7e δ 0.86 (s, 9 H, $C(CH_3)_3$), 1.05 (d, 3 H, *J* = 7.4 Hz, C-2′–CH_3), 1.18–1.42 (m, 4 H), 1.46–1.56 (m, 2 H), 1.65–2.00 (m, 3 H), 2.18–2.34 (m, 1 H), 4.18 (m, 1 H, CHCl); **5e** δ 0.84 (s, 9 H, $C(CH_3)_3$), 1.08 (d, 3 H, *J* = 5.2 Hz, C-2′–CH_3), 1.18–1.42 (m, 4 H), 1.46–1.56 (m, 2 H), 1.65–2.00 (m, 3 H), 2.18–2.34 (m, 1 H), 4.72 (m, 1 H, *J* = 12.7, 4.8 Hz, CHCl). ^{13}C NMR (75.5 MHz, $CDCl_3$): **7e** δ 64.15 (C-1), 40.71 (C-4), 36.53 (C-2), 32.30 ($C(CH_3)_3$), 29.34 (C-3), 27.41 ($C(CH_3)_3$), 26.74 (C-6), 21.13 (C-5), 18.49 (C-2–CH_3); **5e** δ 64.71 (C-1), 39.49 (C-4), 35.39 (C-2), 33.81 (C-3), 31.91 ($C(CH_3)_3$), 29.69 (C-5), 27.88 (C-6), 27.47 ($C(CH_3)_3$), 12.63 (C2′–CH_3). High-resolution MS (EI) calcd for $C_{11}H_{21}$: 153.1643. Found: 153.1639, (M^+ – Cl, 0.5%), 137 (M^+ – HCl – CH_3, 11%), 96 (26%), 57 (*t*-Bu, 100%).

2αβ-Bromo-10-methyl-*trans*-decalin. To 20 mL of benzene are added 3.0 mL of freshly distilled oxalyl chloride and 770 mg (4.6 mmol) of 2β-hydroxy-10-methyl-*trans*-decalin (**12**). After the mixture was stirred for 12 h, the solvent and excess oxalyl chloride are removed in vacuo and the residue taken up in benzene (10 mL) and 1.4 mL of $BrCCl_3$. This solution is added within 5 h to a refluxing suspension of 756 mg (5.1 mmol) of 2-mercaptopyridine *N*-oxide sodium salt and 10 mg (0.08 mmol) of DMAP in benzene (150 mL). Heating is continued for 3 h. The reaction mixture is filtered through anhydrous $MgSO_4$ and the solvent is evaporated. Flash chromatography on silica gel with pentane yields 424 mg (40%) of 2-bromo-10-methyl-*trans*-decalin as a mixture of the 2α- and 2β-isomers in a 91:9 ratio (by ^1H NMR). ^1H NMR (300 MHz, $CDCl_3$): 2α-isomer δ 0.85 (s, 3 H, C-10–CH_3), 1.05–1.85 (m, 13 H), 1.95–2.05 (m, 1 H), 2.25–2.40 (m, 1 H), 4.30 (tt, 1 H, *J* = 12.3, 4.4 Hz, CHBr); 2β-isomer δ 0.88 (s, 3 H, C-10–CH_3), 1.05–1.95 (m, 13 H), 2.15–2.25 (m, 1 H), 4.67 (m, 1 H, CHBr). ^{13}C NMR (75.5 MHz, $CDCl_3$): 2α-isomer δ 53.28 (C-1), 49.79 (C-2), 44.34 (C-5), 41.15 (C-9), 39.09 (C-3), 37.10 (C-10), 30.31 (C-4), 28.03 (C-6), 26.69 (C-7), 21.13 (C-8), 15.84 (C-10–CH_3); β-isomer δ 51.20 (C-2), 48.42 (C-1), 45.85 (C-5), 41.86 (C-9), 36.92 (C-3), 34.20 (C-10), 28.33 + 26.90 (C-6 + C-7), 24.35 (C-4), 20.91 (C-8), 18.34 (C-10–CH_3). MS (EI): 230 (M^+, 0.9%), 151 (M^+ – Br, 85%), 95 (M^+ – 135, 100%). Anal. Calcd for $C_{11}H_{19}Br$: C, 57.15; H, 8.28. Found: C, 57.20; H, 8.10.

2αβ-Chloro-10-methyl-*trans*-decalin. In benzene (10 mL) are placed 1.5 mL of freshly distilled oxalyl chloride and 274 mg (1.63 mmol) of 2β-hydroxy-10-methyl-*trans*-decalin (**12**). After the mixture is stirred for 12 h, the solvent and excess oxalyl chloride are evaporated and the residue taken up in 5 mL of CCl_4. This solution is added within 15 min to a refluxing suspension of 270 mg (1.8 mmol) of 2-mercaptopyridine *N*-oxide sodium salt and 8 mg (0.065 mmol) of DMAP in CCl_4 (150 mL). Heating is continued for 30 min. Then the reaction mixture is filtered through anhydrous $MgSO_4$ and the solvent is evaporated. Flash chromatography on silica gel with pentane yields 223 mg (73%) of 2-chloro-10-methyl-*trans*-decalin as an inseparable mixture of the 2α- and 2β-isomers in a 9:1 ratio (by GC and ^1H NMR). ^1H NMR (300 MHz, $CDCl_3$): 2α-isomer δ 0.85 (s, 3 H, C-10–CH_3), 1.05–1.76 (m, 13 H), 1.84–1.94 (m, 1 H), 2.17–2.27 (m, 1 H), 4.11 (tt, 1 H, *J* = 12.0, 4.4 Hz, CHCl); 2β-isomer δ 0.85 (s, 3 H, C-10–CH_3), 1.05–1.76 (m, 13 H), 1.84–1.94 (m, 1 H), 2.03–2.13 (m, 1 H), 4.47 (m, 1 H, CHCl). ^{13}C NMR (75.5 MHz, $CDCl_3$): 2α-isomer δ 57.15 (C-2), 52.32 (C-1), 44.42 (C-5), 41.20 (C-9), 38.10 (C-3), 36.08 (C-10), 29.27 (C-4), 27.95 (C-6), 26.75 (C-7), 21.12 (C-8), 16.01 (C-10–CH_3); 2β-isomer δ 58.60 (C-2), 47.97 (C-1), 45.90 (C-5), 41.74 (C-9), 35.85 (C-3), 34.10 (C-10), 29.70 (C-4), 28.38 (C-6), 26.92 (C-7), 20.98 (C-8), 18.04 (C-10–CH_3). High-resolution MS (EI) calcd for $C_{11}H_{19}Cl$: 186.117. Found: 186.117 (M^+, 55%), 171 (M^+ – CH_3, 16%), 135 (M^+ – HCl – CH_3, 100%).

Acknowledgment. We are grateful to the Swiss National Fonds and the National Science Foundation for financial support and to M. Zehnder and S. Neuenburger for solving the X-ray crystal structure.

Appendix

New MM2 Parameters. Our MM2 results can be reproduced with the parameters listed here. The radical center is defined as MM2 type 29, while the alkene atom being attacked is of type 28. The alkene carbon atom not attacked remains type 2 (sp^2 carbon). Calculations were carried out with Allinger's MM2 program[29] modified by Spellmeyer and Houk.[21] The modified program version allows the equivalence of two atom types. This enables the user to input only the parameters newly defined for a new atom type. The parameters, which are read in at the beginning of the calculation, are given in Table IV in the MM2 input format. The list contains the 33 parameters developed for the intramolecular 5-hexenyl cyclization and those 10 parameters added in the present study.

Supplementary Material Available: Tables of geometrical data for the ab initio transition states in Figure 1 and the UHF/3-21G geometry of the cyclohexyl radical and data for the X-ray crystal structure and NMR spectra (18 pages). Ordering information is given on any current masthead page.

Photochemical Reactions of Chromium–Alkoxycarbene Complexes with Stabilized Ylides To Produce "Push–Pull" Captodative Allenes

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Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received September 18, 1991*

Abstract: Photolysis of chromium alkoxycarbene complexes in the presence of stabilized ylides produced allenes having electron withdrawing groups on C-1 and electron donating groups on C-3. These highly reactive captodative allenes rearranged to 1,3-substituted-1,3-dienes under mildly acidic conditions and hydrolyzed to γ-keto-α,β-unsaturated esters, both in excellent yield.

Introduction

Over the past several years the photochemical reactions of chromium–carbene complexes has been extensively developed in these laboratories. Photolysis of these complexes (visible light/Pyrex) generates a reactive intermediate that undergoes reactions common to ketenes,[1] and this chemistry has been used to synthesize β-lactams,[2] cyclobutanones,[3] and α-amino acid esters[4] (Scheme I). In an effort to extend the parallels between con-

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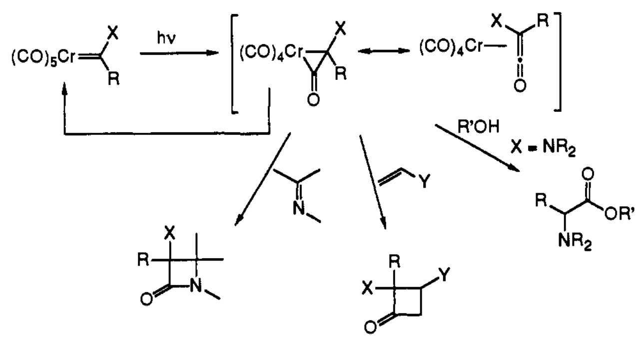
(1) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

(2) (a) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680. (b) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833. (c) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101. (d) Hegedus, L. S.; D'Andrea, S. *J. Org. Chem.* **1988**, *53*, 3113. (e) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109.

Scheme I



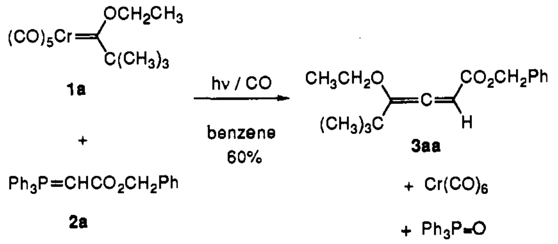
ventional organic ketene chemistry and the photochemical reactions of chromium carbene complexes, reactions with stabilized ylides were examined, and the results are presented below.

Stable ketenes undergo reaction with nonstabilized phosphorous ylides to produce allenes, although high temperatures are often required to promote the elimination of phosphine oxide from the intermediate, resulting in low yields.[5] In contrast, stable ketenes and carbonyl stabilized ylides combine to produce allenic esters under substantially milder conditions and in fair to excellent yield.[6] Allenic esters are also formed by the direct reaction between stabilized phosphorous ylides and acid chlorides having at least one α-hydrogen.[7] Free ketenes are probably not involved in this process.

Chromium alkoxycarbene complexes are also reactive toward some phosphorous ylides.[8] Nonstabilized ylides remove an acidic α-proton from chromium–alkoxycarbene complexes and act as nucleophiles toward complexes lacking α-protons, producing enol ethers in a formal metathesis reaction. However, chromium alkoxycarbene complexes are unreactive toward carbonyl stabilized phosphorous ylides, making these ylides compatible for coupling with photogenerated chromium complexed ketenes. The synthesis of captodative allenes by this procedure is detailed below.

Results and Discussion

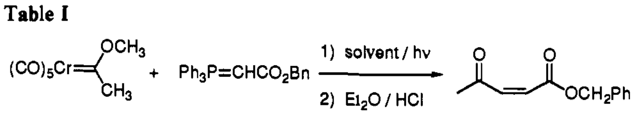
Photolysis (visible light, Pyrex) of a benzene solution of (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) and (ethoxy)(*tert*-butyl)carbene complex **1a** under an atmosphere of CO (100 psi) produced an almost quantitative yield of the allene **3aa**, as determined by ^1H NMR analysis of the crude reaction mixture (eq 1). Purification by basic Al_2O_3 chromatography, using triethylamine/hexanes as the eluent, gave a 60% yield of the allene **3aa** as a colorless oil (some of the allene was lost to hydrolysis during chromatography).



(1)

Allene **3aa** was fully characterized. The infrared spectrum contained the characteristic allene absorption at 1939 cm^{-1} (C=C=C) and an ester absorption at 1723 cm^{-1}. The central allene carbon had a chemical shift of δ 207.7 in the ^{13}C NMR, a value about average for allenes (allene itself = 213 ppm). The lone vinyl proton appeared as a singlet at δ 6.1, a position characteristic for this class of compounds (see below).

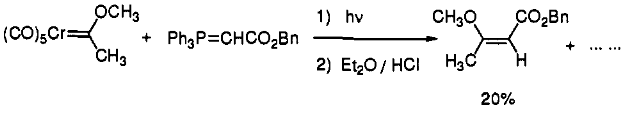
Table I



solvent	CO/(psi)	yield (%)
Et_2O/CH_2Cl_2		0
Et_2O/CH_2Cl_2	80	82
THF	80	46
EtOAc	80	64
benzene		2
benzene	80	68
benzene & 5 mol % hydroquinone	100	78
CH_3CN		56

The photoreaction proved to be general for ester and sulfonyl stabilized ylides and chromium–alkoxycarbene complexes (Scheme II). In many cases, the crude reaction mixtures contained *only* the allene and triphenylphosphine oxide, as determined by ^1H NMR spectroscopy. The allenes **3** had characteristic NMR spectra, while the lone vinyl proton α to the X group appearing at $\sim\delta$ 6.0 coupled with J = 2–3 Hz to the allylic protons at the remote allene terminus.[9,17] This, and the rest of the spectrum, was unmistakable and completely different from that of either the diene **4** or the enone **5**. In the carbon spectrum, the signal for the central allene carbon appeared at δ 207–210 for allenic esters and at δ 198–199 for allenic sulfones. The infrared spectra had a strong band between 1930 and 1940 cm^{-1} for the allene moiety.

In marked contrast to other photochemical reactions of chromium carbene complexes,[1-4] allenes were produced *only* if the reaction was carried out under an atmosphere of carbon monoxide or in strongly coordinating solvent such as acetonitrile (Table I). In the absence of carbon monoxide, the carbene complex was consumed, and a small amount of metathesis product was obtained, along with an intractable mixture of unidentified organic products (eq 2). The role of carbon monoxide is unclear at this time. It is *not* required for ketene generation, since all of the reactions in Scheme I proceed in the absence of added carbon monoxide. It is likely that its role is to prevent the generation of coordinatively unsaturated chromium species, which may either react nonproductively with the ylide or destructively with the product allene. Addition of small amounts of hydroquinone to the reaction mixture led to a modest increase yield as well as to more reproducible results. Captodative compounds are prone to radical reactions,[10] and addition of hydroquinone would suppress these.



(2)

All attempts to purify these allenes failed. Purification by Kugelrohr distillation produced a mixture of allene oligomers and the diene formed by a [1,3] rearrangement of the allene. Purification by basic or neutral alumina chromatography transformed the allene into the diene and an unsaturated keto ester from hydrolysis of the enol ether terminus. Chromatography on silica gel or Florisil gave exclusively hydrolysis products. Thus, only allenes that could not undergo isomerization and were at least moderately resistant to hydrolysis, such as *tert*-butyl allene **3aa**, could be isolated. Because of this most of the allenes **3** were either isomerized to dienes **4** or hydrolyzed to unsaturated keto esters **5** directly.

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(3) (a) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364. (b) Hegedus, L. S.; Bates, R. W.; Söderberg, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 923. (c) Söderberg, B. C.; Hegedus, L. S. *J. Org. Chem.* **1991**, *56*, 2209.

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(6) (a) Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733. (b) Hamlet, Z.; Barker, W. D. *Synthesis* **1970**, 543. (c) Aksnes, G.; Frøyen, P. *Acta Chem. Scand.* **1968**, *22*, 2347.

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(8) Casey, C. P. In *Transition Metals Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 223.

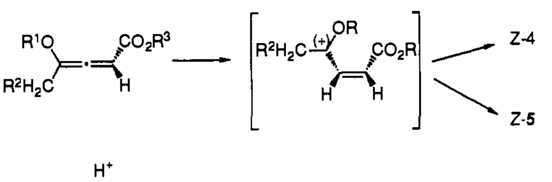
(9) For similar spectra of an alkyl sulfonyl allene, see: Braverman, S.; Mechoulam, H. *Tetrahedron* **1974**, *30*, 3883.

(10) Viehe, H. G.; Janousek, Z.; Merényi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

Optimal conditions for the production of dienes involved a photoreaction under a pressure of carbon monoxide (60–100 psi) with methylene chloride/ether or benzene as the solvent. After the carbene was consumed and the solvent removed, the crude allene was dissolved in CH_2Cl_2 with 5 mol % of the mild acid catalyst, pyridinium *p*-toluenesulfonate (PPTS). Complete isomerization to the diene required 1 day at room temperature. A series of dienes **4** was produced in this manner (Scheme II), all of them possessing *Z* (or cis) stereochemistry about the ester-substituted double bond. The assignment of *Z* stereochemistry was based on the magnitude of the $J_{CH=CH}$ coupling constant of $\approx$12 Hz and was confirmed by isomerizing diene **4ba** to the *E* isomer by treatment with I_2 in hexane. This *E* isomer had a $J_{CH=CH}$ of 15.4 Hz, typical of *E* olefins. In addition, hydrolysis of *Z* dienes **4** produced *Z* unsaturated ketones **5** (see below), again confirming the assigned stereochemistry. Stereochemical control about the other double bond of the diene was not as complete. A 4:1 and 4.7:1 mixture of isomers was obtained for the dienes made from both the ethyl and butyl substituted carbene complexes, respectively. Examples of dienes substituted at the 1-position with an electron withdrawing ester group and at the 3-position with an electron donating alkoxy group are relatively uncommon in the chemical literature,[11] and this process offers relatively easy access to this class of compounds.

All of the allenes **3** were very sensitive toward hydrolysis of the enol ether terminus, producing *Z*-unsaturated ketones **5** under a variety of conditions. Efficient, intentional hydrolysis was best effected by rapidly stirring a biphasic system of the crude reaction mixture with ether/5% aqueous hydrochloric acid (Scheme II). In this way a large number of β-substituted *Z*-unsaturated ketones was synthesized. These should be excellent dienophiles, and their cycloaddition chemistry is currently being studied. Again, the *Z* stereochemistry was based on a $J_{CH=CH}$ of $\approx$12 Hz and was confirmed by NOE studies with **5af**. On standing in solution in the light, isomerization to the more stable *E* isomer with a $J_{CH=CH}$ $\approx$ 16 Hz occurred.

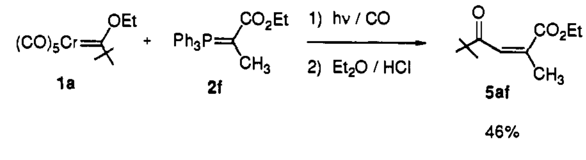
The strong *Z*-stereoselectivity of both the isomerization and hydrolysis reactions warrants comment. Both of these processes involve, at some stage, the delivery of a proton to the central carbon of the allene π-system, and the delivery of that proton from the less sterically hindered face of the allene leads to production of the thermodynamically *less* stable *Z* olefin (eq 3). This same *Z* stereoselectivity has been noted in the basic alumina catalyzed rearrangement of allenic acetic esters ($RCH=C=CHCH_2CO_2R'$)[12] and the acid catalyzed hydrolysis of methoxy allene.[13,14]



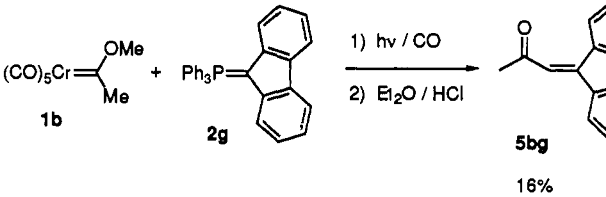
(3)

Disubstituted ylides also underwent photochemical reaction with chromium–alkoxycarbene complexes to produce allenes, although the yields were somewhat lower than those from monosubstituted ylides (eqs 4–6). Unsaturated ylide **2i** underwent a proton transfer to produce a new stabilized ylide **6**, rather than eliminating phosphine oxide (eq 7). Other ylides (**2**, X = CN, $CONH_2$) either failed to react or (X = Ph, $CH_2=CH–$) decomposed the carbene complex upon mixing.

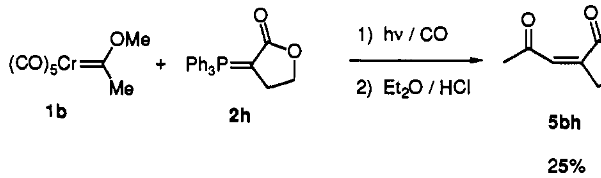
This allene forming reaction was restricted to alkoxycarbene–chromium complexes. Aminocarbene complexes failed to react, undergoing slow photodecomposition over several days. To determine if the aminoketene complexes were too electron-rich to undergo attack by ylides (these same complexes failed to react with olefins[3]), the corresponding carbamate substituted carbene complex **1L** (which does react with olefins to form cyclobutanones) was photolyzed in the presence of ylides **2a** and **2b** (eq 8). Again, proton transfer rather than phosphine oxide elimination occurred.



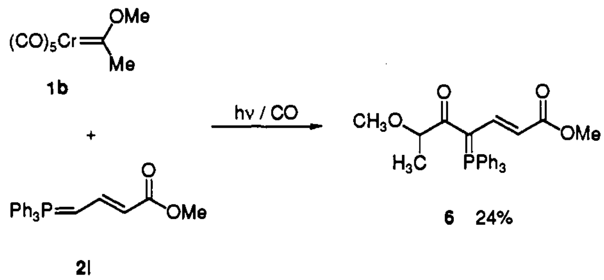
(4)



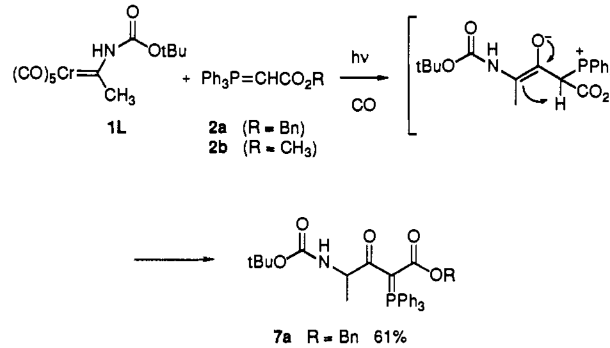
(5)



(6)

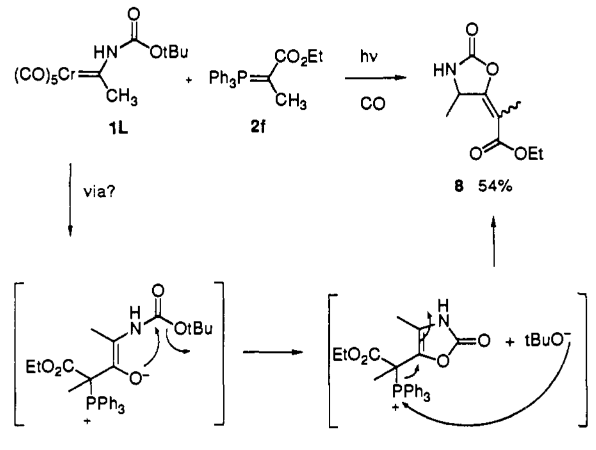


(7)



(8)

To suppress this proton transfer, disubstituted ylide **2f** was used in place of **2a** and **2b** (eq 9). Again, this reaction failed to produce



(9)

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(11) For examples, see: (a) Agosta, W. G.; Lowrance, W. W., Jr. *J. Org. Chem.* **1970**, *35*, 3851. (b) Crombie, L.; Taylor, J. L. *J. Chem. Soc.* **1957**, 2760.

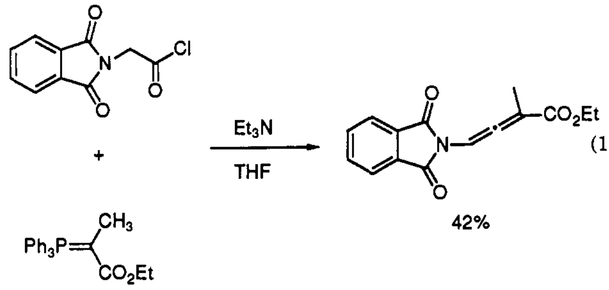
(12) Tsuboi, S.; Masuda, T.; Takeda, A. *J. Org. Chem.* **1982**, *47*, 4478.

(13) Leroux, Y.; Ronan, C. *Tetrahedron Lett.* **1973**, 2585.

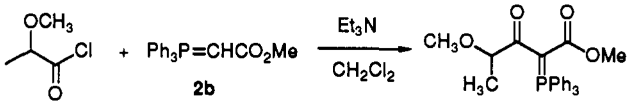
(14) Mantione, R. *Bull. Soc. Chim. Fr.* **1969**, 4523.

an allene, but rather gave the unusual oxazolidinone **8** in modest yield.

Within the limits presented above, photolysis of chromium-alkoxycarbene complexes in the presence of ester or sulfone stabilized ylides provides an efficient method for the synthesis of relatively unstable captodative allenes **3** having both conjugated enone and enol ether functionality. Other examples of captodative allenes are relatively rare. Captodative 1,1-diethoxyallenes were prepared by the reaction of nonenolizable α-diketones or hexafluoroacetone with the ylide $Ph_3P{=}C{=}C(OEt)_2$.[15] Some were isolable while others dimerized ([2 + 2]) upon formation. The central carbon of these allenes also appeared at $\sim\delta$ 200 in the ^{13}C NMR spectrum. A captodative 1-methoxy-3-keto allene was a proposed (but not detected) intermediate in the reaction of 1-methoxy-1-methylallene with butyllithium followed by a dimethyl amide to give (*E*)-diketoolefins.[16] A captodative phthalimido allenic ester was synthesized from an ester stabilized ylide and phthalimidoacetic acid chloride (eq 10).[17] This same procedure[7b] could *not* be used to produce allenes **3**. Treatment of α-methoxypropionyl chloride with ylide **2b** produced an almost quantitative yield of a new stabilized ylide **9** (eq 11).



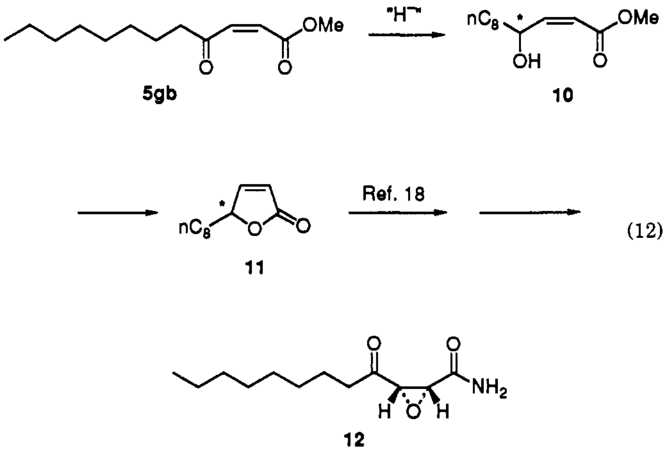
(10)



9 98%

(11)

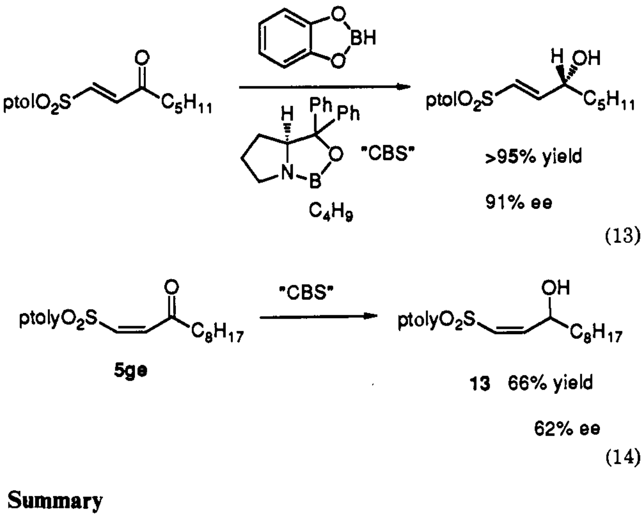
Although the reaction chemistry of the captodative allenes reported above remains to be developed, the structural similarity of hydrolysis product **5gb** to a key intermediate in the synthesis[18] of the antibiotic tetrahydrocerulenin[19] **12** prompted the following studies (eq 12).



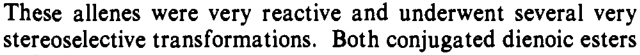
(12)

Asymmetric reduction of the keto group in **5gb** with high enantioselectivity to give **10**, followed by cyclization to **11** would constitute a formal total synthesis of optically active tetrahydrocerulenin, since racemic **11** has been carried onto (±)-tetrahydrocerulenin efficiently.[18] Since both chiral centers are set in the epoxidation of **11**, and since this step went with complete diastereoselectivity,[18] high enantioselectivity in the conversion of **5gb** to **10** should thus be translated into a highly enantioselective synthesis of **12**.

Treatment of **5gb** with 9-BBN,[20] followed by isolation using diethanolamine to remove boron residues produced racemic **11** in 66% yield. This constituted a formal synthesis of (±)-**12**. Use of (−)-B-chlorodiisopinocamphenylborane (Ipc_2BCl)[21] as a reducing agent gave a 53% yield of **11** with a dismal 28% ee, as determined by ^1H NMR spectroscopy using $Eu(hfc)_3$ as a chiral shift reagent. The CBS reagent reduced a γ-ketosulfone with excellent stereoselectivity (eq 13),[22] a reaction thought to provide a good analogy for the asymmetric reduction of **5gb**. In the event, reduction of **5gb** with this system led to a quantitative yield of **11**, with only 41% ee. The corresponding *tert*-butyl ester was reduced with slightly better ee (60%) but still not sufficiently high to be of use. For a more direct comparison, *Z*-vinyl sulfone **5ge** was reduced using this reagent (eq 14). It gave a similarly low ee (62%) suggesting that the geometry of the olefin played a significant role in the asymmetric induction. Thus, the formal synthesis of optically active **12** awaits the development of more effective asymmetric reduction procedures.



(13)



5ge

13 66% yield

62% ee

(14)

Summary

Ester-stabilized ylides and alkoxychromium carbene complexes combined to form captodative allenes under photolytic conditions. These allenes were very reactive and underwent several very stereoselective transformations. Both conjugated dienoic esters and unsaturated 1,4-keto esters were produced from these allenes. The stereochemistry about the double bonds in these products was always cis. The formation of this isomer was explained by a facial-selective protonation of the π-systems of the enol ether. One face was blocked by the ester substituent.

The allene-forming reaction could not be extended to aminocarbene complexes or to any other types of stabilized ylides. A formal total synthesis of (±)-tetrahydrocerulenin was completed by transforming an allene hydrolysis product into a butenolide via the regiospecific reduction of the ketone moiety followed by lactonization.

Experimental Section

General Methods. Irradiation of the reaction mixtures were carried out in (a) a Pyrex pressure tube supplied by Ace Glass fitted with a pressure-retaining head capable of holding at least 150 psi or (b) a Pyrex test-tube for reactions not requiring CO. The reaction mixture was

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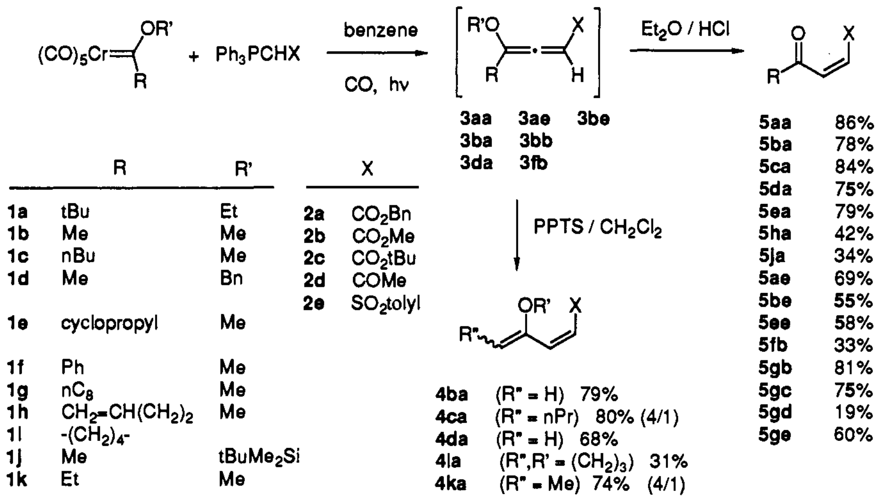
Scheme II



	R	R'
1a	tBu	Et
1b	Me	Me
1c	nBu	Me
1d	Me	Bn
1e	cyclopropyl	Me
1f	Ph	Me
1g	nC_8	Me
1h	$CH_2{=}CH(CH_2)_2$	Me
1l	$-(CH_2)_4-$	
1j	Me	$tBuMe_2Si$
1k	Et	Me

	X
2a	CO_2Bn
2b	CO_2Me
2c	CO_2tBu
2d	COMe
2e	SO_2tolyl

4ba	(R" = H)	79%
4ca	(R" = nPr)	80% (4/1)
4da	(R" = H)	68%
4la	(R",R' = $(CH_2)_3$)	31%
4ka	(R" = Me)	74% (4/1)

5aa	86%
5ba	78%
5ca	84%
5da	75%
5ea	79%
5ha	42%
5ja	34%
5ae	69%
5be	55%
5ee	58%
5fb	33%
5gb	81%
5gc	75%
5gd	19%
5ge	60%

placed 10 cm from a Conrad-Hanovia 7825 medium-pressure mercury lamp operating at 450W, which was placed in a water-cooled immersion well.

Materials. Tetrahydrofuran and diethyl ether were distilled from benzophenone ketyl under a nitrogen atmosphere prior to use. Benzene, methylene chloride, toluene, and acetonitrile were distilled from CaH_2 prior to use. Chromium hexacarbonyl was supplied by Pressure Chemicals. Octyllithium was prepared from octyl bromide and lithium metal according to the published procedure for the production of *n*-BuLi.[23]

The following compounds were prepared according to literature methods: [(methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**),[24] [(methoxy)(ethyl)carbene]pentacarbonylchromium(0) (**1k**),[25] [(benzyloxy)(methyl)carbene]pentacarbonylchromium(0) (**1d**),[26] [(methoxy)(butyl)carbene]pentacarbonylchromium(0) (**1c**),[27] [(methoxy)(cyclopropyl)carbene]pentacarbonylchromium(0) (**1e**),[28] [(methoxy)(phenyl)carbene]pentacarbonylchromium(0) (**1f**),[29] [(methyl)((tetramethylammonio)oxy)carbene]pentacarbonylchromium(0),[30] pyridinium *p*-toluenesulfone (PPTS),[31] (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**),[32] (carbomethoxy)methylenetriphenylphosphorane (**2b**),[33] (carboethoxy)(methyl)methylenetriphenylphosphorane (**2f**),[33] fluorenyldienetriphenylphosphorane (**2g**),[34] acetylmethylenetriphenylphosphorane (**2d**),[35] (3-carbomethoxy-2-propen-1-ylidene)triphenylphosphorane (**2l**),[36] α-methoxypropionyl chloride,[37] butyrolactone-α-triphenylphosphorane (**2h**),[38] (*S*)-tetrahydro-1-*n*-butyl-3,3-diphenyl-1*H*,3*H*-pyrrolo-[1,2-*c*][1,3,2]oxazaborole,[39] tosylmethylenetriphenylphosphorane (**2e**),[40] (carbo-*tert*-butoxy)methylenetriphenylphosphorane (**2c**).[41]

[(Ethoxy)(*tert*-butyl)carbene]pentacarbonylchromium(0) (1a). This carbene complex was prepared via a modification of Semmelhack and Lee's method.[42] An Airless flask containing 10 mmol $K_2Cr(CO)_5$[43] in 100 mL of THF was cooled to −78 °C. Pivaloyl chloride (1.23 mL, 10 mmol) was added under Ar into the flask. The green-black mixture was stirred at −78 °C for 15 min. The mixture was warmed to 25 °C over 2 h, and the volatiles were removed under vacuum. The black-green residue taken up in 150 mL of chilled, degassed H_2O, and $Et_3O^+BF_4^-$ (1.9 g, 10 mmol) was added at 25 °C. The resulting yellow mixture was stirred for 15 min at 25 °C. After filtration through Celite, the aqueous layer was extracted with 4–50 mL portions of hexane. The combined hexane extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude carbene complex was purified by flash chromatography (SiO_2, hexanes) to yield 1.80 g (59%) of **1a** as an orange oil. The material was identical in all respects with that previously described.[26]

[(3-Bromopropyloxy)(methyl)carbene]pentacarbonylchromium(0). To a stirred, −40 °C suspension of [(methyl)[(tetramethylammonio)oxy]-carbene]pentacarbonylchromium(0) (2.30 g, 7.44 mmol) in CH_2Cl_2 (150 mL) under argon was added pivaloyl chloride (0.898 g, 7.44 mmol) over 5 min. After 1.3 h, 3-bromopropanol (1.03 g, 7.44 mmol) was added to the now red suspension. The reaction was slowly warmed to room temperature over 14 h before Al_2O_3 (5 g) was added. All of the volatiles were removed under reduced pressure, and the crude material was purified by column chromatography (SiO_2, 5% Et_2O/hexane) to yield 2.35 g (6.57 mmol, 88%) of the carbene complex as a yellow oil: ^1H NMR (270 MHz, $CDCl_3$) δ 2.53 (quint, 2 H, J = 6.0 Hz, $-CH_2CH_2CH_2-$), 2.97 (s, 3 H, CH_3), 3.63 (t, 2 H, J = 3.6 Hz, $BrCH_2-$), 5.01 (br s, 2 H, $CrOCH_2-$).

(2-Oxacyclohexylidene)pentacarbonylchromium(0) (1l). To a solution of [(3-bromopropyloxy)(methyl)carbene]pentacarbonylchromium(0) (1.97 g, 5.52 mmol) in THF (200 mL) under argon at −78 °C was added a solution of lithium hexamethyldisilazide (6.07 mmol) in THF (10 mL, precooled to −78 °C). The reaction mixture was allowed to warm to room temperature slowly overnight. Al_2O_3 (5 g) was added in one portion to the reaction mixture, and the solvent was removed under reduced pressure. The crude solid material was purified by column chromatography (silica gel, 3% Et_2O/hexanes) to yield 1.01 g (3.67 mmol, 66%) of complex **1l** as and orange solid. Spectroscopic data were consistent with material prepared by a different route:[44] ^1H NMR (300 MHz, $CDCl_3$) δ 1.65 (quint, 2 H, J = 7.1 Hz, CH_2), 1.88 (quint, 2 H, J = 6.6 Hz, CH_2), 3.51 (t, 2 H, J = 6.8 Hz, $-CH_2C{=}Cr$), 4.63 (t, 2 H, J = 6.0 Hz, $-CH_2O-$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.8, 21.3, 52.8, 74.9, 216.7 (cis CO), 224.0 (trans CO), 355.9 ($Cr{=}C$); IR (film) ν 2062 (CO), 1936 (CO) cm^{-1}.

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[(Methoxy)(*n*-octyl)carbene]pentacarbonylchromium(0) (1g). *n*-Octyllithium (16.1 mL of a 2.05 M solution in Et_2O) was added dropwise to a stirred suspension of $Cr(CO)_6$ (6.60 g, 30 mmol) in Et_2O (175 mL) under argon over a period of 5 min. The reaction mixture was allowed to stir at room temperature for 4 h, and the volatiles were removed under reduced pressure. The dark residue was taken up in water (100 mL), and Me_3OBF_4 was added until the suspension became acidic (~5 g). The aqueous suspension was extracted with Et_2O (3 × 100 mL). The combined ether extracts were dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. To remove excess $Cr(CO)_6$, the yellow residue was taken up in absolute EtOH (20 mL) and filtered through a pad of Celite. The ethanol was removed under reduced pressure, and the crude carbene complex was purified by column chromatography (SiO_2, hexanes) to yield 8.46 g (24.3 mmol, 81%) of **1g** as a yellow oil. This material was relatively unstable and would decompose after several hours: ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 7.0 Hz, $-CH_3$), 1.26 (br s, 10 H, $(CH_2)_5$, 1.47 (m, 2 H, CH_2), 3.35 (m, 2 H, $=C(OCH_3)C\mathit{H}_2-$), 4.76 (s, 3 H, OCH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.07, 22.64, 26.33, 29.07, 29.26, 29.30, 31.78 (CH_2), 63.13, 67.57, 216.44 (cis CO), 223.20 (trans CO), 363.78 (carbene C); IR (film) ν 2959, 2928, 2857, 2062 (CO), 1920 (CO), 1455, 1256, 1164, 1122 cm^{-1}; MS (EI) *m/e* 284 (M-2 CO).

[(Methoxy)(3-butenyl)carbene]pentacarbonylchromium(0) (1h). To a solution of [(methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.580 g, 2.32 mmol) in THF (25 mL) under argon at −78 °C was added *n*-BuLi (1.20 mL, 1.93 M solution in hexanes). After 10 min, allyl bromide (0.285 g, 2.32 mmol) was added by syringe. The reaction mixture was allowed to warm to room temperature over 20 h. Silica gel (1.0 g) was added, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (SiO_2, hexanes, R_f 0.36) to yield 0.522 g (1.8 mmol, 78%) of a yellow oil that was comprised of **1h** (75%) and the bisalkylation product (25%): ^1H NMR (270 MHz, $CDCl_3$) δ 2.23 (q, 2 H, J = 7.0 Hz, $=CCH_2$), 3.42 (t, 2 H, J = 7.6 Hz, $Cr{=}CC\mathit{H}_2$), 4.79 (s, 3 H, $OC\mathit{H}_3$), 5.04 (m, 2 H, $=CH_2$), 5.74 (m, 1 H, $=C\mathit{H}$).

[((*tert*-Butyldimethylsilyl)oxy)(methyl)carbene]pentacarbonylchromium(0) (1j). To a solution of [(methyl)[(tetramethylammonio)oxy]carbene]pentacarbonylchromium(0) (1.55 g, 5.0 mmol) in CH_2Cl_2 (100 mL) at 0 °C under argon was added *tert*-butyldimethylsilyl chloride. The temperature was slowly warmed to 24 °C, and after 14 h, the solvent was removed under reduced pressure with the careful exclusion of oxygen. Dry, degassed pentane (3 × 3 mL) was added to the residual solid, and the resulting suspension was filtered through a pad of Celite under airless conditions. The filtrate was concentrated under water aspirator pressure and then under full vacuum (1.0 mmHg) to yield 1.02 g (2.82 mmol, 65%) of **1j** as a yellow solid that melted slightly above room temperature: ^1H NMR (300 MHz, $CDCl_3$) δ 0.37 (s, 6 H, Me_2Si), 1.08 (s, 9 H, Me_3C), 2.97 (s, 3 H, $CH_3C{=}Cr$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −3.1 (Me_2Si), 18.4 ($Me_3\mathit{C}$), 25.3 (Me_3C), 51.7 ($\mathit{C}H_3C{=}Cr$), 216.7 (cis CO), 224.6 (trans CO), 374.9 (carbene C); IR (film) ν 3360, 3019, 2063 (CO), 1943 (s, CO) cm^{-1}; MS (EI) *m/e* 350 (M^+).

[(*N*-Carbonyl(*tert*-butyloxy)amino)(methyl)carbene]pentacarbonylchromium(0) (1L).[45] To a suspension of [(methyl)[(tetramethylammonio)oxy]carbene]pentacarbonylchromium(0) (2.00 g, 6.48 mmol) in CH_2Cl_2 (100 mL) under argon at −35 °C was added acetyl bromide (0.80 g, 6.48 mmol) dropwise over 5 min. The resulting deep red solution was stirred for 15 min before a solution of *O-tert*-butyl carbamate (1.14 g, 9.72 mmol) in CH_2Cl_2 (40 mL, degassed) was added to the reaction mixture. This mixture was stirred at −35 °C for 2 h and was then slowly warmed to 25 °C over 6 h. The reaction mixture was filtered through a pad of Celite, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 hexanes/EtOAc) to yield 1.57 g of complex (**1L**) (4.67 mmol, 72%) as an orange solid. Recrystallization from hexanes yielded an analytically pure sample: mp 73–76 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ major rotomer 1.57 (s, 9 H, $C(CH_3)_3$), 3.38 (s, 3 H, CH_3), 10.11 (s, 1 H, NH); minor rotomer 1.60 (s, 9 H, $C(CH_3)_3$), 3.02 (s, 3 H, CH_3), 9.66 (s, 1 H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ major rotomer 27.75 ($C(\mathit{C}H_3)_3$), 42.51 (CH_3), 85.51 ($\mathit{C}(CH_3)_3$), 143.90 (CO), 216.36 (trans CO), 223.19 (cis CO), 323.96 (carbene C); IR (neat) ν 2060, 1937, 1775 cm^{-1}; MS (EI) 336 (M^+). Anal. Calcd for $C_{12}H_{13}NO_7Cr$: C, 42.99; H, 3.91; N, 4.18. Found: C, 42.80; H, 4.07; N, 4.13.

General Procedures for the Synthesis of Allenes: Photoreaction Procedure A. A solution of chromium–carbene complex (1.0 equiv), phosphorus ylide (1.05–1.1 equiv), and hydroquinone (0.05 equiv) in dry benzene (0.05 M) under carbon monoxide (50–100 psi) was irradiated until the carbene complex was completely consumed, as indicated by TLC analysis (12–16 h). The solvent was removed under reduced pressure, which left the crude allene contaminated with triphenylphosphine oxide and chromium hexacarbonyl.

Photoreaction Procedure B. A solution of chromium–carbene complex (1.0 equiv), phosphorus ylide (1.1 equiv), and hydroquinone (0.05 equiv) in dry CH_3CN (0.05 M) under argon was irradiated until the carbene complex was completely consumed, as indicated by TLC analysis (10–16 h). The solvent was removed under reduced pressure, and the residual material was taken up in ethyl acetate/hexanes (1:1 mixture, 0.025 M). The resulting suspension was filtered through Celite and then was placed in a light box equipped with six 20W Vitalite fluorescent lamps for air oxidation of the chromium-containing byproducts. After 2–3 days the solution was colorless, and the insoluble chromium impurities were removed by filtration through Celite. The clear filtrate was concentrated under reduced pressure, which left triphenylphosphine oxide and a mixture of allene and diene.

Benzyl 5,5-Dimethyl-4-ethoxy-2,3-hexadienoate (3aa). [(Ethoxy)(*tert*-butyl)carbene]pentacarbonylchromium(0) (**1a**) (0.360 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.451 g, 1.1 mmol) were subjected to photolysis procedure A. Purification of the crude material by column chromatography (basic Al_2O_3, 2% Et_3N/petroleum ether, R_f 0.22 on Al_2O_3 TLC plate eluted with hexane) gave 0.163 g (0.60 mmol, 60%) of **3aa** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9 H, $C(CH_3)_3$), 1.24 (t, 3 H, J = 7.0 Hz, $-CH_2C\mathit{H}_3$), 3.58 (dq, 1 H, J = 12.5, 7.0 Hz, $OC\mathit{H}HCH_3$), 3.59 (dq, 1 H, J = 12.5, 7.0 Hz, $OC\mathit{H}HCH_3$), 5.14 (d, 1 H, J = 12.5 Hz, $CO_2C\mathit{H}HPh$), 5.22 (d, 1 H, J = 12.6 Hz, $CO_2CH\mathit{H}Ph$), 6.14 (s, 1 H, allene H), 7.36 (m, 5 H, PhH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.40 (CH_3), 27.74 ($C(\mathit{C}H_3)_3$), 34.42 ($\mathit{C}(CH_3)_3$), 65.29 (OCH_2), 66.28 (OCH_2), 99.53 ($=\mathit{C}H$), 127.83, 128.01, 128.42, 136.10 ($=\mathit{C}$), 145.92, 165.85 (CO), 207.66 ($=\mathit{C}=$); IR (film) ν 1939 ($C{=}C{=}C$), 1723 (CO), 1573 cm^{-1}; MS (EI) *m/e* 274 (M), 275 (M + 1). Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.61; H, 8.22.

Methyl 4-Methoxy-2,3-pentadienoate (3bb). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.250 g, 1.0 mmol) and (carbomethoxy)methylenetriphenylphosphorane (**2b**) (0.367 g, 1.1 mmol) were subjected to photolysis procedure A. The crude reaction mixture was taken up in 1–2 mL of CH_2Cl_2, and hexane (15 mL) was added to precipitate most of the $Ph_3P{=}O$. The mixture was filtered through Celite, and the solvent was removed under reduced pressur to give **3bb** contaminated with $Ph_3P{=}O$: ^1H NMR (270 MHz, $CDCl_3$) δ 1.97 (d, 3 H, J = 2 Hz, $=CC\mathit{H}_3$), 3.42 (s, 3 H, $OC\mathit{H}_3$), 3.72 (s, 3 H, $CO_2C\mathit{H}_3$), 6.11 (q, 1 H, J = 2 Hz, $=CH$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.74 (CH_3), 51.84 ($CO_2\mathit{C}H_3$), 56.84 (OCH_3), 98.58 ($=CH$), 165.22 (CO), 207.61 ($=C=$), one allene signal is underneath $Ph_3P{=}O$ signals IR (film) ν 1939 ($C{=}C{=}C$), 1727 (CO) cm^{-1}.

Benzyl 4-Methoxy-2,3-pentadienoate (3ba). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.250 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.451 g, 1.1 mmol) were subjected to photolysis procedure A. The crude reaction mixture was taken up in 1–2 mL of CH_2Cl_2, and hexane (15 mL) was added to precipitate most of the $Ph_3P{=}O$. The mixture was filtered through Celite, and the solvent was removed under reduced pressure to give **3ba** contaminated with $Ph_3P{=}O$: ^1H NMR (270 MHz, $CDCl_3$) δ 1.90 (d, 3 H, J = 2.5 Hz, $=CC\mathit{H}_3$), 3.34 (s, 3 H, $OC\mathit{H}_3$), 5.09 (d, 1 H, J = 12.5 Hz, $CO_2C\mathit{H}HPh$), 5.15 (d, 1 H, J = 12.5 Hz, $CO_2CH\mathit{H}Ph$), 6.07 (q, 1 H, J = 2.5 Hz, $=C\mathit{H}$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.69 (CH_3), 56.88 (OCH_3), 66.37 ($CO_2\mathit{C}H_2$), 98.72 ($=CH$), 164.51 (CO), 208.12 ($=C=$), one allene signal and Ar*C* signals are underneath $Ph_3P{=}O$ signals; IR (film) ν 1932 ($C{=}C{=}C$), 1724 (CO) cm^{-1}.

Methyl 4-Methoxy-4-phenyl-2,3-butadienoate (3fb). [(Methoxy)(phenyl)carbene]pentacarbonylchromium(0) (**1f**) (0.311 g, 1.0 mmol) and (carbomethoxy)methylenetriphenylphosphorane (**2b**) (0.367 g, 1.1 mmol) were subjected to photolysis procedure A. The crude reaction mixture was taken up in 1–2 mL of CH_2Cl_2, and hexane (15 mL) was added to precipitate most of the $Ph_3P{=}O$. The mixture was filtered through Celite, and the solvent was removed under reduced pressure to give **3fb** contaminated with $Ph_3P{=}O$: ^1H NMR (270 MHz, $CDCl_3$) δ 3.66 (s, 3 H, $OC\mathit{H}_3$), 3.78 (s, 3 H, $CO_2C\mathit{H}_3$), 6.53 (s, 1 H, $=C\mathit{H}$), PhH (underneath $Ph_3P{=}O$ signals); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 51.98 ($CO_2\mathit{C}H_3$), 56.99 (OCH_3), 102.43 ($=CH$), 164.25 (CO), 210.01 ($=C=$), one allene signal and Ar*C* signals are underneath $Ph_3P{=}O$ signals; IR (film) ν 1940 ($C{=}C{=}C$), 1724 (CO) cm^{-1}.

Benzyl 4-(Benzyloxy)-2,3-pentadienoate (3da). [(Benzyloxy)(methyl)carbene]pentacarbonylchromium(0) (**1d**) (0.326 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.451 g, 1.1 mmol) were subjected to photolysis procedure A. The crude reaction mixture was taken up in 1–2 mL of CH_2Cl_2, and hexane (15 mL) was added to precipitate most of the $Ph_3P{=}O$. The mixture was filtered through Celite, and the solvent was removed under reduced pressure to give **3fb** contaminated with $Ph_3P{=}O$: ^1H NMR (270 MHz, $CDCl_3$) δ 2.05 (d, 3 H, J = 2.5 Hz, $C\mathit{H}_3$), 4.56 (d, 1 H, J = 12.5 Hz, $OC\mathit{H}HPh$), 4.63 (d, 1 H, J = 12.5 Hz, $OCH\mathit{H}Ph$), 5.20 (s, 2 H, $CO_2C\mathit{H}_2Ph$), 6.14

(q, 1 H, *J* = 2.4 Hz, =C*H*), PhH (underneath Ph$_3$P=O signals); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 17.86 (CH$_3$), 66.04 (OCH$_2$), 66.33 (OCH$_2$), 98.48 (=CH), 164.34 (CO), 208.20 (=C=), one allene signal and Ar*C* signals are underneath Ph$_3$P=O signals; IR (film) ν 1939 (C=C=C), 1723 (CO) cm^{-1}.

3-Methoxy-1-(*p*-tolylsulfonyl)-1,2-butadiene (3be). [(Methoxy)(methyl)]pentacarbonylchromium(0) (**1b**) (0.063 g, 0.25 mmol) and tosylmethylenetriphenylphosphorane (**2e**) (0.113 g, 0.26 mmol) were subjected to photolysis procedure A. A few milliliters of CH$_2$Cl$_2$ were added to dissolve all of the ylide. The crude reaction mixture was taken up in 1–2 mL of CH$_2$Cl$_2$ and hexane (15 mL) was added to precipitate most of the Ph$_3$P=O. The mixture was filtered through Celite, and the solvent was removed under reduced pressure to give **3be** contaminated with Ph$_3$P=O: ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.91 (d, 3 H, *J* = 2.3 Hz, =CC*H*$_3$), 2.44 (s, 3 H, ArC*H*$_3$), 3.39 (s, 3 H, OC*H*$_3$), 6.61 (q, 1 H, *J* = 2.3 Hz, =C*H*); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 17.91 (CH$_3$), 21.58 (ArCH$_3$), 57.57 (OCH$_3$), 109.83 (=CH), 199.27 (=C=), one allene signal and Ar*C* signals are underneath Ph$_3$P=O signals; IR (film) ν 1947 (C=C=C), 1314, 1144 (SO$_2$) cm^{-1}.

3-Ethoxy-4,4-dimethyl-1-(*p*-tolylsulfonyl)-1,2-pentadiene (3ae). [(Ethoxy)(*tert*-butyl)carbene]pentacarbonylchromium(0) (**1a**) (0.113 g, 0.37 mmol) and tosylmethylenetriphenylphosphorane (**2e**) (0.160 g, 0.37 mmol) were subjected to photolysis procedure A. A few milliliters of CH$_2$Cl$_2$ were added to dissolve all of the ylide. The crude reaction mixture was taken up in 1–2 mL of CH$_2$Cl$_2$, and hexane (15 mL) was added to precipitate most of the Ph$_3$P=O. The mixture was filtered through Celite, and the solvent was removed under reduced pressure to give **3ae** contaminated with Ph$_3$P=O: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.97 (s, 9 H, C(C*H*$_3$)$_3$), 1.23 (t, 3 H, *J* = 7.0 Hz, CH$_2$C*H*$_3$), 2.41 (s, 3 H, ArC*H*$_3$), 3.48 (q, 1 H, *J* = 7.1 Hz, OC*H*H), 3.49 (q, 1 H, *J* = 7.0 Hz, OCH*H*), 6.63 (s, 1 H, =CH), PhH (underneath Ph$_3$P=O signals); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 14.33 (CH$_2$*C*H$_3$), 21.56 (Ar*C*H$_3$), 27.45 (C(*C*H$_3$)$_3$), 35.14 (*C*(CH$_3$)$_3$), 66.12 (OCH$_2$), 110.62 (=CH), 198.39 (=C=), one allene signal and Ar*C* signals are underneath Ph$_3$P=O signals; IR (film) ν 1936 (C=C=C), 1316, 1142 (SO$_2$) cm^{-1}.

General Procedure for Allene to Diene Isomerization. The crude allene from the photoreaction (procedure A or B) and PPTS (0.05 g) were dissolved in dry CH$_2$Cl$_2$ (0.025 M). The yellow solution was stirred at room temperature, under argon, for 24 h. The methylene chloride was removed under reduced pressure, which afforded the crude diene. The diene was purified by column chromatography (silica gel which had been previously washed with hexanes/Et$_3$N (4:1) followed by copious amounts of hexanes to remove any excess Et$_3$N, and then it was thoroughly dried under reduced pressure (1.0 mmHg for 12 h)). Hexanes were used to elute the residual Cr(CO)$_6$ (photoreaction procedure A) followed by hexanes/Et$_2$O (98:2) to elute the diene.

Benzyl (*Z*)-4-Methoxy-2,4-pentadienoate (4ba). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.125 g, 0.5 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.216 g, 0.525 mmol) were subjected to photolysis procedure A and the general allene isomerization procedure to yield 0.086 g (0.4 mmol, 79%) of diene (**4ba**) as a colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.40 (s, 3 H, OCH$_3$), 4.27 (d, *J* = 2.3 Hz, =CH*H*), 4.33 (d, 1 H, *J* = 2.3 Hz, =C*H*H), 5.19 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.82 (d, 1 H, *J* = 12.4 Hz, =CH), 6.11 (d, 1 H, *J* = 12.4 Hz, =CH), 7.26–7.49 (m, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 54.81 (OCH$_3$), 66.35 (OCH$_2$), 89.74 (=C), 120.28, 128.16, 128.47, 128.57, 131.91, 135.92, 157.47, 167.47 (CO); IR (film) ν 1732 (CO), 1644, 1588 cm^{-1}; MS (EI) *m*/*e* 218 (M). Anal. Calcd for C$_{14}$H$_{13}$O$_3$: C, 71.54; H, 6.47. Found: C, 71.39; H, 6.25.

Benzyl 4-Methoxy-2*Z*,4*E*(*Z*)-hexadienoate (4ka). [(Methoxy)(ethyl)carbene]pentacarbonylchromium(0) (**1k**) (0.287 g, 1.09 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.490 g, 1.20 mmol) were subjected to photolysis procedure A (16 h) and the general allene isomerization procedure to yield 0.187 g of **4ka** (0.81 mmol, 81%) as a 4:1 mixture of isomers. Separation of the two isomers by chromatography was not successful: ^{1}H NMR (270 MHz, CDCl$_3$) δ major isomer 1.70 (d, 3 H, *J* = 7.3 Hz, –CH$_3$), 3.45 (s, 3 H, OCH$_3$), 5.18 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.26 (q, 1 H, *J* = 7.3 Hz, =C*H*CH$_3$), 5.72 (d, 1 H, *J* = 12.2 Hz, =CH), 6.09 (d, 1 H, *J* = 12.2 Hz, =CH), 7.28–7.46 (m, 5 H, PhH); minor isomer 1.68 (d, 3 H, *J* = 7.2 Hz, –CH$_3$), 3.34 (s, 3 H, OCH$_3$), 4.77 (q, 1 H, *J* = 7.2 Hz, =C*H*CH$_3$), 5.18 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.85 (d, 1 H, *J* = 12.2 Hz, =CH), 6.44 (d, 1 H, *J* = 12.2 Hz, =CH), 7.28–7.46 (m, 5 H, PhH); ^{13}C NMR (67.9 MHz, CDCl$_3$) δ major isomer 11.06 (CH$_3$), 59.00 (OCH$_3$), 66.31 (CO$_2$CH$_2$), 117.22, 118.52, 128.06, 128.37, 128.58, 133.93, 135.92, 153.06, 167.34 (CO); minor isomer 11.72 (CH$_3$), 54.47 (OCH$_3$), 66.22 (CO$_2$CH$_2$), 99.89, 120.48, 128.37, 128.58, 128.64, 133.93, 136.01, 151.12, 167.51; IR (film) ν 1728 (CO), 1612 (C=C) cm^{-1}; MS (NH$_3$CI) *m*/*e* 233 (M + 1). Anal. Calcd for C$_{14}$H$_{16}$O$_3$: C, 72.39; H, 6.94. Found: C, 72.19; H, 6.87.

When photolysis procedure B was used (photoreaction = 8 h, air oxidation = 36 h), the same carbene complex (0.264 g, 1.0 mmol) and ylide (0.431 g, 1.05 mmol) were transformed into 0.167 g (0.7 mmol, 70%) of diene **4ka** with an identical 4:1 mixture of isomers.

Benzyl 4-Methoxy-2*Z*,4*E*(*Z*)-octadieneoate (4ca). [(Methoxy)(butyl)carbene]pentacarbonylchromium(0) (**1c**) (0.305 g, 1.04 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.490 g, 1.20 mmol) were subjected to photolysis procedure A (16 h, substitute CH$_2$Cl$_2$/Et$_2$O for benzene and no hydroquinone used) and general allene isomerization procedure to yield 0.217 g (0.83 mmol, 80%) of **4ca** as a clear oil. The diene was a 4.7:1 mixture of isomers which were not completely separated: ^{1}H NMR (300 MHz, CDCl$_3$) δ major isomer 0.92 (t, 3 H, *J* = 7.3 Hz, C*H*$_3$), 1.39 (tq, 2 H, *J* = 7.3, 7.4 Hz, –CH$_2$C*H*$_2$CH$_3$), 2.15 (q, 2 H, *J* = 7.4 Hz, =CC*H*$_2$), 3.45 (s, 3 H, OCH$_3$), 5.17 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.18 (t, 1 H, *J* = 7.4 Hz, =C*H*), 5.74 (d, 1 H, *J* = 12.2 Hz, =CH), 6.11 (d, 1 H, *J* = 12.2 Hz, =CH), 7.25–7.45 (m, 5 H, PhH); minor isomer 0.90 (t, 3 H, *J* = 7.3 Hz, C*H*$_3$), 1.39 (hex, 2 H, *J* = 7.3 Hz, –CH$_2$C*H*$_2$CH$_3$), 2.05 (q, 2 H, *J* = 7.4 Hz, =CC*H*$_2$), 3.35 (s, 3 H, OCH$_3$), 4.72 (t, 1 H, *J* = 7.9 Hz, =C*H*Pr), 5.18 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.84 (d, 1 H, *J* = 12.2 Hz, =CH), 6.44 (d, 1 H, *J* = 12.2 Hz, =CH), 7.25–7.43 (m, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ major isomer 13.83 (CH$_3$), 22.44 (CH$_2$), 27.59 (*C*H$_2$C=), 59.36 (OCH$_3$), 66.32 (O*C*H$_2$Ph), 118.65, 122.92, 128.07, 128.38, 134.03, 135.87, 152.20, 167.39 (CO); minor isomer 13.59 (CH$_3$), 23.67 (CH$_2$), 28.61 (*C*H$_2$C=), 54.48 (OCH$_3$), 66.28 (O*C*H$_2$PH), 105.85, 120.36, 128.11, 128.44, 128.51, 128.59, 136.02, 150.70, 167.79 (CO); IR (film) ν 1730 (CO), 1611 cm^{-1}; MS (EI) *m*/*e* 260 (M). Anal. Calcd for C$_{16}$H$_{20}$O$_3$: C, 73.82; H, 7.74. Found: C, 74.00; H, 7.64.

Benzyl (*Z*)-4-(Benzyloxy)-2,4-pentadieneoate (4da). [(Benzyloxy)(methyl)carbene]pentacarbonylchromium(0) (**1d**) (0.326 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.431 g, 1.05 mmol) were subjected to photolysis procedure A (16 h, Et$_2$O/CH$_2$Cl$_2$ substituted for benzene, no hydroquinone) followed by the general allene isomerization procedure to yield 0.200 g (0.68 mmol, 68%) of **4da** as a colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.37 (s, 2 H, =CH$_2$), 4.70 (s, 2 H, OC*H*$_2$Ph), 4.71 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.80 (d, 1 H, *J* = 12.4 Hz, =CH), 6.08 (d, 1 H, *J* = 12.4 Hz, =CH), 7.10–7.70 (m, 10 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 66.08 (O*C*H$_2$Ph), 69.88 (O*C*H$_2$Ph), 90.94, 120.40, 127.89, 127.94, 128.14, 128.22, 128.27, 131.10, 135.60, 136.19, 156.41, 167.37 (CO); IR (film) ν 1731 (CO), 1643 cm^{-1}; MS (NH$_3$CI) *m*/*e* 295 (M + 1), 312 (M + 18). Anal. Calcd for C$_{19}$H$_{18}$O$_3$: C, 77.53; H, 6.16. Found: C, 77.31; H, 6.15.

Benzyl (*Z*)-3-(6-(3,4-Dihydro-2*H*-pyranyl))-2-propenoate (4ia). (2-Oxacyclohexylidene)pentacarbonylchromium(0) (**1i**) (0.166 g, 0.6 mmol) and (benzyloxy)methylenetriphenylphosphorane (**2a**) (0.247 g, 0.60 mmol) were subjected to photolysis procedure A (6 h, CH$_2$Cl$_2$ substituted for benzene, no hydroquinone). The crude material was purified by column chromatography (10:1 silica gel/dry K$_2$CO$_3$ (finely crushed), 5% EtOAc/hexane, R_f 0.19 on SiO$_2$ TLC plate with 5:1 hexane/Et$_2$O) to yield 0.045 g (0.18 mmol, 31%) of **4ia** as a colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.76 (tt, 2 H, *J* = 5.2, 6.2 Hz, –OCH$_2$C*H*$_2$CH$_2$–), 2.10 (dt, 2 H, *J* = 4.2, 6.2 Hz, =CC*H*$_2$), 3.81 (m, 2 H, OC*H*$_2$–), 5.03 (t, 1 H, *J* = 4.2 Hz, =C(*H*)CH$_2$–), 5.18 (s, 2 H, CO$_2$C*H*$_2$Ph), 5.69 (d, 1 H, *J* = 12.4 Hz, =CH), 5.96 (d, 1 H, *J* = 12.4 Hz, =CH), 7.25–7.45 (m, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 20.85, 21.74, 65.78 (OCH$_2$), 66.29 (OCH$_2$), 107.05, 117.59, 128.07, 128.42, 128.53, 131.80, 136.10, 149.91, 167.87 (CO); IR (film) ν 1726 (CO), 1609 cm^{-1}; high resolution mass spectrum calcd for C$_{15}$H$_{16}$O$_3$ [M] 244.1100, found 244.1100.

General Procedure for Allene Hydrolysis. Procedure A. The crude material from the photoreaction (procedure A or B) was taken up in diethyl ether (40 mL per mmol of allene) and an equivalent amount of 5% aqueous HCl solution. The biphasic mixture was stirred vigorously for 16 h (some allenes required shorter times, see individual synthesis). The layers were separated, and the aqueous portion was washed with diethyl ether. The combined ether layers were washed with saturated NaCl solution and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the residue was purified by chromatography as described in each synthesis.

Procedure B. The crude material from the photoreaction was taken up in a mixture of THF and H$_2$O (9:1) made of 0.2 N in sulfuric acid (40 mL per mmol of allene). The solution thus formed was stirred for 4 h and then diluted with saturated NaCl solution. The layers were separated, and the aqueous layer was washed with Et$_2$O. The combined organic layers were dried over MgSO$_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude material was purified by chromatography as described in each synthesis.

Benzyl (*Z*)-5,5-Dimethyl-4-oxo-2-hexenoate (5aa). [(Ethoxy)(*tert*-butyl)carbene]pentacarbonylchromium(0) (**1a**) (0.306 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.452 g, 1.1

mmol) were subjected to photolysis procedure A followed by hydrolysis procedure A (0.5 h). Purification by radial chromatography (2 mm SiO$_2$, 10% Et$_2$O/hexane, R_f 0.12) yielded 0.211 g of **5aa** (0.86 mmol, 86%) as a colorless oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.16 (s, 9 H, C(CH$_3$)$_3$), 5.16 (s, 2 H, CO$_2$CH_2Ph), 6.09 (d, 1 H, J = 12.2 Hz, =CH), 6.76 (d, 1 H, J = 12.2 Hz, =CH), 7.35 (s, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 26.13 (CH$_3$), 43.75 (C(CH$_3$)$_3$), 66.92 (OCH$_2$), 125.79, 128.36, 128.51, 135.20, 139.60, 152.78, 165.21 (CO), 208.40 (CO); IR (film) ν 1727 (CO), 1696 (CO), 1620 (C=C) cm^{-1}; MS (EI) m/e 246 (M). Anal. Calcd for C$_{15}$H$_{18}$O$_3$: C, 73.15; H, 7.37. Found: C, 72.86; H, 7.25.

Benzyl (*Z*)-4-Oxo-2-pentenoate (5ba). Procedure A. [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.125 g, 0.5 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.216 g, 0.525 mmol) were subjected to photolysis procedure A followed by hydrolysis procedure A (12 h). The crude material was purified by column chromatography (silica gel) eluting first with hexanes to remove Cr(CO)$_6$ and then with 2:1 hexane/Et$_2$O to elute **5ba** (0.80 g, 0.39 mmol, 78%) as a colorless oil (R_f 0.14 for 3:1 hexane/Et$_2$O): ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.32 (s, 3 H, CH$_3$), 5.19 (s, 2 H, CO$_2$CH_2Ph), 6.05 (d, 1 H, J = 12.1 Hz, =CH), 6.48 (d, 1 H, J = 12.1 Hz, =CH), 7.37 (s, 5 H, PhH); ^{13}C NMR (67 MHz, CDCl$_3$) δ 29.86 (CH$_3$), 67.02 (OCH$_2$), 124.27, 128.32, 128.47, 128.59, 135.20, 142.08, 164.96 (CO), 200.97 (CO); IR (film) ν 1727 (CO), 1700 (CO), 1633 (C=C) cm^{-1}. Anal. Calcd for C$_{12}$H$_{12}$O$_3$: C, 70.57; H, 5.92. Found: C, 70.17; H, 6.19.

Procedure B. The above procedure was repeated using hydrolysis procedure B to yield 0.075 g of **5ba** (0.37 mmol, 74%).

Procedure C. The procedure in method A was repeated using [(benzyloxy)(methyl)carbene]pentacarbonylchromium(0) (**1d**) (0.163 g, 0.5 mmol) in place of the carbene complex listed to yield 0.076 g (0.37 mmol, 75%) of **5da**.

Procedure D. [((*tert*-Butyldimethylsilyl)oxy)(methyl)carbene]pentacarbonylchromium(0) (**1j**) (0.333 g, 0.95 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.460 g, 1.0 mmol) were subjected to photolysis procedure A (15 h, Et$_2$O/CH$_2$Cl$_2$ substituted for benzene, no hydroquinone) and hydrolysis procedure A (20 h). The crude material was purified by radial chromatography (2 mm silica gel, 5% Et$_2$O/hexanes) to yield 0.65 g (0.32 mmol, 34%) of **5ja**.

***tert*-Butyl (*Z*)-4-Oxo-2-dodecenoate (5gc).** [(Methoxy)(octyl)carbene]pentacarbonylchromium(0) (**1g**) (174 mg, 0.5 mmol) and (carbo-*tert*-butoxy)methylenetriphenylphosphorane (**2c**) (207 mg, 0.55 mmol) were subjected to photolysis procedure A (8 h) followed by hydrolysis procedure A (13 h). The crude material was purified by flash chromatography (SiO$_2$, 9/1 hexanes/ ethyl acetate) to give 100 mg (75%) of **5gc** as a colorless oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.85 (br t, 3 H, CH_3CH$_2$), 1.2–1.4 (m, 10 H, –(CH$_2$)$_5$–), 1.46 (s, 9 H, C(CH$_3$)$_3$), 1.60 (m, 2 H, CH$_2$), 2.56 (t, 2 H, J = 7.5 Hz, CH_2C=O), 5.91 (d, 1 H, J = 12.1 Hz, =CH), 6.35 (d, 1 H, J = 12.1 Hz, =CH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 14.01 (CH$_3$), 22.58, 23.37 (CH$_2$), 27.88 (CH$_3$), 29.05, 29.09, 29.28, 31.76, 42.75 (CH$_2$), 81.88 (OC(CH$_3$)$_3$), 126.68 (=CH), 139.83 (=CH), 164.50 (C=O), 203.60 (C=O); IR (film) ν 1728 (C=O), 1625 (C=C) cm^{-1}. Anal. Calcd for C$_{16}$H$_{28}$O$_3$: C, 71.60; H, 10.51. Found: C, 71.64; H, 10.74.

Methyl (*Z*)-4-Oxo-2-dodecenoate (5gb). Method A. [(Methoxy)(octyl)carbene]pentacarbonylchromium(0) (**1g**) (0.560 g, 1.61 mmol) and (carbomethoxy)methylenetriphenylphosphorane (**2b**) (0.591 g, 1.77 mmol) were subjected to photolysis procedure A (16 h, 30 mL benzene) and hydrolysis procedure A (24 h). Purification by radial chromatography (2 mm SiO$_2$, hexanes followed by 5:1 hexane/Et$_2$O, R_f 0.26 in 3:1 hexane/Et$_2$O) gave 0.296 g (1.31 mmol, 81%) of **5gb** as a colorless oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.88 (br t, 3 H, CH$_3$), 1.24 (br s, 10 H, –(CH$_2$)$_5$–), 1.65 (m, 2 H, –C(O)CH$_2$CH_2–), 2.60 (t, 2 H, J = 7.4 Hz, C(O)CH$_2$–), 3.75 (s, 3 H, OCH$_3$), 6.03 (d, 1 H, J = 12.2 Hz, =CH), 6.50 (d, 1 H, J = 12.2 Hz, =CH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 13.97 (CH$_3$), 22.53, 23.19, 29.01, 29.27, 31.72, 42.56 (CH$_2$), 51.90 (OCH$_3$), 124.19 (=C), 141.82 (=C), 165.67 (CO), 203.64 (CO); IR (film) ν 1728 (CO), 1706 (CO), 1628 (C=C) cm^{-1}; MS (NH$_3$CI) m/e 227 (M + 1), 244 (M + 18). Anal. Calcd for C$_{13}$H$_{22}$O$_3$: C, 68.99; H, 9.80. Found: C, 68.96, H, 9.84.

Procedure B. In a Pyrex test tube, the same carbene complex (1.05 g, 3.0 mmol), ylide (1.10 g, 3.3 mmol), and hydroquinone (8 mg) were dissolved in CH$_3$CN (160 mL). The vessel was purged with argon and was subjected to photolysis for 8 h. The volatiles were removed, and the residual material was subjected to hydrolysis procedure A (100 mL of Et$_2$O, 80 mL of 5% aqueous HCl, 20 h). The crude material was then taken up in EtOAc (50 mL) and hexanes (100 mL) for air oxidation (24 h). The suspension was filtered through a pad of Celite, and the solvent was removed under reduced pressure. The residual brown oily solid was purified by column chromatography (SiO$_2$, 6:1 hexane/Et$_2$O) to yield 0.390 g of **5gb** (1.73 mmol, 58%).

Benzyl (*Z*)-4-Oxo-2-octenoate (5ca). [(Methoxy)(butyl)carbene]pentacarbonylchromium(0) (**1c**) (0.147 g, 0.51 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.229 g, 0.56 mmol) were subjected to photoreaction procedure A (15.5 h, Et$_2$O/CH$_2$Cl$_2$ substituted for benzene) and allene hydrolysis procedure A (25 h). The crude material was isolated by radial chromatography (2 mm SiO$_2$, 5% Et$_2$O/hexane, R_f 0.22 in 3:1 hexane/Et$_2$O) to yield 0.105 g of **5ca** (0.43 mmol, 84%) as a colorless oil: ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.88 (t, 3 H, J = 7.3 Hz, CH_3), 1.30 (hex, 2 H, J = 7.2 Hz, –CH$_2$CH_2CH$_3$), 1.57 (quint, 2 H, J = 7.2 Hz, –CH$_2$CH_2CH$_2$), 2.56 (t, 2 H, J = 7.2 Hz, –CH_2CO), 5.17 (s, 2 H, OCH_2Ph), 6.04 (d, 1 H, J = 12.2 Hz, =CH), 6.50 (d, 1 H, J = 12.2 Hz, =CH), 7.35 (s, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 13.62 (CH$_3$), 21.95 (CH$_2$), 25.05 (CH$_2$), 42.09 (OCH$_2$), 66.71 (CO$_2$CH$_2$), 123.95, 128.21, 128.27, 128.34, 135.01, 142.10, 164.84 (CO), 203.42 (CO); IR (film) ν 1725 (CO), 1699 (CO), 1625 cm^{-1}; MS (EI) m/e 245 (M). Anal. Calcd for C$_{15}$H$_{18}$O$_3$: C, 73.15; H, 7.37. Found: C, 72.99; H, 7.38.

Benzyl (*Z*)-Cyclopropyl-4-oxo-2-propenoate (5ea). [(Methoxy)(cyclopropyl)carbene]pentacarbonylchromium(0) (**1e**) (0.276 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.452 g, 1.1 mmol) were subjected to photolysis procedure A (16 h) followed by hydrolysis procedure A (0.5 h). Purification by radial chromatography (2 mm SiO$_2$, elute first with hexanes then 3:1 hexane/Et$_2$O, R_f 0.34) yielded 0.181 g (0.79 mmol, 79%) of **5ea** along with 0.016 g (0.07 mmol, 7%) of the trans isomer: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.94 (ddd, 2 H, J = 7.9, 7.9, 4.6 Hz, cyclopropyl HCH), 1.12 (ddd, 2 H, J = 7.9, 4.6, 4.6 Hz, cyclopropyl HCH), 2.04 (tt, 1 H, J = 7.9, 4.6 Hz, cyclopropyl CH), 5.18 (s, 2 H, CO$_2$CH_2Ph), 6.09 (d, 1 H, J = 12.1 Hz, =CH), 6.56 (d, 1 H, J = 12.1 Hz, =CH), 7.36 (s, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 11.87 (CH$_2$), 21.45 (CH), 66.86 (OCH$_2$), 124.88, 128.31, 128.43, 135.11, 140.87, 165.01 (CO), 203.00 (CO); IR (film) ν 1727 (CO), 1685 (CO), 1622 (C=C) cm^{-1}; MS (EI) m/e 230 (M). Anal. Calcd for C$_{14}$H$_{14}$O$_3$: C, 73.03; H, 6.13. Found: C, 72.93; H, 6.06.

Benzyl (*Z*)-4-Oxo-2,7-octadienoate (5ha). [(Methoxy)(3-butenyl)carbene]pentacarbonylchromium(0) (**1h**) (0.390 g, 1.07 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.459 g, 1.12 mmol) were subjected to photolysis procedure A (Et$_2$O/CH$_2$Cl$_2$ substituted for benzene, no hydroquinone, 10 h) followed by hydrolysis procedure A (20 h). Purification by radial chromatography (2 mm SiO$_2$, 10% Et$_2$O/hexanes, R_f 0.25 in 3:1 hexanes/Et$_2$O) yielded 0.110 g (0.45 mmol, 42%) of **5ha** as a colorless oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.34 (q, 2 H, J = 7.2 Hz, CH$_2$C=), 2.67 (t, 2 H, J = 7.2 Hz, C(O)CH_2–), 5.00 (m, 2 H, =CH_2), 5.16 (s, 2 H, OCH_2), 5.79 (m, 1 H, CH$_2$=CH–), 6.04 (d, 1 H, J = 12.1 Hz, =CH), 6.48 (d, 1 H, J = 12.1 Hz, =CH), 7.35 (s, 5 H, PhH); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 27.22 (CH$_2$), 41.65 (CH$_2$), 67.02 (OCH$_2$), 115.31, 124.30, 128.47, 128.49, 128.57, 135.10, 136.78, 142.15, 164.95 (CO), 202.79 (CO); IR (film) ν 1725 (CO), 1640 cm^{-1}; MS (EI) m/e 244 (M). Anal. Calcd for C$_{15}$H$_{16}$O$_3$: C, 73.75; H, 6.60. Found: C, 73.68; H, 6.65.

Methyl (*Z*)-4-Oxo-4-phenyl-2-butenoate (5fb). [(Methoxy)(phenyl)carbene]pentacarbonylchromium(0) (**1f**) (0.172 g, 0.5 mmol) and (carbomethoxy)methylenetriphenylphosphorane (**2b**) (0.167 g, 0.5 mmol) were subjected to photolysis procedure A (24 h, no hydroquinone) followed by hydrolysis procedure A (1 h). Purification by radial chromatography (1 mm SiO$_2$, 10% Et$_2$O/hexanes, R_f 0.07 in 20% Et$_2$O/hexanes) gave 0.032 g of **5fb** (0.17 mmol, 33%) as a white solid. Recrystallization from hexanes/Et$_2$O gave an analytically pure sample of **5fb** as white needles: mp 65–66 °C (lit.[46] mp 65–66 °C); ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.60 (s, 3 H, OCH$_3$), 6.30 (d, 1 H, J = 12.1 Hz, =CH), 6.91 (d, 1 H, J = 12.1 Hz, =CH), 7.48 (t, 2 H, J = 7.5 Hz, phenyl H-3), 7.58 (d, 1 H, J = 7.4 Hz, phenyl H-4), 7.93 (d, 2 H, J = 7.5 Hz, phenyl H-2); IR (film) ν 1726 (CO), 1673 (CO) cm^{-1}; MS (EI) m/e 190 (M), 191 (M + 1), 192 (M + 2).

(*Z*)-3-Tridecen-2,5-dione (5gd). [(Methoxy)(octyl)carbene]pentacarbonylchromium(0) (**1g**) (0.348 g, 1.0 mmol) and acetylmethylenetriphenylphosphorane (**2d**) were subjected to photolysis procedure A (12 h, CH$_2$Cl$_2$ substituted for benzene) and hydrolysis procedure A (2 h). Purification by radial chromatography (2 mm SiO$_2$, 5:1 hexane/EtOAc, R_f 0.33) gave 0.039 g (0.19 mmol, 19%) of **5gd** as a white solid: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.88 (br t, 3 H, CH$_3$), 1.3 (br s, 10 H, –(CH$_2$)$_5$–), 1.65 (m, 2 H, CH$_2$), 2.38 (s, 3 H, CH_3CO), 2.65 (t, 2 H, J = 7.3 Hz, –CH_2CO), 6.83 (s, 2 H, =CH); ^{13}C NMR (67.9 Mhz, CDCl$_3$) δ 14.00 (CH$_3$), 22.57, 23.73, 28.09, 29.07, 29.08, 29.28, 31.75, 41.38 (CH$_2$), 136.82 (=C), 137.17 (=C), 198.37 (CO), 200.69 (CO); IR (film) ν 1682 (CO), 1620 (C=C) cm^{-1}; MS (EI) m/e 210 (M). Anal. Calcd for C$_{13}$H$_{22}$O$_2$: C, 74.24; H, 10.54. Found: C, 74.30; H, 10.35.

4,4-Dimethyl-3-oxo-1-(*p*-tolylsulfonyl)-1-pentene (5ae). [(Ethoxy)(*tert*-butyl)carbene]pentacarbonylchromium(0) (**1a**) (113 mg, 0.37 mmol) and tosylmethylenetriphenylphosphorane (**2e**) (160 mg, 0.37

mmol) were subjected to photolysis procedure A (11 h) followed by hydrolysis procedure A (30 min). The crude material was purified by radial chromatography (2 mm $\mathrm{SiO_2}$, 9:1 hexanes/ethyl acetate) to give 68 mg (69%) of **5ae** as a yellow oil: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.23 (s, 9 H, $((\mathrm{CH_3})_3)$), 2.39 (s, 3 H, Ar-CH_3), 6.38 (d, 1 H, J = 11.7 Hz, =CH), 6.77 (d, 1 H, J = 11.7 Hz, =CH), 7.31 (d, 2 H, J = 8.0 Hz, ArH), 7.84 (d, 2 H, J = 8.3 Hz, ArH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$) δ 21.58 ($C\mathrm{H_3Ar}$), 26.50 ($\mathrm{C}(C\mathrm{H_3})_3$), 44.07 ($C(\mathrm{CH_3})_3$), 128.37, 129.82, 133.89 (=CH), 136.34, 139.27 (=CH), 144.92, 208.51 (C=O); IR (film) ν 1698 (C=O), 1317, 1148 ($\mathrm{SO_2}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{14}H_{18}SO_3}$: C, 63.13; H, 6.81. Found: C, 62.94; H, 6.59.

4-Oxo-1-(*p*-tolylsulfonyl)-1-butene (5be). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (125 mg, 0.5 mmol) and tosylmethylenephenylphosphorane (**2e**) (237 mg, 0.55 mmol) were subjected to photolysis procedure A (9.5 h) followed by hydrolysis procedure A (11 h). The crude material was purified by flash chromatography ($\mathrm{SiO_2}$, 2:1 hexanes/ethyl acetate) to give 62 mg (55%) of **5be** as a yellow oil: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 2.40 (s, 3 H, ArCH_3), 2.47 (s, 3 H, $\mathrm{CH_3}$), 6.33 (d, 1 H, J = 11.6 Hz, =CH), 6.54 (d, 1 H, J = 11.6 Hz, =CH), 7.32 (d, 2 H, J = 8.4 Hz, ArH), 7.77 (d, 2 H, J = 8.3 Hz, ArH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$) δ 21.60 (Ar$C\mathrm{H_3}$), 30.87 ($\mathrm{CH_3}$), 128.11 (Ar), 129.99 (Ar), 132.35 (=CH), 136.25 (Ar ipso), 140.92 (=CH), 145.19 (Ar ipso), 200.41 (C=O); IR (film) ν 1707 (C=O), 1595 (C=C), 1304, 1144 ($\mathrm{SO_2}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{11}H_{12}SO_3}$: C, 58.91; H, 5.39. Found: C, 58.96; H, 5.46.

3-Cyclopropyl-3-oxo-1-(tolylsulfonyl)-1-propene (5ee). [(Methoxy)(cyclopropyl)carbene]pentacarbonylchromium(0) (**1e**) (138 mg, 0.5 mmol) and tosylmethylenetriphenylphosphorane (**2e**) (237 mg, 0.55 mmol) were subjected to photolysis procedure A (15.5 h) followed by hydrolysis procedure A (4 h). The crude material was purified by radial chromatography (1 mm $\mathrm{SiO_2}$, 2:1 hexanes/ ethyl acetate) to give 72 mg (58%) of **5ee** as a yellow oil: ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ 1.14 (m, 2 H, $\mathrm{CH_2}$), 1.30 (m, 2 H, $\mathrm{CH_2}$), 2.20 (m, 1 H, CH), 2.44 (s, 3 H, $\mathrm{ArCH_3}$), 6.42 (d, 1 H, J = 11.7 Hz, =CH), 6.66 (d, 1 H, J = 11.7 Hz, =CH), 7.35 (d, 2 H, J = 8.1 Hz, ArH), 7.83 (d, 2 H, J = 8.3 Hz, ArH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$) δ 12.63 ($\mathrm{CH_2}$), 21.60 (Ar$C\mathrm{H_3}$), 22.38 (CH), 128.19, 129.91 (Ar), 133.10 (=CH), 136.47 (Ar ipso), 140.39 (=CH), 145.05 (Ar ipso), 202.51 (C=O); IR (film) ν 1686 (C=O), 1316, 1148 ($\mathrm{SO_2}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{13}H_{14}SO_3}$: C, 62.38; H, 5.64. Found: C, 62.42; H, 5.67.

3-Oxo-1-(tolylsulfonyl)-1-undecene (5ge). [(Methoxy)(octyl)carbene]pentacarbonylchromium(0) (**1g**) (174 mg, 0.5 mmol) and tosylmethylenephenylphosphorane (**2e**) (228 mg, 0.53 mmol) were subjected to photolysis procedure A (16 h) followed by hydrolysis procedure A (22 h). The crude material was purified by radial chromatography (2 mm $\mathrm{SiO_2}$, 5:1 hexanes/ethyl acetate) to give 96 mg (60%) of **5ge** as a yellow oil: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.85 (t, 3 H, J = 6.7 Hz, $\mathrm{CH_2C}H_3$), 1.24 (m, 10 H, $-(\mathrm{CH_2})_5-$), 1.7 (m, 2 H, $\mathrm{CH_2}$), 2.41 (s, 3 H, ArCH_3), 2.73 (t, 2 H, J = 7.5 Hz, $\mathrm{CH_2}$), 6.33 (d, 1 H, J = 11.8 Hz, =CH), 6.55 (d, 1 H, J = 11.7 Hz, =CH), 7.33 (d, 2 H, J = 8.4 Hz, ArH), 7.79 (d, 2 H, J = 8.3 Hz, ArH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$) δ 14.06 ($\mathrm{CH_2}C\mathrm{H_3}$), 21.65 (Ar$C\mathrm{H_3}$), 22.61, 23.02, 29.01, 29.08, 29.34, 31.79, 43.55 ($\mathrm{CH_2}$), 128.22, 129.98 (Ar), 132.57 (=CH), 136.35 (Ar), 141.04 (=CH), 145.12 (Ar), 203.03 (C=O); IR (film) ν 1706 (C=O), 1318, 1149 ($\mathrm{SO_2}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{18}H_{26}SO_3}$: C, 67.05; H, 8.13. Found: C, 66.80; H, 8.00.

Ethyl (*Z*)-5-Dimethyl-2-methyl-4-oxo-2-hexenoate (5af). [(Ethoxy)(*tert*-butyl)carbene]pentacarbonylchromium(0) (**1a**) (0.306 g, 1.0 mmol) and (carbethoxy)(methyl)methylenetriphenylphosphorane (**2f**) (0.398 g, 1.1 mmol) were subjected to photolysis procedure A (13 h) and hydrolysis procedure A (0.5 h). Purification by radial chromatography (2 mm $\mathrm{SiO_2}$, pentane followed by 10% $\mathrm{Et_2O}$/pentane, R_f 0.32 in 3:1 hexane/$\mathrm{Et_2O}$) gave 0.090 g (0.46 mmol, 46%) of **5af** as a colorless oil: ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ 1.16 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.30 (t, 3 H, J = 7.6 Hz, $\mathrm{C}H_3\mathrm{CH_2O}$), 2.05 (d, 3 H, J = 1.1 Hz, =$\mathrm{CCH_3}$), 4.26 (q, 2 H, J = 7.6 Hz, $\mathrm{OC}H_2$), 6.43 (br s, 1 H, =CH); ^{13}C NMR (67 MHz, $\mathrm{CDCl_3}$) δ 13.81 ($\mathrm{CH_3}$), 20.39 ($\mathrm{CH_3}$), 26.10 ($\mathrm{CH_3}$), 43.06 ($C(\mathrm{CH_3})_3$), 61.05 ($\mathrm{OCH_2}$), 126.29 (=C), 142.44 (=C), 169.33 (CO), 204.70 (CO). The NOE experiment of **5gf** revealed a 5.25% enhancement of the allylic methyl signal when the vinyl proton was irradiated. The reverse experiment revealed a 2.84% enhancement of the vinyl proton signal: IR (film) ν 1731 (CO), 1690 (CO), 1624 (C=C) cm^{-1}; MS (EI) m/e 198 (M). Anal. Calcd for $\mathrm{C_{11}H_{18}O_3}$: C, 66.64; H, 9.15. Found: C, 66.42; H, 8.98.

Fluorene Derivative (5bg). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.250 g, 1.0 mmol) and fluorenylidenetriphenylphosphorane (**2g**) (0.426 g, 1.0 mmol) were subjected to photolysis procedure A ($\mathrm{CH_2Cl_2}$ substituted for benzene, no hydroquinone, 22 h) followed by hydrolysis procedure A (3 h). Purification by radial chromatography (2 mm $\mathrm{SiO_2}$, 1% $\mathrm{Et_2O}$/hexane, R_f 0.34 in 10% $\mathrm{Et_2O}$/hexane) gave 0.036 g (0.16 mmol, 16%) of **5bg** as a yellow solid. Recrystallization from hexanes/$\mathrm{Et_2O}$ gave an analytically pure sample as yellow needles: mp 99–100 °C; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ 2.47 (s, 3 H, $\mathrm{CH_3}$), 7.04 (s, 1 H, =CH), 7.2–7.5 (m, 4 H, ArH), 7.67 (m, 3 H, ArH), 8.77 (d, 1 H, J = 7.6 Hz, 1 H, ArH); IR (film) ν 1682 (CO), 1618, 1590 cm^{-1}; MS (EI) m/e 200 (M), 221 (M + 1). Anal. Calcd for $\mathrm{C_{16}H_{12}O}$: C, 87.25; H, 5.49. Found: C, 87.35; H, 5.58.

(*Z*)-2-(1-(2-Oxo)propylidene)-γ-butyrolactone (5bh). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (250 mg, 1 mmol) and γ-butyrolactone-2-triphenylphosphorane (**2h**) (381 mg, 1.1 mmol) were subjected to photolysis procedure A (23.5 h) followed by hydrolysis procedure A (3 h). The crude material was purified by radial chromatography (2 mm $\mathrm{SiO_2}$, 2:1 hexanes/ethyl acetate) to give 32 mg (25%) of **5bh** as a colorless solid: ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ 2.34 (s, 3 H, CH_3), 3.30 (dt, 2 H, J = 3.3, 7.0 Hz, $\mathrm{C}H_2\mathrm{C}$=), 4.43 (t, 2 H, J = 7.1 Hz, $\mathrm{C}H_2\mathrm{O}$), 7.04 (t, 1 H, J = 3.2 Hz, =CH); ^{13}C NMR (67.5 MHz, $\mathrm{CDCl_3}$) δ 28.09 ($C\mathrm{H_2C}$=), 31.69 ($\mathrm{CH_3}$), 66.51 ($\mathrm{CH_2O}$), 128.5 (=CH), 138.78 (=CH), 170.74 (OC(O)), 197.92 (C=O); IR (film) ν 1747, 1698 (C=O), 1643 (C=C) cm^{-1}. Anal. Calcd for $\mathrm{C_7H_8O_3}$: C, 60.00; H, 5.75. Found: C, 59.89; H, 5.78.

[((*E*)-2-Carbomethoxyethenyl)(2-methoxypropionyl)]methylenetriphenylphosphorane (6). [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.250 g, 1.0 mmol) and (3-carbomethoxy-2-propenylyliden)triphenylphosphorane (**2i**) (0.360 g, 1.0 mmol) were subjected to photolysis procedure A. The crude material was purified by radial chromatography (2 mm $\mathrm{SiO_2}$, 10:1 hexanes/ethyl acetate) followed by silica gel flash chromatography (100:3 $\mathrm{CH_2Cl_2}$/MeOH) to yield 0.107 g of **6** (0.24 mmol, 24%) as a pale yellow solid: mp 69–70 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.36 (d, 3 H, J = 6.5 Hz, $-\mathrm{CHC}H_3$), 3.34 (s, 3 H, $\mathrm{OCH_3}$), 3.60 (s, 3 H, $\mathrm{CO_2CH_3}$), 4.93 (q, 1 H, J = 6.5 Hz, $\mathrm{C}H\mathrm{CH_3}$), 7.02 (br s, 1 H, =CH), 7.5–7.8 (m, 16 H, =CH, PhH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, J_{PC} in parentheses) δ 19.12 ($\mathrm{CH_3}$), 49.95 ($\mathrm{OCH_3}$), 56.98 ($\mathrm{CO_2}C\mathrm{H_3}$), 73.27 (101.1 Hz, C=P), 79.64 (CH), 101.87 (15.9 Hz, =CH), 123.52 (89.7 Hz), 129.44 (12.4 Hz), 133.42, 133.55, 155.07 (9.7 Hz, =CH), 169.62 (C=O), 196.65 (C=O); IR (film) ν 1660 (CO), 1598 cm^{-1}; MS ($\mathrm{NH_3CI}$) m/e 447 (M + 1). Anal. Calcd for $\mathrm{C_{22}H_{27}O_4P}$: C, 72.63; H, 6.10; P, 6.94. Found: C, 72.41; H, 6.26; P, 6.97.

[(2-(*N*-Carbonyl(*tert*-butyloxy)amino)propionyl)(benzyloxycarbonyl)]methylentriphenylphosphorane (7a). [(*N*-Carbonyl(*tert*-butyloxy)amino)(methyl)carbene]pentacarbonylchromium(0) (**1L**) (0.323 g, 1.0 mmol) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.410 g, 1.0 mmol) were subjected to photolysis procedure A ($\mathrm{CH_2Cl_2}$ substituted for benzene, no hydroquinone, 18 h). Purification of the crude material by column chromatography ($\mathrm{SiO_2}$, 2:1 hexanes/ethyl acetate, R_f 0.38 with 1:1 hexanes/ethyl acetate) gave 0.352 g (0.61 mmol, 61%) of **7a** as a white solid. An analytical sample was obtained upon recrystallization from petroleum ehter/ethyl acetate: mp 134–135 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.39 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.43 (d, 3 H, J = 6.4 Hz, $\mathrm{CH_3}$), 4.59 (d, 1 H, J = 12.1 Hz, $\mathrm{OCH}H\mathrm{Ph}$), 4.71 (d, 1 H, J = 12.1 Hz, $\mathrm{CO_2C}H\mathrm{HPh}$), 5.48 (m, 2 H, N$H$, $-\mathrm{C}H\mathrm{CH_3}$), 6.90 (m, 2 H, ArH), 7.18 (m, 3 H, ArH), 7.4 (m, 6 H, ArH), 7.58 (d, 2 H, J = 12.6 Hz, ArH), 7.61 (d, 2 H, J = 12.7 Hz, ArH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, J_{PC} in parentheses) δ 20.14 ($\mathrm{CH_3}$), 28.32 ($\mathrm{C}(C\mathrm{H_3})_3$), 52.00 (8.3 Hz, CH), 64.71 ($\mathrm{CH_2O}$), 68.42 (110.7 Hz, C=P), 78.12 ($C(\mathrm{CH_3})_3$), 125.93 (93.4 Hz), 127.40, 128.11, (21.4 Hz), 128.33, 128.49, 131.62 (1.5 Hz), 132.81 (9.9 Hz), 136.47, 155.16, 166.35 (14.3 Hz, CO), 195.57 (CO); IR (film) ν 1709 (CO), 1669 (CO), 1563 cm^{-1}; MS ($\mathrm{NH_3CI}$) m/e 583 (M + 1). Anal. Calcd for $\mathrm{C_{35}H_{36}NO_5P}$: C, 72.27; H, 6.24; P, 5.33. Found: C, 72.49; H, 6.31; P, 5.47.

[(2-(*N*-Carbonyl(*tert*-butyloxy)amino)propionyl)(carbomethoxy)methylenetriphenylphosphorane (7b). [(*N*-Carbonyl(*tert*-butyloxy)amino)(methyl)carbene]pentacarbonylchromium(0) (**1L**) (0.323 g, 1.0 mmol) and (carbomethoxy)methylenetriphenylphosphorane (**2b**) (0.334 g, 1.0 mmol) were subjected to photolysis procedure A ($\mathrm{CH_2Cl_2}$ substituted for benzene, no hydroquinone, 13.5 h). The crude material was purified by column chromatography ($\mathrm{SiO_2}$, 2:1 hexanes/ethyl acetate, R_f 0.34) to yield 0.335 g of (**7b**). Recrystallization from petroleum ether/ethyl acetate gave an analytically pure sample as white prisms: mp 169–170 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.30 (s, 9 H, $\mathrm{C(CH_3)_3}$, 1.34 (d, 3 H, J = 6.5 Hz, $-\mathrm{CH_3}$), 3.14 (s, 3 H, $\mathrm{OCH_3}$), 5.30 (m, 1 H, $\mathrm{C}H\mathrm{CH_3}$), 5.38 (m, 1 H, NH), 7.36–7.61 (m, 15 H, PhH); ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, J_{PC} in parentheses) δ 20.02 ($\mathrm{CH_3}$), 28.27 ($\mathrm{C}(C\mathrm{H_3})_3$), 49.64 ($\mathrm{OCH_3}$), 51.87 (8.3 Hz, $C\mathrm{H(CH_3)}$), 68.94 (108.0 Hz, C=P), 78.17 ($C(\mathrm{CH_3})_3$), 125.83 (93.7 Hz), 128.38 (12.6 Hz), 131.66 (1.6 Hz), 132.95 (9.7 Hz), 155.16 (CO), 166.91 (15.5 Hz, CO), 195.22 (CO); IR (film) ν 1707 (CO), 1672 (CO), 1560 cm^{-1}; MS ($\mathrm{NH_3CI}$) m/e 506 (M + 1), 505 (M). Anal. Calcd for $\mathrm{C_{29}H_{32}NO_5P}$: C, 68.90; H, 6.38; N, 2.77. Found: C, 68.90; H, 6.32; N, 2.80.

Cyclic Carbamate 8. [(*N*-Carbonyl(*tert*-butyloxy)amino)(methyl)carbene]pentacarbonylchromium(0) (**1L**) (0.323 g, 1.0 mmol) and (carbethoxy)(methyl)methylenetriphenylphosphorane (**2f**) (0.398 g, 1.1 mmol) were subjected to photolysis procedure A followed by the allene isomerization procedure. Purification of the crude material by flash chromatography (SiO_2, 3:1 hexanes/ethyl acetate, R_f 0.20) yielded 0.113 g of **8** as a clear oil which solidified upon standing: mp 81.5–82.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, 3 H, $J = 7.1$ Hz, OCH_2CH_3), 1.49 (d, 3 H, $J = 6.3$ Hz, $-CHCH_3$), 1.91 (d, 3 H, $J = 1.2$ Hz, $=CCH_3$), 4.22 (q, 2 H, $J = 7.1$ Hz, OCH_2), 5.05 (q, 1 H, $J = 6.3$ Hz, $-CHCH_3$), 6.97 (br s, 1 H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.49 (CH_3), 14.04 (CH_3), 20.62 (CH_3), 53.34 (CH), 60.48 (CH_2), 104.08 (=C), 155.13 (=C), 161.74 (CO), 166.78 (CO); IR (film) ν 3323 (br, NH), 1796 (CO), 1708 (CO), 1662 (C=C) cm^{-1}; MS (EI) *m/e* 199 (M). Anal. Calcd for $C_9H_{13}NO_4$: C, 54.27; H, 6.58; N, 7.03. Found: C, 54.46; H, 6.66; N, 7.03.

[(Carbomethoxy)(2-methoxypropionyl)]methylenetriphenylphosphorane (9). To a solution of (carbomethoxy)methylenetriphenylphosphorane (**2b**) (0.444 g, 1.33 mmol) and triethylamine (0.135 g, 1.33 mmol) in CH_2Cl_2 (6.7 mL) was added 2-methoxypropionyl chloride (0.163 g, 1.33 mmol) as a solution in CH_2Cl_2 (1 mL). After 3 h of stirring at room temperature, the solvent was removed under reduced pressure. The residual solid was purified by silica gel column chromatography (EtOAc, R_f 0.10 with 1:1 hexanes/ethyl acetate) to yield 0.547 g of **9** (0.547 mmol, 98%) as a white solid. An analytically pure sample was obtained upon crystallization from hot ethyl acetate/petroleum ether: mp 184.5–185 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.45 (d, 3 H, $J = 6.5$ Hz, CH_3), 3.14 (s, 3 H, OCH_3), 3.24 (s, 3 H, CO_2CH_3), 5.02 (q, 1 H, $J = 6.5$ Hz, $-CHCH_3$), 7.4–7.8 (m, 15 H, ArH); ^{13}C NMR (67.9 MHz, $CDCl_3$, J_{PC} in parentheses) δ 18.01 (CH_3), 49.27 (OCH_3), 56.65 (OCH_3), 70.07 (109.2 Hz, C=P), 78.51 (8.5 Hz, CH), 126.25 (93.6 Hz), 128.16 (12.5 Hz), 131.51, 132.99, (10.5 Hz), 167.39 (15.2 Hz, CO), 196.23 (CO); IR (film) ν 1660 (br, CO), 1565 cm^{-1}; MS (NH_3CI) *m/e* 421 (M + 1). Anal. Calcd for $C_{25}H_{25}O_4P$: C, 71.42; H, 5.99; P, 7.37. Found: C, 71.31; H, 5.97; P, 7.29.

Dodec-2-enoic Acid γ-Lactone (11). Procedure A. To a solution of methyl (*Z*)-4-oxo-2-dodecanoate (**5gb**) (0.239 g, 1.06 mmol) in THF (0.270 mL) under argon at 0 °C was added 9-BBN (2.22 mL of a 0.5 M solution in THF) dropwise over 15 min. The reaction mixture was allowed to stir for 3 h at 0 °C and then was warmed to room temperature over 1 h. A few drops of methanol was added to quench the remaining 9-BBN, and the solvent was removed under reduced pressure. The residue was taken up in Et_2O (5 mL) and diethanolamine (0.203 mL, 2.2 mmol) was added. The mixture was allowed to stir for 12 h and was then filtered through Celite. The filtrate was washed with 5% aqueous HCl solution, saturated NaCl solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (SiO_2, 9:1 hexanes/ethyl acetate, R_f 0.29 in 3:1 hexanes/ethyl acetate) to yield 0.138 g (0.70 mmol, 66%) of butenolide **11** as a colorless oil. The physical data were identical to those reported in the literature.[18]

Procedure B. A degassed solution of keto ester **5gb** (0.313 g, 1.38 mmol) in THF (75 mL) was added to a solution of (−)-B-chlorodiisopinocamphenylborane (0.497 g, 1.55 mmol) in THF (25 mL) precooled to −15 °C. After 4 h, the reaction mixture was allowed to warm to room temperature, and the solvent was removed under reduced pressure (1 mmHg for 2 h). The crude oily material was taken up in Et_2O (5 mL), and diethanolamine (0.263 g, 2.5 mmol) was added. After 1.5 h, the white ppt was removed by filtration through Celite, and the ether solution was washed with water (30 mL) and brine (30 mL) and dried over $MgSO_4$. The crude material was purified by flash chromatography (SiO_2, 10:1 hexanes/ethyl acetate) to yield 0.143 g (0.173 mmol, 53%) of butenolide **11** as a colorless oil. ^1H NMR chiral shift reagent study with $Eu(hfc)_3$ (60 mol %) revealed a 28% ee.

Procedure C. A 0.5 M solution of the chiral *n*-butyloxazaborolidine in toluene was prepared according to the published procedure.[39] The keto ester **5gb** (0.113 g, 0.50 mmol) in 2 mL of toluene and 0.10 mmol (200 mL) of the oxazaborolidine solution were cooled to −78 °C, and catecholborane (0.75 mL of a 1.0 M solution in toluene) was added over 10 min. After 18 h at −78 °C, water (2 mL) was added to the reaction, and the mixture was allowed to warm to room temperature. One hour later, the reaction mixture was diluted with toluene (10 mL), transferred to a separatory funnel, and washed with 1 N NaOH (2 × 10 mL), 5% HCl solution (2 × 10 mL), saturated NaCl solution, and then dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was taken up in Et_2O (25 mL) with *p*-toluenesulfonic acid (10 mg, 0.10 mol %) and was allowed to stir overnight. The Et_2O was washed with saturated $NaHCO_3$ and saturated NaCl solutions, dried over $MgSO_4$, and filtered. The Et_2O was removed under reduced pressure to give a quantitative yield of butenolide **11**. A ^1H NMR chiral shift reagent study with $Eu(hfc)_3$ (60 mol %) revealed a 41% ee.

The same reduction was performed on keto ester (**5gc**) to give the butenolide **11** in quantitative yield. A ^1H NMR chiral shift reagent study with $Eu(hfc)_3$ (60 mol %) revealed a 60% ee.

3-Hydroxy-1-(*p*-tolylsulfonyl)-1-undecene (13). The keto sulfone (**5ge**) (48 mg, 0.15 mmol) was reduced via procedure C (CBS). The crude material was purified by radial chromatography (1 mm SiO_2, 4:1 hexane/diethyl ether) to give 32 mg (66%) of the allylic alcohol **13** as a yellow oil: ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, 3 H, $J = 6.7$ Hz, CH_2CH_3), 1.1–1.7 (m, 15 H, $(CH_2)_7$ and OH), 2.42 (s, 3 H, $ArCH_3$), 5.1–5.2 (m, 1 H, *H*COH), 6.19 (dd, 1 H, $J = 11.4$, 7.7 Hz, =CH), 6.25 (d, 1 H, $J = 11.4$ Hz, =CH), 7.33 (d, 2 H, $J = 8.4$ Hz, ArH), 7.78 (d, 2 H, $J = 8.2$ Hz, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.08 (CH_3), 21.61 ($ArCH_3$), 22.62, 25.02, 29.19, 29.40, 29.45, 31.83, 36.55 (CH_2), 66.32 (*C*OH), 127.43, 129.99 (Ar*C*), 130.55 (=*C*H), 137.93, 144.75 (ArC), 147.63 (=*C*H); IR (film) 3482 (OH), 1302, 1146 (SO_2) cm^{-1}. Anal. Calcd for $C_{18}H_{28}SO_3$: C, 66.63; H, 8.70. Found: C, 66.45; H, 8.90. The preparation of the Mosher's ester was identical to that previously reported.[47] The ^1H NMR spectrum in $CDCl_3$ (300 MHz) focused on one of the vinylic protons (dd) at 5.9–6.1 ppm. Integration of the peaks revealed a 62% ee.

Benzyl 3-Methoxy-2-butenoate. [(Methoxy)(methyl)carbene]pentacarbonylchromium(0) (**1b**) (0.5 mmol, 125 mg) and (benzyloxycarbonyl)methylenetriphenylphosphorane (**2a**) (0.5 mmol, 205 mg) were subjected to photolysis procedure A (4 mL of THF, no CO). The crude material was taken up 25 mL of EtOAc/25 mL of hexanes and oxidized (sunlight) for 3 h followed by hydrolysis procedure A (0.5 h). The solution was filtered and concentrated to give a yellow oil. The crude material was purified by radial chromatography (1 mm SiO_2, 1:1 hexane/ether) to give 3-methoxy-2-butenoate (20 mg, 20%) as a colorless oil: ^1H NMR (270 MHz, $CDCl_3$) δ 2.02 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 4.97 (s, 1 H, =CH), 5.11 (s, 2 H, CH_2Ph), 7.2–7.5 (m, 5 H, PhH).

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Registry No. 1 (R = Me; R′ = $(CH_2)_3Br$), 139915-37-0; **1a**, 117041-04-0; **1b**, 20540-69-6; **1c**, 99038-42-3; **1d**, 117041-03-9; **1e**, 52149-50-5; **1f**, 27436-93-7; **1g**, 139915-38-1; **1h**, 103637-16-7; **1i**, 98703-36-7; **1j**, 139915-39-2; **1k**, 54040-22-1; **1l**, 122846-97-3; **2a**, 15097-38-8; **2b**, 2605-67-6; **2c**, 35000-38-5; **2d**, 1439-36-7; **2e**, 5554-81-4; **2f**, 5717-37-3; **2g**, 4756-25-6; **2h**, 34932-07-5; **2i**, 65866-00-4; **3aa**, 139915-05-2; **3ae**, 139915-06-3; **3ba**, 139915-07-4; **3bb**, 139915-08-5; **3be**, 139915-09-6; **3da**, 139915-10-9; **3fb**, 139915-11-0; **4ba**, 139915-12-1; (*Z*,*Z*)-**4ca**, 139915-13-2; (*E*,*Z*)-**4ca**, 139915-14-3; **4da**, 139915-15-4; **4ia**, 139915-16-5; (*Z*,*Z*)-**4ka**, 139915-17-6; (*E*,*Z*)-**4ka**, 139915-18-7; **5aa**, 139915-19-8; **5ae**, 139915-20-1; **5af**, 139943-01-4; **5ba**, 139915-21-2; **5be**, 88726-08-3; **5bg**, 83759-76-6; **5bh**, 139915-22-3; **5ca**, 139915-23-4; **5ea**, 139915-24-5; **5ee**, 139915-25-6; **5fb**, 19522-28-2; **5gb**, 139915-26-7; **5gc**, 139915-27-8; **5gd**, 139915-28-9; **5ge**, 139915-29-0; **5ha**, 139915-30-3; **6**, 139915-31-4; **7a**, 139915-32-5; **7b**, 139915-33-6; **8**, 139915-34-7; **9**, 139915-35-8; **11**, 58949-91-0; **12**, 64838-72-8; **13**, 139915-36-9; $K_2Cr(CO)_5$, 107799-34-8; $HO(CH_2)_3Br$, 627-18-9; *t*-$BuOCONH_2$, 4248-19-5; $Cr(CO)_6$, 13007-92-6; pivaloyl chloride, 3282-30-2; [(methyl)[(tetramethylammonio)oxy]carbene]pentacarbonylchromium(0), 139915-41-6; *n*-octyllithium, 3314-49-6; allyl bromide, 106-95-6; *tert*-butyldimethylsilyl chloride, 18162-48-6; 2-methoxypropionyl chloride, 56680-75-2.