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PREPARATION AND REACTIVITY OF FUNCTIONALIZED ALKENYL-ZINC, -COPPER, AND -CHROMIUM ORGANOMETALLICS

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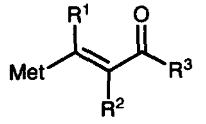
Key words: functionalized organozinc halides, alkenylchromium(III) compounds, copper-zinc organometallics.

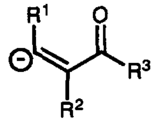
Abstract: β-Halogeno-α,β-unsaturated carbonyl derivatives were converted to the corresponding zinc organometallics **2a** *under mild conditions in THF (Zn dust, 25-45°C, 1-4h). These functionalized alkenylzinc iodides react with a variety of alkenyl and aromatic iodides affording the desired coupling products in 40-97% yield. The addition of a THF solution of CuCN·2LiCl to* **2a** *affords the corresponding organocopper derivatives* **2b** *which react with electrophiles, such as alkynyl and allylic halides, nitro olefins, enones, and chlorotrimethylstannane providing polyfunctional unsaturated carbonyl compounds in 71-95% yield. The insertion of chromium (II) chloride to β-iodo and to some β-(p-tosyl)enones in DMF furnishes new functionalized chromium (III) organometallics* **2c** *which react with aldehydes providing γ-hydroxy unsaturated carbonyl derivatives in 40-91% yield. The synthetic scope and the limitations of this methodology are discussed.*

Introduction

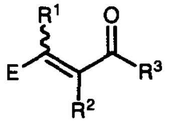
Highly functionalized organometallics are important intermediates for the preparation of complex organic molecules. They avoid the necessity of performing many protection and deprotection steps. The preparation of polyfunctional alkyl organozincs by the direct insertion of zinc metal[2] and organocoppers by the direct insertion of activated copper metal[3], or more conveniently by transmetallation from organozinc reagents[2d], allows the preparation of a variety of polyfunctional organometallics. In fact, the presence of most organic functional groups (ester, ketone, nitrile, halide, phosphonate, primary and secondary amines and amides, aldehydes) is tolerated in these compounds. Significant applications, such as the synthesis of prostaglandins[4], have been performed with the reagents RCu(CN)ZnI. Whereas, the insertion of zinc into primary and secondary carbon-iodine bonds proceeds under very mild conditions (zinc dust (2.5 eq.), THF, 20-40°C, 1-4h), the insertion into aromatic or vinylic carbon-iodine bonds requires the use of polar solvents (DMF or DMA (N,N-dimethylacetamide))[5] or the use of highly activated zinc.[2k,6] We recently reported that the substitution of alkenyl iodides with electron withdrawing groups greatly accelerates the zinc insertion. This led to the preparation of several new types of functionalized alkenylzinc and copper organometallics.[7] We describe herein the preparation and the reactivity of these reagents as well as related organochromium (III) derivatives. Of special interest are the organometallic compounds **1**, which bear a carbonyl function in the β position to the carbon-metal bond, since they are direct synthetic equivalent of vinylogous acyl anions[8] **1b**.



1a : M = ZnX, Cu(CN)ZnX or CrX_2



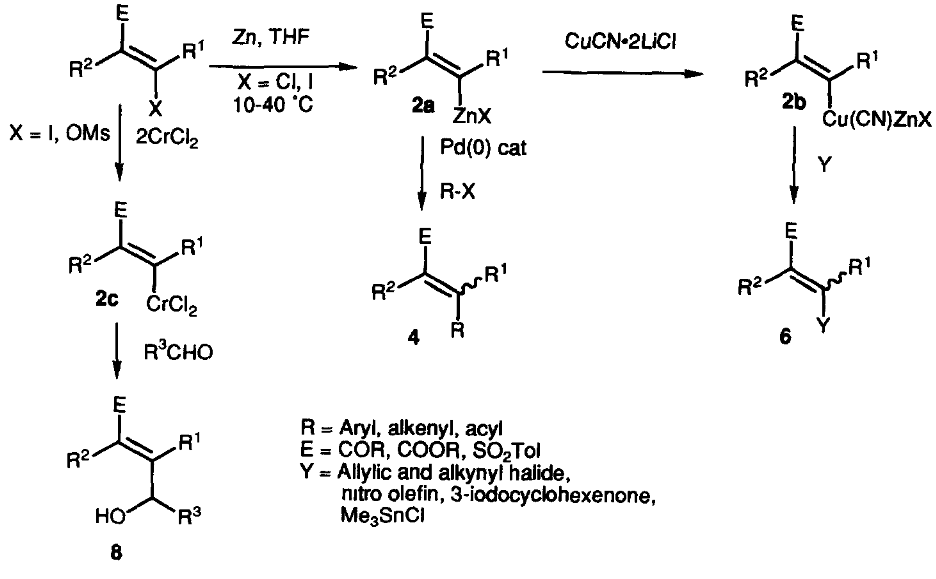
1b



1c

This umpolung of the usual reactivity pattern (d^3 reactivity)[9] allows the formation of new carbon-carbon bonds with electrophilic reagents at position 3 leading to products of type **1c** The exceptional chemoselectivity displayed by the d^3 reagent **1a** (M = ZnX, Cu(CN)ZnX or CrX_2) precludes any protection of the carbonyl group or the double bond. As will be shown below, the three metals, Zn, Cu, and Cr, each confer different and complementary reactivities to the carbon-metal bond making these reagents very versatile intermediates. The general reactivity pattern of the functionalized alkenyl organometallics **2** is described in Scheme I.

Scheme I



R = Aryl, alkenyl, acyl
E = COR, COOR, SO_2Tol
Y = Allylic and alkynyl halide, nitro olefin, 3-iodocyclohexenone, Me_3SnCl

Results and Discussion

(E)-1-Iodo-1-octene reacts with zinc dust in DMF only under forcing conditions (70°C, 14h) affording a mixture of (E) and (Z) octenylzinc iodides.[5] In strong contrast, 3-iodo-2-cyclohexen-1-one[10] reacts in THF, as a 3M solution, in an exothermic manner with zinc dust (first activated with dibromoethane and chlorotrimethylsilane[2d]) leading to a quantitative formation of (3-oxo-1-cyclohexenyl)zinc iodide[3a] (25°C, 1h). 5,5-Dimethyl-3-iodo-2-cyclohexen-1-one[10] was similarly converted to the corresponding zinc compound **3b** (25°C, 1.5h; Table I). Interestingly, the reaction can be extended to β-haloesters and 4-chlorocoumarin[11], which reacts smoothly with zinc dust (45°C, 4h) to give the zinc organometallic **3c** in over 80%, as shown by GC analysis of hydrolyzed and iodolyzed reaction aliquots. It must be emphasized that zinc dust does not usually insert into the carbon-chlorine bond of alkyl chlorides and even the activated allyl- or benzyl-chloride do not react with zinc in THF.[12] In strong contrast, the electron withdrawing functionality (ester) linked to the unsaturated chloride makes this molecule such a good electron acceptor that the first electron transfer from zinc occurs very easily, leading to a radical anion which is eventually converted to **3c**. Using the acyclic unsaturated ester (Z)-ethyl 3-iodoacrylate[13], we observed the formation of two isomeric zinc reagents **3d** (E:Z mixture of 11:89 determined by the iodolysis of GC reaction aliquots). 1-Chloro-1-octen-3-one[14] was also converted to the zinc compound **3e** at low temperature (-15°C to +10°C, 2h), but in a moderate yield. The best conditions involve the generation of **3e** in the presence of the electrophile (entry 12 of Table I). An iodolysis of **3e** shows that this organometallic is a mixture of E and Z isomers (ca. 1:1). The low yield obtained in the preparation of **3e** is partially due to the instability of this zinc reagent, which rapidly decomposes at 25°C.

Attempts to prepare the zinc reagents derived from 3-iodo-2-methyl-2-cyclopenten-1-one[10] were not successful. Interestingly, the β-iodosulfone (E)-2-iodo-1-octenyl-p-tolylsulfone[15] inserts zinc dust within 4h at 25°C providing an E/Z mixture of the organozinc iodide **3f** (ca. 60% yield; E:Z = 9:1). This organometallic shows remarkable stability considering the presence of a β-leaving group (p-TolSO$_2$). The half-life time of the (E)-reagent **3f** was ca. 4h at 25°C and the formation of increasing quantities of 1-octyne and TolSO$_2$ZnI was observed during the course of the reaction. In the presence of catalytic amounts of bis-(dibenzylideneacetone)palladium[16] (Pd(dba)$_2$) (1-2 mol%) and PPh$_3$ (4-8 mol%), the functionalized zinc reagents **3a-f** reacted with aromatic and alkenyl iodides and benzoyl chloride[16,17] affording the polyfunctional unsaturated compounds **4a-k** (Table I). The reactions generally proceed under mild conditions (25°C, 1-24h) and in fair to good yields (40-97% yield). Of special interest is the formation of the 5-substituted uracil derivatives **4a** and **4i** in 97% and 87% yields respectively by the reaction of **3a** and **3d** respectively with N,N-dimethyl 5-iodouracil[18] (entries 1 and 9 of Table I). The cross-coupling reactions of the cyclic organozinc compounds **3a-c** with (E)-1-iodo-1-octene (entries 3, 4, 7, 8, 12, and 13), ethyl (Z)-3-iodoacrylate (entry 6) and (E)-2-iodo-1-octenyl-p-tolylsulfone[15] (entry 11) give stereochemically pure dienes in fair to good yields (40-87% yield). In the case of the

Table I. Products **4a-l** obtained by the palladium (0) catalyzed reactions of the functionalized alkenylzinc reagents of **3a-f** with unsaturated iodides or benzoyl chloride.

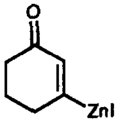
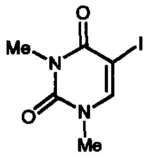
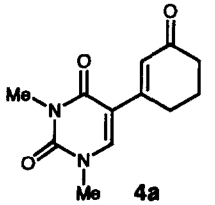
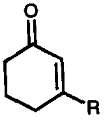
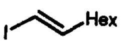
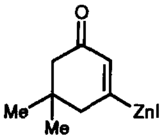
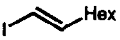
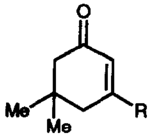
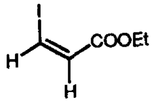
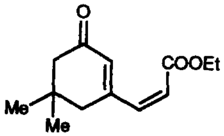
Entry	Organozinc Reagent	Unsaturated Iodide	Reaction Conditions (°C, h)	Product **4**	Yield (%)[a]
1	 **3a**		(25,24)	 **4a**	97
2	**3a**	PhI	(25,8)	 **4b**: R = Ph	71
3	**3a**		(25,1)	**4c**:R = (E)-CH = CH-Hex	73
4	 **3b**		(25,1.5)	 **4d**:R = (E)-CH = CH-Hex	82
5	**3b**	PhCOCl	(25,1)	**4e**:R = COPh	72
6	**3b**		(25,1)	 **4f**: (E:Z = 5:95)	93

Table I (continued)

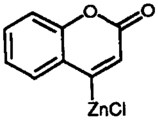
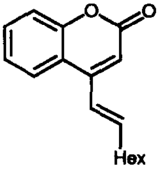
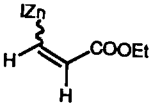
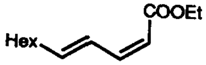
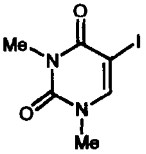
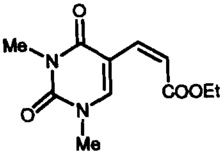
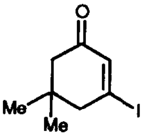
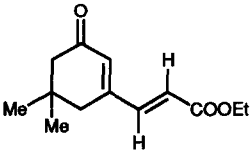
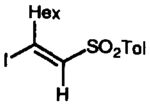
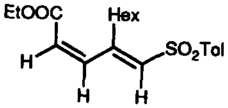
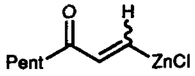
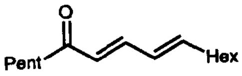
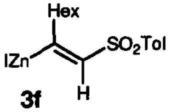
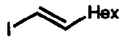
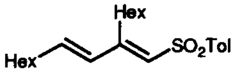
Entry	Organozinc Reagent	Unsaturated Iodide	Reaction Conditions (°C, h)	Product **4**	Yield (%)[a]
7	 **3c**		(25,5)	 **4g**: (100%E)	71
8	 **3d** (E:Z = ca. 11:89)		(25.2)	 **4h**:(100%, 2Z,4E)	81
9	**3d**		(25,24)	 **4i**: (100% Z)	87
10	**3d**		(25,24)	 **4f**: (E:Z = 88:12)	88
11	**3d**		(25,24)	 **4j**: (E:Z = 4·96)	87

Table I (continued)

Entry	Organozinc Reagent	Unsaturated Iodide	Reaction Conditions (°C, h)	Product **4**	Yield (%)[a]
12	 **3e**		(25,4)	 **4k**: (100% EE)	55
13	 **3f**		(25,24)	 **4l**: (100% E)	40

[a] All yields refer to isolated yields of analytically pure products.

unstable β-keto organozinc chloride **3e**, the formation of the zinc reagent was performed in the presence of $Pd(dba)_2$ and 1-iodooctene (THF, 25°C, 4h; 55% yield, entry 12). The reaction of alkenyl iodide with 2-(carbethoxy)vinylzinc iodide **3d** (E:Z = ca. 11:89) affords a mixture of stereoisomeric products reflecting the E/Z ratio of the zinc reagent. However, with 1-iodooctene (0.8 equiv.) only the (2Z, 4E)-dienic ester **4h** is obtained (81% yield, entry 8). The cross-coupling of **3d** with 5,5-dimethyl-3-iodo-2-cyclohexen-1-one provides mostly the (E)-ketoester **4f** (E:Z = 88:12). The pure (Z)-ketoester **4f** (E:Z = 5:95) was prepared independently by the reaction of **3b** with ethyl 3-iodoacrylate (entry 6). Similarly, the reaction of **3d** with (E)-2-iodooctenyl p-tolylsulfone provides the diene **4j** in 87% yield (E:Z = 4:96; entry 11). The coupling of **3a** or **3b** with acid chlorides in the presence of Pd(0) does not proceed efficiently[16e,19] However, the reaction of benzoyl chloride with **3b** (25°C, 1h) provides the 1,4-diketone **4e** in 72% yield (entry 5). Finally, the cross-coupling reaction between the β-p-(tolylsulfonyl)alkenylzinc iodide and 1-iodooctene gives the pure E,E-diene **4l** in 40% yield (25°, 24h; entry 13).

The transmetallation of the alkenylzinc halides **2a** with the THF soluble copper salt CuCN 2LiCl[2d] provides functionalized copper reagents of type **2b** (Scheme I). Some of these alkenyl copper compounds are thermally unstable, thus **5a** undergoes a reductive coupling if warmed to 0°C

Table II. Products **6a-k** obtained by the reaction of the copper reagents **5a-c** with electrophiles.

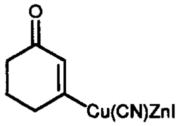
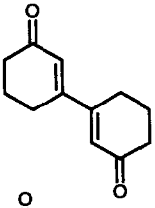
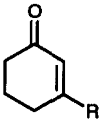
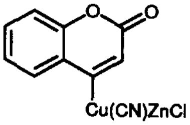
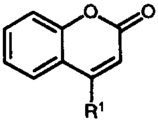
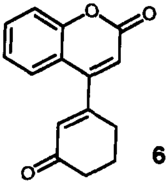
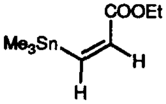
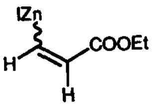
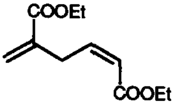
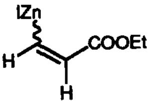
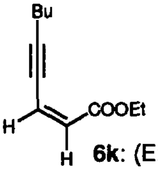
Entry	Organocopper Reagent 5	Electrophile	Product 6	Yield (%)[a]
1	 **5a**	Thermolysis of the copper derivative	 **6a**	83
				
2	**5a**	Me_3SnCl	**6b**:R=$SnMe_3$	93
3	**5a**	1-iodohexyne	**6c**:R= -C≡C—Bu	92
4	**5a**	ethyl α-(bromomethyl) acrylate	**6d**:R=$CH_2C(CO_2Et)=CH_2$	83
5	**5a**	1-nitro-1-pentene	**6e**:R=$CH(Pr)CH_2NO_2$	76
6	 **5b**	ethyl α-(bromomethyl) acrylate	 **6f**:$R^1=CH_2C(CO_2Et)=CH_2$	71
7	**5b**	Me_3SnCl	**6g**:$R^1=Me_3Sn$	69
8	**5b**	3-iodo-2-cyclohexen-1-one	 **6h**	70
9	**5b**	Me_3SnCl	 **6i**: (100% E)	95

Table II (continued)

Entry	Organocopper Reagent **5**	Electrophile	Product **6**	Yield (%)[a]
10	 **5c**	ethyl α-(bromomethyl) acrylate	 **6j**: (100%Z)	95
11	 **5c**	1-iodo-1-hexyne	 **6k**: (E:Z=11:89)	81

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[a] All yields refer to isolated yields of analytically pure products.

furnishing the 1,4-dienic diketone **6a** in 83% yield (entry 1 of Table II). However, if dimethylsulfide (THF:Me_2S, 1:1) is added as a cosolvent[20], the copper reagent **5a** is stable at -40° to -30°C for several hours and reactions with various electrophiles such as allylic and alkynyl halides, Me_3SnCl and some Michael-acceptors afford the desired adducts in 71-95% yield. The allylation of **5a-c** with ethyl α-(bromomethyl)acrylate[21] occurs under very mild conditions (-30 to 0°C, 0.5 h), giving the polyfunctional adducts **6d** (83%; entry 4), **6f** (71%; entry 6) and **6j** (95%; entry 10). Interestingly, the 1,4-dienic diester **6j** has pure (Z)-stereochemistry indicating that the copper compound (Z)-**5c** is more reactive than the (E)-isomer of **5c**. On the other hand the coupling of **5c** with 1-iodohexyne[22] (entry 11 of Table II) gives an E/Z mixture of the ester **6k** (E.Z = 11:89) which is identical with the E/Z ratio of the zinc-copper reagent **5c**. A stannylation of **5a-c** with Me_3SnCl (0°C, 1h) gives the vinylic stannanes **6b**, **6g**, and **6i** (100% Z) in 69-95% yield (entries 2, 7, and 9). The Michael addition of **5b** to 3-iodo-2-cyclohexen-1-one[10] provides the 1,4-addition-elimination product **6h** (-30 to -5°C, 16h; 70% yield; entry 8) In the case of **5b**, it was found that the addition of Me_2S was not necessary and no reductive dimerization of **5b** was observed. Whereas nitrostyrene did not undergo a Michael addition with **5a**, the addition of **5a** to a reactive aliphatic nitro olefin such as 1-nitro-1-pentene[23] proceeds smoothly and affords the nitro adduct **6e** (-60°C to 0°C, 3h; 76% yield, entry 5) 1,4-Additions to less reactive Michael-acceptors such as benzylideneacetone and cyclohexenone did not occur under our reaction conditions. Also the addition of these alkenylcoppers to aldehydes in the presence of $BF_3 OEt_2$ did not proceed. However, we found that the addition of 3-iodo-2-cyclohexen-1-one (1 equiv.) to a suspension of $CrCl_2$[25] (2 equiv) and an aldehyde (0.5 equiv.) in DMF at 25°C led to the rapid formation of functionalized allylic alcohols (entries 1-2 of Table III).

Table III. Products **8a-k** obtained by the reaction of aldehydes with the intermediate chromium(III) reagents **7a-k**.

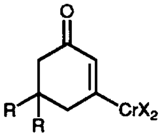
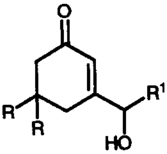
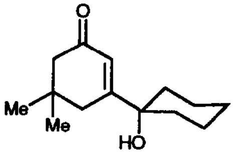
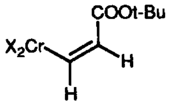
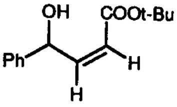
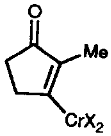
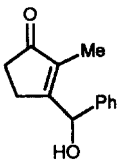
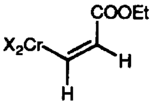
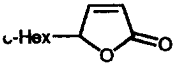
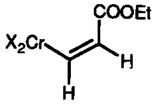
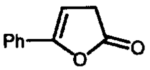
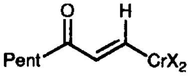
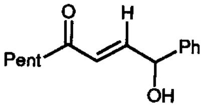
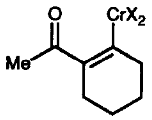
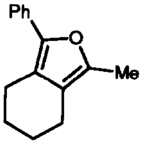
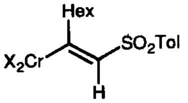
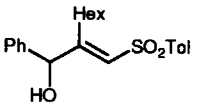
Entry	Organochromium Intermediate	Aldehyde	Product **8**	Yield (%)[a]
				
1	**7a**: R=H	PhCHO	**8a**:R=H,R^1=Ph	91(71)[b]
2	**7a**:R=H	PentCHO	**8b**:R=H,R^1=Pent	72
3	**7b**:R=CH_3	c-HexCHO	**8c**:R=CH_3;R^1=c-Hex	97
4	**7b**:R=CH_3	cyclohexanone	 **8d**	43
5	**7c** 	PhCHO	 **8e** (100% Z)	39
6	**7d** 	PhCHO	 **8f**	57
7	**7e** 	c-HexCHO	 **8g**	50

Table III (continued)

Entry	Organochromium Intermediate	Aldehyde	Product 8	Yield (%)[a]
8	**7e** 	PhCHO	 **8h**	50
9	**7f** 	PhCHO	 **8i**	56
10	**7g** 	PhCHO	 **8j**	44
11	**7k** 	PhCHO	 **8k**	40

[a] All yields refer to isolated yields of analytically pure products

[b] Reaction performed with 3-mesyloxy-2-cyclohexen-1-one

[c] Prepared from 1-acetyl-2-mesyloxycyclohexene

A vinylic mesylate[26] can be used instead of the vinylic iodide, but this results in lower yields (entries 1 and 9 of Table III) The reaction proceeds with good to excellent yields with 3-iodo cyclohexenone derivatives, although lower yields were obtained with other functionalized alkenyl iodides. For example, 3-iodo-2-methyl-2-cyclopenten-1-one reacts with benzaldehyde in the presence of $CrCl_2$ (DMF, 25°C, 3h) providing the allylic alcohol **8f** in only 57% yield (entry 5). The tert-butyl 3-iodoacrylate reacts with benzaldehyde and $CrCl_2$ (50°C, 2h) giving the pure cis γ-hydroxy tert-butyl acrylate **8e** (39%, entry 6), whereas the use of ethyl 3-iodoacrylate provides, with cyclohexanecarboxaldehyde, the unsaturated butyrolactone **8g** (50°C, 24h, 50% yield, entry 7) The use of benzaldehyde gives the isomerized unsaturated lactone **8h** (25°C, 3h, 50% yield, entry 8). β-Chloro enones undergo the chromium insertion under similar conditions (25°C, 3h) and the reaction of 1-chloro-1-octen-3-one[14] with benzaldehyde gives the γ-(hydroxy)enone **8i** in 56% yield. By using 1-acetyl-2-mesyloxycyclohexene[26] and benzaldelyde, the furan **8j** can be isolated in 44% yield (entry 9) Finally, the reaction of (E)-2-iodo-1-octenyl p-tolylsulfone with benzaldehyde (0.5 equiv.; $CrCl_2$ (2 equiv.), 25°C, 2h) furnishes the γ-(hydroxy)unsaturated sulfone[27] **8k** in 40% yield (entry 10).

Conclusion

In conclusion, we have shown that the insertion of zinc metal or chromium (II) chloride into a variety of alkenyl iodides bearing election withdrawing groups provides new polyfunctional alkenyl organometallics which react with several important classes of electrophiles to afford a wide range of organic molecules.

Experimental Section

General Methods. Unless otherwise indicated, all reactions were carried out under an argon atmosphere. Solvents (THF and diethyl ether) were dried and freshly distilled from sodium/benzophenone. Zinc dust (-325 mesh) and $CrCl_2$ were purchased from Aldrich Chemical Company. Reactions were monitored by gas-liquid phase chromatography (GC) analysis of reaction aliquots. Unless otherwise indicated, the reactions were worked up as follows. the reaction mixture was poured into a mixture of ether and sat. aqueous NH_4Cl. The two phase mixture was filtered to remove insoluble salts and the two layers were separated. The aqueous layer was extracted with ether (2 x ca.50ml) The combined ethereal extracts were then washed with water (50 ml) and sat. aqueous NaCl (20ml), dried ($MgSO_4$) and filtered. The residue obtained after evaporation of the solvents was purified by flash-chromatography. Fourier transform infrared spectra (FT-IR) were recorded under a nitrogen atmosphere on a Nicolet 5DXB FT-IR spectrometer. Proton and carbon nuclear magnetic resonance spectra (^1H and ^{13}C NMR) was recorded on a Bruker WM-300 (300 MHz (proton) and 75.5 MHz (carbon)). Mass Spectra (MS) and exact mass calculations were recorded on a VG-70-250 S mass spectrometer. The ionization methods used were desorption chemical ionization (CI) and electron impact ionization (EI).

Starting Materials. The following starting materials were prepared according to the literature: (E)-1-iodo-1-octene[28], 3-iodo-2-cyclohexen-1-one[10], 5,5-dimethyl-3-iodo-2-cyclohexen-1-one[10], 4-chlorocoumarin[11], (Z)-ethyl 3-iodoacrylate[13], 1-chloro-1-octen-3-one[14], 3-iodo-2-methyl- 2-cyclopenten-1-one[10], (E)-2-iodo-1-octenyl p-tolylsulfone[15], bis-(dibenzylideneacetone) palladium[16], N,N-dimethyl-5-iodouracil[18], ethyl α-(bromomethyl)acrylate[21], 1-iodohexyne[22], 1-nitro-1-pentene[23], 3-mesyloxy-2-cyclohexen-1-one[26], 1-acetyl-3-mesyloxy-2-cyclohexen-1-one[26]

Typical Procedure A: Preparation of a functionalized alkenylzinc halide: Preparation of 3-oxo-1-cyclohexen-1-ylzinc iodide (**3a**): A dry, three-necked, 50 mL flask equipped with an argon inlet, a magnetic stirring bar and a low temperature thermometer was charged with zinc dust (1 95 g, 30mmol, Aldrich, -325 mesh) and flushed with argon.
1,2-Dibromoethane (200 mg, 1mmol) in THF (3 mL) was added. The zinc suspension was heated with a heat gun to ebullition, allowed to cool and heated again. This process was repeated three times. Then Me_3SiCl (0.15 mL, ca. 1 2 mmol) was added, and after 10 min of stirring, a solution of 3-iodo-2-cyclohexen-1-one (2.22 g, 10 mmol) in THF (3 mL) was added dropwise over 15-20 min. During the addition, the temperature rose to 55°C. The reaction mixture was stirred for 1 h at room temperature and the progress of the reaction was monitored by GC analysis of hydrolyzed reaction aliquots. After completion of the reaction, THF (8 mL) was added and the zinc was allowed to settle for 1-2 h at 25°C. GC analysis of a reaction aliquot indicates complete

conversion of the alkenyl iodide to the zinc organometallic as well as the formation of less than 8% of dimer **6a** (entry 1 of Table II). The yield of 3-oxo-1-cyclohexen-1-ylzinc iodide **3a** was estimated to be 85%. The organozinc reagents **3b-3f** were prepared using procedure A and the following reaction times and temperatures: **3b** (25°C, 1.5h, ca. 90% yield); **3c** (45°C, 4h, ca. 80% yield); **3d** (25°C, 2-3h, ca. 90% yield); **3e** (-15 to 10°C, 2h, ca.50% yield); **3f** (25°C, 4h, ca. 60% yield).

Typical Procedure B: Reaction of a functionalized alkenylzinc halide with an unsaturated iodide in the presence of catalytic amounts of Pd(dba)$_2$: Preparation of (E)-1-octenyl-2-cyclohexen-1-one (**4c**): A dry, three-necked 50mL flask equipped as described above (Procedure A) was charged with bis(dibenzylideneacetone) palladium (0) (Pd(dba)$_2$, 27 mg, 0.05 mmol) and triphenylphosphine (52 mg, 0.2mmol). The flask was flushed with argon and THF (10 mL) was added. After 10 min (E)-iodo-1-octene (0.833 g, 3.5 mmol), and a THF solution of 3-oxo-1-cyclohexen-1-ylzinc iodide **3a** (5 mmol) were sequentially added at 25°C. During the addition, the temperature rises to 40°C. The reaction mixture was stirred for 1 h at 25°C. GC analysis of a reaction aliquot indicates the completion of the reaction which was worked up as described above. The crude residue was purified by flash chromatography (EtOAc/hexane 1/10) yielding 530 mg of (E)-1-octenyl-2-cyclohexen-1-one **4c** as an analytically pure oil (73% yield).

Typical Procedure C: Conversion of 3-oxo-1-cyclohexenylzinc iodide (3a) to the corresponding copper reagent (5a) and its reaction with ethyl α-(bromomethyl) acrylate: Preparation of ethyl 2-(3-oxo-1-methylcyclohexenyl)-2-propenoate **6d** (see entry 4 of Table II): A dry, three-necked 50 mL flask equipped as described above, was charged with LiCl (0.85 g, 20 mmol, previously dried under vacuum at 130°C for 2 h), copper cyanide (0.89 g, 10 mmol). THF (8 mL) and Me$_2$S (12 mL) were added and the resulting solution was cooled to -70°C. The previously prepared THF solution of the zinc reagent **3a** was slowly added via. The reaction mixture was allowed to warm to -30°C, stirred 5 min at this temperature, cooled back to -70°C and ethyl α-(bromomethyl) acrylate (1.35 g, 7 mmol ca. 0.8 equiv.) was added. The cooling bath was removed and the reaction mixture was allowed to warm to 0°C. After 1 h at this temperature, the reaction was complete as indicated by GC analysis and was worked up as described above. After evaporation of the solvents, the resulting crude oil was purified by flash chromatography (EtOAc /hexane 1/4) to furnish 1.22 g of the ketoester **6d** as an analytically pure oil (83% yield)

Typical Procedure D: Reaction of functionalized alkenyl halides or mesylates with an aldehyde in the presence of CrCl$_2$: 3-(1-Hydroxy-1-hexyl)-2-cyclohexen-1-one **8b**: A dry, three-necked 50mL flask equipped with an argon inlet, a magnetic stirring bar, and a a low temperature thermometer was charged with chromium (II) chloride (Aldrich, 0.98 g, 8.0 mmol) and flushed with argon. Freshly distilled DMF (8 mL) was added and stirred for 10 min at 25°C. A solution of hexane (0.220 g, 2 mmol) in DMF (3 mL) and a solution of 3-iodo-2-cyclohexen-1-one (0.88 g, 4 mmol) in DMF (3 mL) were added successively. The reaction mixture was stirred 4 h at 25°C. After completion as indicated by GC analysis, the reaction was worked up as described above. After evaporation of the solvent, the resulting crude product was purified by flash chromatography (EtOAc /lhexane, 3/10), yielding **8b** (283 mg, 72%) as an analytically pure oil.

Analytical Data for the Products 4a - 4l (Table I)

1,3-Dimethyl-5-(3-oxo-1-cyclohexenyl)-uracil (4a): 796 mg (97% yield) obtained by the reaction of 1,3-dimethyl-5-iodouracil (930 mg, 3.5 mmol) with **3a** (5 mmol); 25°C, 24 h (Typical Procedure A and B). Purified by flash chromatography (EtOAc), solid m.p. 46-48°C. IR (neat): 3010 (s), 2950 (s), 2850 (m), 1708 (s), 1654 (s), 1453 (m), 1344 (m), 1215 (m), 1197 (s), 1010 (m), 754 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.44 (s, 1H), 6.48 (s, 1H), 3.47 (s, 3H), 3.36 (s, 3H), 2.72 (t, 2H, J = 6.1 Hz), 2.46 (t, 2H, J = 6.7 Hz), 2.08 (quintet, 2H, J = 6.1 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 200.8, 160.9, 155.7, 150.8, 141.9, 126.2, 112.4, 37.4, 37.2, 28.1, 28.0, 22.6; MS (EI): 42 (100), 149 (36), 150 (28), 178 (76), 179 (13), 206 (68), 233 (70), 234 (96). Exact mass calcd. for $C_{12}H_{14}N_2O_3$: 234.1004 Observed: 234.1005.

3-Phenyl-2-cyclohexen-1-one (4b): 388 mg (71 % yield) obtained by the reation of iodobenzene (612 mg, 3 mmol) with **3a** (5 mmol); 25°C, 8 h (Typical Procedures A and B)

Purified by flash chromatography (EtOAc/hexane: 3/10). IR: (neat): 3083 (s), 3017 (s), 2950 (s), 2890 (s), 1662 (s), 1576 (s), 1446 (m), 1415 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.56 (m, 2H), 7.41 (m, 3H). 6.42 (s, 1H), 2.78 (m, 2H), 2.46 (t, 2H, J=7.3 Hz), 2.12 (quintet, 2H J=7.3 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 199.8, 159.5, 139.0, 129.7, 128.5, 125.8, 125.2, 37.0, 27.8, 22.6; MS (EI): 115 (55), 116 (38), 144 (100), 172 (68). Exact mass calcd. for $C_{12}H_{12}O$: 172.0888. Observed: 172.0878.

(E)-3-(1-octenyl)-2-cyclohexen-1-one (4c): 530 mg (73% yield) obtained by the reaction of (E)-1-iodo-1-octene (833 mg, 3.5 mmol) with **3a** (5 mmol); 25°C, 1 h (Typical Procedures A and B). Purified by flash chromatography (EtOAc /hexane: 1/10) IR (neat): 3018 (s), 2930 (s), 2858 (s), 1662 (s), 1632 (s), 1586 (m), 1456 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.17 (m, 2H), 5.85 (s, 1H), 2.44 (t, 2H, J=5.8 Hz), 2.37 (t, 2H, J=5.1 Hz), 2.18 (q, 2H, J=5.6 Hz), 2.02 (quintet, 2H, J=6.2 Hz), 1.41 (t, 2H, J=6.6 Hz), 1.28 (m, 6H), 0.89 (m, 3H) ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 200.1, 157.4, 139.0, 131.3, 126.3, 37.6, 33.1, 31.5, 29.5, 28.7, 25.0, 22.4, 22.2, 13.8; MS (EI): 121 (100), 122 (26), 206 (26). Exact mass calcd. for $C_{14}H_{22}O$: 206.1670. Observed: 206.1657.

(E)-5,5-Dimethyl-3-(1-octenyl)-2-cyclohexen-1-one (4d): 667 mg (82% yield) obtained by the reaction of (E)-1-iodo-1-octene (833 mg, 3.5 mmol) with **3b** (5 mmol); 25°C, 1.5 h (Typical Procedures A and B). Purified by flash chromatography (EtOAc /hexane; 1/5). IR (neat): 3027 (s), 2958 (s), 2926 (s), 2857 (s), 1664 (s), 1635 (s), 1590 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): d 6.2 (s, 2H), 5.84 (s, 1H), 2.31 (s, 2H), 2.24 (s, 2H), 2.16 (m, 2H), 1.41 (m, 2H), 1.30 (m, 6H), 1.06 (s, 6H), 0.9 (m, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): d 199.9, 155.0, 138.7, 131.4, 125.1, 51.3, 39.1, 33.2, 33.1, 31.5, 28.8, 28.3, 22.4, 13.9; MS (EI): 108 (61), 109 (33), 121 (39), 138 (35), 149 (85), 150 (48), 151 (52), 178 (32), 219 (29), 234 (100). Exact mass calcd for $C_{16}H_{26}O$: 234.1983 Observed· 234.1483.

5,5-Dimethyl-3-benzoyl-2-cyclohexen-1-one (4e): 495 mg (72% yield) obtained by the reaction of benzoyl chloride (426 mg, 30 mmol) with **3b** (5 mmol); 25°C, 1 h (Typical Procedures A and B). Purified by flash chromatography (EtOAc /hexane; 1/10) solid m.p. 116°C. IR (KBr): 3058 (m), 2963 (s), 2947 (s), 2887 (m), 1718 (s), 1678 (s), 1650 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): d 7.79 (d, 2H, J=7.2 Hz), 7.58 (t, 1H, J=7.7 Hz), 7.47 (t, 2H, J=7.7 Hz), 6.2 (s, 1H), 2.56 (s, 2H), 2 39 (s, 2H), 1.14 (s, 6H); ^{13}C NMR (CDCl$_3$, 75.5 MHz). d 199.9, 196.8, 153.6, 135 6, 133.2, 131 2, 129.4, 128.5, 51.4, 39.3, 33.7, 28.0, MS (EI): 105 (100), 144 (17), 211 (18), 213 (9), 228 (38) Exact mass calcd for $C_{15}H_{16}O_2$: 228.1150. Observed 228.1134.

(Z)-Ethyl 3-(1-oxo-5,5-dimethyl-2-cyclohexenyl)acrylate (4f): 726 mg (93% yield) obtained by the reaction of (Z)-ethyl 3-iodo acrylate (791 mg, 3 5 mmol) with **3b** (5 mmol); 25°C, 1h (Typical Procedures A and B). Purified by flash chromatography (EtOAc/hexane; 1/20). IR (neat): 2960 (s), 2942 (s), 2871 (s), 1730, (s), 1676 (s), 1630 (s) cm^{-1}, ^{1}H NMR (CDCl$_3$, 300 MHz): d 6.50 (d, 1H, J=12.2 Hz), 5.98 (s, 1H), 5.93 (d, 1H, J=12.2 Hz), 4.17 (q, 2H, J=7.1 Hz), 2.37 (s, 2H), 2.26 (s, 2H), 1.27 (t, 3H, J=7.1 Hz), 1 06 (s, 6H), ^{13}C NMR (CDCl$_3$, 75.5 MHz): d 199.1, 165.3, 154.2, 140.6, 128.0, 123.4, 60.5, 51.0, 41.9, 33.6, 28.1, 13.9; MS (EI): 110 (70), 121 (30), 133 (43), 138 (41), 161 (46), 165 (100), 194 (32), 222 (51) Exact mass calcd for $C_{13}H_{18}O_3$: 222.1255. Observed: 222.1252.

(E)-Ethyl 3-(1-oxo-5,5-dimethyl-2-cylohexenyl)acrylate 4f: 586 mg (78% yield) obtained by the reaction of 5,5-dimethyl-3-iodo-2-cyclohexen-1-one (750 mg, 3.0 mmol) with **3d** (5 mmol); 25°C, 24 h (Typical Procedures A and B) Purified by flash chromatography (EtOAc /hexane, 1/10) IR (neat): 2960 (m), 1720 (s), 1670 (s), 1631 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): d 7 35 (d, 1H, J=16.1 Hz), 6.26 (d, 1H, J=16.1 Hz), 6.15 (s, 1H,) 4 20 (q, 2H, J=7.6 Hz), 2.36 (s, 2H), 2.31 (s, 2H), 1.30 (t, 3H, J=7 6 Hz), 1 07 (s, 6H), ^{13}C NMR (CDCl$_3$, 75 5 MHz): d 199.5, 165.6, 154.2, 151.4, 144.2, 140.6, 131.3, 127 9, 123.9, 123.3, 60.7, 60 6, 51.2, 50.9, 41 8, 38 8, 33 6, 33.1, 28.2, 28.1, 14.1; MS (EI). 94 (62), 110 (100), 138 (90), 149 (85), 166 (51), 177 (41), 222 (76). Exact mass calcd for $C_{13}H_{18}O_3$. 222 1255. Observed: 222.1257.

(E)-4-(octenyl)coumarin (4g) 539 mg (71% yield) obtained by the reaction of (E) 1-iodo-1-octene (714 mg, 3 mmol) with **3c** (5 mmol); 25°C, 5 h (Typical Procedures A and B) Purified by flash chromatography (EtOAc /hexane, 1/20) solid m.p. 68°C. IR (neat): 2958 (s), 2929 (s), 2872 (s), 1755 (s), 1731 (s), 1684 (s), 1646 (s), 1561 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): d 7.69 (dd, 1H, J=7.9, 1.3 Hz), 7.50 (td, 1H, J=7.5, 1.4 Hz), 7.31 (m, 2H), 6.68 (d, 1H, J=15.6 Hz), 6.51 (dd, 1H, J=13.4, 6.6 Hz), 6.42 (s, 1H), 2.34 (q, 2H, J=7.2 Hz), 1.53 (t, 2H, J=6.9 Hz), 1.36 (m, 6H), 0.90 (t, 3H, J=6.3 Hz). ^{13}C NMR (CDCl$_3$, 75.5 MHz): d 161.1, 153.7, 150.8, 141.4, 131.5, 124.4, 123.9, 122.4, 118.6, 117.1, 110.3, 33.3, 31.5, 28.7, 28.5, 22.4, 13.9; MS (EI): 171 (100), 172 (14), 185 (3), 256 (11). Exact mass calcd. for $C_{17}H_{20}O_2$: 256.1463. Observed: 256.1451.

(2Z,4E)-Ethyl 2,4-undecadienoate (4h): 514 mg (81% yield) obtained by the reaction of (E) 1-iodo-1-octene (714 mg, 3 mmol) with **3d** (5 mmol); 25°C, 2 h (Typical Procedures A and B) (100% 2Z, 4E). The stereochemistry of the double bonds was established by comparison with the literature.[29] Purified by flash chromatography (hexane). IR (neat): 2979 (s), 2957 (s), 2856 (s), 1715 (s), 1637 (s), 1601 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.38 (dd, 1H, J=11.3, 1.8 Hz), 6.55 (t, 1H, J=11.3 Hz), 6.08 (quintet, 1H, J=7.8 Hz), 5.56 (d, 1H, J=11.3 Hz), 4.18 (q, 2H, J=6.1 Hz), 2.20 (q, 2H, J=6.1 Hz), 1.42 (m, 2H), 1.28 (m, 9H), 0.92 (t, 3H, J=4.8 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 166.4, 145.5, 145.2, 126.9, 115.5, 59.7, 32.9, 31.6, 28.9, 28.7, 22.5, 14.3, 13.9. MS (EI): 125 (100), 165 (13), 210 (24). Exact mass calcd. for $C_{13}H_{22}O_2$: 210.1619. Observed: 210.1626.

(Z)-5-(2-Carboethoxyethenyl)-1,3-dimethyluracil (4i): 628 mg (87% yield) obtained by the reaction 1,3-dimethyl-5-iodouracil (798 mg, 3 mmol) with **3d** (5 mmol); 25°C, 26 h (Typical Procedure A and B). Purified by flash chromatography (EtOAc /hexane; 1/5). IR (neat): 2982 (s), 2957 (s), 2927 (s), 1707 (s), 1656 (s), 1634 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.18 (s, 1H), 7.05 (d, 1H, J=13.8 Hz), 5.90 (d, 1H, J=13.8 Hz), 4.15 (q, 2H, J=7.6 Hz), 3.51 (s, 3H), 3.38 (s, 3H), 1.33 (t, 3H, J=7.6 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz): d 167.8, 166.8, 162.6, 161.1, 151.1, 150.5, 146.8, 144.7, 136.8, 135.2, 118.9, 117.9, 107.9, 107.3, 61.1, 60.5, 37.8, 37.3, 28.4, 27.8, 14.2. MS (EI): 43 (100), 209 (3), 238 (7). Exact mass calcd. for $C_{11}H_{14}O_4H_2$: 238.0953. Observed: 238.0948.

Compound **4i** slowly isomerized to (E)-5-(2-Carboethoxyethenyl)-1,3-dimethyluracil. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.46 (s, 1Hz), 7.34 (d, 1H, J=15.7 Hz), 6.95 (d, 1H, J=15.7 Hz), 4.15 (q, 2H, J=7.6 Hz), 3.51 (s, 3H), 3.38 (s, 3H), 1.33 (t, 3H, J=7.6 Hz).

(2Z, 4E) Ethyl 4-hexyl-5-p-tolylsulfonyl-2,4-pentadienoate (4j): 950 mg (87% yield) obtained by the reaction of (E)-2-iodooctene-p-tolylsulfone (1.17 g, 3 mmol) with **3d** (5 mmol); 25°C, 24 h (Typical Procedures A and B). Purified by flash chromatography (EtOAc /hexane: 1/5). IR (neat): 3022 (s), 2981 (s), 2872 (s), 1713 (s), 1631 (s), 1596 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.81 (d, 2H, J=10.4 Hz), 7.32 (d, 2H, J=10.4 Hz), 7.51 (d, 1H, J=15.4 Hz), 6.45 (s, 1H), 6.16 (d, 1H, J=15.4 Hz), 4.22 (q, 2H, J=7.1 Hz), 2.73 (t, 2H, J=6.9 Hz), 2.42 (m, 3H), 1.3 (m, 11H), 0.85 (m, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 165.5, 150.7, 144.7, 143.8, 138.8, 134.1, 129.9, 127.5, 124.5, 60.9, 31.4, 29.5, 29.3, 27.4, 22.6, 21.5, 14.1, 13.9; MS (EI): 136 (30), 365 (2). Exact mass calcd. for $C_{20}H_{28}O_4SH^+$: 365.1786. Observed: 365.1796.

(7E,9E)-6-Oxo-7,9 hexadecadiene (4k): 389 mg (55% yield) obtained by the reaction of (E)-1-iodo-1-octene (714 mg, 3 mmol) with **3e** (5 mmol); 25°C, 4 h (Typical Procedures A and B) (100% E,E). Purified by flash chromatography (EtOAc /hexane; 1/50). IR (neat): 3029 (s), 2928 (s), 2871 (s), 1689 (s), 1637 (s), 1596 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.15 (m, 1H), 6.18 (m, 2H), 6.08 (d, 1H, J=13.0 Hz), 2.55 (t, 2H, J=6.8 Hz), 2.19 (m, 2H), 1.65 (m, 2H), 1.37 (m, 12H), 0.88 (m, 6H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 200.9, 145.4, 142.8, 129.0, 128.0, 40.5, 33.1, 31.6, 31.5, 28.8, 28.7, 24.1, 22.5, 22.4, 13.9, 13.8. MS (EI): 95 (100), 151 (56), 165 (43), 180 (35), 236 (5). Exact mass calcd. for $C_{18}H_{28}$: 236.2140. Observed: 236.2126.

2-Hexyl-1-p-tolylsulfonyl-1,3-decadiene (4l): 456 mg (40% yield) obtained by the reaction (E)-1-iodo-1-octene (714 mg, 3 mmol) with **3f** (5 mmol), 25°C, 24 h (Typical Procedures A and B). Purified by flash chromatography (EtOAc /hexane; 1/50). IR (neat): 2955 (s), 2870 (s), 1637 (s), 1597 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.79 (d, 2H, J=10.4 Hz), 7.32 (d, 2H, J=10.4 H), 6.1 (m, 2H), 5.85 (d, 1H, J=17.4 Hz), 2.65 (m, 2H), 2.45 (s, 3H), 2.15 (m, 2H), 1.28 (m, 16H), 0.90 (m, 6H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 154.4, 143.7, 140.0, 138.7, 130.2, 129.6, 127.1, 126.6, 32.9, 31.5, 29.5, 28.7, 27.6, 22.4, 21.4, 13.9. MS (EI): 151 (100), 157 (24), 163 (29), 220 (50), 221 (45), 376 (25). Exact mass calcd. for $C_{23}H_{36}O_2S$: 376.2476. Observed: 376.2432.

Analytical Data for the Products (6a) - (6k) (Table II)

3,3'-Dioxo-1,1'-bicyclohexenyl (6a): 403 mg (83% yield) obtained by thermolysis of **5a** (5 mmol); -60^{0}C to 0^{0}C, 1 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane; 1/2) solid, m.p 98^{0}C. IR (neat): 3018 (s), 2955 (s), 2890 (s), 1669 (s), 1581 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz)· δ 6.25 (s, 1H), 2 55 (t, 2H, J=4.6 Hz), 2.45 (t, 2H, J=6 1 Hz), 2.05 (dt, 2H, J=6.1, 4.6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 199.3, 156.4, 127.8, 37.2, 25.7, 22.0; MS (EI): 78 (68), 91 (68), 119 (35), 134 (100), 162 (36), 190 (197). Exact mass calcd for $C_{12}H_{14}O_2$· 190.0993. Observed 190 1001

3-Trimethylstannyl-2-cyclohexen-1-one (6b)^{30}· 841 mg (93% yield) obtained by the reaction of Me_3SnCl (693 mg, 3.5 mmol), with **5a** (5 mmol); -78^{0}C to 0^{0}C, 1 h (Typical Procedures A and C). Purified by flash chromatography (EtOAc /hexane, 3/20) IR (neat): 2979 (s), 2921 (s), 2862 (s), 2330 (s), 1673 (s), 1575 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz). δ 6.22 (t, 1H, J=2.0 Hz), 2.49 (tt, 2H, J=5.8, 2.0 Hz), 2.39 (t, 2H, J=6.4 Hz), 1.98 (td, 2H, J=6.4, 5.1 Hz), 0.20 (t, 9H J=57.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz)· δ 196.7, 173 5, 138 3, 38.0, 31.7, 23.5, 10.4; MS (EI): 163 (64), 165 (81), 245 (100), 258 (24), 260 (31) Exact mass calcd for $C_9H_{15}O^{120}Sn$: 260.0223. Observed: 260.0213.

3-(1-Hexynyl)-2-cyclohexen-1-one (6c)· 587 mg (92% yield) obtained by the reaction of 1-iodohexyne (728 mg, 3.5 mmol), with **5a** (5 mmol); -60^{o}C, 24 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane; 2/20). IR (neat): 3016 (s), 2959 (s), 2216 (s), 1658 (s), 1541 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.08 (s, 1H), 2.38 (m, 6H), 1.98 (quintet, 2H, J=6.3 Hz), 1.51 (m, 2H), 1 48 (m, 2H), 0 89 (t, 3H, J=6.3 Hz); ^{13}C NMR ($CDCl_3$, 75 5 MHz). δ 198.3, 144.2, 131.6, 102.0, 80 2, 37.0, 30.7, 30.2, 22.4, 21.7, 19.3, 13.3; MS (EI): 134 (73), 148 (81), 161 (6), 176 (100); Exact mass calcd. for $C_{12}H_{16}O$. 176.1201. Observed: 176.1207.

Ethyl 2-(3-oxo-1-methylcyclohex-1-enyl)-2-propenoate (6d): 600mg (83% yield) obtained by the reaction of ethyl α-(bromomethyl)acrylate (680 mg, 3 5 mmol) with **5a** (5 mmol); -60^{o}C to 0^{o}C, 1h. (Typical Procedures A and C) Purified by flash chromatography (EtOAc /hexane; 1/4) IR (neat): 3018 (s), 2955 (s), 2890 (s), 1712 (s), 1666 (s) cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz)· δ 6.28 (d, 1H, J=1.6 Hz), 5.82 (t, 1H, J=1 4 Hz), 5 58 (t, 1H, J=1 1 Hz), 4 15 (q, 2H, J=7.2 Hz), 3.17 (s, 2H), 2.32 (m, 4H), 1.97 (quintet, 2H, J=6 3 Hz), 1 25 (t, 3H, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 199.2, 166.1, 162.8, 136 6, 127 4, 126 7, 60.8, 39 7, 37.1, 29.4, 22.4, 13.9; MS (EI) 135 (94), 162 (100), 163 (90), 179 (12), 208 (46) Exact mass calcd for $C_{12}H_{16}O_3$: 208 1099 Observed: 208.1091

3-(-1-Propyl-2-nitroethyl)-2-cyclohexen-1-one (6e): 565 mg (71% yield) obtained by the reaction of 1-nitro-1-pentene (402 mg, 3 5 mmol) with **5a** (5 mmol); -60^{o}C to 0^{o}C, 3 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane; 1/5). IR (neat) 3019 (s), 2962 (s), 2875 (s), 1706 (m), 1668 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.87 (s, 1H), 4.43 (d, 2H, J=6.7 Hz), 3.04 (quintet, 1H, J=6.9 Hz), 2.37 (t, 2H, J=6.4 Hz), 2.28 (t, 2H, J=6.2 Hz), 2.00 (quintet, 2H, J=6.0 Hz), 1.48 (m, 2H), 1.28 (m, 2H), 0 91 (t, 3H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 5 MHz): δ 198.8, 162.2, 127.9, 77 8, 45 5, 37.4, 32 4, 26 7, 22.5, 20.0, 13 6; MS (EI): 95 (100), 121 (30), 123 (34), 135 (46), 211 (16) Exact mass calcd. for $C_{11}H_{17}NO_3$: 211.1208. Observed 211.1207.

4-(2-Carboethoxy-2-propenyl)-coumarin (6f)· 555 mg (71% yield) obtained by the reaction of ethyl α-(bromomethyl)acrylate (579 mg, 3.0 mmol) with **5b** (5 mmol); -78^{o}C to 0^{o}C, 1 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane; 1/5). IR (neat) 3076 (s), 3044 (s), 2982 (s), 2907 (s), 1755 (s), 1734 (s), 1605 (m) cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (m, 2H), 7.32 (m, 2H), 6 42 (s, 1H), 6.26 (s, 1H), 5.62 (s, 1H), 4.23 (q, 2H, J=7.2 Hz), 3 80 (s, 2H), 1.31 (t, 3H, J=7.2 Hz), ^{13}C NMR ($CDCl_3$, 75 5 MHz) d 165.8, 160.4, 153.5, 153 0, 136 0, 131.7, 128.3, 124 4, 124.1, 118 8, 117 0, 115 1, 61 1, 33 4, 14.0; MS (EI) 128 (45), 129 (24), 156

(20), 157 (48), 184 (33), 185 (100), 258 (33). Exact mass calcd. for $C_{15}H_{14}O_4$: 258.0892. Observed: 2580887.

4-Trimethylstannyl coumarin (6g): 736 mg (69% yield) obtained by the reaction of Me_3SnCl (693 mg, 3.5 mmol) with **5b** (5 mmol), -68°C to 0°C, 1 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane; 1/25) solid m.p. 100°C. IR (neat): 3019 (s), 1723 (s), 1702 (s), 1604 (m) cm^{-1}; NMR ($CDCl_3$, 300 MHz): δ 7.47 (d, 1H, J=8.5 Hz), 7.43 (d, 1H, J=7.8 Hz), 7.29 (m, 2H), 6.58 (t, 1H, J=2.7 Hz), 0.46 (t, 9H, J=2.8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.4, 158.5, 152.8, 131.0, 129.6, 125.0, 124.2, 123.5, 117.3, -8.6; MS (EI): 125 (98), 145 (100), 267 (52), 293 (42), 295 (55), 308 (27), 309 (13), 310 (36). Exact mass calcd. for $C_{12}H_{14}O_2{}^{120}Sn$: 310.0015. Observed: 310.0015.

4-(3-Oxo-1-cyclohexenyl)-coumarin (6h): 510 mg, (70% yield) obtained by the reaction of 3-iodo-2-cyclohexen-1-one (666 mg, 3.0 mmol) with **5b** (5 mmol); -30°C to -5°C, 16 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane; 3/10) solid m.p. 146°C. IR (neat): 2955 (s), 2930 (s), 1728 (s), 1681 (s), 1606 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, 1H, J=5.7 Hz), 7.41 (dd, 2H, J=9.5, 1.59 Hz), 7.30 (d, 1H, J=6.0 Hz), 6.29 (s, 1H), 6.17 (s, 1H), 2.63 (t, 2H, J=5.7 Hz), 2.59 (t, 2H, J=6.0 Hz), 2.25 (quintet, 2H, J=6.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 197.6, 159.7, 155.1, 153.9, 153.8, 132.2, 129.6, 125.6, 124.4, 117.4, 116.8, 113.0, 37.1, 27.8, 22.8; MS (EI): 184 (100), 212 (38), 240 (72). Exact mass calcd. for $C_{15}H_{12}O_3$: 240.0786. Observed: 240.0768.

(Z)-Ethyl 3-trimethylstannylacrylate 6i) [31]: 940 mg (99% yield) obtained by the reaction of Me_3SnCl (693 mg, 3.5 mmol) with **5c** (5 mmol) -30°C to 0°C, 3 h (Typical Procedure A and C): Purified by flash chromatography (hexane). IR (neat): 3014 (s), 2917 (s), 2363 (s), 1711 (s), 1669 (m), 1585 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.15 (d, 1H, J=12.3 Hz), 6.70 (d, 1H, J=12.3 Hz), 4.21 (q, 2H, J=6.7 Hz), 1.32 (t, 3H, J=6.7 Hz), 0.20 (t, 9H, J=60 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 167.6, 160.2, 135.0, 60.5, 14.3, -7.8; MS (EI): 219 (71), 221 (81), 245 (46), 247 (76), 249 (100). Exact mass calcd. for $(MCH_3{}^+)C_7H_{13}O_2{}^{120}Sn$: 248.9937. Observed: 248.9938.

(Z)-Ethyl 4-carbethoxy-2,5-hexadienoate (6j): 708 mg (95% yield) obtained by the reaction of ethyl 2-(bromomethyl)acrylate (675 mg, 3.5 mmol) with **5c** (5 mmol); -60°C to 0°C, 1 h (Typical Procedures A and C): Purified by flash chromatography (EtOAc /hexane). IR (neat): 2983 (s), 1719 (s), 1645 (s), 1631 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.28 (m, 1H), 6.21 (s, 1H), 5.86 (d, 1H, J=12 Hz), 5.65 (s, 1H), 4.21 (m, 4H), 3.69 (d, 1H, J=7.5 Hz), 1.3 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.0, 165.5, 145.5, 138.6, 125.8, 120.9, 61.0, 59.9, 31.6, 14.2; MS (EI): 39 (100), 138 (23), 139 (12), 166 (24), 167 (20). Exact mass calcd. for (MH^+) $C_{11}H_{16}O_4H$: 213.1126. Observed: 213.1118.

(Z)-Ethyl 4-nonyn-2-ene (6k): (E/Z mixture: 11/89) 510 mg (81% yield) obtained by the reaction 1-iodo-1-hexyne (735 mg, 3.5 mmol) with **5c** (5 mmol); -55°C, 48 h (Typical Procedures A and C).

(Z)-Ethyl 4-nonyn-2-ene (11c): (E/Z mixture: 11/89) The stereochemistry of the double bond was established by an independent synthesis of **11c**: hexynylzinc bromide and ethyl 3-iodoacrylate in the presence of $Pd(dba)_2$, $4PPh_3$, as a catalyst (THF, 25°C, 1h, 80% yield). Purified by flash chromatography (EtOAc /hexane; 1/50). IR (neat): 2979 (s), 2935 (s), 2873 (s), 2209 (s), 1724 (s), 1509 (s), 1447 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.15 (d, 1H, J=12.2 Hz), 5.97 (d, 1H, J=12.2 Hz), 4.20 (q, 2H, J=6.7 Hz), 2.42 (t, 2H, J=6.1 Hz), 1.58 (m, 2H), 1.45 (q, 2H, J=9.1 Hz), 1.32 (t, 3H, J=9.1 Hz), 0.93 (t, 3H, J=7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.3, 165.0, 137.8, 127.3, 124.2, 123.6, 103.9, 77.8, 60.5, 60.0, 30.5, 22.1, 19.4, 14.5, 13.7. MS (EI): 110 (100), 123 (41), 125 (25), 135 (33), 152 (37), 181 (3). Exact mass calcd. for $C_{11}H_{16}O_2H^+$: 181.1228. Observed: 181.1230.

Analytical Data for the Products (8a) - (8k) (Table III).

3-(1-Hydroxybenzyl)-2-cyclohexen-1-one (8a): 368 mg (91% yield) obtained by the reaction of benzaldehyde (212 mg, 2mmol) with $CrCl_2$ (980 mg, 8 mmol) and 3-iodo-2-cyclohexen-1-one

(883 mg, 4 mmol); 25°C, 2 h (Typical Procedure D): Purified by flash chromatography (EtOAc /Hexane; 2/5) IR (neat): 3417 (s), 3085 (m), 3037 (m), 2948 (s), 2870 (s), 1667 (s), 1602 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.33 (m, 5H), 6.31 (s, 1H), 5.19 (s, 1H), 3.18 (s, 1H), 2.33 (t, 2H, J=6.6 Hz), 2.12 (t, 2H, J=6.3 Hz), 1.91 (m, 2H); ^{13}C NMR (CDCl$_3$, 75.5 Hz): δ 200.3, 166.1, 140.8, 128.6, 128.2, 126.7, 124.0, 76.5, 37.6, 25.7, 22.5; MS (EI): 97 (100), 105 (37), 107 (31), 129 (41), 146 (37), 173 (25), 202 (14). Exact mass calcd. for $C_{13}H_{14}O_2$: 202.0993. Observed: 202.0988.

3-(1-Hydroxy-1-hexyl)-2-cyclohexen-1-one (8b): 283 mg (72 % yield), (Typical Procedure D). Purified by flash chromatography: (EtOAc /hexane, 3/10). IR (neat): 3404 (s), 2953 (m), 2931 (s), 1664 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.03 (s, 1H), 4.18 (s, 1H), 2.35 (m, 4H), 2.26 (t, 1H, J=6.7 Hz), 2.02 (m, 2H), 1 58 (m, 2H), 1.33 (m, 6H), 0.87 (t, 3H, J=2.2 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 200.5, 167.9, 124.1, 74.4, 37.8, 35.1, 31.6, 25.4, 25.0, 22.7, 22.4, 13.9; MS (EI): 97 (100), 98 (20), 125 (31), 126 (11), 140 (29), 196 (2). Exact mass cacld. for $C_{12}H_{20}O_2$: 196.1463. Observed: 196.1461.

3-(1-Hydroxycyclohexylmethyl)-5,5-dimethyl-2-cyclohexen-1-one (8c): 460 mg (97% yield) obtained by the reaction of cyclohexanecarboxaldehyde (225 mg, 2 mmol) with CrCl$_2$ (980 mg, 8 mmol) and 5,5-dimethyl-3-iodo-2-cyclohexen-1-one (1.0 g, 4 mmol); 45°C, 5h, (Typical Procedure D). Purified by flash chromatography: (EtOAc /hexene; 3/10) solid m.p. 77°C. IR (KBr): 3419 (s), 2941 (s), 2920 (s), 2885 (m), 2853 (m), 1649 (s) cm^{-1}, ^{1}H NMR (CDCl$_3$, 360 MHz): δ 5.98 (s, 1H), 3.9 (s, 1H), 2.26 (m, 4H), 2.19 (d, 1H, J=4 2 Hz), 1 76 (m, 4H), 1.52 (d, 2H, J=2.5 Hz), 1.15 (m, 5H), 1.1 (s, 6H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 200.4, 164.2, 124.4, 79.0, 51.5, 40.9, 39.6, 33.5, 29.8, 28.2, 28.1, 27.4, 26 2, 26.1, 25 9; MS (EI): 154 (100), 155 (11), 176 (1), 236 (3). Exact mass calcd for $C_{15}H_{24}O_2$: 236.1776 Observed. 236.1765.

3-(1-Hydroxy-1-cyclohexyl)-5,5-dimethyl-2-cyclohexen-1-one (8d): 195 mg (43% yield) obtained by the reaction of cyclohexanone (196 mg, 2 mmol) with CrCl$_2$ (980 mg, 8mmol) and 3-iodo-5,5-dimethyl-2-cyclohexen-1-one (1.0 g, 4 mmol); 55°C, 24h (Typical Procedure D) Purified by flash chromatography (EtOAc /hexane; 1/4): solid m.p. 95°C. IR (KBr): 3420 (s), 2951 (m), 2944 (s), 2921 (s), 2851 (m), 1645 (s), 1612 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.16 (s, 1H), 2.26 (s, 2H), 2.20 (s, 2H), 1.82 (s, 1H), 1.65 (m, 1H), 1 02 (s, 6H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 201.1, 169.5, 122.0, 73.4, 51 1, 39 8, 34 8, 33.7, 28.0, 25.3, 21.3; MS (EI): 151 (100), 153 (43), 179 (34), 194 (35), 222 (23) Exact mass calcd. for $C_{14}H_{22}O_2$: 222.1619. Observed: 222.1611.

(Z)-t-Butyl 4-hydroxy-4-phenyl-2-butenoate (8e) (100% Z): 185 mg (39% yield) obtained by the reaction of benzaldehyde (212 mg, 2 mmol) with CrCl$_2$ (980 mg, 8 mmol) and (Z)-t-butyl 3-iodoacrylate (1.01 g, 4 mmol), 25°C, 2 h (Typical Procedure D): Purified by flash chromatography (EtOAc /hexane; 1/10): solid m.p. 47°C IR (KBr): 3436 (s), 2973 (m), 2926 (s), 2854 (m), 1756 (s), 1599 (s), 1495 (s), 1450 (m) cm^{-1}, ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.44 (m, 2H), 7 32 (m. 3H), 6.32 (dd, 1H, J=7.4, 11.7 Hz), 6.07 (m, 1H), 5 82 (dd, 1H, J=1.3, 11 7 Hz), 3.78 (d, 1H, J=4.3 Hz), 1.50 (s, 9H); ^{13}C NMR (CDCl$_3$, 75.5 MHz). δ 166.2, 149.2, 142.4, 128.5, 127.6, 126.1, 121.9, 81.4, 69.7, 28.1; MS (EI): 57 (100), 133 (37), 159 (21), 160 (35), 178 (68). Exact mass calcd for $C_{14}H_{18}O_3H$ (M^+H^+): 235 1334 Observed: 235 1334

3-(1-Hydroxyl-1-benzyl)-2-methyl-2-cyclopenten-1-one (8f): 233 mg (57% yield) obtained by the reaction of benzaldehyde (212 mg, 2 mmol) with CrCl$_2$ (980 mg, 8 mmol) and 3-iodo-2-methyl-2-cyclopenten-1-one (888 mg, 4 mmol), 25°C, 5h (Typical Procedure D): Purified by flash chromatography (EtOAc /hexane, 2/5): solid m.p. 108°C IR (KBr): 3819 (s), 3066 (m), 3052 (m), 3024 (m), 2923 (s), 1680 (s), 1639 (s), 1598 (s), 1571 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz). δ 7.36 (m, 5H), 5.84 (s, 1H), 2 71 (m, 2H), 2.43 (m, 1H), 1.82 (s, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz). δ 210.6, 172.3, 141.1, 136.0, 128 7, 128 1, 125 9, 71 8, 33 7, 24.8, 8 4, MS (EI): 97 (100), 105 (50), 107 (68), 108 (66), 202 (7) Exact mass calcd for $C_3H_{14}O_2$: 202 0993 Observed 202.0996

5-Cyclohexyl-5H-furan-2-one (8g): 165 mg (50% yield) obtained by the reaction of cyclohexanecarboxadehyde (225 mg, 2mmol) with CrCl$_2$ (980 mg, 8mmol), NiCl$_2$ (52 mg, 0.06 mmol), and (Z)-ethyl 3-iodoacrylate (904 mg, 4 mmol), 50°C, 24 h (Typical Procedure D): Purified by flash chromatography (EtOAc /hexane; 3/25): solid m.p. 71°C, IR (KBr): 2930 (s), 2861 (s), 1756 (s), 1603 (m), 1443 (s), 1332 (m), 1158 (s), 116 (m), 1088 (m), 1026 (m), 1026 (m), 901 (m), 784 (s), 760 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (dd, 1H, J=1.5, 5.7 Hz), 6.11 (dd, 1H, J=2.0, 5.7 Hz), 4.83 (td, 1H, J=3.3, 5.4 Hz), 1.69 (m, 6H), 1.15 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 Hz): δ 173.0, 155.0, 124.8, 87.4, 41.2, 28.5, 28.1, 26.0, 25.7, 25.6; MS (EI): 84 (100), 166 (2). Exact mass calcd. for $C_{10}H_{14}O_2$: 166.0993. Observed: 166.0998.

5-Phenyl-3H-furan-2-one (8h): 158 mg (50% yield) obtained by the reaction of benzaldehyde (212 mg, 2 mmol) with $CrCl_2$ (980 mg, 8 mmol) and (Z)-ethyl 3-iodo-acrylate (904 mg, 4 mmol); 25°C, 3 h (Typical Procedure D): Purified by flash chromatography (EtOAc /hexane; 2/25): IR (neat): 3019 (s), 2962 (m), 2926 (m), 1707 (s), 1599 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 (m, 2H), 7.14 (m, 3H), 5.5 (t, 1H, J=2.7 Hz), 3.17 (d, 2H, J=2.7 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 175.9, 154.0, 122.6, 128.7, 128.5, 124.8, 97.7, 34.6; MS (EI): 105 (100), 115 (12), 131 (41), 160 (99). Exact mass calcd. for $C_{10}H_8O_2$: 160.0524. Observed: 160.0522.

(E)-1-hydroxy-1-phenyl-4-oxo-2-nonene (8i): 261 mg (56% yield) obtained by the reaction of benzaldehyde (212 mg, 2 mmol) with $CrCl_2$ (980 mg, 8 mmol) and (E)-1-chloro-1-octen-3-one (640 mg, 4 mmol); 25°C, 3 h (Typical Procedure D): Purified by flash chromatography (EtOAc /hexane; 1/5) IR (neat): 3426 (s), 3068 (m), 3026 (m), 2956 (s), 2871 (m), 1694 (s), 1668 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (m, 5H), 6.85 (dd, 1H, J=4.6, 15.8 Hz), 6.42 (dd, 1H, J=2.2, 15.8 Hz), 5.34 (bs, 1H), 2.53 (t, 2H, J=7.3 Hz), 1.59 (m, 2H), 1.27 (m, 5H), 0.87 (t, 3H, J=6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 200.9, 146.3, 141.1, 128.7, 128.2, 128.0, 126.5, 126.2, 73.6, 40.6, 40.3, 31.4, 23.7, 22.4, 13.8; MS (EI): 105 (100), 115 (30), 117 (17), 125 (27), 133 (55), 161 (24), 203 (33). Exact mass calcd. for $C_{15}H_{20}O_2$: 232.1463. Observed: 232.1462.

1-Methyl-3-phenyl-4H,5H,6H,7H,isobenzo-furan (8j): 185 mg (44% yield) obtained by the reaction of benzaldehyde (212 mg, 2 mmol) with $CrCl_2$ (1.96 g, 16 mmol) and 2-(methanesulfonyloxy)-1-acetylcyclohexene (872 mg, 4 mmol), 50°C, 3 h (Typical Procedure D). Purified by flash chromatography (hexane): IR (neat): 3087 (m), 2926 (s), 2855 (s), 1636 (s), 1602 (s), 1559 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, 2H, J=7.3 Hz), 7.38 (t, 2H, J=7.7 Hz), 7.20 (t, 1H, J=7.4 Hz), 2.77 (t, 2H, J=5.4 Hz), 2.47 (t, 2H, J=5.5 Hz), 2.26 (s, 3H), 1.74 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 145.0, 144.7, 132.5, 128.5, 126.0, 125.6, 125.0, 123.9, 119.3, 118.3, 23.5, 23.3, 23.0, 20.6, 11.6; MS (EI): 185 (26), 197 (7), 211 (16), 212 (100). Exact mass calcd. for $C_{15}H_{16}O$: 212.1201. Observed: 212.1186.

2-Hexyl-3-hydroxy-3-phenyl-1-propenyl p-tolylsulfone (8k): 276 mg (40% yield) obtained by the reaction of benzaldehyde (212 mg, 2mmol) with $CrCl_2$ (980 mg, 8 mmol) and (E)-2-iodo-1-octenyl p-tolylsulfone (1.56 g, 4 mmol), 25°C, 24 h (Typical Procedure D). Purified by flash chromatography: (EtOAc /hexane; 3/10). IR (neat): 3478 (s), 3064 (m), 3033 (s), 2965 (s), 2928 (s), 2860 (s), 1625 (s), 1607 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82 (m, 2H), 7.31 (m, 7H), 6.8 (d, 1H, J=1.3 Hz), 5.1 (d, 1H, J=1.4 Hz), 2.83 (m, 1H), 2.44 (s, 3H), 2.09 (d, 1H, J=3.3 Hz), 1.88 (m, 1H), 1.21 (m, 8H), 0.84 (t, 3H, J=5.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 159.9, 144.0, 140.2, 139.6, 129.8, 128.9, 128.8, 127.4, 127.2, 127.1, 125.3, 76.2, 31.3, 29.5, 29.1, 28.9, 22.4, 21.5, 13.9; MS (EI): 107 (100), 108 (70), 199 (3), 217 (5), 267 (1). Exact mass calcd. for $C_{22}H_{28}O_3SH$ (M^+H^+): 373.1837. Observed: 373.1827.

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