Studies on the Competitive Nickel-Promoted Carbonylative Intramolecular Cyclization of Vinyl and Aryl Halides with Hydroxyalkenes

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$Ni(CO)_4$ promotes carbonylative intramolecular cyclization of bromovinyl or iodoaryl substrates bearing suitable hydroxyalkene substituents. In O-protected substrates, alkene insertion takes place exclusively whereas lactonization is observed in substrates having a free hydroxyl group. Reaction products different from those arising under similar Pd-catalyzed conditions for carbonylations of hydroxyalkenes are observed in the present case. Alternative reaction pathways are proposed to account for the products obtained, and the selectivity of these processes is deduced from the nature of the resulting organic compounds.

Applications of organotransition metal complexes in organic synthesis are gaining increasing interest.[1,2] Due to the central role played by the carbonyl group in organic chemistry, the easy activation of carbon monoxide by transition metals to further carbonylate organic substrates represents a very attractive approach.[3,4] Palladium compounds have been used in catalytic carbonylations,[5] specially in cyclic acylmetalations when a heteroatom is present in the substrate to give lactones[6] or lactams.[7] On the contrary, acyl metalations to give cyclic ketones from suitable acyclic precursors are rather scarce in the literature[3a] and drastic conditions are usually required. Nickel-promoted carbonylations[8] are also attractive, and in general, they require milder conditions. In this context, during the last years we have been interested in the development of nickel-promoted cyclocarbonylation reactions and their application to potentially useful intermediates for the synthesis of bioactive natural products.[9] In particular, we planned to extend the scope of the intramolecular cyclization of vinyl halides with alkenes by means of tetracarbonylnickel in the presence of methanol and triethylamine[10] to vinyl or aryl halides bearing hydroxyalkene substituents of general structure A (Scheme I), in order to study the internal selectivity of these systems *versus* an external alcohol present in the solvent system. Thus, whereas lactones B (Scheme I) could be expected to be formed by initial oxidative addition followed by carbonylation and intramolecular reductive elimination with the corresponding hydroxyl group (path a) an alternative carbonylation of this moiety (path b) with further reductive elimination or olefin insertion would provide access to structures B or C, respectively, in analogy with palladium chemistry.[6b,11] On the other hand, the protection of the hydroxyl group would allow for a diversity of reaction pathways, as depicted in Scheme II.

The initially formed intermediate D, arising from oxidative addition of $Ni(CO)_4$ by the starting halide A, can either be carbonylated to E or inserted into the olefin double bond to give F or G, *via* an *exo* or *endo* cyclization process, respectively. While carbonylation of intermediates F and G followed by alcoholysis would ultimately lead to cycloalkenyl derivatives K and L, double bond insertion at E could lead similarly to cycloalkenes I and J through an *endo* or *exo* cyclization pathway, respectively. Finally, alcoholysis of E prior to alkene insertion would account for the formation of α,β-unsaturated esters H.

In the light of these considerations, this work was directed to elucidate the above preferred reaction pathways. This knowledge would be of capital importance from a synthetic standpoint, since unwanted side reactions could be minimized or even avoided by a proper choice of reaction conditions.

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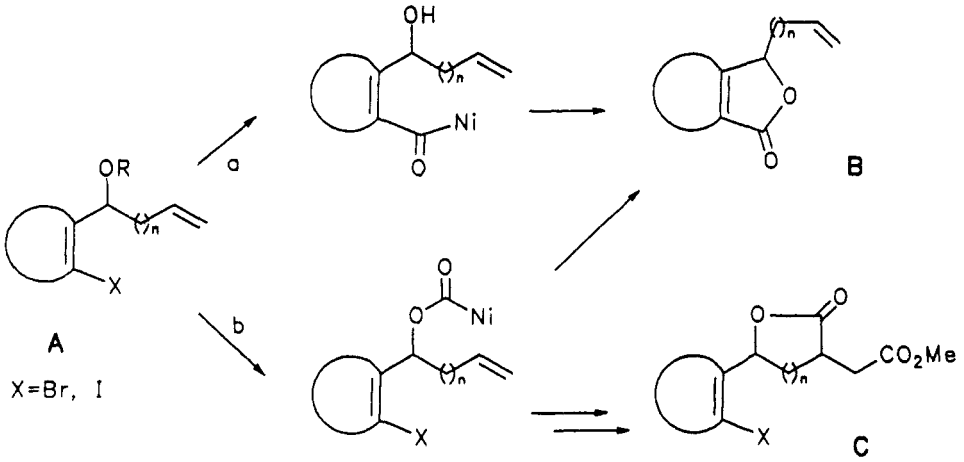
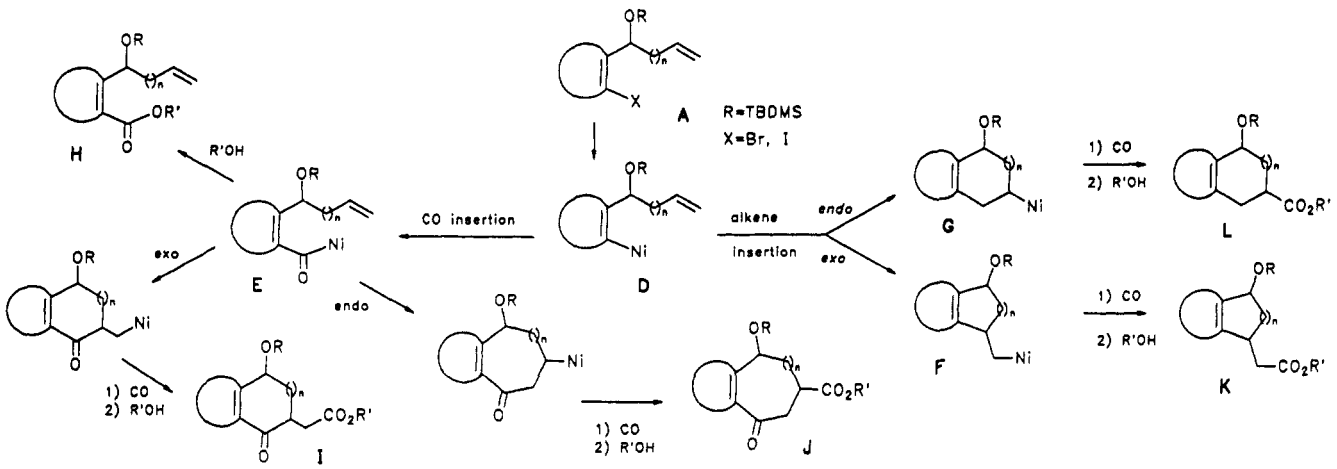
Scheme I. Alternative Pathways in Nickel-Promoted Cyclization of Vinyl and Aryl Halides with a Supplementary Hydroxyalkene Function (R = H)



Scheme II. Different Pathways in O-Protected Derivatives (R = TBDMS)



Results and Discussion

Nickel-promoted intramolecular cyclization of vinyl and aryl halides **1a–e** (Table I), afforded the corresponding lactones **2a–e** in good to excellent yields in all cases. Extensive and highly stereoselective double bond isomerization, presumably due to the formation of a π-allylnickel hydride species, was also observed in some cases (Table I, entries 1 and 4). As indicated above (see Scheme I), two alternative mechanisms (paths a and b) can account for the formation of **2a–e**. Support for path a stems from the results obtained from substrates **1f** and **1g** (Table I), which seem to rule out the second mechanism, since unreacted starting material was recovered in both cases. As expected, both substrates were reactive under the Pd-catalyzed conditions recently described by Tamaru *et al.*[6b] giving **6f** and **6g** (Table II), in analogy with the lactonization of related hydroxyolfefins, in which initial formation of an (alkoxycarbonyl)palladium species was postulated. Interestingly, application of the above palladium-catalyzed carbonylation to **1c** afforded lactone **6c** (1:1 mixture of diastereomers) as a result of a selective reaction at the hydroxyolefin moiety. Concerning selectivity in the attack at the acyl–nickel intermediate, its preference is clear by the hydroxyl group (instead of that of the alkene) since no cyclopentenones (or cyclohexenones) were ever detected (Table I).

The protection of the hydroxyl group drastically alters the course of the cyclization process. Thus, when compounds **7a–f** were submitted to our standard reaction conditions, as indicated in Table III, CO insertion to give a nickel–acyl intermediate E (see Scheme II) was the major or exclusive pathway in all cases and double bond insertion of this intermediate *via* a 5-*exo-trig* process was strongly favored. Vinyl derivatives **7a–c**, afforded the corresponding cyclopentenones **8a–c** in modest stereoselectivity and in moderate to good yields. The observed stereoselectivity can reasonably be assumed to arise from the cyclization process rather than from equilibration of the resulting enone, since **7a** afforded results comparable to those obtained from **7b**, where equilibration is not possible. In cases where a 5-*exo-trig* carbonylative cyclization cannot take place, methanolysis of the nickel–acyl intermediate E becomes a competitive process in front of the alternative 6-*exo-trig* cyclization (entries 4 and 5, compound **9** vs **11**). Finally, double bond insertion in intermediate D (Scheme II) through a noncarbonylative Heck type process represents a minor pathway (entries 3–5), although, once again, a 6-*exo-trig* process is the only one observed for the acyl–nickel intermediate of type E.[12]

It was thought that a bulkier, less nucleophilic alcohol, such as *t*-BuOH, would avoid formation of **9**.[10] However, when *t*-BuOH was used, complex mixtures were obtained, suggesting that polyinsertion is favored under these conditions.

In order to further explore the chemoselectivity of the nickel-promoted cyclization of vinyl and aryl halides with

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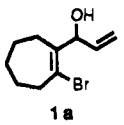
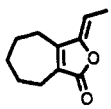
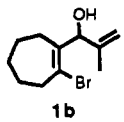
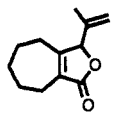
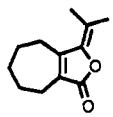
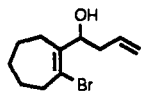
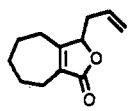
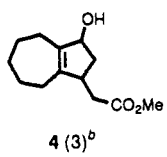
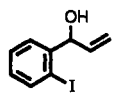
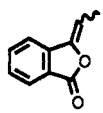
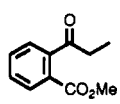
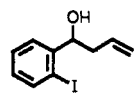
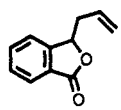
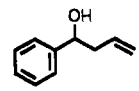
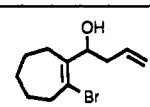
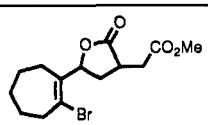
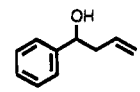
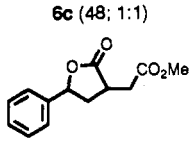
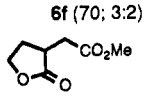
Table I. $Ni(CO)_4$-Promoted Lactonizations of Vinyl and Aryl Halides

entry	substrate	product (isolated yield, %)	
1	 **1a**	 **2a** (71)[a]	
2	 **1b**	 **2b** (92)	 **3** (2)
3	 **1c**	 **2c** (93)	 **4** (3)[b]
4	 **1d**	 **2d** (70)[a,c]	 **5** (16)[d,e]
5	 **1e**	 **2e** (79)	
6	 **1f**	no reaction	
7	 **1g**	no reaction	

[a] Stereochemistry confirmed by NOE experiments. [b] 3:1 mixture of isomers. [c] 9:1 *Z/E*. [d] from Methanolysis of **2d**. [e] Reference 13.

Table II. Pd-Promoted Lactonization of 1c, 1f, and 1g

entry	substrate	product (isolated yield, %; isomeric ratio)
1	 **1c**	 **6c** (48; 1:1)
2	 **1f**	 **6f** (70; 3:2)
3	 **1g**	 **6g** (76)[a]

[a] See ref 6b.

alkenes, we tested the reaction on substrates **14a–c** (Table IV), where two simultaneous and competitive oxidative addition processes might occur. From the observed results, we conclude that vinyl bromides are more reactive than aryl bromides under our standard reaction conditions (entries 1 and 3). However, the more reactive aryl iodides showed extensive polyinsertion reactions and, as a consequence, low yields of cyclic compounds were obtained (compare entries 1 and 5). Once again, a strong preference for a 5-*exo-trig* cyclization process was observed in all cases and only low yields of 6-*endo-trig* adducts (compounds **18** and **19**) were obtained. It is worth noting that, whereas 5-*exo-trig* adducts were almost invariably obtained as a diastereomeric mixture, single isomers were produced as a result of 6-*endo-trig* process (see also compounds **13**, Table III). As above, formation of the major products can be explained through the participation of a nickel–acyl intermediate such as E (Scheme I), followed by sequential double bond insertion, carbonylation, and methanolysis. In these reactions, replacement of methanol with *t*-BuOH showed inconsistent results. Thus, whereas the less reactive aryl bromide **14b** afforded a major cyclization product in high yield (entry 4), reaction of **14a** and **14c** afforded low yields and complex mixtures, respectively (entries 2 and 6).

In summary, intramolecular nickel-promoted cyclizations of vinyl or aryl halides with hydroxyalkenes, unlike those of palladium, afford good to excellent yields of the corresponding lactones through an initial oxidative addition of the tetracarbonylnickel followed by carbonylation to an acylnickel intermediate and nucleophilic intramolecular displacement by the hydroxyl group. On the other hand, reaction with O-protected hydroxyalkenes proves to be useful from a synthetic standpoint only when a 5-*exo-trig* insertion of the acylnickel intermediate is feasible, thus leading to cyclopentenone adducts, although in modest diastereoselectivity. Further work in our group will be addressed to apply this methodology to the total synthesis of natural products.

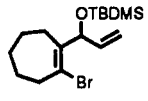
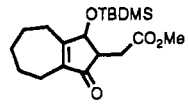
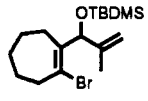
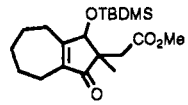
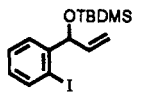
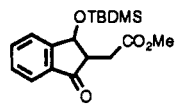
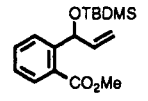
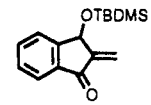
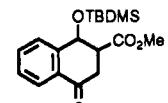
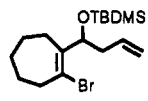
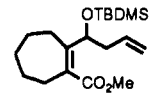
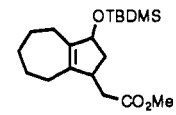
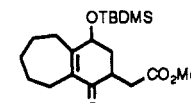
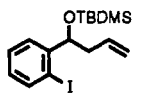
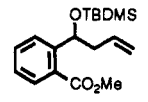
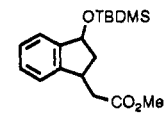
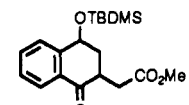
Experimental Section

CAUTION! $Ni(CO)_4$ is an extremely harmful chemical and special precautions have to be taken when it is used.

IR spectra were recorded with a Perkin-Elmer 399B spectrometer and are reported in cm^{-1}. ^1H NMR and ^{13}C NMR were recorded with WP-80-SY Bruker, Gemini 200 Varian, and Unity 300 Varian machines. Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane, or in ppm relative to the singlet at 7.26 ppm for chloroform-d_1. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; b, broad. Coupling constants are reported in hertz (Hz). ^{13}C NMR are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-d_1. Routine ^{13}C NMR spectra were fully decoupled by broad-band decoupling. Elemental analyses were performed with a Carlo Erba apparatus (1107 and 1500 Models). Mass spectra were taken with a VG-updated AEI MS-902 instrument. GC–MS were determined on a HP 5995 mass spectrometer coupled to a gas chromatograph equipped with a fused silica capillary column SPB-5 (30 m × 0.32-mm i.d.). GC analyses were performed with a Carlo Erba Fractovap Series 2350 instrument, fitted with a 2-m column, type OV-101, a Shimadzu Chromatopac C-R1B recorder, and a flame ionization detector. TLC was run on Merck 60 F_{254} silica gel plates. Flash chromatography was performed on 230–400-mesh Merck 60 silica gel. $Ni(CO)_4$ was supplied by Strem.

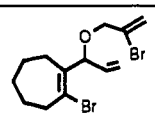
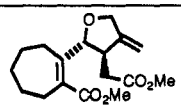
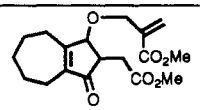
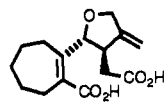
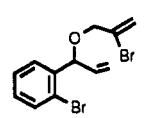
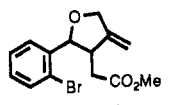
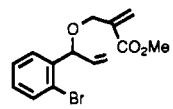
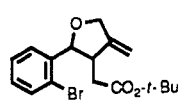
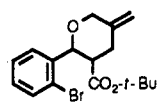
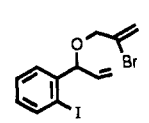
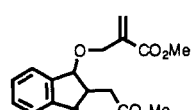
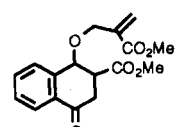
General Procedure for the Nickel-Promoted Intramolecular Cyclization. A typical procedure is as follows. A three-necked flask with magnetic stirring fitted with a thermometer, a gas inlet, a graduated addition funnel, and a condenser with the top outlet connected to a mercury valve, was installed in an argon-filled glovebox. The outlet of the mercury valve was connected outside the glovebox to a cold trap containing a methanolic solution of iodine maintained at −20 to 0 °C. The trap outlet was directly connected to the exterior. Prior to start, the system was purged with Ar, then a solution of the aryl or vinyl halide (1.0 mmol), the alcohol (3.0 mmol), and Et_3N (3.0 mmol) in acetonitrile (10 mL) or acetonitrile–THF (8/2, v/v) was introduced, and finally, $Ni(CO)_4$ (0.5 mL, 3.9 mmol) was added

Table III. $Ni(CO)_4$-Promoted Cyclizations of O-Protected Alkenyl and Aryl Halides

entry	substrate	product (isolated yield, %)			
1	 **7a**	 **8a** (73)[a]			
2	 **7b**	 **8b** (64)[b]			
3	 **7c**	 **8c**[c]	 **9c** (16)	 12 (10)	 **13**[c,d]
4	 **7d**		 **9d** (31)	 **10d** (23)[e]	 **11d** (10)[f]
5	 **7e**		 **9e** (20)	 **10e** (23)	 **11e** (10)[g]

[a] *cis:trans* 3:2. [b] 3:2 mixture of isomers. [c] Mixture of **8c** (*cis:trans* 1:2) and **13** in a 3:1 ratio, respectively. Overall yield 56%. [d] Single isomer. [e] 2.3:1 mixture of isomers. [f] 2:1 mixture of isomers. [g] 2.7:1 mixture of isomers.

Table IV. $Ni(CO)_4$-Promoted Cyclization of Dihalides

entry	substrate	product (isolated yield, %)	
1	 **14a**	 **15a** (12)[a]	 **16a** (46)[b]
2[c]	**14a**	 **15b** (27)[d]	
3	 **14b**	 **15c** (20)[b]	 **17c** (45)
4[c]	**14b**	 **15d** (80)[e]	 **18** (9)[f]
5	 **14c**	 **16c** (17)[g]	 **19** (11)[f]
6[c]	**14c**	complex mixture	

[a] *trans* isomer. [b] 1:1 mixture of isomers. [c] *t*-BuOH was used instead of MeOH. [d] Presumably originated from the corresponding di-*tert*-butyl diester. [e] 1.8:1 mixture of isomers. [f] Single isomer. [g] 4:1 mixture of isomers.

directly from a pressure bottle to a graduated funnel and from this to the reaction flask. The reaction mixture is heated to 30–35 °C while a liquid at −5 °C is passed through the condenser. A slow stream of pure Ar was admitted into the flask. The reaction mixture turned gradually from colorless to yellow, orange, red, and dark purple. At the end of the reaction a black solid deposited. The condenser was removed and the outlet of the flask directly attached to the trap containing iodine. Most of the solvent and any unreacted $Ni(CO)_4$ were evaporated to dryness by increasing the Ar stream passing through the flask. The residue was taken out of the glovebox and treated with CH_2Cl_2. After filtration through a Celite pad, washing (NH_4Cl and NaCl saturated solutions), drying (Na_2SO_4), and evaporation, final flash column chromatography of the residue afforded the products.

3-Ethylidene-3,4,5,6,7,8-hexahydrocyclohepta[*c*]furan-1-one (2a): conventional column chromatographic separation of the reaction mixture on neutral alumina (pentane–diethyl ether 10:3, R_f = 0.25), 71% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 1.48–1.63 (m, 4H), 1.68–1.75 (m, 2H), 1.82 (d, 1H, J = 7.5 Hz), 2.34–2.42 (m, 4H), 5.20 (q, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (s), 152.9 (s), 149.8 (s), 129.4 (s), 105.6 (d), 30.8 (t), 26.7 (t), 26.6 (t), 25.9 (t), 24.7 (t), 11.6 (q); IR ($CHCl_3$) 2930, 2850, 1830, 1760; mp 36–38 °C. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.28; H, 8.07.

3-Isopropenyl-3,4,5,6,7,8-hexahydrocyclohepta[*c*]furan-1-one (2b): flash chromatography (hexane–*tert*-butyl methyl ether 90:10, R_f = 0.20), 92% yield; ^1H NMR (300 MHz, $CDCl_3$) δ 1.46 (s, 3H), 1.55–1.80 (m, 6H), 2.20–2.26 (m, 2H), 2.38–2.42 (m, 2H), 5.03 (m, 1H), 5.10–5.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1 (s), 163.3 (s), 139.4 (s), 129.9 (s), 117.7 (d), 86.5 (d), 30.4 (t), 27.7 (t), 26.8 (t), 26.6 (t), 24.9 (t), 15.2 (q); IR (CCl_4) 2930, 2860, 1760, 1680; mp 48–50 °C. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.96; H, 8.41.

3-Allyl-3,4,5,6,7,8-hexahydrocyclohepta[*c*]furan-1-one (2c): flash chromatography (hexane–*tert*-butyl methyl ether 5:2, R_f = 0.21), 93% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 1.50–1.90 (m, 6H), 2.22–2.46 (m, 3.5H), 2.60–2.76 (m, 0.5H), 4.77 (bt, 1H, J = 6.3 Hz), 5.08–5.21 (m, 2H), 5.60–5.77 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.7 (s), 162.2 (s), 131.4 (d), 129.8 (s), 118.9 (t), 81.5 (d), 35.8 (t), 30.5 (t), 28.2 (t), 26.8 (t), 26.6 (t), 24.8 (t); IR

($CHCl_3$) 2940, 2860, 1710, 1680; mp 25–30 °C. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.07; H, 8.40.

3-Ethylidene-3*H*-isobenzofuran-1-one (2d): product separation on neutral alumina (hexane–*tert*-butyl methyl ether 10:1, R_f = 0.3), 70% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (d, 3 H, J = 7.2 Hz), 5.67 (d, 1H, J = 7.2 Hz), 7.49 (ddd, 1H, J = 7.8 Hz, J' = 6.9 Hz, J'' = 1.5 Hz), 7.60–7.69 (m, 2H), 7.88 (dt, 1H, J = 7.8 Hz, J' = 2.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1 (s), 146.3 (s), 139.5 (s), 134.2 (d), 129.3 (d), 125.2 (d), 124.4 (s), 119.5 (d), 104.2 (d), 11.3 (q); IR (neat) 2960, 1785, 1700, 1480. Anal. Calcd for $C_{10}H_8O_2$: C, 74.97; H, 5.05. Found: C, 74.90; H, 5.14.

3-Allyl-3*H*-isobenzofuran-1-one (2e): flash chromatography (hexane–*tert*-butyl methyl ether 90:10, R_f = 0.12), 79% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55–2.85 (m, 2H), 5.08–5.21 (m, 2H), 5.51 (t, 1H, J = 10 Hz), 5.62–5.86 (m, 1H), 7.42–7.58 (m, 2H), 7.61–7.70 (m, 2H), 7.83–7.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 (s), 149.2 (q), 133.8 (d), 131.1 (d), 129.1 (d), 126.1 (q), 125.5 (d), 121.9 (d), 119.6 (t), 80.1 (d), 38.5 (t); IR (neat) 3090, 2940, 1770, 1650, 1620, 1600. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78. Found: C, 75.85; H, 5.86.

Methyl 2-propionylbenzoate (5): product separation on neutral alumina (hexane–*tert*-butyl methyl ether 10:1, R_f = 0.65), 16% yield. Spectroscopic data are according to ref 13.

Methyl 5-(2-bromo-1-cycloheptenyl)-2-oxo-3-oxolaneacetate (6c): flash chromatography (hexane–*tert*-butyl methyl ether 3:1), 48% yield. Isomer A: R_f = 0.29; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35–1.85 (m, 8H), 2.05–2.25 (m, 2H), 2.45–2.65 (m, 2H), 2.65–2.85 (m, 3H), 2.85–3.05 (m, 1H), 3.82 (s, 3H), 5.37 (dd, 1H, J = 11 Hz, J' = 6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.2 (s), 171.3 (s), 137.6 (s), 126.0 (s), 81.5 (d), 51.9 (q), 41.6 (t), 37.1 (d), 33.7 (t), 32.0 (t), 31.3 (t), 27.0 (t), 26.0 (t), 25.0 (t); IR (CCl_4): 2930, 2850, 1785, 1745, 1435. Anal. Calcd for $C_{14}H_{19}BrO_4$: C, 50.77; H, 5.78. Found: C, 51.01; H, 5.88. Isomer B: R_f = 0.25; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.38–1.63 (m, 4H), 1.63–1.85 (m, 2H), 2.05–2.25 (m, 4H), 2.50–2.80 (m, 4H), 2.85–3.10 (m, 1H), 3.68 (s, 3H), 5.51 (dd, 1H, J = 8.2 Hz, J' = 6.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.2 (s), 171.3 (s), 138.8 (s), 125.5 (s), 81.3 (d), 52.1 (q), 41.5 (t), 36.3 (d), 35.0 (t), 31.9 (t), 31.2 (t), 27.4 (t), 26.0 (t), 24.9 (t); IR (CCl_4) 2940, 2880, 1785, 1750, 1430. Anal. Calcd for $C_{14}H_{19}BrO_4$: C, 50.77; H, 5.78. Found: C, 51.22; H, 5.90.

Methyl 2-oxo-5-phenyl-3-oxolaneacetate (6f): flash chromatography (hexane–*tert*-butyl methyl ether 7:3), 70% yield. Isomer A: R_f = 0.27; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.43–2.70 (m, 3H), 2.80–3.10 (m, 2H), 3.85 (s, 3H), 5.63 (bt, 1 H, J = 5.5 Hz), 7.23–7.45 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.8 (s), 171.3 (s), 139.5 (s), 128.6 (d), 128.0 (d), 124.7 (d), 78.4 (d), 51.9 (q), 35.6 (t), 34.8 (d), 34.1 (t); IR (CCl_4): 2950, 1790, 1750, 1440, 1160. Anal. Calcd for $C_{13}H_{14}O_4$: C, 77.95; H, 3.98. Found: C, 77.86; H, 3.94. Isomer B: R_f = 0.25; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.80–2.20 (m, 1H), 2.48–2.72 (m, 1H), 2.80–3.05 (m, 2H), 3.10–3.35 (m, 1H), 3.70 (s, 3H), 5.39 (dd, 1H, J = 10.8 Hz, J' = 5.8 Hz), 7.35 (bs, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.0 (s), 171.4 (s), 138.6 (s), 128.6 (d), 128.5 (d), 125.6 (d), 79.6 (d), 51.9 (q), 37.9 (t), 37.6 (d), 33.8 (t); IR (CCl_4) 2950, 1790, 1750, 1440, 1160. Anal. Calcd for $C_{13}H_{14}O_4$: C, 77.95; H, 3.98. Found: C, 77.84; H, 3.90.

Methyl 3-[(*tert*-butyldimethylsilyl)oxy]-1-oxo-1,2,3,4,5,6,7,8-octahydro-2-azuleneacetate (8a): mixture of *cis* and *trans* isomers, 73% combined yield; flash chromatography (hexane–*tert*-butyl methyl ether 6:1). *cis* isomer: R_f = 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 3H), 0.08 (s, 3H), 0.81 (s, 9H), 1.42–1.78 (m, 6H), 2.16–2.60 (m, 4H), 2.54 (m, 2H), 2.87 (ddd, 1H, J = 6.9 Hz, J' = 6.0 Hz, J'' = 5.5 Hz), 3.61 (s, 3H), 4.69 (d, 1H, J = 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.5 (s), 173.7 (s), 173.1 (s), 142.3 (s), 73.2 (d), 51.6 (q), 46.6 (d), 31.0 (t), 30.6 (t), 30.5 (t), 26.4 (t), 26.3 (t), 25.8 (q), 23.2 (t), 18.2 (s), –4.2 (q), –4.5 (q); IR (neat) 2960, 2940, 2860, 1745, 1710, 1705, 1470, 1460, 1435, 1410; mp 73–75 °C. Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 64.80; H, 9.25. *trans* isomer, R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 3H), 0.06 (s, 3H), 0.83 (s, 9H), 1.43–1.75 (m, 6H), 2.23–2.56 (m, 4H), 2.40 (dt, 1H, J = 5.1 Hz, J' = 2.4 Hz), 2.58 (A of an ABC, 1H, J_{AB} = 17.1 Hz, J_{AC} = 5.1 Hz), 2.79 (B of an ABC, 1H, J_{AB} = 17.1 Hz, J_{BC} = 5.1 Hz), 3.58 (s, 3H), 4.45 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.9 (s), 173.4 (s), 172.1 (s), 142.3 (s), 76.7 (d), 51.7 (q), 51.4 (d), 31.8 (t), 31.0 (t), 29.5 (t), 26.4 (t), 26.3 (t), 25.7 (q), 23.3 (t), 18.0 (s), –4.0 (q), –4.6 (q); IR (neat) 2960, 2940, 2860, 1740, 1710, 1655, 1435. Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 64.73; H, 9.25.

Methyl 3-[(*tert*-butyldimethylsilyl)oxy]-1-oxo-1,2,3,4,5,6,7,8-octahydro-2-methyl-2-azuleneacetate (8b): mixture of isomers, 64% combined yield; flash chromatography (hexane–Et_2O 90:10, R_f = 0.36, minor isomer), R_f = 0.34 (major isomer)); ^{1}H NMR (300 MHz, $CDCl_3$) (major isomer) δ 0.13 (s, 6H), 0.88 (s, 9H), 1.12 (s, 3H), 1.51–1.82 (m, 6H), 2.25–2.55 (m, 4H) (AB system, 2H: δ_A 2.39, J_{AB} = 15.9 Hz; δ_B 2.51, J_{AB} = 15.9 Hz), 3.52 (s, 3H), 4.25 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) (minor isomer) δ 207.8 (s), 171.2 (s), 171.0 (s), 141.8 (s), 81.3 (d), 51.0 (q), 48.8 (s), 39.8 (t), 31.1 (q), 29.4 (t), 26.1 (q), 25.7 (q), 23.3 (t), 23.2 (t), 17.9 (s), –3.6 (q), –4.7 (q); IR (mixture of both isomers; CCl_4) 2960, 2940, 2860, 1740, 1705, 1650. Anal. Calcd for $C_{20}H_{34}SiO_4$ (mixture of isomers): C, 65.53; H, 9.35. Found: C, 65.49; H, 9.49.

Methyl 3-[(*tert*-butyldimethylsilyl)oxy]-1-oxo-2-indaneacetate (8c) (mixture of isomers) and Methyl 1-(*tert*-butyldimethylsiloxy)-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (13) were obtained as an inseparable mixture from **7c** (see Table III); flash chromatography (hexane–*tert*-butyl methyl ether 15:1, R_f = 0.16). Significant spectroscopic data for **8c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.21 (d, 1H, J = 3.9 Hz, major isomer), 5.50 (d, 1H, J = 6.3 Hz, minor isomer); ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.2 (s, CO major isomer), 204.8 (s, CO minor isomer).

Methyl 2-[1-[(*tert*-butyldimethylsilyl)oxy]-2-propenyl]-benzoate (9c): flash chromatography (hexane–*tert*-butyl methyl ether 15:1, R_f = 0.53), 16% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.06 (s, 3H), 0.90 (s, 9H), 3.89 (s, 3H), 4.99 (dt, 1H, J = 10.5 Hz, J' = 1.8 Hz), 5.29 (dt, 1H, J = 17.1 Hz, J' = 1.8 Hz), 5.93–6.05 (m, 1H), 6.19 (dt, 1H, J = 4.5 Hz, J' = 1.8 Hz), 7.27 (dt, 1H, J = 7.5 Hz, J' = 1.5 Hz), 7.51 (dt, 1H, J = 7.5 Hz, J' = 1.5 Hz), 7.75 (dd, 1H, J = 7.8 Hz, J' = 0.3 Hz), 7.83 (dd, 1H, J = 7.8 Hz, J' = 1.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.8 (s), 145.9 (s), 141.2 (d), 132.3 (d), 129.8 (d), 127.3 (s), 127.2 (d), 126.6 (d), 112.6 (t), 70.9 (d), 52.0 (q), 25.8 (q), 18.3 (s), –4.8 (q), –4.9 (q).

Methyl 2-[1-[(*tert*-butyldimethylsilyl)oxy]-3-butenyl]-1-cycloheptenecarboxylate (9d): flash chromatography (hexane–*tert*-butyl methyl ether 90/10, R_f = 0.55), 31% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ –0.10 (s, 3H), –0.05 (s, 3H), 0.85 (s, 9H), 1.25–1.40 (m, 2H), 1.40–1.55 (m, 4H), 2.05–2.45 (m, 6H), 3.70 (s, 3H), 4.87 (dd, 1H, J = 11.2 Hz, J' = 7.8 Hz), 4.95–5.05 (m, 2H), 5.65–5.85 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.0 (s), 154.1 (s), 135.3 (t), 130.7 (s), 116.4 (t), 72.0 (d), 51.2 (q), 40.9 (t), 32.6 (t), 32.5 (t), 30.5 (t), 27.8 (t), 26.3 (q), 25.8 (q), 25.7 (t). 18.1 (s), –4.8 (q), –5.0 (q); IR (neat) 2960, 2930, 2860, 1720, 1435, 1255, 1205. Anal. Calcd for $C_{19}H_{34}SiO_3$: C, 67.40; H, 10.12; Found: C, 67.36; H, 10.09.

Methyl 2-[1-[(*tert*-butyldimethylsilyl)oxy]-3-butenyl]-benzoate (9e): flash chromatography (hexane–*tert*-butyl methyl ether 97:3, R_f = 0.50), 31% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ –0.10 (s, 3H), 0.05 (s, 3H), 2.15–2.75 (m, 2H), 3.95 (s, 3H), 4.90–5.10 (m, 2H), 5.65 (dd, 1H, J = 7.4 Hz, J' = 4.0 Hz), 5.78–5.95 (m, 1H), 7.20–7.35 (m, 1H), 7.45–7.52 (m, 1H), 7.76–7.81 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.7 (s), 147.5 (s), 135.5 (d), 132.0 (d), 129.8 (d), 127.3 (d), 127.0 (s), 126.4 (d), 116.7 (d), 70.5 (d), 51.9 (q), 45.1 (t), 25.8 (q), 18.2 (s), –4.8 (q), –4.9 (q); IR (neat) 3080, 2960, 2935, 2860, 1760, 1435, 1245. Anal. Calcd for $C_{18}H_{28}SiO_3$: C, 67.45; H, 8.80. Found: C, 67.40; H, 8.77.

Methyl 3-[(*tert*-butyldimethylsilyl)oxy]-1,2,3,4,5,6,7,8-octahydro-1-azuleneacetate (10d): flash chromatography (hexane–*tert*-butyl methyl ether 90:10, R_f = 0.35, mixture of isomers), 23% yield; ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of isomers) δ 0.10 (s, 6H), 0.95 (s, 9H), 1.30–1.80 (m, 8H), 1.95–2.90 (m, 7H), 3.65 (s, 3H), 3.98 (bt, 0.3H), 4.19 (bt, 0.7H); ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of isomers) δ 176.7 (s), 175.4 (s), 137.2 (s), 135.8 (s), 135.5 (s), 135.3 (s), 71.1 (d), 69.8 (d), 51.7 (q), 38.7 (t), 35.3 (d), 34.8 (t), 34.3 (d), 32.4 (t), 29.0 (t), 27.0 (t), 26.7 (t), 25.8 (q), 18.1 (s), –3.8 (q), –4.2 (q), –4.5 (q), –4.9 (q); IR (CCl_4) (mixture

(13) Bowden, K.; Taylor, G. R. *J. Chem. Soc. B* 1971, 1395–1399.

of isomers) 2960, 2930, 2860, 1740, 1430, 1250. Anal. Calcd for $C_{19}H_{34}SiO_3$: C, 67.40; H, 10.12. Found: C, 67.36; H, 10.09.

Methyl 3-[(*tert*-butyldimethylsilyl)oxy]-1-indaneacetate (10e): flash chromatography (hexane–*tert*-butyl methyl ether 97:3, R_f = 0.32, mixture of isomers), 23% yield; ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of isomers) δ 0.10 (s, 6H), 0.95 (s, 9H), 1.55–1.68 (m, 0.65H), 2.05–2.15 (m, 0.65H), 2.20–2.82 (m, 2.4H), 2.85–3.05 (m, 0.65H), 3.40–3.55 (m, 0.65H), 3.78 (s, 1.05H), 3.80 (s, 1.95H), 5.19 (t, 0.65H, J = 7.3 Hz), 5.34 (t, 0.35H, J = 6.5 Hz), 7.25–7.40 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of isomers) δ 173.1 (s), 145.7 (s), 143.8 (s), 128.1 (d), 127.8 (d), 127.3 (d), 127.2 (d), 124.5 (d), 123.9 (d), 123.1 (d), 75.0 (d), 74.9 (d), 51.6 (q), 43.7 (t), 42.7 (t), 40.3 (t), 39.8 (t), 38.9 (d), 37.9 (d), 25.8 (q), 18.2 (s), −4.4 (q), −4.5 (q), −4.6 (q); IR (neat) 2960, 2930, 2860, 1745, 1435, 1260. Anal. Calcd for $C_{18}H_{28}SiO_3$: C, 67.45; H, 8.80. Found: C, 67.74; H, 8.94.

Methyl 4-[(*tert*-butyldimethylsilyl)oxy]-1-oxo-2,3,4,5,6,7,8,9-octahydro-1*H*-2-benzocycloheptenacetate (11d): flash chromatography (hexane–*tert*-butyl methyl ether 90:10, R_f = 0.10, mixture of isomers), 10% yield; ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of isomers) δ 0.10 (s, 6H), 0.92 (s, 9H), 1.20–2.05 (m, 8H), 2.15–2.50 (m, 4H), 2.55–2.95 (m, 2.35H), 3.15–3.35 (m, 0.65H), 3.68 (s, 1.95H), 3.70 (s, 1.05H), 4.21 (t, 0.65H, J = 3 Hz), 4.45 (dd, 0.35H, J = 10 Hz, J' = 4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of isomers) δ 219.9 (s), 198.6 (s), 172.9 (s), 158.9 (s), 137.7 (s), 70.2 (d), 69.7 (d), 51.6 (q), 41.7 (t), 39.0 (t), 37.0 (t), 36.5 (t), 34.8 (t), 34.7 (t), 34.6 (t), 32.3 (t), 30.5 (t), 26.0 (t), 25.7 (q), 24.3 (t), 18.0 (s), −3.9 (q), −4.5 (q), −4.8 (q), −5.0 (q); IR (neat) 2925, 2915, 2830, 1740, 1670, 1435, 1250. Anal. Calcd for $C_{20}H_{34}SiO_4$: C, 65.53; H, 9.35. Found: C, 65.61; H, 9.42.

Methyl 4-[(*tert*-butyldimethylsilyl)oxy]-1-oxo-1,2,3,4-tetrahydro-2-naphthaleneacetate (11e): flash chromatography (hexane–*tert*-butyl methyl ether 97:3, R_f = 0.15, mixture of isomers), 10% yield; ^{1}H NMR (200 MHz, $CDCl_3$) (major isomer) δ 0.06 (s, 3H), 0.18 (s, 3H), 0.87 (s, 9H), 2.18–2.25 (m, 2H), 2.50–2.65 (m, 1H), 2.85–3.05 (m, 1H), 3.58–3.75 (m, 1H), 3.83 (s, 3H), 4.95 (t, 1H, J = 3 Hz), 7.30–7.65 (m, 3H), 8.05 (dd, 1H, J = 7.5 Hz, J' = 1.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) (major isomer) δ 198.3 (s), 172.6 (s), 143.9 (s), 133.7 (d), 131.1 (s), 128.6 (d), 128.4 (d), 127.4 (d), 67.5 (d), 51.6 (q), 38.5 (d), 37.4 (t), 34.7 (t), 25.8 (q), 18.0 (s), −4.4 (q), −4.5 (q); ^{1}H NMR (200 MHz, $CDCl_3$) (minor isomer) δ 0.20 (s, 3H), 0.24 (s, 3H), 0.99 (s, 9H), 5.07 (dd, 1H, J = 11.2 Hz, J' = 4.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) (minor isomer) δ 194.5 (s), 165.3 (s), 147.3 (s), 133.8 (d), 130.6 (s), 127.5 (d), 127.2 (d), 125.9 (d), 69.0 (d), 51.7 (q), 43.1 (d), 39.7 (t), 34.8 (t), 25.7 (q), 18.0 (s), −4.2 (q), −4.7 (q); IR (mixture of both isomers; CCl_4) 2950, 2930, 2860, 1745, 1690, 1605. Anal. Calcd for $C_{19}H_{28}SiO_4$: C, 65.48; H, 8.10. Found: C, 65.52; H, 8.25.

3-[(*tert*-Butyldimethylsilyl)oxy]-2-methyleneindan-1-one (12): flash chromatography (hexane–*tert*-butyl methyl ether 15:1, R_f = 0.28), 10% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 3H), 0.25 (s, 3H), 0.95 (s, 9H), 5.66 (b, 1H), 5.78 (d, 1 H, J = 1.5 Hz), 6.42 (d, 1H, J = 1.5 Hz), 7.48 (bt, 1 H, J = 7.5 Hz), 7.60–7.73 (m, 2H), 7.84 (bd, 1 H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4 (s), 152.0 (s), 148.6 (s), 137.4 (s), 135.4 (d), 129.3 (d), 125.8 (d), 123.8 (d), 120.7 (t), 70.1 (d), 25.8 (q), 18.1 (s), 3.8 (q); IR (neat) 2960, 2940, 2860, 1735, 1605, 1475.

Methyl 2-[2-(methoxycarbonyl)-1-cycloheptenyl]-4-methylene-3-oxolaneacetate (15a): flash chromatography (hexane–*tert*-butyl methyl ether 7:3, R_f = 0.45), 12% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22–1.80 (m, 6H), 2.20–2.42 (m, 4H), 2.43 (A of an ABX, 1H, J_{AB} = 16.6 Hz, J_{AX} = 5.2 Hz), 2.59 (B of an ABX, 1H, J_{AB} = 16.6 Hz, J_{BX} = 7.4 Hz), 2.85 (b, 1H), 3.83 (s, 3H), 3.85 (s, 3H), 4.0–4.5 (AB system: δ_A 4.25, δ_B 4.44, J_{AB} = 13 Hz), 4.61 (d, 1H, J = 9.2 Hz), 4.78–4.85 (m, 1H), 4.85–4.92 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$,) δ 172.6 (s), 169.9 (s), 150.7 (s), 148.7 (s), 135.5 (s), 104.1 (t), 83.1 (d), 71.3 (t), 51.6 (q), 42.7 (d), 34.4 (t), 32.5 (t), 30.8 (t), 27.9 (t), 26.2 (t); IR (neat) 2920, 2845, 1740, 1710, 1440. Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.42; H, 7.75.

2-(2-Carboxy-1-cycloheptenyl)-4-methylene-3-oxolaneacetic acid (15b): flash chromatography (hexane–*tert*-butyl methyl ether 1:1, R_f = 0.63), 27% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42–1.63 (m, 4H), 1.64–1.82 (m, 2H), 2.20–2.35 (m, 2H), 2.55–2.62 (m, 2H), 2.73–2.81 (m, 2H), 2.83 (b, 1H), 4.30–4.50 (AB system: δ_A 4.32, δ_B 4.52, J_{AB} = 13 Hz), 4.63 (d, 1H, J = 9.8 Hz), 4.84–5.08 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.0 (s), 150.2 (s), 138.9 (s), 126.5 (s), 140.4 (t), 86.5 (d), 71.2 (t), 42.6 (d), 41.9 (t), 31.8 (t), 27.7 (t), 26.3 (t), 25.2 (t); IR (CCl_4) 3500–2800 (b), 2950, 2860, 1720; MS (EI) m/z (%) 235 (100), 203 (13), 175 (17), 147 (17), 112 (22), 95 (43).

Methyl 2-(2-bromophenyl)-4-methylene-3-oxolaneacetate (15c): flash chromatography (hexane–*tert*-butyl methyl ether 90:10), 20% yield. Isomer A: R_f = 0.42; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.90–2.10 (m, 2H), 3.45 (s, 3H), 3.60–3.80 (b, 1H), 4.35–4.70 (AB system: δ_A 4.40, δ_B 4.65, J_{AB} = 12 Hz), 5.0 (b, 1H), 5.12 (b, 1H), 5.22 (d, 1H, J = 5.2 Hz), 7.10–7.60 (m, 4H). Isomer B: R_f = 0.40; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.55–2.80 (m, 2H), 3.05–3.15 (b, 1H), 3.6 (s, 3H), 4.50–4.70 (AB system: δ_A 4.55, δ_B 4.68, J_{AB} = 14 Hz), 4.90 (b, 1H), 5.0 (b, 1H), 5.08 (d, 1H, J = 7.3 Hz), 7.10–7.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9 (s), 149.5 (s), 140.1 (s), 132.7 (d), 129.3 (d), 128.0 (d), 127.7 (d), 122.6 (s), 105.4 (d), 84.3 (d), 71.4 (t), 51.5 (q), 48.1 (d), 36.1 (t); IR (CCl_4) 2850, 1740, 1430, 1160. Anal. Calcd for $C_{14}H_{15}BrO_3$ (mixture of isomers): C, 54.03; H, 4.85. Found: C, 54.27; H, 4.92.

***tert*-Butyl 2-(2-bromophenyl)-4-methylene-3-oxolaneacetate (15d)**: flash chromatography (hexane–*tert*-butyl methyl ether 5:1), 80% yield. Isomer A: R_f = 0.63; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0 (s, 9H), 1.86 (A of an ABX, 1H, J_{AB} = 15.6 Hz, J_{AX} = 5.7 Hz), 1.94 (B of an ABX, 1H, J_{AB} = 15.6 Hz, J_{BX} = 9.6 Hz), 3.69 (m, 1H), 4.40–4.70 (AB system: δ_A 4.41, δ_B 4.67, J_{AB} = 13.2 Hz), 5.01 (b, 1H), 5.14 (b, 1H), 5.23 (d, 1 H, J = 5.4 Hz), 7.14 (dt, 1H, J = 7.8 Hz, J' = 1.8 Hz), 7.3 (t, 1H, J = 7.8 Hz), 7.50–7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 (s), 150.5 (s), 137.7 (s), 132.4 (d), 128.9 (d), 128.4 (d), 127.2 (d), 121.9 (s), 106.3 (t), 82.6 (d), 80.4 (s), 70.1 (t), 42.4 (d), 36.6 (t), 28.0 (q). Isomer B: R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9H), 2.52 (A of an ABX, 1H, J_{AB} = 15.9 Hz, J_{AX} = 8.1 Hz), 2.63 (B of an ABX, 1H, J_{AB} = 15.9 Hz, J_{BX} = 5.4 Hz), 3.0–3.1 (m, 1H), 4.53 (ddd, 1H, J = 12.9 Hz, J' = 4.2 Hz, J'' = 2.1 Hz), 4.67 (dt, 1H, J = 12.9 Hz, J' = 1.8 Hz), 4.96 (dd, 1H, J = 4.5 Hz, J' = 2.1 Hz), 5.0 (dd, 1H, J = 4.5 Hz, J' = 2.1 Hz), 5.06 (d, 1H, J = 7.2 Hz), 7.14 (dt, 1H, J = 7.5 Hz, J' = 1.8 Hz), 7.33 (dt, 1H, J = 7.5 Hz, J' = 1.2 Hz), 7.45–7.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7 (s), 149.7 (s), 140.0 (s), 132.6 (d), 129.3 (d), 128.1 (d), 127.7 (d), 122.8 (s), 105.0 (t), 84.3 (d), 80.7 (s), 71.4 (t), 48.2 (d), 37.0 (t), 27.9 (q). Anal. Calcd for $C_{17}H_{39}BrO_3$: C, 55.03; H, 10.59. Found: C, 54.88; H, 10.33.

Methyl 3-[2-(methoxycarbonyl)-2-propenyloxy]-1-oxo-1,2,3,4,5,6,7,8-octahydro-2-azuleneacetate (16a): flash chromatography (hexane–*tert*-butyl methyl ether 7:3, R_f = 0.15, mixture of isomers), 46% yield; ^{1}H NMR (200 MHz, $CDCl_3$) (mixture of isomers) δ 1.25–1.85 (m, 6H), 2.10–2.95 (m, 7H), 3.56 (s, 1.4 H), 3.60 (1.4 H), 3.70 (s, 3.6H), 4.10–4.50 (m, 3H), 5.7–5.85 (m, 1H), 6.18–6.28 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) (mixture of isomers) δ 205.8 (s), 203.8 (s), 173.2 (s), 172.3 (s), 172.1 (s), 171.4 (s), 166.0 (s), 165.9 (s), 143.7 (s), 143.0 (s), 136.9 (s), 136.8 (s), 126.4 (t), 84.0 (d), 80.9 (d), 71.0 (t), 68.1 (t), 51.8 (q), 51.7 (q), 51.6 (q), 48.1 (d), 45.5 (d), 33.4 (t), 30.9 (t), 30.8 (t), 30.7 (t), 30.6 (t), 29.7 (t), 26.2 (t), 26.2 (t), 23.4 (t), 23.1 (t); IR (neat) (mixture of isomers) 2930, 2850, 1735, 1710, 1650, 1440. Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.31; H, 7.42.

Methyl 3-[[2-(methoxycarbonyl)-2-propenyl]oxy]-1-oxo-2-indaneacetate (16c) (mixture of isomers) and methyl 1-[[2-(methoxycarbonyl)-2-propenyl]oxy]-4-oxo-1,2,3,4-tetrahydro-2-naphthalenecarboxylate (19) were obtained as an inseparable mixture from **14c** (see Table IV). Significant spectroscopic data for **16c** (mixture of isomers) (17% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (d, 1H, J = 3 Hz, major isomer), 5.20 (d, 1H, J = 6.4 Hz, minor isomer), 5.75 (b, 1H, minor isomer), 5.93 (b, 1H, major isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.8 (s, CO minor isomer), 202.1 (s, CO major isomer). GC–MS (retention time 26.9 min) m/z (%): (major isomer) 287 (1), 259 (9), 219 (84), 204 (5), 187 (31), 159 (100), 131 (9); (minor isomer) (retention time 27.0 min) 287 (5), 259 (6), 219 (100), 204 (10), 187 (30), 159 (85), 131 (12). Data for **19** (11% yield): ^{1}H NMR (300 MHz, $CDCl_3$)

δ 4.94 (d, 1H, J = 5.6 Hz), 5.84 (b, 1H), 6.27 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6 (s, CO); GC–MS, m/z (%): (retention time 26.7 min), 318 (1), 259 (2), 219 (100), 187 (30), 159 (35). Anal. Calcd for $C_{17}H_{18}O_6$ (mixture of **16c** and **19**): C, 64.14; H, 5.59. Found: C, 64.27; H, 5.77.

Methyl 2-[[(2-bromo-α-vinylbenzyl)oxy]methyl]acrylate (17c): flash chromatography (hexane–*tert*-butyl methyl ether 90:10, R_f = 0.45), 45% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.75 (s, 3H), 4.20 (b, 2H), 5.15–5.40 (m, 3H), 5.80–5.95 (m, 1H), 5.95 (b, 1H), 6.30 (b, 1H), 7.05–7.18 (m, 1H), 7.25–7.35 (m, 1H), 7.45–7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1 (s), 139.7 (s), 136.9 (s), 136.7 (d), 132.6 (d), 129.1 (d), 128.1 (d), 127.7 (t), 125.9 (d), 123.0 (s), 116.6 (t), 80.7 (d), 66.8 (t), 51.7 (q); IR (CCl_4) 2960, 2940, 2860, 1740, 1435, 1120. Anal. Calcd for $C_{14}H_{15}BrO_3$: C, 54.03; H, 4.85; Found: C, 54.32; H, 4.83.

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Supplementary Material Available: Textual presentation of experimental procedures and compound characterization NMR data for **1a–g**, **7a–e**, and **14a–c** (17 pages). Ordering information is given on any current masthead page.

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