syringe pump. The reaction mixture was cooled, and water (20 mL) and ether (40 mL) were added. The phases were separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase was washed with brine. The solvent was removed under reduced pressure and the crude product (68 mg) was purified by column chromatography using neutral alumina (elution with 4% ethyl acetate/hexane) to furnish **6b** (12 mg, 23%). − ^{1}H NMR (300 MHz): δ = 7.26−7.07 (m, 4 H, C_6H_4), 6.24, 6.09 (br s, m_c, each 1 H, 3′-H), 5.19 (d, J = 7.5 Hz, 1 H, 1-H), 3.92 (td, J_1 = 8.8 Hz, J_2 = 7.5 Hz, 1 H, 2-H), 3.70 (s, 3 H, CO_2Me), 3.40, 3.24 (part of AB-system: J_1 = 16.1 Hz, J_2 = 8.8 Hz, 2 H, 3-H), 1.99 (m_c, 3 H, Me). − ^{13}C NMR (75.5 MHz): δ = 199.9 (s, C=O), 174.6, 52.1 (s, q, CO_2Me), 145.7, 126.8 (s, t, C-2′, C-3′), 141.9, 140.2, 127.7, 126.7, 124.8, 124.0 (2s, 4d, Ar), 53.9 (d, C-1), 46.4 (d, C-2), 35.2 (t, C-3), 18.0 (q, 2′-Me). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1735 (C=O), 1675 (C=O), 1245, 1220, 750. − MS (EI, 70 eV): *m*/*z* (relative intensity) = 244 [M^+] (26), 212 (6), 184 (12), 175 (34), 143 (16), 131 (10), 115 (100), 91 (11), 69 (39), 41 (21). − $C_{15}H_{16}O_3$ (244.3): calcd. C 73.75, H 6.60; found C 73.49, H 6.67.

The compounds **10** and **11** were observed under the reaction conditions mentioned in entry 1, Table 2.

Compound 10: Position of methyl signals in crude ^{1}H NMR (300 MHz): δ = 3.69 (s, 3 H, CO_2Me), 1.48, 1.39 (2s, each 3 H, 1-Me). The other signals are not obvious from the mixture spectrum. MS (EI, 70 eV): *m*/*z* (relative intensity) = 246 [M^+] (34), 228 (31), 215 (15), 199 (32), 187 (15), 173 (60), 160 (19), 143 (100), 129 (44), 115 (76), 91 (33), 41 (18).

Compound 11:[27] MS (EI, 70 eV): *m*/*z* (relative intensity) = 246 [M^+] (14), 215 (15), 186 (10), 163 (91), 131 (100), 117 (23), 91 (48), 69 (44), 41 (34).

One-Pot Procedure Starting from Cyclopropane Derivative 4b (Method A): To a mixture of K_2CO_3 (60 mg, 0.43 mmol), benzyltriethylammonium chloride (20 mg, 0.09 mmol), CsF (66 mg, 0.43 mmol) and $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) in DMF (15 mL) at 110 °C was added a solution of **4b** (105 mg, 0.22 mmol) in DMF (10 mL) over a period of 4.5 h using a syringe pump. The reaction mixture was stirred for an additional 30 min. After the usual workup (as above), the crude material was purified by column chromatography using neutral alumina (elution with 5% ethyl acetate/hexane) to furnish **6b** (16 mg, 30%).

One-Pot Procedure Starting from Cyclopropane Derivative 4b (Method C): To a stirred solution of **4b** (243 mg, 0.50 mmol) in THF (3 mL) at room temperature were added solutions of Bu_4NF (470 mg, 1.49 mmol) in THF (5 mL), and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) in THF (5 mL), over the course of 15 h via two separate syringes, using a syringe pump. The reaction mixture was stirred for an additional 2 h at room temperature. Ether (20 mL) and brine (10 mL) were introduced into the mixture. The layers were separated and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic phase was washed with water and brine, and dried. The solvent was removed under reduced pressure and the residue was purified by column chromatography using neutral alumina and elution with 10% ethyl acetate/hexane to furnish **5b** (44 mg, 24%). Compound **6b** was not detected in this case.

Methyl 1-(1-Cyclohex-1-enylmethanoyl)indan-2-carboxylate (6c). − One-Pot Procedure Starting from Cyclopropane Derivative 4c (Method B): To a suspension of CsF (110 mg, 0.72 mmol), tetrabutylammonium chloride (296 mg, 1.0 mmol), and K_2CO_3 (83 mg, 0.60 mmol) in MeCN (10 mL) at 92 °C (bath temperature) were added solutions of **4c** (269 mg, 0.51 mmol) in MeCN (10 mL) and a mixture of $Pd(OAc)_2$ (11 mg, 0.05 mmol) with PPh_3 (26 mg, 0.1 mmol) in MeCN (10 mL), over a period of 8 h, through two separate syringes, using a syringe pump. [The $Pd(OAc)_2/PPh_3$ solution was prepared by heating the turbid solution initially formed upon mixing MeCN, $Pd(OAc)_2$, and PPh_3. The solution turned to brownish, and on further heating to a clear greenish]. The reaction mixture was further heated for 1 h. The reaction mixture was cooled and diluted with dichloromethane (25 mL) and water (20 mL). The phases were separated and the aqueous layer was extracted twice with dichloromethane. The combined organic phase was washed with brine and dried. The solvent was removed under reduced pressure and the residue was purified by column chromatography using neutral alumina (elution with 5% ethyl acetate/hexane) to furnish **6c** (43 mg, 37%). − ^{1}H NMR (300 MHz): δ = 7.29−7.02 (m, 5 H, C_6H_4, 3′-H), 5.15 (d, J = 7.7 Hz, 1 H, 1-H), 3.95 (td, J_1 = 8.9 Hz, J_2 = 7.7 Hz, 1 H, 2-H), 3.70 (s, 3 H, CO_2Me), 3.39, 3.22 (part of AB-system: J_1 = 16.1 Hz, J_2 = 8.9 Hz, 2 H, 3-H), 2.42−2.20 (m, 4 H, 4′ to 7′-H), 1.69 (m_c, 4 H, 4′ to 7′-H). − ^{13}C NMR (75.5 MHz): δ = 199.0 (s, C=O), 174.8, 52.0 (s, q, CO_2Me), 142.4, 141.9 (d, s, C-3′, C-2′), 140.7, 140.3, 127.5, 126.7, 124.6, 123.9 (2s, 4d, Ar), 53.4 (d, C-1), 46.3 (d, C-2), 35.3 (t, C-3), 26.5, 23.6, 22.0, 21.6 (4t, C-4′ to C-7′). $C_{18}H_{18}O_3$ (284.4): calcd. C 76.03, H 7.09; found C 74.84, H 7.06. Because of the limited amount of product, no correct elemental analysis could be obtained.

One-Pot Procedure Starting from Cyclopropane Derivative 4c (Method C): The reaction was performed as described in method **C**, applied to **4c**. Thus, **4c** (263 mg, 0.50 mmol) in THF (2 mL), Bu_4NF (466 mg, 1.47 mmol) in THF (5 mL), and $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in THF (5 mL) were used. The crude product after column purification using neutral alumina and elution with 10% ethyl acetate/hexane furnished **6c** (46 mg, 33%), followed by **5c** (36 mg, 17%).

Methyl 1-Benzoylindan-2-carboxylate (6d). − One-Pot Procedure Starting from Cyclopropane Derivative 4d (Method B): The reaction was performed as described in method **B** for **6c**. Thus, CsF (91 mg, 0.60 mmol), tetrabutylammonium chloride (296 mg, 1.0 mmol), K_2CO_3 (83 mg, 0.60 mmol) in MeCN (5 mL), **4d** (261 mg, 0.50 mmol) in MeCN (10 mL), and $Pd(OAc)_2$ (11 mg, 0.05 mmol)

and PPh_3 (26 mg, 0.10 mmol) in MeCN (10 mL) were used. The crude product was purified by column chromatography using neutral alumina (elution with 10% ethyl acetate/hexane) to furnish **6d** (66 mg, 47%) as the major fraction and a minor mixed fraction (5 mg), the ^1H NMR of which indicated it to be the diastereomer of **6d**.

Starting from γ-Oxo Ester Derivative: To a stirred solution of **5d** (242 mg, 0.60 mmol) in dry THF (5 mL) at room temperature was added $Pd(PPh_3)_4$ (141 mg, 0.12 mmol). The reaction mixture was stirred for 10 min until a light brown, homogeneous solution resulted. A solution of *t*BuOK/*t*BuOH (0.54 mL of 1.35 M solution; corresponding to 82 mg, 0.73 mmol, of *t*BuOK) in THF (5 mL) was added, by syringe pump, over the course of 3 h. KI precipitated from the mixture as the reaction proceeded. The mixture was stirred for an additional 5 h at room temperature. Ether (20 mL) and brine (10 mL) were added. The layers were separated and the aqueous layer was extracted twice with ether (2x20 mL). The combined organic phase was washed with brine and dried. The solvent was removed under reduced pressure and the residue was purified by column chromatography using neutral alumina (elution with 5% ethyl acetate/hexane) to furnish **6d** (70 mg, 42%) which was recrystallized (toluene/hexane), m.p. 91−92 °C. − ^1H NMR (300 MHz): δ = 8.11, 7.67−7.49, 7.26−7.13, 7.05, 6.89 (m_c, 2m, $2m_c$, 2 H, 3 H, 2 H, 1 H, 1 H, Ar), 5.46 (d*, J = 7.5 Hz, 1 H, 1-H), 4.08 (td*, J_1 = 9.0 Hz, J_2 = 7.5 Hz, 1 H, 2-H), 3.69 (s, 3 H, CO_2Me), 3.45, 3.31 (part of AB-system: J_1 = 16.1 Hz, J_2 = 9.0 Hz, each 1 H, 3-H); * the exact nature and magnitude of coupling was determined from decoupling experiments. − ^{13}C NMR (75.5 MHz): δ = 198.6 (s, C=O), 174.5, 52.0 (s, q, CO_2Me), 141.8, 140.1, 137.2 (3s, Ar), 133.5, 129.1*, 128.8*, 127.7, 126.8, 124.7, 124.2 (7d, Ar), 54.9 (d, C-1), 46.3 (d, C-2), 35.2 (t, C-3), *signal has double intensity. − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1720 (C=O), 1680 (C=O), 1595, 1445, 1305, 1290, 1195, 1170, 750, 700. $C_{18}H_{16}O_3$ (280.3): calcd. C 77.13, H 5.75; found C 77.36, H 5.84.

Methyl 1-Acetylindan-2-carboxylate (6e). − One-Pot Procedure Starting from Cyclopropane Derivative 4e (Method B): The reaction was performed as described in method **B** for **6d**. Thus, **4e** (230 mg, 0.50 mmol), CsF (91 mg, 0.60 mmol), tetrabutylammonium chloride (296 mg, 1.0 mmol), K_2CO_3 (83 mg, 0.60 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and PPh_3 (26 mg, 0.10 mmol) in MeCN (10 mL) were used. The crude product after column purification using neutral alumina furnished ca. 3−5% **6e** as a mixture with **5e**.

One-Pot Procedure Starting from Cyclopropane Derivative 4e (Method C): The reaction was performed as described in method **C** for **6b**. Thus, **4e** (460 mg, 1.00 mmol) in THF (4 mL), Bu_4NF (1.12 g, 3.54 mmol) in THF (10 mL), and $Pd(PPh_3)_4$ (232 mg, 0.20 mmol) in THF (10 mL) were used. The crude product after column purification using neutral alumina and elution with 10% ethyl acetate/hexane furnished **6e** as a colorless liquid, 112 mg (51%).

Starting from γ-Oxo Ester Derivative 5e: The reaction was performed as described for **6d**. Thus, **5e** (208 mg, 0.60 mmol), $Pd(PPh_3)_4$ (141 mg, 0.12 mmol), *t*BuOK/*t*BuOH (0.54 mL of 1.35 M solution; corresponding to 82 mg, 0.73 mmol, of *t*BuOK), and THF (10 mL) were used. After the usual workup, the residue was purified by column chromatography using neutral alumina and elution with 10% ethyl acetate/hexane to furnish **6e** (8 mg, 6%), followed by a mixture of **6e+5e** (11 mg), and unchanged **5e** (20 mg, 10%). − Compound **6e**: ^1H NMR (300 MHz): δ = 7.29−7.19 (m, 4 H, Ar), 4.52 (d, J = 6.2 Hz, 1 H, 1-H), 3.78 (m_c, 1 H, 2-H), 3.72 (s, 3 H, CO_2Me), 3.30 (m_c, 2 H, 3-H), 2.36 (s, 3 H, Me). − ^{13}C NMR (75.5 MHz): δ = 206.4 (s, C=O), 174.5, 52.2 (s, q, CO_2Me), 141.9, 139.1, 128.0, 127.0, 124.9, 124.2 (2s, 4d, Ar), 61.3 (d, C-1), 45.9 (d, C-2), 35.0 (t, C-3), 28.9 (q, Me). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1735 (C=O), 1710 (C=O), 1435, 1355, 1245, 1215, 1170, 760. − $C_{13}H_{14}O_3$ (218.3): calcd. C 71.54, H 6.47; found C 71.10, H 6.54.

Methyl 1-Pivaloylindan-2-carboxylate (6f). − One-Pot Procedure Starting from Cyclopropane Derivative 4f (Method B): The reaction was performed as described in method **B** for **6c**. Thus, CsF (380 mg, 2.50 mmol), tetrabutylammonium chloride (740 mg, 2.50 mmol), K_2CO_3 (83 mg, 0.60 mmol) in MeCN (20 mL), **4f** (251 mg, 0.50 mmol) in MeCN (10 mL), and $Pd(OAc)_2$ (11 mg, 0.05 mmol) and PPh_3 (26 mg, 0.10 mmol) in MeCN (10 mL) were used. The crude product, ca. 90%, was an inseparable mixture consisting of three components − **4f**, **5f**, and **6f** − in a ratio of 3.7:3.5:1, as determined from the ^1H NMR of the crude reaction mixture. The presence of **6f** could again be inferred from the characteristic signals at 4.99 (d, J = 6.6 Hz, 1 H, 1-H) and 3.70 (s, 3 H, CO_2Me) in the ^1H NMR spectrum of the mixture.

One-Pot Procedure Starting from Cyclopropane Derivative 4f (Method C): The reaction was performed as described in method **C** for **6b**. Thus, **4f** (202 mg, 0.40 mmol) in THF (2 mL), Bu_4NF (400 mg, 1.27 mmol) in THF (4 mL), and $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) in THF (4 mL) were used. The crude product after column purification using neutral alumina and elution with 5% ethyl acetate/hexane furnished three fractions, corresponding to *trans*-**6f** (50 mg), *trans*/*cis*-**6f** (3:1, 20 mg), and *cis*-**6f** (1 mg), respectively, in 68% total yield. Ratio of *trans*/*cis* = 89:11, determined from ^1H NMR of the crude mixture. − Isomer *trans*-**6f**: ^1H NMR (300 MHz): δ = 7.25−7.09, 7.01−6.97 (2m, 3 H, 1 H, Ar), 4.99 (d, J = 7 Hz, 1 H, 1-H), 3.70 (s, 3 H, CO_2Me), 3.56−3.20 (series of m, 3 H, 2-H, 3-H), 1.29 (s, 9 H, *t*Bu). − ^{13}C NMR (75.5 MHz): δ = 216.3 (s, C=O), 174.5, 52.0 (s, q, CO_2Me), 142.4, 141.9, 127.5, 126.9, 124.5, 123.9 (2s, 4d, Ar), 54.0 (d, C-1), 49.2 (d, C-2), 44.9 (s, *t*Bu), 36.1 (t, C-3), 26.0 (q, *t*Bu). − IR (neat): $\tilde{\nu}$ = 3050−2850 cm^{-1} (C-H), 1735, 1705 (C=O), 1480, 1460, 1435, 1365, 1170. − $C_{16}H_{20}O_3$ (260.3): calcd. C 73.82, H 7.74; found C 73.87, H 8.09. − Isomer *cis*-**6f**: ^1H NMR (300 MHz): δ = 7.31−7.13 (series of m, 4 H, Ar), 4.95 (d, J = 8 Hz, 1 H, 1-H), 3.81 (dd, J_1 = 15 Hz, J_2 = 9 Hz, 1 H, 3-H), 3.70 (s, 3 H, CO_2Me), 3.57 (td, J_1 = 9 Hz, J_2 = 8 Hz, 1 H, 2-H), 3.16 (dd, J_1 = 15 Hz, J_2 = 9 Hz, 1 H, 3-H), 1.28 (s, 9 H, *t*Bu). − ^{13}C NMR (75.5): δ = 215.5 (s, C=O), 173.0, 51.7 (s, q, CO_2Me), 143.7, 141.1, 127.6, 126.3, 125.3, 124.7 (2s, 4d, Ar), 52.7 (d, C-1), 49.9 (d, C-2), 44.9 (s, *t*Bu), 35.1 (t, C-3), 27.1 (q, *t*Bu).

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