Addition of Zinc Homoenolates to Acetylenic Esters and Amides: A Formal [3 + 2] Cycloaddition

Michael T. Crimmins,* Philippe G. Nantermet, B. Wesley Trotter, Isabelle M. Vallin, Paul S. Watson, Lynne A. McKerlie, Tracy L. Reinhold, Adrian Wai-Hing Cheung, Katherine A. Stetson, Dimitra Dedopoulou, and Jeffrey L. Gray

Department of Chemistry, The Venable and Kenan Laboratories, University of North Carolina, Chapel Hill, North Carolina 27599-3290

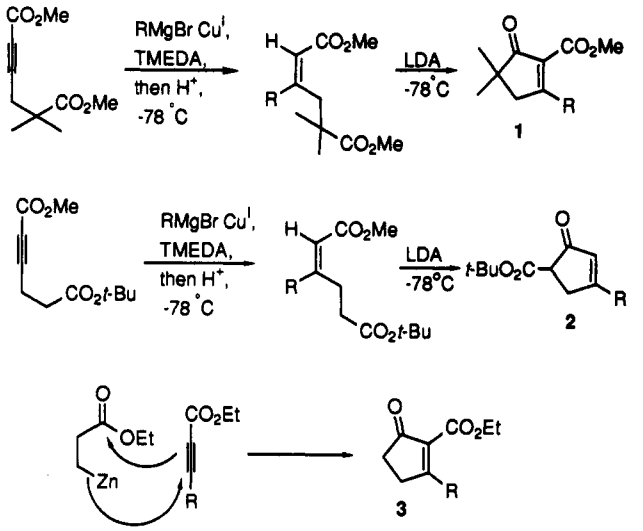
Received August 25, 1992

The copper-catalyzed conjugate addition–cycloacylation reaction of zinc homoenolates with acetylenic esters or acetylenic amides is described. The zinc homoenolate is prepared from [(ethoxycyclopropyl)-oxy]trimethylsilane and zinc chloride in ether. Addition of an acetylenic amide or ester provides 2-carboxamido- or 2-carboalkoxy-3-alkylcyclopent-2-en-1-ones in good to excellent yields. The reaction can be carried out in the presence of a variety of sensitive functional groups including epoxides, α,β-unsaturated esters, acetals, silyl ethers, and furans.

Introduction

While numerous useful methods are known for the synthesis of substituted cyclohexenones,[1] there are comparatively few general methods for the preparation of substituted cyclopentenones.[2] Most of these methods rely on the use of preformed five-membered rings. Highly substituted cyclopentenones have been widely utilized in radical cyclizations, [2 + 2] photocycloadditions,[3] and other reactions leading to the total synthesis of complex natural products. A general method for the synthesis of 3-substituted 4,4-dimethyl 2-carbomethoxycyclopentenones 1 was developed in our laboratories earlier[4] and utilized in the total synthesis of several natural products[5] through intramolecular [2 + 2] photocycloadditions. However, when this method was applied to unsubstituted acetylenic diesters, 5-carbethoxycyclopent-2-en-1-ones 2 were formed. Since a rapid entry into 2-carbethoxy-3-alkylcyclopentenones was required for other ongoing projects, various protocols for their preparation were investigated. We recently reported a general method for the synthesis of such cyclopentenones using zinc homoenolates.[6] Since an ester homoenolate is formally a 1,3 nucleophile–electrophile tandem, these reagents have the potential for the formation of two carbon–carbon bonds in a single reaction as shown in Scheme I. This strategy was applied in the tandem copper-catalyzed conjugate addition–cyclization reaction of zinc homoenolates with

Scheme I



acetylenic esters resulting in the formation of 3-substituted 2-carbethoxycyclopentenones such as **3**. This new method has now been tested with numerous acetylenic esters and acetylenic amides bearing a variety of sensitive electrophilic functional groups which remain intact after the reaction. The results of the studies which have been performed on this novel reaction are reported here.

Results

The starting acetylenic esters and amides were prepared according to methods previously described in the literature (Scheme II). Acetylenic esters and amides bearing an α-hydroxy substituted side chain (entries 1–8, 16–18, 20, 21, and 24 in Table I) were synthesized by an addition reaction between the the lithium acetylide of the propiolate

(1) Jung, M. E. *Tetrahedron* **1976**, *32*, 3. Taber, D. F.; Gunn, B. P.; Chiu, I. *Org. Synth.* **1983**, *61*, 59. Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979**, *4*, 3275. Pramod, K.; Ramanathan, H.; Rao, S. *J. Chem. Soc., Perkin Trans. 1* **1983**, 7. Corey, E. J.; Boger, D. *Tetrahedron Lett.* **1978**, *28*, 2461. Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. Stork, G.; Danheiser, R. *J. Org. Chem.* **1973**, *38*, 1775.

(2) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. Negishi, E.; Zhang, Y.; Cederbaum, F. E.; Webb, M. B. *J. Org. Chem.* **1986**, *51*, 4080. Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429. Burk, S. D.; Grieco, P. A. *Org. React.* **1979**, 361. Smith, A. B.; Dieter, R. K. *Tetrahedron* **1981**, *37*, 2407. Taber, D. F.; Amedio, J. C.; Sherill, R. G. *J. Org. Chem.* **1986**, *51*, 3382. Ho, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1149.

(3) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453. Crimmins, M. T.; Reinhold, T. L. *Org. React.*, in press.

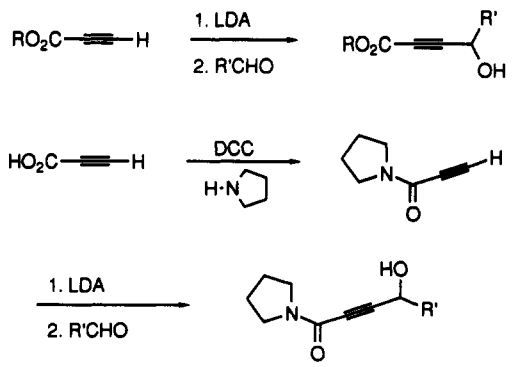
(4) Crimmins, M. T.; Marscarella, S. W.; DeLoach, J. A. *J. Org. Chem.* **1984**, *49*, 3033.

(5) Crimmins, M. T.; Marscarella, S. W. *J. Am. Chem. Soc.* **1986**, 3435. Crimmins, M. T.; Gould, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 6199. Crimmins, M. T.; DeLoach, J. A. *J. Am. Chem.* 4Soc. **1986**, *108*, 800. Crimmins, M. T.; DeLoach, J. A. *J. Org. Chem.* **1984**, *49*, 2077.

(6) Crimmins, M. T.; Nantermet, P. G. *J. Org. Chem.* **1990**, *55*, 4235. For a recent review on homoenolate chemistry, see: Kuwajima, I.; Nakamura, E. *Top. Curr. Chem.* **1990**, *155*, 1. For leading references in the application of functionalized organozinc reagents, see: Knochel, P.; Yeh, M. C. P.; Berk, S.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390. Yeh, M. C. P.; Knochel, P.; Santa, L. *Tetrahedron Lett.* **1988**, *29*, 3887. Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1989**, *30*, 4799. Chou, T.; Knochel, P. *J. Org. Chem.* **1990**, *55*, 4791 and 6232. Retherford, C.; Chou, T.; Schelkoun, R.; Knochel, P. *Tetrahedron Lett.* **1990**, *31*, 1833. Berk, S.; Yeh, M. C. P.; Nakcheol, J.; Knochel, P. *Organometallics* **1990**, *9*, 3053. Knoess, P.; Furlong, M.; Rozema, M.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 5974.

0022-3263/93/1958-1038$04.00/0

Scheme II



ester or amide[7] and the appropriate aldehyde.[8] Protection of the hydroxyl by known methods provided the methoxymethyl ether, trimethylsilyl ether, or acetate protected substrates represented in entries 1 and 2. Other acetylenic esters or amides were prepared by deprotonation of terminal alkynes and subsequent trapping of the acetylide with ethyl or methyl chloroformate (entries 9, 22, and 25). Quenching of the acetylide with carbon dioxide provides the corresponding acetylenic acids which can be converted to acetylenic amides and esters through coupling the desired alcohol or amine to the acid with dicyclohexyl carbodiimide[9] (entries 11 and 12) or through mixed anhydride[10] activation of the acid (entries 13–15). Use of the Corey–Fuchs method[11] (entry 19) also gives access to acetylenic esters and acids which lack the α-hydroxy substitution. Some acetylenic amides were obtained from the corresponding esters using the Weinreb method[12] (entries 10 and 23).

The zinc homoenolate 4 utilized in the reaction is prepared according to Nakamura's procedure[13] by ultrasonic irradiation of an ether solution of [(ethoxycyclopropyl)oxy]trimethylsilane and zinc chloride for 40 min. The resulting solution is cooled to 0 °C and stirred for 5 min. After addition of CuBr–Me_2S, a THF solution of the starting acetylenic ester or acetylenic amide followed by HMPA are added at once. The reaction mixture is warmed to room temperature and stirred until the starting material has been consumed. The reaction progress can easily be followed by thin-layer chromatography; reaction times of 4–6 h are typical. The resulting cyclopentenones are shown in Table I.

The early examples (entries 1–3) were performed using only 3% copper catalyst and required approximately 9 h at room temperature to reach completion. Initially, low yields (about 40%) were obtained with acetylenic esters bearing an unsubstituted alkyl chain such as entry 9. It was found that increasing the quantity of CuBr–Me_2S to 10–25% gave higher yields of cyclopentenones and reduced the reaction time to 6 h. This procedure also provided cyclopentenone **26** in 78% yield (71% with 3% CuBr–Me_2S). All the examples except entries 1–3 were carried out with at least 15% copper catalyst. Somewhat higher yields could be expected for entries 1–3 with higher catalyst ratios.

Acetylenic esters bearing free hydroxyl groups can be directly utilized in the reaction to give cyclopentenones with the hydroxyl group protected as the trimethyl silyl ether, although 4.2 equiv (twice the normal quantity) of zinc homoenolate must be employed. Acetylenic esters with MOM-protected hydroxyls gave similar results, but acetates (entries 1 and 2) gave somewhat lower yields due to selectivity problems (vide infra).

It is important to note that higher yields are obtained when an acetylenic amide is used instead of the corresponding acetylenic ester. This is illustrated by entries 6, 8, 21, and 23 and appears to be general. The amide analog is especially useful for substrates bearing nonsubstituted alkyl chains, which typically give lower yields than substrates bearing α-hydroxy-substituted alkyl chains. For example, acetylenic esters from entries 4, 16, and 17 give higher yields than the corresponding unsubstituted acetylenic esters from entries 11 and 12. However, use of the unsubstituted acetylenic amide (entry 13) gave the corresponding cyclopentenone in 80% yield. Compare also entries 9 to 10 and 11 to 13.

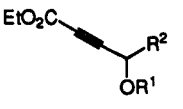
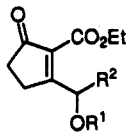
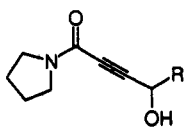
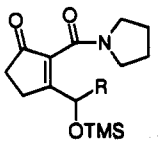
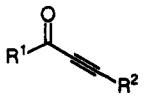
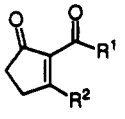
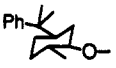
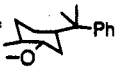
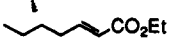
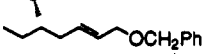
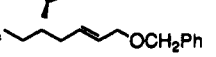
This reaction has been performed successfully on acetylenic esters and amides bearing somewhat sensitive functional groups. As shown with entries 14 and 17, α,β-unsaturated esters, furans (entries 5, 20, 21, and 24), and epoxides also remain intact (entries 22–24).

Discussion

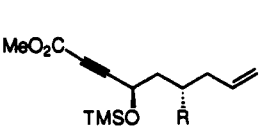
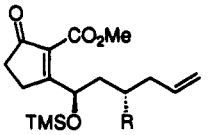
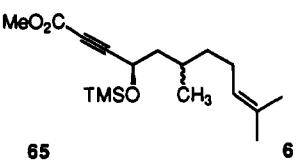
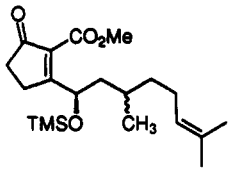
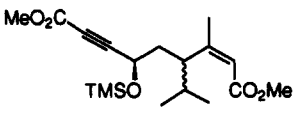
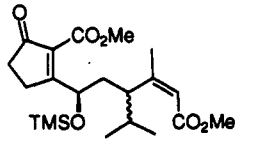
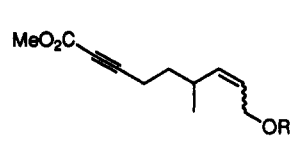
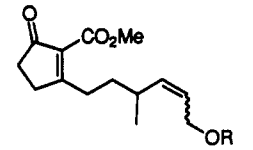
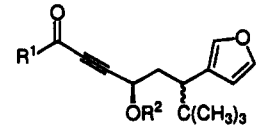
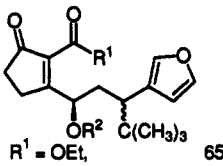
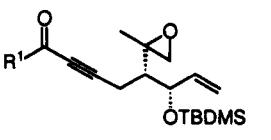
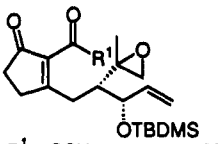
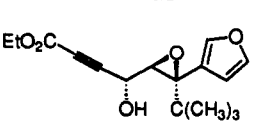
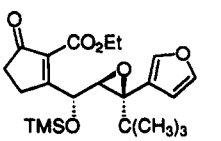
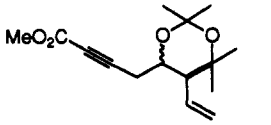
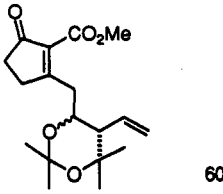
The following mechanistic interpretation is proposed to account for the results. The first step of the reaction is a conjugate addition of a zinc/copper homoenolate to the acetylenic ester or amide to generate the allenolate **5**, although the intermediacy of a vinylcopper species cannot be excluded and may also be involved. The allenolate **5** is trapped by trimethylsilyl chloride generated in situ during the formation of the zinc homoenolate to form the silyl ketene acetal **6**. Allenolates have been implicated in a variety of copper-catalyzed additions to acetylenes.[14] Klein and Levine[15] reported infrared data to support the presence of an allenolate, and Marino and Linderman[16] have trapped an allenolate as the trimethylsilyl ether (no C-silylation was observed) in the presence of HMPA. In the presence of a proton source such as trace water the silyl ketene acetal **6** is converted to the corresponding alkenes **7**. Such alkenes are always isolated in variable quantities as byproducts of the reaction and tend to be more a problem when the reaction is conducted on small quantities of material. There may also be some protonation of the intermediate by the acidic γ-proton of the product. The intermediate **6** can also undergo intramolecular acylation to produce the cyclopentenone **3** (Scheme III). This step may be assisted by Lewis acid catalysis from the zinc salts in the reaction.

(7) Banner, C. B.; Pandit, U. K. *Tetrahedron* **1982**, *38*, 3597.
(8) Midland, M. M.; Tramontano, A.; Cable, J. R. *J. Org. Chem.* **1980**, *45*, 28. Carlson, R. M.; Peterson, J. R.; Hoop, B. J.; Jensen, K. J. *Synth. Commun.* **1982**, *12*, 977. Hirama, M.; Shigemoto, T.; Ito, S. *J. Org. Chem.* **1987**, *52*, 3342.
(9) Mikolajczyk, M.; Kielbasinski, P. *Tetrahedron* **1981**, *37*, 233. Williams, A.; Ibrahim, I. T. *Chem. Rev.* **1981**, *81*, 589.
(10) Porter, N. A.; Scott, D. M.; Rosenstein, I. J.; Giese, B.; Viet, A.; Zeitz, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 1791.
(11) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *36*, 3769.
(12) Weinreb, S. M.; Lipton, M.; Basha, A. *Tetrahedron Lett.* **1977**, *48*, 4171. Weinreb, S. M.; Basha, A.; Lipton, M. *Org. Synth.* **1979**, *59*, 49. Weinreb, S. M.; Turos, E.; Levin, J. I. *Synth. Commun.* **1982**, *12*, 989.
(13) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. Nakamura, E.; Aoki, S.; Sekia, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056.
(14) Corey, E. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 1851. Siddall, J. B.; Biskup, M.; Fried, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1853. Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4623.
(15) Klein, J.; Levine, R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1971.
(16) Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1981**, *46*, 3696.

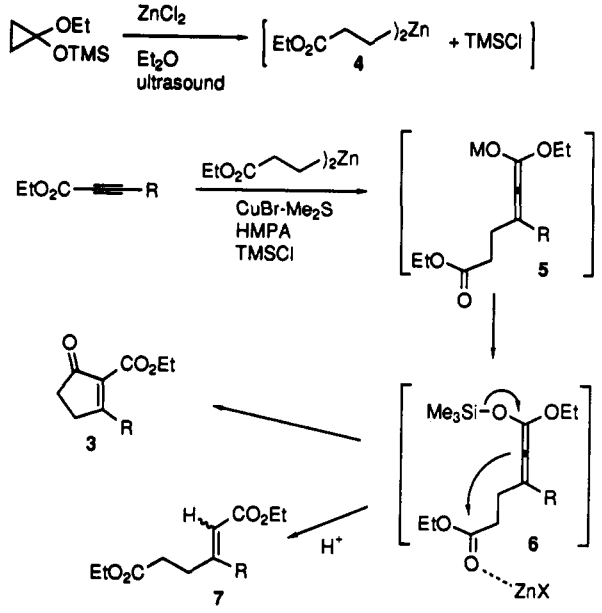
Table I

	entry	substrate	product, (no.), yield
			
1	**23**	R^1 = MOM, R^2 = $(CH_2)_4CH_3$	**26** R^1 = MOM, R^2 = $(CH_2)_4CH_3$ 78%
	24	R^1 = Ac, R^2 = $(CH_2)_4CH_3$	**27** R^1 = Ac, R^2 = $(CH_2)_4CH_3$ 50%
	25	R^1 = H, R^2 = $(CH_2)_4CH_3$	**28** R^1 = TMS, R^2 = $(CH_2)_4CH_3$ 70%
2	**29**	R^1 = MOM, R^2 = $CH(CH_3)_2$	**32** R^1 = MOM, R^2 = $CH(CH_3)_2$ 72%
	30	R^1 = Ac, R^2 = $CH(CH_3)_2$	**33** R^1 = Ac, R^2 = $CH(CH_3)_2$ 49%
	31	R^1 = H, R^2 = $CH(CH_3)_2$	**34** R^1 = TMS, R^2 = $CH(CH_3)_2$ 70%
3	**35**	R^1 = H, R^2 = $(CH_2)_2Ph$	**36** R^1 = TMS, R^2 = $(CH_2)_2Ph$ 65%
4	**37**	R^1 = H, R^2 = $(CH_2)_2C(CH_3)=CH_2$	**38** R^1 = TMS, R^2 = $(CH_2)_2C(CH_3)=CH_2$ 86%
5	**39**	R^1 = H, R^2 = $(CH_2)_2$(3-furyl)	**40** R^1 = TMS, R^2 = $(CH_2)_2$(3-furyl) 65%
			
6	**41**	R = $(CH_2)_4CH_3$	**42** R = $(CH_2)_4CH_3$ 85%
7	**43**	R = $CH(CH_3)_2$	**44** R = $CH(CH_3)_2$ 40%[a]
8	**45**	R = $(CH_2)_2Ph$	**46** R = $(CH_2)_2Ph$ 85%
			
9	**47**	R^1 = CH_3O, R^2 = $(CH_2)_3CH_3$	**48** R^1 = OCH_3, R^2 = $(CH_2)_3CH_3$ 65%
10	**49**	R^1 =  , R^2 = $(CH_2)_3CH_3$	**50** R^1 =  , R^2 = $(CH_2)_3CH_3$ 80%
11	**51**	R^1 = $C_6H_{11}O$, R^2 = $(CH_2)_3CH=CH_2$	**52** R^1 = OC_6H_{11}, R^2 = $(CH_2)_3CH=CH_2$ 54%
12	**53**	R^1 =  , R^2 = $(CH_2)_3CH=CH_2$	**54** R^1 =  , R^2 = $(CH_2)_3CH=CH_2$ 28%
13	**55**	R^1 =  , R^2 = $(CH_2)_3CH=CH_2$	**56** R^1 =  , R^2 = $(CH_2)_3CH=CH_2$ 80%
14	**57**	R^1 =  , R^2 = 	**58** R^1 =  , R^2 =  89%
15	**59**	R^1 =  , R^2 = 	**60** R^1 =  , R^2 =  79%

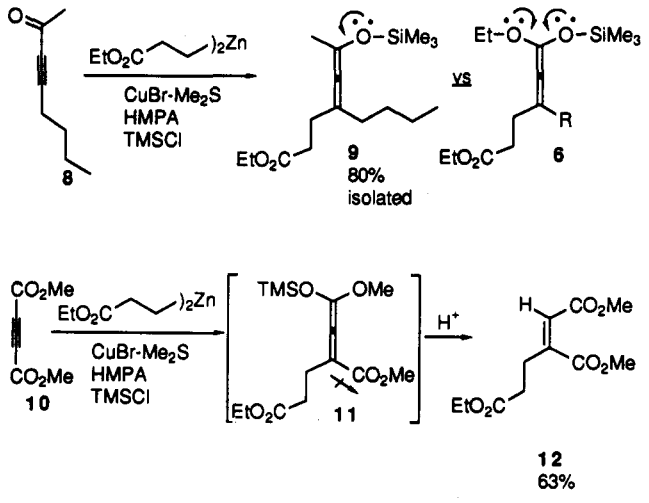
[a] 43% starting material also recovered.

entry	substrate	product, (no.), yield
		
16	**61** R = H, **62** R = CH_3	**63** R = H 69%, **64** R = CH_3 67%
		
17	**65**	**66** 70%
		
18	**67** (syn)	**68** (syn) 66%, **69** (anti) 66%
		
19	**70** R = THP (E alkene), **71** R = CH_2Ph (Z alkene)	**72** R = THP (E alkene), **73** R = CH_2Ph (Z alkene) 51%, 55%
		
20	**74** R^1 = OEt, R^2 = MOM (anti); **75** R^1 = OEt, R^2 = H (anti); **76** R^1 = OEt, R^2 = H (syn)	**77** R^1 = OEt, R^2 = MOM 65%; **78** R^1 = OEt, R^2 = TMS 82%; **79** R^1 = OEt, R^2 = TMS 83%
21	**80** R^1 =  , R^2 = H (2:1 syn:anti)	**81** R^1 =  , R^2 = TMS 86%
		
22	**82** R^1 = OCH_3	**83** R^1 = OCH_3 38%
23	**84** R^1 = $N(CH_3)_2$	**85** R^1 = $N(CH_3)_2$ 71%
		
24	**86**	**87** 52%
		
25	**88** (anti), **89** (syn)	**90**, **91** 60%, 72%

Scheme III



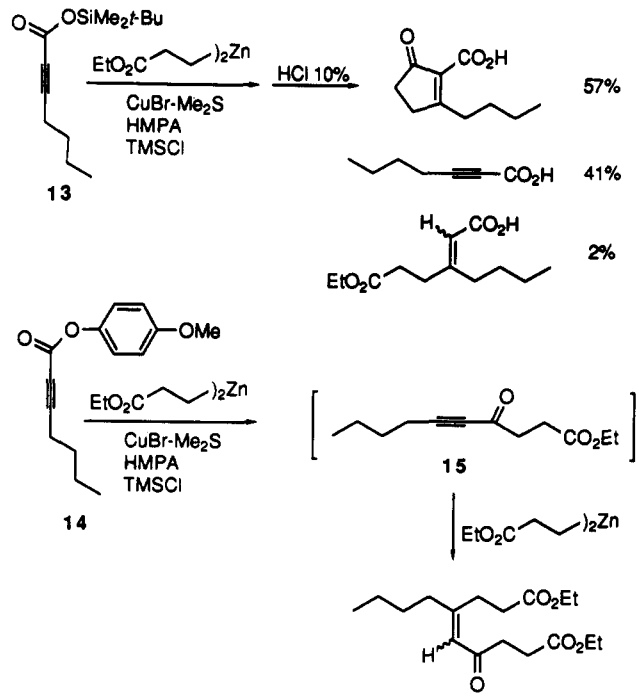
Scheme IV



The two steps proposed in the mechanism, conjugate addition and cyclization of **6**, have opposite electronic requirements: The conjugate addition requires an electrophilic π system while the cyclization step calls for a nucleophilic allenolic carbon. Attempts to modify the reactivity of the system to improve the efficiency of one step could therefore impede the other step. For example, the acetylenic ketone **8** is a better Michael acceptor than the corresponding acetylenic ester but no cyclization is observed because the allenolic carbon of the product **9** is not sufficiently nucleophilic (no second alkoxy lone pair is present). The same probelm is encountered with the acetylenic diester **10** where the presence of an electron-withdrawing ester group on the allenolic carbon of the intermediate **11** inhibits cyclization. The alkene **12** is the only product isolated (Scheme IV).

In an attempt to improve the nucleophilicity of the allenolic carbon of the silyl ketene acetal **6**, the nature of the ester was modified. It was hoped that the use of a more electron-rich ester such as *tert*-butyldimethylsilyl ester **13** would increase the nucleophilicity of the allenolic carbon and therefore promote faster cyclization. Esters of this type gave almost no alkenes **7**, implying fast cyclization of the intermediate **6**. However, the resulting

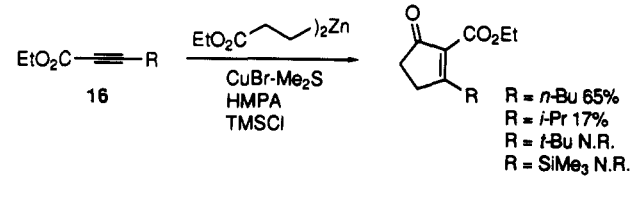
Scheme V



decreased electrophilicity of the starting acetylenic ester **13** resulted in slower conjugate addition, and large quantities of starting material were recovered as shown in Scheme V. When 3% CuBr–Me_2S is used instead of 10%, the yield of cyclopentenone is lower and the quantity of recovered starting material is greater. This may be due to decomposition of the organocopper intermediate to Cu^0 resulting in termination of the catalytic cycle. Additional Cu^I compensates for the loss of catalyst. The higher yield of cyclopentenone when more CuBr–Me_2S is used is consistent with this interpretation.

In the case of the *p*-methoxybenzyl ester **14** 1,2 addition of the homoenolate on the ester is the initial event, followed by 1,4 addition of another homoenolate on the more reactive acetylenic ketone **15**.

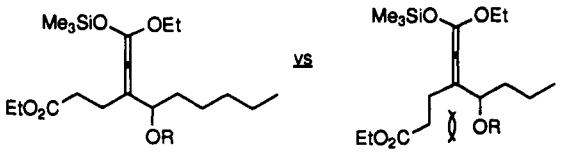
Increasing the bulkiness of the alkyl side chain in acetylenic esters **16** apparently slows initial conjugate addition of the homoenolate giving lower yields of cyclopentenones with recovery of unreacted starting material or no reaction at all in the most hindered cases.



In the case of acetylenic amides the allenolic carbon of the silyl ketene acetal intermediate is more nucleophilic than in the corresponding ester cases since the NR_2 group is a better donor than the OR group. However, the acetylenic amides are still sufficiently electrophilic to undergo fairly rapid conjugate addition with the zinc homoenolate especially in the presence of TMSCl.[17] Cyclization rates are higher without significantly impeding conjugate addition. This results in smaller quantities of

(17) Alexis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047.

Chart I



proton trapping products of type **7** and therefore higher yields of the amide cyclopentenone in all examples tested.

Slower cyclization usually results in lower yields of cyclopentenones, and larger quantities of alkenes of type **7** are isolated. Acetylenic esters bearing an unsubstituted alkyl chain typically provide lower yields of cyclopentenones than the corresponding alkoxy α-substituted acetylenic esters (entries 9, 11, 12 versus 4, 5). The cyclization on a system presenting a branched side chain versus a linear side chain is expected to be faster because of the steric interaction between the OR group and the ester chain which would help place the ester carbonyl in the correct geometry for cyclization, as shown in Chart I.

The low yield obtained for the acetylenic esters bearing an acetate as a protecting group (entries 1 and 2) was originally attributed to the electron-withdrawing effect of the acetate which would decrease the nucleophilicity of the allenolic carbon of the silyl ketene acetal intermediate, resulting in slower addition. Careful analysis of the reaction byproducts for the acetylenic ester **17** did not show alkenes of type **7** but alkene **18** and allene **19**. Alkene **18** is obtained from nucleophilic attack of the allenolic carbon on the acetate carbonyl instead of the ethyl ester carbonyl, as shown in Scheme VI. Allene **19** is the product of a S_N2' reaction on the acetylenic acetate.

When the reaction is performed on the acetylenic diester **20** the presence of two ester carbonyls during the cyclization results in the formation of two cyclopentenones **21** and **22** as shown in Scheme VII. The known *gem*-dimethyl effect favors the formation of **21**.

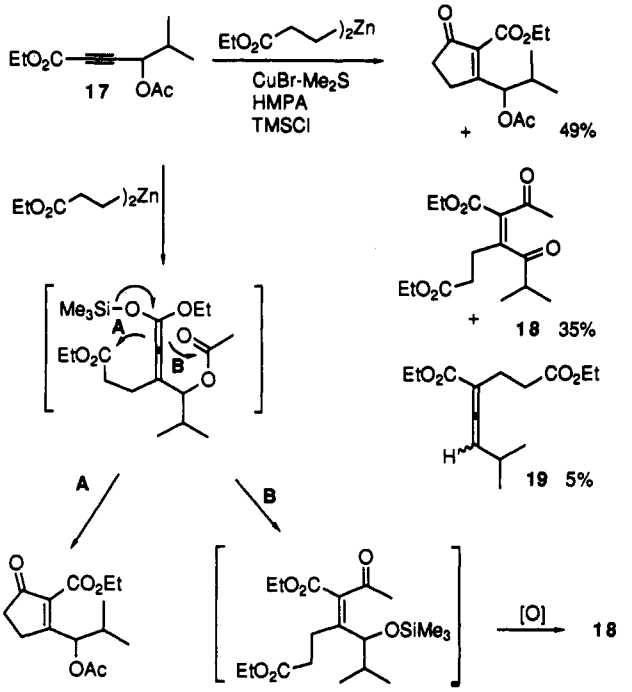
Conclusion

In conclusion, these results demonstrate that the conjugate addition–cyclization (formal [3 + 2] cycloaddition) of zinc homoenolates to acetylenic esters and amides provides easy access to highly functionalized cyclopentenones. The reaction tolerates a variety of sensitive functional groups and proceeds in good to excellent yields. Studies are underway to generalize this reaction to the synthesis of cyclohexenones and higher membered ring systems.

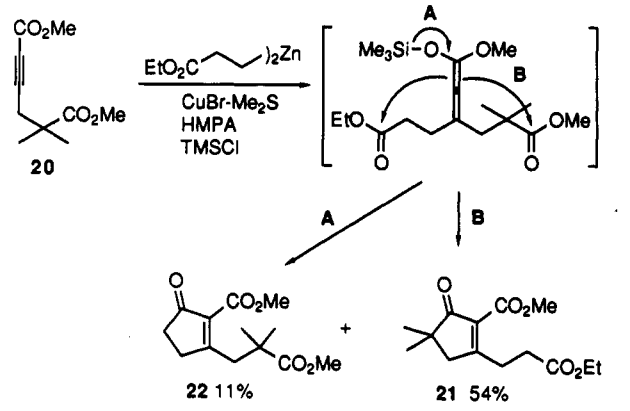
Experimental Section

Infrared (IR) spectra were obtained on an IR-4210 infrared spectrophotometer. The values are reported in cm^{-1} for thin films on NaCl plates unless otherwise noted. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on the following instruments: a Bruker AC200 200-MHz spectrometer, a Bruker WM-250 250-MHz spectrometer, or a Varian XL-400 400-MHz spectrometer. Data are reported as follows: chemical shift (multiplicity, coupling constants, integrated intensity, assignment). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian XL-400 400-MHz spectrometer. Chemical shifts are reported as δ values in parts per million downfield from tetramethylsilane (δ = 0.0 ppm) as an internal standard or from the residual chloroform signal (δ = 7.24 ppm for ^1H NMR or δ = 77.0 ppm for ^{13}C NMR). Analytical combustion analyses were performed by Atlantic Microlabs, Atlanta, GA. Mass spectral analyses were performed by The

Scheme VI



Scheme VII



University of North Carolina Mass Spectroscopy Facility on a VG 70-250 SEQ Tandem Hybrid/MS system, operated in the "MS-only" mode. Chromatography was performed according to the method of Still using silica gel with an average mesh of 40 μm. "Dry" solvents were distilled immediately prior to use from an appropriate drying agent. Diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl. Dimethoxyethane, methylene chloride, benzene, toluene, and acetonitrile were distilled from calcium hydride. Trimethylsilyl chloride, diisopropylamine, and all alkylamines were distilled from calcium hydride immediately prior to use. Dimethyl sulfoxide and hexamethylphosphoramide were distilled at 1 mmHg and stored over 4-Å Linde molecular sieves. All other reagents and solvents were reagent grade. All reactions involving air- or moisture-sensitive processes were carried out under a nitrogen atmosphere and in glassware which had been flame dried with continuous nitrogen flushing.

Typical Procedure for the Preparation of Hydroxyacetylenic Esters and Amides. A solution of *n*-butyllithium (2.5 M, 4.8 mL, 12 mmol) in hexanes was added to a solution of diisopropylamine (1.67 mL, 12 mmol) in 20 mL of dry THF at −78 °C, and the solution was stirred for 20 min.[18] Then, ethyl propiolate (1.08 g, 11 mmol) in 10 mL of THF was slowly added

(18) While all of the preparations for compounds described in this paper were carried out with LDA, we have since determined that reactions are cleaner and yields are higher when lithium hexamethyldisilazide is used as the base to deprotonate the propionate ester.

dropwise over 20 min. After an additional 20 min of stirring, the aldehyde (10 mmol) in 5 mL of THF was rapidly added dropwise, and the mixture was stirred for 30 min at −78 °C. The mixture was quenched with saturated NH_4Cl and warmed to room temperature. The reaction mixture was diluted with ether, and the organic layer was washed with water and saturated NaCl and dried over magnesium sulfate. The solvent was removed at reduced pressured, and the crude oil was flash chromatographed to provide the pure hydroxy acetylenic ester (70–90% yield).

Typical Procedure for the Preparation of 2-Carbalkoxy- and 2-Carboxamidocyclopent-2-en-1-ones from a Starting Acetylenic Ester or Amide without Free Hydroxyl. To a stirring solution of 2.4 mL (12 mmol) of [(1-ethoxycyclopropyl)-oxy]trimethylsilane (purchased from Aldrich) in 9 mL of diethyl ether was added 9 mL (9 mmol) of zinc chloride (1.0 M in ethyl ether, purchased from Aldrich) via syringe in one portion at room temperature. This mixture was than sonicated for 40 min followed by stirring at room temperature for an additional 10 min. At this point the heterogeneous mixture was cooled to 0 °C, and to this was added successively 154 mg (0.75 mmol) of copper(I) bromide dimethyl sulfide complex, 5 mmol of acetylenic ester or amide in 18 mL of THF, and 2.1 mL (12 mmol) of hexamethylphosphoramide (HMPA). After addition, the mixture was allowed to stir 5 min at 0 °C, and then the ice bath was removed and the stirring was continued for 4 h. The reaction was quenched with saturated ammonium chloride solution, and the organic layer was washed with half-saturated ammonium hydroxide solution until no blue color appeared in the wash. The resulting organic layer was washed with water and saturated sodium chloride solution and dried over magnesium sulfate. Concentration followed by chromatography of the crude oil (25% ethyl acetate/hexanes) gave the corresponding cyclopentenone.

Typical Procedure for the Preparation of 2-Carbalkoxy- and 2-Carboxamidocyclopent-2-en-1-ones from a Starting Acetylenic Ester or Amide with an Unprotected Hydroxyl. To a stirring solution of 4.8 mL (24 mmol) of [(1-ethoxycyclopropyl)oxy]trimethylsilane (purchased from Aldrich) in 18 mL of diethyl ether was added 18 mL (18 mmol) of zinc chloride (1.0 M in ethyl ether, purchased from Aldrich) via syringe in one portion at room temperature. This mixture was then sonicated for 40 min followed by stirring at room temperature for an additional 10 min. At this point the heterogeneous mixture was cooled to 0 °C, and to this was added successively 308 mg (1.5 mmol) of copper(I) bromide dimethyl sulfide complex, 5 mmol of acetylenic ester or amide in 18 mL of THF, and 4.2 mL (24 mmol) of hexamethylphosphoramide (HMPA). After addition, the mixture was allowed to stir for 5 min at 0 °C, and then the ice bath was removed and the stirring was continued for 4 h. The reaction was quenched with saturated ammonium chloride solution, and the organic layer was washed with half-saturated ammonium hydroxide solution until no blue color appeared in the wash. The resulting organic layer was washed with water and saturated sodium chloride solution and dried over magnesium sulfate. Concentration followed by chromatography of the crude oil (10% ethyl acetate/hexanes) gave the corresponding trimethylsilyl-protected hydroxy cyclopentenone.

Analytical Data. Acetylenic ester 23: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (bt, 6.8 Hz, 3 H, $(CH_2)_4CH_3$), 1.25 to 1.55 (band, 6 H, $CH_2(CH_2)_3CH_3$), 1.31 (t, J = 7.6 Hz, 3 H, $CO_2CH_2CH_3$), 1.77 (m, 2 H, $CH_2(CH_2)_3CH_3$), 3.39 (s, 3 H, OCH_2OCH_3), 4.23 (q, J = 7.6 Hz, 2 H, $CO_2CH_2CH_3$), 4.43 (t, J = 6.7 Hz, 1 H, $CHOCH_2OCH_3$), 4.6 (d, J = 7.6 Hz, 1 H, OCH_2OCH_3), 4.88 (d, J = 7.6 Hz, 1 H, OCH_2OCH_3); ^{13}C NMR ($CDCl_3$) δ 13.91; 22.40; 24.75; 31.28; 34.85; 55.69; 61.96; 65.20; 77.01; 86.00; 94.52; 153.22. IR (neat): 2950, 2220, 1720, 1465, 1360 1245 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.36; H, 9.13.

Acetylenic ester 24: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (t, J = 6.5 Hz, 3 H, $(CH_2)_4CH_3$), 1.15–1.55 (band, 6 H, $CH_2(CH_2)_3CH_3$), 1.23 (t, J = 7.2 Hz, 3-H, $CO_2CH_2CH_3$), 1.75 (m, 2 H, $CH_2(CH_2)_3CH_3$), 2.03 (s, 3 H, $COCH_3$), 4.18 (q, J = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 5.38 (t, J = 6.7 Hz, 1 H, $CHOAc$); ^{13}C NMR ($CDCl_3$) δ 13.82; 13.88; 20.68; 22.29; 24.42; 31.07; 33.81; 62.07; 63.04; 76.70; 84.05; 152.96; 169.57; IR (neat) 2950, 2920, 2860, 2230, 1750, 1715, 1460, 1365, 1250, 1215 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.90; H, 8.36.

Acetylenic ester 25: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 3H, $(CH_2)_4CH_3$), 1.15–1.55 (band, 6 H, $CH_2(CH_2)_3CH_3$), 1.29 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.75 (m, 2 H, $CH_2(CH_2)_3CH_3$), 2.64 (broad s, 1 H, OH), 4.22 (q, J = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 4.27 (t, J = 6.6 Hz, 1 H, $CHOH$); ^{13}C NMR ($CDCl_3$) δ 13.50; 22.09; 24.29; 30.98; 61.34; 61.76; 75.69; 88.27; 153.39; IR (neat) 3410 (broad), 2950, 2930, 2860, 2230, 1720, 1455, 1365, 1250 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.61; H, 9.16.

Cyclopentenone 26: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (broad t, J = 6.3 Hz, 3 H, $(CH_2)_4CH_3$), 1.15–1.85 (band, 8 H, $(CH_2)_4CH_3$), 1.33 (t, J = 7.5 Hz, 3 H, $CO_2CH_2CH_3$), 2.49 (X of ABX_2, t, J = 5.25 Hz, 2 H, $COCH_2CH_2$), 2.73 (AB of ABX_2, $\Delta\nu$ = 22.8 Hz, J = 20, 5.25 Hz, 2 H, $COCH_2CH_2$), 3.37 (s, 3 H, OCH_2OCH_3), 4.32 (q, J = 7.5 Hz, 2 H, $CO_2CH_2CH_3$), 5.05 (dd, J = 8, 4.5 Hz, 1 H, $CHOMOM$); ^{13}C NMR ($CDCl_3$) δ 13.66; 13.86; 22.19; 24.97; 25.73; 31.18; 33.84; 34.38; 55.61; 60.71; 74.21; 95.6; 132.77; 162.68; 184.7; 203.1; IR (neat) 2940, 1755, 1725, 1645, 1470 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.40; H, 8.78. Found: C, 64.34; H, 8.78.

Cyclopentenone 27: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (broad t, J = 6 Hz, 3 H, $(CH_2)_4CH_3$), 1.2–1.45 (band, 6 H, $CH_2(CH_2)_3CH_3$), 1.33 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.65–1.85 (band, 2 H, $CH_2(CH_2)_3CH_3$), 2.07 (s, 3 H, $COCH_3$), 2.44 (t, J = 4.5 Hz, 2 H, $COCH_2CH_2$), 2.45–2.8 (band, 2 H, $COCH_2CH_2$), 4.31 (m, 2 H, $CO_2CH_2CH_3$), 6.0 (dd, J = 8.4, 4.5 Hz, 1 H, $CHOAc$); ^{13}C NMR ($CDCl_3$) δ 13.57; 13.82; 20.29; 22.06; 24.83; 25.19; 30.95; 32.76; 34.12; 60.71; 72.24; 131.78; 162.32; 169.88; 182.30; 202.50; IR (neat) 1755, 1745, 1720, 1645, 1630 cm^{-1}; HRMS for $C_{16}H_{24}O_5$ calcd 254.1518, found 254.1505.

Cyclopentenone 28: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.09 (s, 9 H, $OSi(CH_3)_3$), 0.87 (broad t, J = 6 Hz, 3 H, $(CH_2)_4CH_3$), 1.1–1.65 (band, 8 H, $(CH_2)_4CH_3$), 1.33 (t, J = 6.75 Hz, 3 H, $CO_2CH_2CH_3$), 2.47 (X of ABX_2, t, J = 4.8 Hz, 2 H, $COCH_2CH_2$), 2.73 (AB of ABX_2, $\Delta\nu$ = 28.5 Hz, J = 20, 4.8 Hz, 2 H, $COCH_2CH_2$), 4.3 (q, J = 6.75 Hz, 2 H, $CO_2CH_2CH_3$), 5.18 (dd, J = 8.2, 4.5 Hz, 1 H, $CHOSiMe_3$); ^{13}C NMR ($CDCl_3$) δ 0.91; 13.29; 13.54; 21.85; 24.54; 25.05; 30.81; 33.92; 35.70; 60.03; 69.42; 13.37; 162.28; 187.10; 202.48; IR (neat) 2950, 2920, 2860, 1750, 1725, 1625 cm^{-1}; HRMS for $C_{17}H_{30}O_4Si$ calcd 311.1683, found 311.1684.

Acetylenic ester 29: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (d, J = 3 Hz, 3 H, $CH(CH_3)_2$), 1.04 (d, J = 3 Hz, 3 H, $CH(CH_3)_2$), 1.3 (t, J = 7.3 Hz, 3 H, $CO_2CH_2CH_3$), 2.1 (m, 1 H, $CH(CH_3)_2$), 3.38 (s, 3 H, OCH_2OCH_3), 4.21 (d, J = 6 Hz, 1 H, $CHOMOM$), 4.22 (q, J = 7.3 Hz, 2 H, $CO_2CH_2CH_3$), 4.59 (d, J = 7.6 Hz, 1 H, OCH_2OCH_3), 4.91 (d, J = 7.6 Hz, 1 H, OCH_2OCH_3); ^{13}C NMR ($CDCl_3$) δ 13.83; 17.79; 18.07; 32.75; 55.56; 61.82; 70.52; 77.69; 84.92; 94.51; 153.07; IR (neat) 2960, 2890, 2220, 1725, 1465, 1360, 1240 cm^{-1}.

Acetylenic ester 30: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (d, J = 4.5 Hz, 3 H, $CH(CH_3)_2$), 1.02 (d, J = 4.5 Hz, 3 H, $CH(CH_3)_2$), 1.28 (t, J = 7.3 Hz, 3 H, $CO_2CH_2CH_3$), 2.04 (m, 1 H, $CH(CH_3)_2$), 2.07 (s, 3 H, $COCH_3$), 4.2 (q, J = 7.3 Hz, 2 H, $CO_2CH_2CH_3$), 5.27 (d, J = 6 Hz, 1 H, $CHOAc$); ^{13}C NMR ($CDCl_3$) δ 13.85; 17.46; 17.91; 20.59; 32.07; 62.01; 67.90; 77.29; 82.14; 152.88; 169.55; IR (neat) 2970, 2940, 2235, 1755, 1720, 1465, 1370 cm^{-1}.

Acetylenic ester 31: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.0 (d, J = 3 Hz, 3 H, $CH(CH_3)_2$), 1.04 (d, J = 3 Hz, 3 H, $CH(CH_3)_2$), 1.3 (t, J = 6.7 Hz, 3 H, $CO_2CH_2CH_3$), 1.95 (m, 1 H, $CH(CH_3)_2$), 2.31 (broad s, 1 H, OH), 4.23 (q, J = 6.7 Hz, 2 H, $CO_2CH_2CH_3$), 4.28 (d, J = 6 Hz, 1 H, $CHOH$); ^{13}C NMR ($CDCl_3$) δ 13.58; 17.16; 17.70; 33.83; 61.87; 66.92; 76.56; 87.25; 153.43; IR (neat) 3420 (broad), 2960, 2930, 2900, 2870, 2220, 1725, 1685, 1465, 1385, 1365, 1250 cm^{-1}.

Cyclopentenone 32: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (d, J = 6.75 Hz, 3 H, $CH(CH_3)_2$), 1.07 (d, J = 6.45 Hz, 3 H, $CH(CH_3)_2$), 1.33 (t, J = 7.5 Hz, 3 H, $CO_2CH_2CH_3$), 1.98 (m, 1 H, $CH(CH_3)_2$), 2.5 (X of ABX_2, t, J = 5.25 Hz, 2 H, $COCH_2CH_2$), 2.71 (AB of ABX_2, $\Delta\nu$ = 31.35 Hz, J = 18, 5.25 Hz, 2 H, $COCH_2CH_2$), 3.37 (s, 3 H, OCH_2OCH_3), 4.31 (q, J = 7.5 Hz, 2 H, $CO_2CH_2CH_3$), 4.56 (AB, $\Delta\nu$ = 4.7 Hz, J = 8 Hz, 2 H, OCH_2OCH_3), 4.72 (d, J = 7.5 Hz, 1 H, $CHOMOM$); ^{13}C NMR ($CDCl_3$) δ 13.83; 18.46; 18.55; 25.91; 31.75; 34.39; 55.73; 60.71; 70.05; 95.81; 134.65; 162.81; 182.99; 203.18; IR (neat) 2980, 1755, 1730, 1650 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.21. Found: C, 62.10; H, 8.21.

Cyclopentenone 33: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$), 0.98 (d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.32 (t, J = 7.5 Hz, 3 H, $CO_2CH_2CH_3$), 2.07 (s, 3 H, $COCH_3$), 2.11 (m, 1 H, $CH(CH_3)_2$), 2.44 (t, J = 5.2 Hz, 2 H, $COCH_2CH_2$), 2.45–2.75 (band, 2 H, $COCH_2CH_2$), 4.29 (q, m, 2 H, $CO_2CH_2CH_3$), 5.84 (d, J = 6 Hz, 1 H, CHOAc); ^{13}C NMR ($CDCl_3$) δ 14.12; 17.85; 18.87; 20.57; 27.0; 31.79; 34.44; 61.15; 76.46; 133.84; 162.84; 170.22; 180.80; 202.92; IR (neat): 1755, 1730, 1720, 1645 cm^{-1}; HRMS for $C_{14}H_{20}O_5$ calcd 268.1311, found 268.1355.

Cyclopentenone 34: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9 H, $OSi(CH_3)_3$), 0.8 (d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$), 0.96 (d, J = 6.3 Hz, 3 H, $CH(CH_3)_2$), 1.33 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.84 (m, 1 H, $CH(CH_3)_2$), 2.45 (X of ABX_2, t, J = 5.25 Hz, 2 H, $COCH_2CH_2$), 2.62 (AB of ABX_2, $\Delta\nu$ = 44.3 Hz, J = 20.2, 5.25 Hz, 2 H, $COCH_2CH_2$), 4.29 (q, J = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 4.83 (d, J = 7.5 Hz, 1 H, $CHOSiMe_3$); ^{13}C NMR ($CDCl_3$) δ 0.15; 14.22; 18.64; 18.67; 25.98; 33.78; 34.68; 60.96; 74.80; 132.46; 163.13; 187.17; 203.83; IR (neat) 2950, 1745, 1715, 1625 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_4Si$: C, 60.36; H, 8.78. Found: C, 60.32; H, 8.76.

Acetylenic ester 35: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (t, J = 7.6 Hz, 3 H, $CO_2CH_2CH_3$), 1.84 (bs, 1 H, OH), 2.1 (dt, J = 6.7, 7.5 Hz, 2 H, $PhCH_2CH_2$), 2.82 (t, J = 7.5 Hz, 2 H, $PhCH_2CH_2$), 4.25 (q, J = 7.6 Hz, 2 H, $CO_2CH_2CH_3$), 4.48 (t, J = 6.7 Hz, 1 H, CHOH), 7.13–7.35 (band, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 13.84; 30.98; 38.10; 60.98; 62.18; 76.69; 87.80; 126.02; 128.37; 140.56; 153.52; IR (neat) 3400 (broad), 2220, 1700, 1485, 1445, 1360, 1240 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.16; H, 6.98.

Cyclopentenone 36: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 9 H, $OSi(CH_3)_3$), 1.33 (t, J = 7.5 Hz, 3 H, $CO_2CH_2CH_3$), 1.8–2.05 (band, 2 H, CH_2CH_2Ph), 2.43 (t, J = 5 Hz, 2 H, $COCH_2CH_2$), 2.5–2.9 (band, 4 H, $COCH_2CH_2$ and CH_2CH_2Ph), 4.25 (q, J = 7.5 Hz, 2 H, $CO_2CH_2CH_3$), 5.22 (dd, J = 8, 4.5 Hz, 1 H, CHOTMS), 7.1–7.3 (band, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.27; 14.07; 25.65; 31.70; 34.49; 37.80; 60.80; 69.72; 125.87, 128.17; 128.25; 130.94; 141.03; 162.74; 187.53; 203.38; IR (neat) 2970, 1755, 1730, 1635 cm^{-1}. Anal. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83. Found: C, 66.70; H, 7.89.

Acetylenic ester 37: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3 (t, J = 7.6 Hz, 3 H, $CO_2CH_2CH_3$), 1.72 (bs, 3 H, $CH_2C(=CH_2)CH_3$), 1.9 (m, 2 H, $CH(OH)CH_2CH_2$), 2.18 (m, 2 H, $CH(OH)CH_2CH_2$), 4.22 (q, J = 7.6 Hz, 2 H, $CO_2CH_2CH_3$), 4.48 (t, J = 6.8 Hz, 1 H, CHOH), 4.73 (m, 2 H, $C=CH_2$).

Cyclopentenone 38: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9 H, TMS), 1.31 (t, J = 7.6 Hz, 3 H, $CO_2CH_2CH_3$), 1.68 (bs, 3 H, $CH_2C(=CH_2)CH_3$), 1.56–2.2 (band, 4 H, $CH(OTMS)(CH_2)_2$), 2.43 (X of ABX_2, t, J = 5.7 Hz, 2 H, $(CO)CH_2CH_2$), 2.72 (AB of ABX_2, dt, J = 20.8, 5.7 Hz, $\Delta\nu$ = 43.5 Hz, 2 H, $(CO)CH_2CH_2$), 4.27 (q, J = 7.6 Hz, 2 H, $CO_2CH_2CH_3$), 4.68 (bd, J = 13.3 Hz, 2 H, $C=CH_2$), 5.14 (dd, J = 9.5, 5.7 Hz, 1 H, CHOTMS).

Acetylenic ester 39: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (t, J = 7.5 Hz, 3 H, $CO_2CH_2CH_3$), 2.04 (m, 2 H, $CH(OH)CH_2CH_2$), 2.2 (d, J = 6.5 Hz, 1 H, OH), 2.63 (broad t, J = 7.9 Hz, 2 H, $CH(OH)CH_2CH_2$), 4.24 (q, J = 7.5 Hz, 2 H, $CO_2CH_2CH_3$), 4.5 (m, 1 H, CHOH), 6.29 (m, 1 H, OCH=CH), 7.25 (m, 1 H, OCH=CH), 7.37 (m, 1 H, OCH=CC).

Cyclopentenone 40: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.1 (s, 9 H, OTMS), 1.33 (t, J = 7.5 Hz, 3 H, $CO_2CH_2CH_3$), 1.9 (m, 2 H, $CH(OTMS)CH_2CH_2$), 2.35–2.95 (band, 6 H, $CH(OTMS)CH_2CH_2$ and $COCH_2CH_2$), 4.3 (q, J = 7.5 Hz, 2 H, $CO_2CH_2CH_3$), 5.23 (dd, J = 8.3 Hz, 4.5 Hz, 1 H, CH(OTMS)), 6.27 (m, 1 H, OCH=CH), 7.24 (m, 1 H, OCH=CH), 7.37 (m, 1 H, OCH=CC).

Acetylenic amide 41: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.04 (broad t, J = 6.1 Hz, 3 H, $(CH_2)_4CH_3$), 1.10–1.55 (band, 6 H, $CH_2(CH_2)_3CH_3$), 1.60–1.78 (band 2 H, $CH_2)CH_2)_3CH_3$), 1.86 (m, 4 H, $NCH_2(CH_2)_2CH_2$), 3.40 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 3.56 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 4.10–4.38 (band, 1 H, OH), 4.46 (broad t, J = 9.1 Hz, 1 H, CH(OH)); ^{13}C NMR ($CDCl_3$) δ 13.95; 22.49; 24.63; 24.74; 25.29; 31.36; 37.06; 45.31; 48.17; 62.11; 78.08; 91.19; 152.38; IR(CH_2Cl_2) 3420 (broad), 3050, 2978, 2865, 2240, 1734, 2240, 1734, 1615, 1423, 1369, 1240 (broad) cm^{-1}.

Cyclopentenone 42: ^{1}H NMr (200 MHz, $CDCl_3$) δ 0.04 (s, 9 H, $Si(CH_3)_3$), 0.80 (t, J = 5.8 Hz, 3 H, $(CH_2)_4CH_3$), 1.12–1.32 (band, 6 H, $CH_2(CH_2)_3CH_3$), 1.45–1.62 (band, 2 H, $CH(OTMS)CH_2$), 1.75–1.90 (band, 4 H, $NCH_2(CH_2)_2CH_2$), 2.39 (X of ABX_2, t, J = 5.8 Hz, 2 H, $(CO)CH_2CH_2$), 2.62 (AB of ABX_2, dt, J = 19.7, 5.8 Hz, $\Delta\nu$ = 36.4 Hz, 2 H, $(CO)CH_2CH_2$), 3.23 (t, J = 6.4 Hz, 2 H, $NCH_2(CH_2)_2CH_2$), 3.49 (t, J = 6.4 Hz, 2 H, $NCH_2(CH_2)_2CH_2$), 4.77 (dd, J = 8.8, 6.0 Hz, 1 H, CH(OTMS)); ^{13}C NMR ($CDCl_3$) δ 1.89; 13.99; 22.50; 24.19; 25.00; 25.79; 27.40; 31.59; 33.97; 34.69; 45.83; 47.37; 71.06; 137.96; 164.52; 182.96; 204.18; IR (CH_2Cl_2) 2993, 2985, 2909, 1712, 1620, 1443 cm^{-1}. Anal. Calcd for $C_{19}H_3H_{33}NSi$: C, 64.91; H; 9.46. Found: C, 64.81; H, 9.44.

Acetylenic amide 43: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (m, 6 H, $CH(CH_3)_2$), 1.79–2.01 (band, 5 H, $NCH_2(CH_2)_2CH_2$ and $CH(CH_3)_2$), 2.55–3.04 (band, 1 H, OH), 3.48 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 3.63 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 4.32 (d, J = 5.8 Hz, 1 H, CH(OH)); ^{13}C NMR ($CDCl_3$) δ 17.08; 17.73; 24.11; 24.76; 33.66; 44.84; 47.78; 66.54; 77.72; 90.53; 152.06; IR (CH_2Cl_2) 3380, 2960, 2925, 2870, 2230, 1610, 1435, 1335 cm^{-1}.

Cyclopentenone 44: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.78 (d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$), 0.92 (d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$), 1.6–2.01 (band 5 H, $NCH_2(CH_2)_2CH_2$ and $CH(CH_3)_2$), 2.38 (X of ABX_2, t, J = 4.9 Hz, 2 H, $(CO)CH_2CH_2$), 2.68 (AB of ABX_2, dt, J = 21.2, 5.6 Hz, $\Delta\nu$ = 56.1 Hz, 2 H, $(CO)CH_2CH_2$), 3.12–3.59 (band, 4 H, $NCH_2(CH_2)_2CH_2$), 4.55 (d, J = 7.6 Hz, 1 H, $CH(OSiMe_3)$); ^{13}C NMR ($CDCl_3$) δ 0.04; 18.62; 24.16; 25.95; 26.06; 33.82; 34.52; 46.83; 47.36; 60.24; 74.79; 138.36; 162.69; 182.62; 204.71; IR (CH_2Cl_2) 2960, 2878, 1710, 1635, 1442 cm^{-1}. Anal. Calcd for $C_{17}H_{29}O_3NSi$: C, 63.11; H, 9.04. Found: C, 62.98; H, 9.26.

Acetylenic amide 45: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.82–1.98 (band, 4 H, $NCH_2(CH_2)_2CH_2$), 2.0–2.2 (band, 2 H, CH_2CH_2Ph), 2.8 (t, J = 5.8 Hz, 2 H, CH_2Ph), 2.65–3.1 (band, 1 H, OH), 3.45 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 3.61 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 4.55 (dd, J = 10.9, 6.4 Hz, 1 H, CH(OH)), 7.11–7.36 (band, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 24.31; 24.95; 31.05; 38.41; 45.11; 48.0; 60.63; 77.52; 91.61; 125.64; 128.09; 128.17; 140.87; 152.27; IR (CH_2Cl_2) 3360 (broad), 3058, 2983, 2882, 2245, 1611, 1435, 1263 cm^{-1}.

Cyclopentenone 46: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.12 (s, 9 H, $OSi(CH_3)_3$), 1.26–2.1 (band, 8 H, $NCH_2(CH_2)_2CH_2$ and $(CH_2)_2Ph$), 2.43 (X of ABX_2, t, J = 3.3 Hz, 2 H, $(CO)CH_2CH_2$), 2.71 (AB of ABX_2, dt, J = 15.2, 3.3 Hz, $\Delta\nu$ = 34.6 Hz, 2 H, $(CO)CH_2CH_2$), 3.28 (t, J = 4.6 Hz, 2 H, $NCH_2(CH_2)_2CH_2$), 3.56 (t, J = 4.9 Hz, 2 H, $NCH_2(CH_2)_2CH_2$), 4.92 (dd, J = 6.1, 3.6 Hz, 1 H, $CH(OSiMe_3)$), 7.9–7.31 (band, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 0.25; 24.01; 25.67; 31.33; 34.30; 37.70; 45.26; 46.79; 69.62; 125.70; 128.11; 137.44; 141.12; 162.69; 182.32; 204.34; IR (CH_2Cl_2) 2950, 2878, 1705, 1625, 1447 cm^{-1}. Anal. Calcd for $C_{21}H_{31}O_3NSi$: C, 68.53; H, 8.11. Found: C, 68.46; H, 8.07.

Acetylenic ester 47: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (t, J = 7.6 Hz, 3 H, $(CH_2)_3CH_3$), 1.3–1.7 (band, 4 H, $CH_2(CH_2)_2CH_3$), 2.33 (t, J = 6.7 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 3.75 (s, 3 H, CO_2CH_3).

Cyclopentenone 48: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 3 H, $(CH_2)_3CH_3$), 1.38 (m, 2 H, $(CH_2)_2CH_2CH_3$), 1.55 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.45 (m, 2 H, $COCH_2CH_2$), 2.65 (m, 2 H, $COCH_2CH_2$), 2.74 (t, J = 8.2 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 3.8 (s, 3 H, CO_2CH_3); ^{13}C NMR ($CDCl_3$) δ 13.43; 22.46; 29.46; 30.11; 32.08; 34.62; 51.44; 131.89; 163.46; 188.53; 203.38; IR (neat) 1750, 1720, 1620 cm^{-1}; HRMS for $C_{11}H_{17}NO$ calcd 196.1099, found 196.1115.

Acetylenic amide 49: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81 (t, J = 7.3 Hz, 3 H, $CH_2(CH_2)_2CH_3$), 1.20–1.58 (band, 4 H, $CH_2(CH_2)_2CH_3$), 1.70–1.98 (band, 4 H, $NCH_2(CH_2)_2CH_2$), 2.24 (t, J = 6.7 Hz, $CH_2(CH_2)_2CH_3$), 3.34 (m, 2 H, $NCH_2(CH_2)_2CH_2$), 3.49 (m, 2 H, $NCH_2(CH_2)_2CH_2$); ^{13}C NMR ($CDCl_3$) δ 13.40; 18.40; 21.84; 24.64; 25.26; 29.79; 45.03; 48.00; 75.08; 91.43; 152.85; IR (CH_2Cl_2) 3420, 3055, 2980, 2295, 1733, 1617, 1320, 1262 cm^{-1}.

Cyclopentenone 50: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.78 (t, J = 7.6 Hz, 3 H, $(CH_2)_3CH_3$), 1.12–1.32 (m, 4 H, $CH_2(CH_2)_2CH_3$), 1.77 (m, 4 H, $NCH_2(CH_2)_2CH_2$), 2.22–2.58 (band, 6 H, $(CO)CH_2CH_2$ and $CH_2(CH_2)_2CH_3$), 3.16 (t, J = 6.4 Hz, 2 H, $NCH_2(CH_2)_2CH_2$), 3.42 (t, J = 6.4 Hz, 2 H, $NCH_2(CH_2)_2CH_2$); ^{13}C NMR ($CDCl_3$) δ 13.56; 22.48; 24.17; 25.67; 29.15; 29.85; 31.65; 34.75; 45.23; 46.81; 139.32; 163.62; 180.45; 204.56; IR (CH_2Cl_2) 2960, 2878, 1709, 1633, 1442 cm^{-1}. Anal. Calcd for $C_{14}H_{21}O_2N$: C, 71.45; H, 9.00. Found: C, 71.24; H, 9.08.

Acetylenic ester 51: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22–1.27 (band, 6 H, $OCHCH_2(CH_2)_3CH_2$), 1.75 (m, 2 H, $CH_2CH_2CH_2CH=CH_2$), 1.75–2.1 (band, 4 H, $OCHCH_2(CH_2)_3CH_2$), 2.24 (m, 2 H, $(CH_2)_2CH_2CH=CH_2$), 2.41 (t, J = 4.8 Hz, 2 H, $CH_2(CH_2)_2$-

$CH{=}CH_2$), 4.88 (m, 1 H, $OCH(CH_2)_5$), 5.0–5.2 (band, 2 H, $CH{=}CH_2$), 5.84 (m, 1 H, $CH{=}CH_2$).

Cyclopentenone 52: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2–2.04 (band, 12 H, $OCH(CH_2)_5$ and $CH_2CH_2CH_2CH{=}CH_2$), 2.15 (m, 2 H, $(CH_2)_2CH_2CH{=}CH_2$), 2.45 (m, 2 H, $COCH_2CH_2$), 2.6–2.8 (band, 4 H, $COCH_2CH_2$ and $CH_2(CH_2)_2CH{=}CH_2$), 4.88–5.13 (band, 3 H, $OCH(CH_2)_5$ and $CH{=}CH_2$), 5.8 (m, 1 H, $CH{=}CH_2$).

Acetylenic ester 53: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (d, J = 8.5 Hz, 3 H, $OCHCH(CH_3)(CH_2)_2CH(CMe_2Ph)CH_2$), 0.7–2.1 (band, 8 H, $OCHCH(CH_3)(CH_2)_2CH(CMe_2Ph)CH_2$), 1.27 (s, 3 H, $CH(CMe_2Ph)$), 1.35 (s, 3 H, $CH(CMe_2Ph)$), 1.65 (m, 2 H, $CH_2CH_2CH_2CH{=}CH_2$), 2.15 (m, 2 H, $(CH_2)_2CH_2CH{=}CH_2$), 2.27 (t, J = 12 Hz, 2 H, $CH_2(CH_2)_2CH{=}CH_2$), 4.87 (td, J = 6, 4.5 Hz, 1 H, $OCHCH(CH_3)(CH_2)_2CH(CMe_2Ph)CH_2$), 4.95–5.15 (band, 2 H, $CH{=}CH_2$), 5.77 (m, 1 H, $CH{=}CH_2$), 7.1–7.35 (band, 5 H, Ph).

Cyclopentenone 54: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (d, J = 8.5 Hz, 3 H, $OCHCH(CH_3)(CH_2)_2CH(CMe_2Ph)CH_2$), 0.8–2.2 (band, 12 H), 2.35 (m, 2 H, $COCH_2CH_2$), 2.4–2.53 (band, 4 H, $COCH_2CH_2$ and $CH_2(CH_2)_2CH{=}CH_2$), 4.9–5.1 (band, 3 H, $OCHCH(CH_3)(CH_2)_2$ and $CH{=}CH_2$), 5.78 (m, 1 H, $CH{=}CH_2$), 6.95–7.3 (band, 5 H, Ph).

Acetylenic amide 55: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17 (d, J = 6.53 Hz, 3 H, $NCH(CH_3)$), 1.26 (d, J = 6.46 Hz, 3 H, $NCH(CH_3)$), 1.42–1.72 (band, 4 H, $CH_2CH_2CH_2CH{=}CH_2$), 1.79–2.2 (band, 6 H, $NH(CH_3)CH_2CH_2$ and $C{\equiv}CCH_2$), 4.05–4.35 (band, 2 H, $NH(CH_3)$), 5.01 (m, 2 H, $CH{=}CH_2$), 5.76 (m, 1 H, $CH{=}CH_2$); ^{13}C NMR ($CDCl_3$) δ 18.19; 18.67; 21.50; 27.01; 29.57; 30.07; 32.77; 52.95; 55.16; 57.08; 89.91; 115.60; 137.32; 152.43; IR (neat) 2253, 1604, 1414, 909, 734, 651 cm^{-1}.

Cyclopentenone 56: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (d, J = 6.54 Hz, 3 H, $NCH(CH_3)$), 1.1 (d, J = 6.38 Hz, 3 H, $NCH(CH_3)$), 1.41 (m, 2 H) and 1.54 (m, 2 H) ($CH_2CH_2CH{=}CH_2$), 1.99 (m, 4 H, $NCH(CH_3)CH_2CH_2$), 2.22–2.45 (band, 4 H, CH_2CH_2CO), 2.45–2.55 (band, 2 H, $CH_2CH_2CH_2CH{=}CH_2$), 3.7 (m, 1 H, $NCH(CH_3)$), 4.17 (m, 1 H, $NCH(CH_3)$), 4.86 (m, 2 H, $CH_2CH{=}CH_2$), 5.64 (m, 1 H, $CH_2CH{=}CH_2$); ^{13}C NMR ($CDCl_3$) δ 18.66; 21.68; 25.97; 28.75; 29.34; 30.37; 31.34; 33.37; 34.67; 52.94; 53.34; 115.15; 137.18; 139.63; 163.15; 204.47; IR (neat) 2951, 1702, 1618, 1425 cm^{-1}.

Acetylenic amide 57: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (d, J = 6.36 Hz, 3 H, $NCH(CH_3)$), 1.07 (t, J = 7.15, 3 H, $CO_2CH_2CH_3$), 1.08 (d, J = 6.47 Hz, 3 H, $NHCH(CH_3)$), 1.38 (m, 2 H) and 1.54 (m, 2 H), ($CH_2CH_2CH_2CH{=}CH$), 1.95 (m, 2 H, $CH_2CH_2CH_2CH{=}CH$), 2.05–2.25 (band, 4 H, $NCH(CH_3)CH_2CH_2$), 3.97 (q, J = 7.22 Hz, 2 H, $CO_2CH_2CH_3$), 3.87–4.07 (band, 2 H, $NCH(CH_3)$), 5.64 (dt, J = 15.56, 1.59 Hz, 1 H, $CH{=}CHCO_2CH_2CH_3$), 6.71 (dt, J = 15.54, 6.86 Hz, 1 H, $CH{=}CHCO_2Et$); ^{13}C NMR ($CDCl_3$) δ 13.77; 17.77; 18.12; 21.01; 25.72; 29.06; 29.57; 30.56; 52.49; 54.68; 59.70; 76.02; 88.52; 121.85; 146.81; 151.69; 165.80; IR (neat) 2963, 2244, 1608, 1410, 913, 733 cm^{-1}. Anal. Calcd for $C_{17}H_{23}O_3N$: C, 70.07; H, 8.65. Found: C, 69.94; H, 8.59.

Cyclopentenone 58: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (d, J = 6.54 Hz, 3 H, $NCH(CH_3)$), 1.12 (d, J = 6.38 Hz, 3 H, $NCH(CH_3)$), 1.15 (t, J = 6.87 Hz, 3 H, $CO_2CH_2CH_3$), 1.43 (m, 2 H) and 1.65 (m, 2 H) ($CH_2CH_2CH{=}CH$), 1.82–2.02 (band, 4 H, $NCH(CH_3)CH_2CH_2$), 2.23–2.58 (band, 6 H, $COCH_2CH_2$ and $CH_2CH_2CH_2CH{=}CH$), 3.73 (m, 1 H, $NCH(CH_3)$), 4.04 (q, J = 7.01 Hz, 2 H, $CO_2CH_2CH_3$), 4.20 (m, 1 H, $NCH(CH_3)$), 5.71 (dt, J = 15.5, 1.53 Hz, 1 H, $CH{=}CHCO_2Et$), 6.8 (dt, J = 15.6, 7 Hz, 1 H, $CH{=}CHCO_2Et$); ^{13}C NMR ($CDCl_3$) δ 14.0; 18.70; 21.78; 25.26; 28.8; 29.37; 30.44; 31.42; 31.77; 34.74; 53.12; 53.38; 59.96; 121.99; 140.04; 147.24; 163.09; 166.12; 204.36; IR (neat): 2959, 1707, 1616, 1434 cm^{-1}. Anal. Calcd for $C_{20}H_{27}O_4N$: C, 69.14; H, 8.41. Found: C, 68.90; H, 8.50.

Acetylenic amide 59: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17 (d, J = 6.5 Hz, 3 H, $NCH(CH_3)$), 1.25 (d, J = 6.5 Hz, 3 H, $NCH(CH_3)$), 1.45–1.78 (band, 4 H, $(CH_2)_2CH{=}CH$), 2.02–2.25 (band, 4 H, $NCH(CH_3)CH_2CH_2$), 2.33 (t, J = 7.3 Hz, 2 H, $CH_2(CH_2)_2CH{=}CH$), 3.96 (d, J = 4.7 Hz, 2 H, $CH{=}CHCH_2OBz$), 4.18 (m, 2 H, $NCH(CH_3)$), 4.48 (s, 2 H, OCH_2Ph), 5.64 (m, 2 H, $CH{=}CH$), 7.25–7.35 (band, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 18.26; 18.64; 21.49; 27.19; 29.55; 30.05; 31.32; 52.94; 55.14; 70.67; 72.03; 76.19; 88.07; 89.77; 127.58; 127.74; 128.34; 132.79; 138.31; 152.37; IR (neat) 2959, 2245, 1605, 1412 cm^{-1}.

Cyclopentenone 60: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (d, J = 6.6 Hz, 3 H, $NCH(CH_3)$), 1.17 (d, J = 6.5 Hz, 3 H, $NCH(CH_3)$), 1.35–1.7 (band, 4 H, $(CH_2)_2CH{=}CH$), 1.9–2.2 (band, 4 H, $NCH(CH_3)CH_2CH_2$), 2.25–2.6 (band, 6 H, $COCH_2CH_2$ and $CH_2(CH_2)_2CH{=}CH$), 3.77 (m, 1 H, $NCH(CH_3)$), 3.89 (d, J = 4.7 Hz, 2 H, $CH{=}CHCH_2OBz$), 4.24 (m, 1 H, $NCH(CH_3)$), 4.4 (s, 2 H, OCH_2Ph), 5.59 (m, 2 H, $CH{=}CH$), 7.15–7.3 (band, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.95; 18.64; 21.68; 26.18; 28.71; 29.31; 30.34; 31.45; 32.0; 34.65; 52.95; 53.3; 65.3; 65.46; 70.35; 71.64; 127.10; 127.19; 127.38; 127.98; 132.66; 138.01; 139.65; 163.11; 204.12; IR (neat) 2952, 2246, 1701, 1612, 1435 cm^{-1}. Anal. Calcd for $C_{24}H_{29}O_3N$: C, 75.92; H, 8.41. Found: C, 75.80; H, 8.43.

Acetylenic ester 61: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.15 (s, 9 H, TMS), 1.4–1.78 (band, 4 H, $(CH_2)_2CH_2CH{=}CH_2$), 2.04 (m, 1 H, $CH_2CH{=}CH_2$), 3.74 (s, 3 H, CO_2CH_3), 4.41 (t, J = 7 Hz, 1 H, CHOTMS), 4.9–5.05 (band, 2 H, $CH{=}CH_2$), 5.75 (m, 1 H, $CH{=}CH_2$).

Acetylenic ester 62: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.16 (s, 9 H, TMS), 0.87 (d, J = 7.6 Hz, 3 H, $CHCH_3$), 1.43 (m, 1 H, $CHCH_3$), 1.65–2.15 (band, 4 H), 3.74 (s, 3 H, CO_2CH_3), 4.49 (dd, J = 9.1, 5.2 Hz, 1 H, CHOTMS), 4.94 (m, 1 H, $CH{=}CH_2$), 5.02 (m, 1 H, $CH{=}CH_2$), 5.6–5.83 (band, 1 H, $CH{=}CH_2$).

Cyclopentenone 63: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9 H, TMS), 1.18–1.8 (band, 4 H, $(CH_2)_2CH_2CH{=}CH_2$), 2.5 (m, 1 H, $CH_2CH{=}CH_2$), 2.45 (X of ABX_2, t, J = 5.4 Hz, 2 H, $(CO)CH_2CH_2$), 2.73 (AB of ABX_2, dt, J = 19.7, 5.4 Hz, $\Delta\nu$ = 38 Hz, 2 H, $(CO)CH_2CH_2$), 3.82 (s, 3 H, CO_2CH_3), 4.89–5.04 (band, 2 H, $CH{=}CH_2$), 5.2 (m, 1 H, CHOTMS), 5.77 (m, 1 H, $CH{=}CH_2$).

Cyclopentenone 64: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9 H, TMS), 0.95 (d, J = 6.6 Hz, 3 H, $CHCH_3$), 1.19 (m, 1 H, $CHCH_3$), 1.62–2.12 (band, 4 H), 2.46 (X of ABX_2, t, J = 6 Hz, 2 H, $(CO)CH_2CH_2$), 2.74 (AB of ABX_2, dt, J = 20.9, 6 Hz, $\Delta\nu$ = 40 Hz, 2 H, $(CO)CH_2CH_2$), 3.82 (s, 3 H, CO_2CH_3), 4.95 (m, 1 H, $CH{=}CH_2$), 5.01 (m, 1 H, $CH{=}CH_2$), 5.32 (dd, J = 9.5, 2.9 Hz, 1 H, CHOTMS), 5.74 (m, 1 H, $CH{=}CH_2$); ^{13}C NMR ($CDCl_3$) δ 0.00; 18.65; 25.99; 28.88; 29.14; 34.85; 42.10; 43.20; 52.06; 68.32; 116.30; 129.86; 136.94; 163.32; 191.12; 203.79.

Acetylenic esters 65: 1:1 mixture of syn/anti (not separated); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.15 (s, 9 H, TMS), 0.87 (d, J = 6 Hz, 3 H, $CHCH_3$), 0.9 (d, J = 6 Hz, 3 H, $CHCH_3$), 1.05–2.05 (band, 6 H), 1.58 (s, 3 H, $CH{=}CMe_2$), 1.65 (s, 3 H, $CH{=}CMe_2$), 3.75 (s, 3 H, CO_2Me), 4.49 (m, 1 H, CHOTMS), 5.07 (m, 1 H, $CH{=}CMe_2$).

Cyclopentenones 66: 1:1 mixture of syn:anti (not separated); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.09 (s, 9 H, TMS), 0.91 (d, J = 6 Hz, 3 H, $CHCH_3$), 0.94 (d, J = 6 Hz, 3 H, $CHCH_3$), 1.01–2.07 (band, 6 H), 1.58 (s, 3 H, $CH{=}CMe_2$), 1.65 (s, 3 H, $CH{=}CMe_2$), 2.45 (X of ABX_2, t, J = 5.6 Hz, 2 H, $(CO)CH_2CH_2$), 2.74 (AB of ABX_2, dt, J = 20.8, 6 Hz, $\Delta\nu$ = 45 Hz, 2 H, $(CO)CH_2CH_2$), 3.81 (s, 3 H, CO_2Me), 5.07 (m, 1 H, $CH{=}CMe_2$), 4.321 (m, 1 H, CHOTMS); ^{13}C NMR ($CDCl_3$) δ 0.15; 17.64; 18.58; 20.32; 25.26; 25.41; 25.56; 25.71; 25.88; 28.47; 28.78; 34.68; 35.85; 37.78; 37.83; 43.70; 43.84; 51.90; 51.94; 68.08; 68.26; 124.51; 129.58; 130.21; 131.29; 163.18; 163.26; 189.99; 191.23; 203.71; 203.77. Anal. Calcd for $C_{20}H_{34}O_4Si$: C, 65.53; H, 9.35. Found: C, 9.33; H, 65.62.

Syn acetylenic ester 67: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80 (d, J = 6.8 Hz, 3 H, $RCH(CH_3)CH_3$), 1.0 (d, J = 6.8 Hz, 3 H, $RCH(CH_3)CH_3$), 1.28 (t, J = 6.8 Hz, 3 H, $RCO_2CH_2CH_3$), 1.5–1.8 (band, 3 H), 1.76 (s, 3 H, $RC(CH_3){=}CCO_2Et$), 2.2 (m, 1 H, $RC(OH)CH(H)R$), 3.27 (m, 1 H, $RC(OH)CH(H)R$), 3.78 (s, 3 H, RCO_2CH_3), 4.18 (q, J = 6.8 Hz, 2 H, $RCO_2CH_2CH_3$), 4.32 (m, 1 H, ipr-CHR_2), 4.75 (bs, 1 H, $HOCHR_2$), 5.88 (s, 1 H, $CR_2{=}CHCO_2Et$); ^{13}C NMR ($CDCl_3$) 14.13, 19.12, 20.85, 21.48, 29.58, 38.25, 44.43, 52.70, 59.72, 60.73, 75.32, 88.45, 120.72, 153.91, 159.42, 168.33.

Syn cyclopentenone 68: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.04 (s, 9 H, $ROSi(CH_3)_3$), 0.80 (d, J = 6.8 Hz, 3 H, $RCH(CH_3)CH_3$), 0.95 (d, J = 6.8 Hz, 3 H, $RCH(CH_3)CH_3$), 1.2 (t, J = 6.8 Hz, 3 H, $RCO_2CH_2CH_3$), 1.25–1.65 (band, 2 H), 1.74 (s, 3 H, $RC(CH_3){=}CCO_2Et$), 1.7–2.0 (band, 1 H), 2.4 (t, J = 5.1 Hz, 2 H, $-CH_2CH_2C(O)-$), 2.7 (m, 2 H, $-CH_2CH_2C(O)-$), 3.76 (s, 3 H, RCO_2CH_3), 4.04 (q, J = 6.8 Hz, 2 H, $RCO_2CH_2CH_3$), 5.0 (m, 1 H, $TMSOCHR_2$), 5.80 (s, 1 H, $CR_2{=}CHCO_2Et$); ^{13}C NMR ($CDCl_3$) δ 0.29, 0.54, 0.58. 14.84, 20.69, 21.33, 21.37, 26.02, 31.86, 35.20, 37.68, 42.81, 52.50, 59.91, 68.54, 120.26, 131.24, 161.59, 163.87, 166.39, 188.97, 204.26; HRMS for $C_{22}H_{36}O_6Si$ calcd 424.2281, found 424.2279.

Anti cyclopentenone 69: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.03 (s, 9 H, ROSi(CH_3)$_3$), 0.75 (d, J = 6.8 Hz, 3 H, RCH(CH_3)CH_3), 0.97 (d, J = 6.8 Hz, 3 H, RCH(CH_3)CH_3), 1.2 (t, J = 6.8 Hz, 3 H, ROC$_2$H$_2$$CH_3$), 1.3–2.0 (band, 2 H), 1.8 (s, 3 H, RC(CH_3)=CCO$_2$Et), 2.4–2.9 (band, 4 H), 3.78 (s, 3 H, RCO$_2$$CH_3$), 4.0 (q, J = 6.8 Hz, 2 H, RCO$_2$$CH_2$$CH_3$), 5.2 (m, 1 H, TMSOC$HR_2$), 5.65 (s, 1 H, CR_2=CHCO$_2$Et).

Acetylenic ester 70: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.0 (d, J = 7.5 Hz, 3 H, CHCH_3), 1.41–1.9 (band, 6 H), 2.28 (m, 2 H, Csp-CH_2), 3.4–4.23 (band, 6 H), 3.92 (s, 3 H, CO$_2$$CH_3$), 4.6 (m, 2 H, C$H_2$OTHP), 6.1 (m, 2 H, C$H$=C$H$).

Acetylenic ester 71: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.0 (d, J = 6 Hz, 3 H, CHCH_3), 1.33–1.72 (m, 2 H, CH_2CHCH$_3$), 2.22 (m, 2 H, Csp-CH_2), 2.48–2.79 (m, 1 H, CHCH$_3$), 3.95 (s, 3 H, CO$_2$$CH_3$), 4.1 (dd, J = 6, 1.5 Hz, 2 H, CH_2OCH$_2$Ph), 4.5 (s, 2 H, OCH_2Ph), 5.27 (m, 1 H, CH=CHCH$_2$), 5.5 (m, 1 H, CH=CHCH$_2$), 7.2–7.4 (band, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.78; 20.99; 31.42; 34.69; 52.69; 66.0; 72.33; 72.98; 89.64; 126.67; 127.63; 127.82; 128.40; 137.33; 138.34; 150.42; IR (film) 2880, 2840, 2220, 1730, 1420, 1450, 1250 cm^{-1}; HRMS for $C_{18}H_{22}O_3$ calcd 286.1568, found 286.1583.

Cyclopentenone 72: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (d, J = 7.5 Hz, 3 H, CHCH_3), 1.4–1.9 (band, 6 H), 2.22 (1 H, CHCH$_3$), 2.38–2.8 (band, 6 H), 3.78 (s, 3 H, CO$_2$$CH_3$), 4.58 (m, 2 H, C$H_2$-OTHP), 5.54 (m, 2 H, C$H$=C$H$).

Cyclopentenone 73: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.0 (d, J = 6 Hz, 3 H, CHCH_3), 1.32–1.7 (m, 2 H, CH$_2$$CH_2$CH), 2.4–2.8 (band 7 H), 3.8 (s, 3 H, CO$_2$$CH_3$), 4.06 (c, C$H_2OCH_2$Ph), 4.5 (s, 2 H, OC$H_2$Ph), 5.38 (m, 1 H, C$H$=CHCH$_2$), 5.62 (m, 1 H, CH=C$HCH_2$), 7.2–7.4 (band, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 20.22; 30.46; 30.79; 34.45; 34.92; 36.80; 51.83; 70.7; 72.06; 125.9; 127.58; 127.72; 127.76; 128.36; 132.05; 138.58; 159.8; 188.75; 203.61; IR (film): 2940, 2830, 1740, 1705, 1615, 1450, 1430, 1350 cm^{-1}; HRMS for $C_{21}H_{26}O_4$ calcd 342.1831, found 342.1829.

Anti acetylenic ester 74: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (s, 9 H, tBu), 1.31 (t, J = 7.3 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.83–2.32 (band, 2 H, CH_2CH(tBu)), 2.48 (dd, J = 12.8, 3 Hz, 1 H, CH$_2$CH(tBu)), 3.28 (s, 3 H, OCH$_2$OCH_3), 4.1 (dd, J = 11.3, 4.5 Hz, 1 H, CHOMOM), 4.23 (q, J = 7.3 Hz, 2 H, CO$_2$CH_2CH$_3$), 4.53 (d, J = 7.6 Hz, 1 H, OCH_2OCH$_3$), 4.78 (d, J = 7.6 Hz, 1 H, OCH_2-OCH$_3$), 6.26 (m, 1 H, OCH=CH), 7.23 (m, 1 H, OCH=CH), 7.36 (m, 1 H, OCH=CC).

Anti acetylenic ester 75: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (s, 9 H, tBu), 1.32 (t, J = 7.6 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.68 (broad s, 1 H, OH), 1.88–2.18 (band, 2-H, CH_2CH(tBu)), 2.45 (dd, J = 12.4, 4 Hz, 1 H, CH$_2$CH(tBu)), 4.1–4.27 (band, 1 H, CHOH), 4.24 (q, J = 7.6 Hz, 2 H, CO$_2$CH_2CH$_3$), 6.27 (m, 1 H, OCH=CH), 7.23 (m, 1 H, OCH=CH), 7.36 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 13.6; 27.48; 32.72; 37.04; 42.72; 61.43; 61.81; 76.68; 87.69; 110.3; 124.28; 140.07; 142.24; 153.34; IR (CH_2Cl_2) 3400 (broad), 2955, 2220, 1705, 1360, 1245 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.97; H, 8.02.

Syn acetylenic ester 76: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (s, 9 H, tBu), 1.3 (t, J = 7.3 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.64 (broad, s, 1 H, OH), 1.76–2.2 (band, 2 H, CH_2CH(tBu)), 2.62 (dd, J = 12.7, 4 Hz, 1 H, CH$_2$CH(tBu)), 4.12–4.28 (band, 1 H, CHOH), 4.23 (q, J = 7.6 Hz, 2 H, CO$_2$CH_2CH$_3$), 6.23 (m, 1 H, OCH=CH), 7.22 (m, 1 H, OCH=CH), 7.38 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 13.91; 27.85; 32.90; 37.54; 42.01; 59.93; 62.11; 75.98; 88.55; 110.72; 124.25; 140.70; 142.6; 153.46; IR (CH_2Cl_2) 3430 (broad), 2960, 2220, 1710, 1360, 1250 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.94; H, 7.99.

Cyclopentenone 77: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (s, 9 H, tBu), 1.21 (t, J = 6.6 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.22–1.4 (band, 1 H, CH$_2$CH(tBu)), 1.95–2.22 (band, 2 H, CH_2CH(tBu)), 2.45 (X of ABX_2, t, J = 5.25 Hz, 2 H, COCH_2CH$_2$), 2.67 (AB of ABX_2, $\Delta\nu$ = 39 Hz, J = 20.25, 5.25 Hz, 2 H, COCH$_2$CH_2), 3.31 (s, 3 H, OCH$_2$OCH_3), 4.13 (qd, J = 6.5, 2.3 Hz, 2 H, CO$_2$CH_2CH$_3$), 4.52 (AB, $\Delta\nu$ = 9.1 Hz, J = 9 Hz, 2 H, OCH_2OCH$_3$), 4.87 (m, 1 H, CHOMOM), 6.23 (m, 1 H, OCH=CH), 7.12 (m, 1 H, OCH=CH), 7.35 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) 13.78; 13.97; 22.3; 25.09; 25.94; 31.3; 33.98; 34.45; 55.75; 60.76; 74.35; 95.72; 132.86; 162.80; 184.91; 203.28; IR (CH_2Cl_2) 1735, 1710, 1260 cm^{-1}. Anal. Calcd for $C_{21}H_{30}O_6$: C, 66.64; H, 7.99. Found: C, 66.46; H, 8.00.

Cyclopentenone 78: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.06 (s, 9 H, TMS), 0.82 (s, 9 H, tBu), 1.15–1.4 (band, 1 H, CH$_2$CH(tBu)), 1.22 (t, J = 6.6 Hz, 3 H, CO$_2$CH$_2$CH_3), 1.82–2.18 (band, 2 H, CH_2CH(tBu)), 2.43 (X of ABX_2, t, J = 5.25 Hz, 2 H, COCH_2CH$_2$), 2.67 (AB of ABX_2, $\Delta\nu$ = 50 Hz, J = 20.3, 5.25 Hz, 2 H, COCH$_2$CH_2), 4.16 (m, 2 H, CO$_2$CH_2CH$_3$), 5.0 (m, 1 H, CHOTMS), 6.24 (m, 1 H, OCH=CH), 7.1 (m, 1 H, OCH=CH), 7.34 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ –0.54; 13.7; 24.43; 27.33; 32.86; 34.14; 36.66; 41.73; 60.53; 67.93; 110.46; 124.58; 132.53; 140.32; 142.87; 162.48; 183.16; 203.54; IR (CH_2Cl_2) 1750, 1725, 1640 cm^{-1}. Anal. Calcd for $C_{22}H_{34}O_5Si$: C, 64.99; H, 8.43. Found: C, 65.08; H, 8.45.

Cyclopentenone 79: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.02 (s, 9 H, TMS), 0.83 (s, 9 H, tBu), 1.18 (t, J = 6.9 Hz, 3 H, CO$_2$-CH$_2$CH_3), 1.56 (m, 1 H, CH_2CH(tBu)), 1.98 (m, 1 H, CH_2CH-(tBu)), 2.4–2.62 (band, 3 H, COCH_2CH$_2$ and CH$_2$CH(tBu)), 2.55–2.98 (band, 2 H, COCH$_2$CH_2), 4.14 (m, 2 H, CO$_2$CH_2CH$_3$), 4.83 (dd, J = 10.1, 2.6 Hz, 1 H, CHOTMS), 6.22 (m, 1 H, OCH=CH), 7.16 (m, 1 H, OCH©H), 7.34 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 0.0; 14.24; 25.79; 28.07; 33.0; 35.5; 36.92; 42.67; 61.18; 60.0; 111.9; 126.0; 131.5; 140.77; 142.22; 162.5; 187.5; 204.0; IR (CH_2Cl_2) 2950, 1745, 1710, 1630 cm^{-1}. Anal. Calcd for $C_{22}H_{34}O_5$-Si: C, 64.99; H, 8.43. Found: C, 64.92; H, 8.42.

Acetylenic amides 80: mixture of syn and anti (1:2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (s, 9 H, tBu), 1.75–2.2 (band, 2 H, CH_2-CH(tBu)), 1.92 (m, 4 H, NCH$_2$(CH_2)$_2$CH$_2$), 2.44 (dd, J = 12.6, 3.8 Hz, $^2/_3$ H, CH$_2$CH(tBu) anti), 2.64 (dd, J = 12.6, 3.8 Hz, $^3/_3$ H, CH$_2$CH(tBu) syn), 3.15 (bs, 1 H, OH), 3.46 (m, 2 H, NCH_2-(CH$_2$)$_2$CH_2), 3.61 (m, 2 H, NCH_2(CH$_2$)$_2$CH_2), 4.19 (m, 1 H, CHOH), 6.22 (m, $^1/_3$ H, OCH=CH syn), 6.25 (m, $^2/_3$ H, OCH=CH anti), 7.19 (m, $^2/_3$ H, OCH=CH anti), 7.21 (m, $^1/_3$ H, OCH=CH syn), 7.35 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 24.52; 25.15; 25.18; 27.77; 27.84; 32.82; 32.99; 37.45; 37.87; 41.91; 43.07; 45.19; 45.24; 48.12; 59.64; 61.65; 77.34; 78.42; 91.14; 92.23; 110.64; 111.79; 124.46; 124.65; 140.12; 140.64; 142.30; 142.34; 152.36; IR (CH_2Cl_2) 3300, 2965, 2880, 2230, 1610 (broad), 1440 cm^{-1}. Anal. Calcd for $C_{18}H_{25}O_3N$: C, 71.26; H, 8.31. Found: C, 71.19; H, 8.37.

Cyclopentenones 81: anti cyclopentenone, free OH; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.8 (s, 9 H, tBu), 1.7–2.15 (band, 6 H, CH_2-CH(tBu) and NCH$_2$(CH_2)$_2$CH$_2$), 2.3–2.7 (band, 5 H, CH$_2$CH(tBu) and COCH_2CH$_2$), 3.3 (m, 2 H, NCH_2(CH$_2$)$_2$CH_2), 3.45 (m, 2 H, NCH_2(CH$_2$)$_2$CH_2), 4.2 (broad, s, 1 H, OH), 4.3 (dd, J = 8.2, 3.6 Hz, 1 H, CHOH), 6.28 (m, 1 H, OCH=CH), 7.15 (m, 1 H, OCH=CH), 7.35 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 24.02; 25.66; 27.21; 27.55; 33.26; 34.55; 35.51; 43.04; 45.69; 47.16; 69.5; 110.84; 125.09; 138.24; 140.14; 142.38; 163.68; 182.17; 204.25; IR (CH_2Cl_2): 3390, 2960, 2880, 1705, 1605, 1445 cm^{-1}. Anal. Calcd for $C_{21}H_{29}O_4N$: C, 70.17; H, 8.13. Found: C, 69.91; H, 8.07.

Syn cyclopentenone, free OH: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81 (s, 9 H, tBu), 1.6–2.0 (band, 6 H, CH_2CH(tBu), and NCH$_2$(CH_2)$_2$CH$_2$), 2.3–2.75 (band, 5 H, CH$_2$CH(t-Bu) and COCH_2CH$_2$), 3.2 (m, 2 H, NCH_2(CH$_2$)$_2$CH_2), 3.45 (m, 2 H, NCH_2-(CH$_2$)$_2$CH_2), 3.92 (bs, 1 H, OH), 4.13 (bd, J = 10.3 Hz, 1 H, CHOH), 6.18 (m, 1 H, OCH=CH), 7.15 (m, 1 H, OCH=CH), 7.3 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 24.15; 25.69; 27.26; 27.90; 32.93; 34.56; 35.87; 42.36; 45.63; 47.23; 69.31; 110.77; 124.56; 137.24; 140.76; 142.27; 164.35; 182.98; 204.21; IR (CH_2Cl_2) 3390, 2960, 2880, 1705, 1610, 1445 cm^{-1}.

Acetylenic ester 82: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.0 (s, 3 H, Si(tBu)Me_2), 0.09 (s, 3 H, Si(tBu) Me_2), 0.88 (s, 9 H, tBu), 1.3 (s, 3 H, OC(CH_3)), 1.43 (dt, J = 7.5, 5 Hz, 1 H, CHCH(OTBS)), 2.35–2.72 (band, 4 H), 3.73 (s, 3 H, CO$_2$$Me$), 4.34 (t, J = 6.5 hz, 1 H, CH(OTBS)), 5.08–5.3 (m, 2 H, CH=CH_2), 5.68–5.95 (m, 1 H, CH=CH$_2$).

Cyclopentenone 83: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 3 H, Si(tBu)Me_2), 0.05 (s, 3 H, Si(tBu)Me_2), 0.87 (s, 9 H, tBu), 1.3 (s, 3 H, OC(CH_3)), 2.4–2.95 (band, 8 H), 3.18 (dd, J = 13.5, 9 Hz, 1 H, –C=CCH_2), 3.83 (s, 3 H, CO$_2$$Me$), 4.07 (t, J = 7.5 hz, 1 H, CH(OTBS)), 5.2 (m, 2 H, CH=CH_2), 5.65–5.9 (m, 1 H, CH=CH$_2$).

Acetylenic amide 84: ^{1}H NMR (200 MHz, $CDCl_3$) δ –0.5 (s, 3 H, Si(tBu)Me_2), 0.02 (s, 3 H, Si(tBu)Me_2), 0.82 (s, 9 H, tBu), 1.25 (s, 3 H, OC(CH_3)), 1.39 (m, 1 H, CHCH(OTBS)), 2.25–2.7 (band, 4 H), 2.68 (s, 3 H, NMe_2), 3.14 (s, 3 H, NMe_2), 4.27 (t, J = 6 Hz, 1 H, CH(OTBS)), 5.12 (m, 2 H, CH=CH_2), 5.62–5.95 (m, 1 H, CH=CH$_2$); ^{13}C NMR ($CDCl_3$) δ –5.17; –4.13; 17.61; 17.92; 18.55; 25.69; 33.88; 38.07; 51.07; 56.05; 56.7; 73.94; 74.79; 91.09; 115.97; 139.34; 154.44; IR (film) 3450 (broad), 3015, 2950, 2925, 1615, 1395, 1210 cm^{-1}.

Cyclopentenone 85: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.02 (s, 3 H, Si(tBu)Me_2), 0.03 (s, 3 H, Si(tBu)Me_2), 0.83 (s, 9 H, tBu), 1.18 (s, 3 H, OC(CH_3)), 1.53 (m, 1 H, CHCH(OTBS)), 2.3–2.6 (band, 8 H), 2.88 (s, 3 H, NMe_2), 2.99 (s, 3 H, NMe_2), 3.96 (t, J = 7.5 Hz, 1 H, CH(OTBS)), 5.14 (m, 2 H, CH=CH_2), 5.55–5.80 (m, 1 H, CH=CH_2); ^{13}C NMR ($CDCl_3$) δ -4.73, -3.39; 16.94; 18.24; 26.02; 30.61; 31.42; 35.02; 35.24; 38.38; 51.02; 55.63; 57.78; 77.97; 117.89; 139.78; 139.91; 165.56; 181.67; 205.13; IR (film) 2950, 2920, 1740, 1710, 1640, 1390, 1250, 1130, 1085 cm^{-1}; HRMS for $C_{22}H_{37}O_4Si$ calcd 407.2492, found 407.2508.

Acetylenic ester 86: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (s, 9 H, tBu), 1.33 (t, J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 3.46 (d, J = 7.9 Hz, 1 H, CH(tBu)), 3.83 (d, J = 7.9 Hz, 1 H, CHOH), 4.27 (q, J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 6.41 (m, 1 H, OCH=CH), 7.37–7.41 (band, 2 H, OCH=C); ^{13}C NMR ($CDCl_3$) δ 1.99; 25.77; 34.09; 62.12; 62.37; 63.16; 66.07; 78.11; 83.06; 111.09; 120.61; 141.05; 142.47; 153.02; 189.19; IR (film) 2223, 1718, 1374, 1260 cm^{-1}.

Cyclopentenone 87: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.11 (s, 9 H, TMS), 0.94 (s, 9 H, tBu), 1.27 (t, J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 2.46–2.59 (band, 2 H, OCH_2CH_2), 2.81–2.97 (band 2 H, OCH_2CH_2), 3.4 (d, J = 7.9 Hz, 1 H, CH(tBu)), 4.15 (m, 2 H, $CO_2CH_2CH_3$), 4.51 (d, J = 7.8 Hz, 1 H, CHOTMS), 6.3 (m, 1 H, OCH=CH), 7.26 (m, 1 H, OCH=CH), 7.35 (m, 1 H, OCH=CC); ^{13}C NMR ($CDCl_3$) δ 0.06; 14.08; 26.01; 34.38; 34.70; 61.05; 62.22; 66.13; 69.13; 95.74; 111.07; 121.41; 127.57; 140.93; 142.53; 162.55; 178.18; 203.57; IR (CH_2Cl_2) 1750, 1725, 1272 cm^{-1}. Anal. Calcd for $C_{22}H_{32}O_6Si$: C, 62.82; H, 7.67. Found: C, 62.81; H, 7.67.

Anti acetylenic ester 88: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35 (s, 3 H, -OC(CH_3)(CH_3)CH-), 1.38 (s, 3 H, -OC(CH_3)(CH_3)CH-), 1.42 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.52 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.77 (dt, J = 5.6, 11.2 Hz, 1 H, -CH_2CH-), 2.35 (d, J = 5.6 Hz, 2 H, -CH_2CH-), 3.76 (s, 3 H, -CO_2CH_3), 4.24 (dd, J = 7.5, 11.2 Hz, 1 H, -C(H)O-), 5.31 (2 multiplets, J = 9.3 Hz, 1 H, -CH=CH(H)), 5.43 (2 multiplets, J = 16.8 Hz, 1 H, -CH=CH-(H)), 5.82 (ddd, J = 7.5, 9.3, 16.8 Hz, 1 H, -CH=CH_2); ^{13}C NMR ($CDCl_3$) δ 153.91, 136.65, 119.03, 98.35, 87.67, 74.48, 73.96, 71.87, 52.53, 45.82, 31.67, 25.05, 24.47, 17.32; IR (film) 3420 (broad, m), 3080 (w), 2980, 2950, 2910, 2210, 1770, 1750, 1435, 1375, 1260, 1195 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.79; H, 8.31.

Syn acetylenic ester 89: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (s, 3 H, -OC(CH_3)(CH_3)CH-), 1.37 (s, 3 H, -OC(CH_3)(CH_3)CH-), 1.47 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.48 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.63 (m, 1 H, -CH_2CH-), 2.51 (d, (2.50), s (2.52), AB, 2 H, -CH_2-CH-), 3.74 (s, 3 H, -CO_2CH_3), 4.76 (m, 1 H, -C(H)O-), 5.24–5.40 (band, 2 H, -CH=CH_2), 5.82 (ddd, J = 3.6, 10.5, 18.0 Hz, 1 H, -CH=CH_2); ^{13}C NMR ($CDCl_3$) δ 137.17, 115.88, 99.05, 85.76, 74.30, 69.02, 68.66, 45.16, 31.51, 29.45, 28.60, 25.02, 14.01; IR (film) 3300, 2980, 2920, 2220 (w), 2100 (w), 1975 (w), 1270, 1245, 1190 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.49; H, 8.31.

Cyclopentenone 90: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.17 (s, 3 H, -C(CH_3)(CH_3)O-), 1.28 (s, 3 H, -C(CH_3)(CH_3)O-), 1.31 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.41 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.85 (m, J = 1.9, 5.6 Hz, 1 H, -$C(CH_3)_2CH$-), 2.39 (t, J = 5.6 Hz, 2 H, -CH_2CH-), 2.48 (t, J = 6.3 Hz, 1 H, -$COCH_2CH$(H)-), 2.52–2.65 (m, 2 H, -$COCH_2CH$(H)- and -$COCH$(H)CH_2-), 2.82 (dd, J = 6.7, 16.8 Hz, 1 H, -$COCH$(H)CH_2-), 3.76 (s, 3 H, -CO_2CH_3), 4.08 (m, 1 H, =CHC(H)O-), 5.08 (dd, J = 1.1, 9.3 Hz, 1 H, -CH=CH(H)), 5.25 (dd, J = 17.9 Hz, 1 H, -CH=CH(H)), 5.62 (ddd, J = 7.5, 9.3, 17.9 Hz, 1 H, -CH=CH_2); ^{13}C NMR ($CDCl_3$) δ 202.96, 163.64, 136.44, 133.13, 118.94, 98.07, 74.00, 72.66, 51.71, 45.94, 34.51, 31.57, 31.06, 30.79, 29.99, 24.76, 23.68, 13.95; IR (film) 2980, 2940, 2240, 1780, 1720, 1710, 1620, 1430, 1370, 1345, 1250, 1195, 1045, 1020 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 67.10; H, 8.17.

Cyclopentenone 91: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.15 (s, 3 H, -C(CH_3)(CH_3)O-), 1.43 (s, 3 H, -C(CH_3)(CH_3)O-), 1.47 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.49 (s, 3 H, -OC(CH_3)(CH_3)O-), 1.79 (m, J = 5.6 Hz, 1 H, -$C(CH_3)_2CH$-), 2.45 (t, J = 5.6 Hz, 2 H, -CH_2CH-), 2.58 (t, J = 5.6 Hz, 1 H, -$COCH_2CH$(H)-), 2.67 (t, J = 5.6 Hz, 1 H, -$COCH_2C$(H)(H)-), 2.82 (dd, J = 6.7, 16.8 Hz, 1 H, -$COCH$(H)CH_2-), 3.19 (dd, J = 6.7, 16.8 Hz, 1 H, -$COCH$(H)-CH_2-), 3.84 (s, 3 H, CO_2CH_3), 4.77 (m, 1 H, =CHC(H)O-), 5.18 (2 triplets, J = 11.2 Hz, 1 H, -CH=CH(H)), 5.34 (2 triplets, J = 16.8 Hz, 1 H, -CH=CH(H)), 5.76 (ddd, J = 3.7, 11.2, 16.8 Hz, 1 H, -CH=CH_2); ^{13}C NMR ($CDCl_3$) δ 203.43, 163.91, 137.13, 133.13, 115.90, 99.26, 74.39, 69.11, 51.83, 43.09, 34.73, 31.54, 30.79, 29.22, 28.57, 28.50, 24.99; IR (film) 2980, 2940, 1740, 1710, 1620, 1430, 1370, 1350, 1290, 1250, 1220, 1190, 1020 cm^{-1}.

Acknowledgment. We thank the National Science Foundation (CHE-9014641), The National Institutes of Health (GM-38904), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Rhone Poulenc, Inc., for generous financial support.

Supplementary Material Available: ^{1}H NMR spectra for compounds **27–31, 33, 37–41, 43, 45–49, 51–56, 59, 61–65, 67–74, 81–86,** and **91** and ^{13}C NMR spectra for compounds **27–31, 33, 37, 38, 41, 43, 45, 46, 48, 49, 55, 56, 59, 62, 64, 67, 68, 71, 73, 74, 81, 84–86,** and **91** (45 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.