An Intramolecular Allenic [2+2+1] Cycloaddition.

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A new stereo-and regioselective method for the preparation of α-methylene and 4-alkylidene cyclopentenones is described. These substructures were achieved by an intramolecular [2+2+1] cycloaddition of an allene, alkyne and carbon monoxide moieties to afford the target compounds stereoselectively and in good yields. In some cases, the target compounds were obtained as mixtures but it is demonstrated that the formation of either the α-methylene or 4-alkylidene cyclopentenone can be controlled by the allene structure or reaction conditions. Monosubstituted allenes afford α-methylene cyclopentenones as the only cycloadduct. Disubstitution on the allene alters the course of the allenic [2+2+1] reaction. 3,3-Disubstituted allenes undergo cycloaddition with the least substituted π-bond of the allene. This affords the bicyclo[4.3.0]nonane ring system. Cycloaddition of 1,3-disubstituted allenes afford mixtures of several possible cycloadducts. However, it has been shown that good control over the product ratio can be obtained by altering the cycloaddition conditions and that the regiochemistry can be directed depending upon the metal used.

Introduction

Since the discovery of the Pauson-Khand (P-K) reaction (formally a [2+2+1] cycloaddition) in the early 70's[1] a great deal of work has transpired to increase the synthetic value of this method and is now regarded as a method of choice when preparing cyclopentenones.[2] Curiously at the initiation of this research, no successful examples of using allenes in place of the olefin component in this [2+2+1] cycloaddition had been reported.[3] We felt this would be an interesting process to investigate since there are two π-

bonds with which the cyclization process can occur (Scheme 1). If this reaction occurs with the internal π-bond (reaction pathway A) the resulting cycloadduct will be an α-methylene cyclopentenone. If the reaction occurs with the external π-bond of the allene (reaction pathway B) the resulting adduct will be a 4-alkylidene cyclopentenone. Either cyclization pathway gives interesting substructures which are present in a variety of biologically important compounds such as the illudins[4] and the prostaglandins.[5]

Scheme 1

Results and Discussion

Monosubstituted Allenes. The feasibility of this allenic [2+2+1] cycloaddition was initially established by preparing alkynyl allene **1** according to the sequence shown in Scheme 2. Addition of lithium trimethylsilylacetylide to 1,3-dibromopropane followed by treatment of the resulting bromoalkyne with magnesium, copper bromide and propargyl methyl ether afforded the desired alkynyl allene **1**. All attempts to effect a Pauson-Khand type cycloaddition of compound **1** using dicobalt octacarbonyl [$Co_2(CO)_8$] were unsuccessful.[6] However, use of conditions reported by Jeong and coworkers[7] proved to be quite successful in the formation of α-methylene cyclopentenone **2**. Treatment of alkynyl allene **1** with molybdenum hexacarbonyl [$Mo(CO)_6$] and dimethylsulfoxide at 100 °C gave compound **2** in a 68% yield. The ^{1}H NMR spectrum showed new resonances at δ 5.92 and 5.27 characteristic of the exocyclic methylene protons and a new absorption appeared at 1692 cm^{-1} in the IR inferring an unsaturated cyclic ketone. The reaction can be monitored reliably by GC-MS and the color of the reaction media has also proven to be diagnostic of the progress of the reaction. As the reaction temperature approaches 100 °C the molybdenum dissolves and the clear heterogeneous mixture turns bright yellow and homogeneous. At this point no product is observed by GC-MS. Soon afterward the

solution turns to a greenish-gray and GC-MS shows that product formation is occurring. Eventually a blue precipitate is formed on the walls of the flask and the starting material is no longer being consumed. It is assumed that these color changes are associated with the varying degrees of complexation of the molybdenum, with the final blue precipitate being a molybdenum carbonyl species that is no longer useful in the reaction sequence.

Scheme 2

Other monosubstituted allenes were also submitted to the cyclization conditions and are depicted in Table 1. Alkynyl allenes **3** and **5** were prepared possessing substituents on C-4 and C-5 of the tether. When R=H (compound **3**, Table 1), the cyclization occurred in 47% yield to give α-methylene cyclopentenone **4** as a 3:1 mixture of diastereomers. These diastereomers were separated by flash column chromatography and it was determined that the major isomer possesses an *anti* relationship between the proton at the ring fusion and the proton geminal to the hydroxyl moiety. This conclusion is based upon the observed coupling constant for these vicinal protons (10.1 Hz) which is in agreement with the calculated coupling constant from the geometry minimized structure using Macromodel (10.2 Hz). The minor isomer possessing the *syn* relationship between these protons shows no coupling which is in close agreement with the calculated coupling (3.2 Hz). Protection of the hydroxyl moiety as the MOM ether (compound **5**, Table 1) did not produce significant changes in the yield (54%) and gave compound **6** in a 1:1 diastereomeric ratio of products. Lengthening the tether was examined next. Alkynyl allene **7** cyclized to give the bicyclo[4.3.0]nonane **8** in 30% yield based upon recovered starting material. The incorporation of a four-carbon tether in this P-K cycloaddition gives very low yields and is thought to be a result of the sensitivity of the cycloaddition to entropic effects and competing polymerization of the allene moiety. In all these examples

using monosubstituted allenes, cycloaddition occurred exclusively with the internal π-bond of the allene (Pathway A, Scheme 1).

Table 1

1,3-Disubstituted Allenes. Next, substitution patterns on the allenes were varied in order to examine its effect on the regiochemical outcome of the cycloaddition. There are numerous natural products possessing substitution at the terminus of the exocyclic olefin moiety of the α-methylene cyclopentenone and the allenic [2+2+1] cycloaddition provides a direct route to this structure. Initially, the cyclizations of 1,3-disubstituted allenes possessing a seven carbon chain appended to the terminus of the allene were examined. The long alkyl chain was selected so that volatility of the starting materials and the products would not affect the observed yields. When 1,3-disubstituted alkynyl allene **9** was treated with molybdenum hexacarbonyl/DMSO cycloaddition occurred exclusively via pathway A to give the bicyclo[3.3.0]octane ring system **10** as a mixture of *E*:*Z* isomers (2:1 ratio) in a 75% yield (entry 1, Table 2).[8] To determine if the *E/Z* ratio was an artifact of the cyclization conditions, an isomerization study was done by submitting both pure **10-*E*** and pure **10-*Z*** to the molybdenum cyclization conditions. The isomers **10-E** and **10-Z** were separated using column chromatography (3% ether/hexanes). When **10-*E*** was submitted to the reaction conditions, no isomerization was observed after 3 days but small amounts of an isomeric dienone began forming after 24 hours. Alternatively, **10-*Z*** showed some isomerization to **10-*E*** after 24 h with concomitant formation of the same dienone isomer seen in the *E* system. However, we feel that isomerization of the product was not a significant factor in the *E:Z* ratio since the duration of the original cycloaddition (**9** → **10**) was only 10 h. Phenyl substituted allene **11** cyclized with slightly

higher stereoselectivity (5:1, *E:Z*) to form cyclopentanone **12**. This modest increase in stereoselectivity may be attributed to a stereoelectronic effect caused by hindered rotation around the allene phenyl bond.

Table 2

Since we are interested in using this [2+2+1] cycloaddition to prepare chiral α-methylene cyclopentenones this apparent lack of facial selectivity resulting in *E* and *Z* isomers concerned us. The *Z*-isomer results from the addition of the metal-alkyne complex from the same face of the allene as the R group and the *E*-isomer results from the addition of the alkyne-metal complex form the opposite face of the R group (Scheme 3). Thus in an effort to increase the facial selectivity, we turned to

Scheme 3

dicobalt octacarbonyl [$Co_2(CO)_8$] as a metal promoter, since dicobalt octacarbonyl has been used successfully in the selective formation of diastereomers.[9] Complexation of the alkynyl allene **9** with $Co_2(CO)_8$ under standard conditions affords metal complex **13**. Subjection of **13** to a variety of cycloaddition conditions indeed resulted in reactions that proceeded with much higher facial selectivity however, π-bond selectivity eroded resulting in nearly 1:1 mixtures of bicyclo[4.3.0]nonane **14** and the bicyclo[3.3.0]octane ring systems **15** (entries 3,4,5, Table 2). In the cobalt-mediated cyclizations, the highest yields were obtained when the alkynes were precomplexed with the cobalt and purified before being subjected to cyclization conditions. The reaction proceeded much more rapidly when

trimethylamine-N-oxide was used as a promoter[10] instead of DMSO however the observed facial selectivity was lower (compare entries 3 and 4, Table 2).

The separation of compounds **14,15-*E*** and **15-*Z*** was effected by HPLC (silica column) eluting with 0.75% EtOAc/hexanes and the assignment of the cycloadduct structures was based upon the ^{1}H NMR spectra and nOe studies (Figure 1). In particular, the most diagnostic resonances appear as triplets at δ5.86, 6.40 and 5.97 corresponding to the olefin protons H_e of **15-*Z*** and **15-*E*** and H_a of the bicyclo[4.3.0]nonane ring system **14**, respectively. In the **15-*Z*** isomer, an nOe (3.2%) was observed between the olefin proton resonance and the allylic methine proton resonance (H_e and H_a). There was no observable nOe for these same proton resonances in the **15-*E*** isomer. This assignment is also in agreement with the chemical shifts observed for the vinyl protons where H_e of **15-*E*** is shifted 0.51 ppm further downfield than the same proton of **15-*Z***. Decoupling and correlation experiments helped to characterize the bicyclo[4.3.0]nonane structure **14**. In particular, irradiation of the allylic protons (H_b) resulted in a singlet for vinylic proton H_a showing them to be vicinal. Additionally, irradiation of H_c simplifies H_b to a doublet and H_d to a singlet.

Figure 1

Finally, when the cyclization was effected in the presence of $Cp_2Zr(n\text{-}Bu)_2$,[11] the bicyclo[3.3.0]octane **15-*E*** was isolated as the major product in good yields (entry 6, Table 2). We have subsequently determined that this notable facial selectivity is an artifact of the workup conditions which involve the addition of 3M HCl to the reaction media. Treatment of the bicyclo[3.3.0]octane **15-*Z*** (independently synthesized) to these workup conditions resulted in the complete isomerization of the **15-*Z*** to **15-*E*** in less than 15 minutes. In an effort to determine the true stereochemical outcome of the zirconium-mediated cyclization,

we hydrolyzed zirconacycle intermediate **17** affording dienes **18** and **19** in a 10:1 ratio (eq. 1). This selectivity remains synthetically appealing and can be rationalized

Equation 1

on the basis of the steric bulk of the cyclopentadienyl ligands as shown in the two extreme precyclization conformers **A** and **B** (Scheme 4). Conformer **B** is predicted to be disfavored due to a severe steric interaction between the alkyl group on the terminus of the allene and the cyclopentadienyl rings. The observed π-bond selectivity can be rationalized as follows. The internal π-bond orbitals of conformer **C** are projected toward the reactive zirconium-carbon bond. Whereas the external π-bond orbitals are perpendicular to the zirconium-carbon bond. Thus, we have shown that the allenic [2+2+1] cycloaddition of 1,3-disubstituted allenes could be directed to react with the internal π-bond of the allene to afford α-methylene cyclopentenones stereoselectively by simply changing the metal catalyst.

Scheme 4

3,3-Disubstituted Allenes. Next the cyclizations of 3,3-disubstituted allenes were investigated. The inefficient processing of 2,2-disubstituted olefins appears to be a weakness in many Pauson-Khand (P-K) systems[12] and the analogous 3,3-disubstituted allenes were predicted to be affected similarly. However, unlike the olefinic P-K reaction, in the allenic variant cycloaddition can occur with an alternate π-bond. The alkynyl allenes utilized in this study were prepared via the addition of the requisite alkynyl magnesium bromide to the appropriate propargylic mesylate in the presence CuBr•LiBr.[13] Treatment of

3-*n*-butyl-1,2-octadien-7-yne (**20**) to molybdenum conditions resulted in the formation of the bicyclo[4.3.0]nonane ring system **21** as the only product in a 60% yield (entry 1, Table 3). This product arises from cyclization with the external π-bond of the allene (pathway B, Scheme 1). *This result demonstrates a dependence of the π-bond selectivity of the allenic* [2+2+1] *reaction upon the substrate structure*. Mono- and 1,3-disubstituted allenes undergo cyclization with the internal π-bond whereas 3,3-disubstituted allenes utilize the external π-bond. To date, there are only a few examples of this type of substrate dependence in the [2+2+1] reaction.[14] Attempts to effect the cyclization of an analog of **20** (possessing a TMS moiety on the terminus of the alkyne) using dicobalt octacarbonyl resulted in the immediate decomposition of the starting material. Likewise the zirconium-promoted cyclization gave very low conversions (0-16%) to the cycloadduct.

Table 3

In an attempt to sterically direct the cyclization reaction toward the internal double bond of the allene, a silicon moiety was placed at the terminus of the allene to give **22**. Treatment of trisubstituted alkynyl allene **22** to molybdenum conditions gave the desilylated bicyclo[4.3.0]nonane ring system **21** in 59% yield (entry 2, Table 3). Based upon GC-MS data the desilylation occurred prior to cyclization. Attempts to prepare the less labile TBS-substituted allene in a manner similar to that used for the preparation of **22** (n-BuLi, TBSCl or TBSOTf) resulted in recovery of starting material. Cyclization of a more functionalized precursor **23** occurred to give the [5.6.5] ring system **24** in 42% yield (entry 3, Table 3).

The [2+2+1] cycloaddition of 3,3-disubstituted allenes has also been used to prepare some interesting carbocyclic skeletons possessing functionality that can easily be

manipulated to other substrates. Alkynyl allenes **25, 28** and **31** were prepared using a method developed in our laboratories for the direct conversion of ketones to allenes.[15] The conjugate addition of organomagnesium reagent **36** to 1-acetyl-1-cyclopentene[16] and 1-acetyl-1-cyclohexene was effected using catalytic manganese (II) chloride (30%) and copper (I) chloride (3%)[17] followed by an *in situ* trap of the enolate with diethyl chlorophosphate to afford the desired enol phosphates (Scheme 5). Elimination of the phosphate to give the allene is then carried out by the addition of LDA at low temperature. The trimethylsilyl moiety can be removed from the alkyne terminus with tetra-*n*-butylammonium fluoride. Exposure of the alkynyl allenes to molybdenum hexacarbonyl/DMSO affords the cycloadducts **26**, **29** and **32** (entries 4-6, Table 3). The subjection of the alkynyl allene **34** to molybdenum [2+2+1] cycloaddition conditions gave only the linear [5.5.5] ring system **35** in a 66% yield with no evidence of the angular [5.4.5] ring system. The rapid assembly of these ring systems demonstrates the applicability of these two methods and provides skeletons visible in naturally occurring compounds.[18]

Scheme 5

Finally, we have shown that trisubstituted allenes undergo cyclization exclusively with the less substituted π-bond of the allene as evidenced by entries 1 and 2 in Table 4. Treatment of alkynyl allene **37** and **39** to the standard molybdenum cyclization conditions afforded dienones **38** and **40**.

Table 4

These preliminary studies have demonstrated a substrate structure dependence upon the course of the allenic [2+2+1] reaction. Monosubstituted allenes afford α-methylene cyclopentenones as the only cycloadduct. Disubstitution on the allene alters the course of

the allenic [2+2+1] reaction. Cycloaddition of 1,3-disubstituted allenes afford mixtures of several possible cycloadducts. However, we have shown that good control over the product ratio can be obtained by altering the cycloaddition conditions and that the regiochemistry can be directed to the internal π-bond depending upon the metal used. 3,3-Disubstituted and trisubstituted allenes undergo cycloaddition with the least substituted π-bond of the allene. This affords the bicyclo[4.3.0]nonane ring system selectively. We are continuing to explore the scope and limitations of the allenic variant of the [2+2+1] cycloaddition and its application to synthesis.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR of all alkynyl allenes and cycloadducts are available (90 pages). This material is contained in the 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.

Experimental Section

General Methods. Unless otherwise note, all reactions were carried out under Ar in flame-dried glassware using standard syringe, cannula, and septa techniques. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl. Dimethylsulfoxide and toluene were distilled from calcium hydride and stored over molecular sieves 4Å. Dichloromethane and benzene were freshly distilled from calcium hydride. Thin-layer chromatography was performed using precoated Kieselgel 60 F-254 plates. Flash chromatography was performed using Baker flash silica gel 60 (40μ). Molybdenum hexacarbonyl, dicobalt octacarbonyl and biscyclopentadienyl zirconium dichloride were all purchased from Strem chemicals, used as purchased and stored under

Ar. 5-Trimethylsilyl-1-chloro-4-pentyne was purchased from Farchan. NMR spectra were obtained on a 270 MHz NMR. ^{1}H NMR shifts were obtained in $CDCl_3$ and reported in ppm relative to the solvent shift of residual chloroform of δ 7.26. ^{13}C NMR shifts were obtained in $CDCl_3$ and reported in ppm relative to $CDCl_3$ 77.0. GC mass spectra were obtained at an ionization potential of 70 eV on a GC/MSD. IR spectra were obtained on a 1600 FT-IR spectrometer. High Resolution MS were obtained from the Department of Chemistry, University of California at Riverside.

1-(Trimethysilyl)-6,7-octadien-1-yne (1): 1-(Trimethylsilyl)-5-bromo-1-pentyne was prepared according to the procedure described by Bailey and Aspris.[19] A solution of 1-(trimethylsilyl)-5-bromo-1-pentyne (3.14 g, 14.3 mmol) in Et_2O (65 mL) was added dropwise to a suspension of magnesium turnings (0.696 g, 28.6 mmol) in Et_2O. The reaction was initiated with slight heating then allowed to stir at rt for 2 h. The Grignard reagent was added to a cooled (-5 °C) mixture of CuBr (20.5 mg, 0.143 mmol) and methyl propargyl ether (1.51 g, 21.5 mmol) in Et_2O (50 mL). The reaction was stirred at -5 °C for 2 h then diluted with Et_2O (50 mL) and poured into an ice-cold 1:1 mixture of 1N HCl: sat'd NH_4Cl (100 mL). The aqueous layer was separated and washed with Et_2O (20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo.* Chromatography (1% Et_2O/pentane) afforded 1.54 g (61%) of the alkynyl allene **1** as a colorless oil. ^{1}H NMR (270MHz, $CDCl_3$) δ5.08 (dt, *J* =13.3, 6.7 Hz, 1H), 4.66 (dt, *J* =6.7, 3.2 Hz, 2H), 2.25 (t, *J* =7.2 Hz, 2H), 2.08 (m, 2H), 1.62 (quin, *J* =7.2 Hz, 2H), 0.12 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 208.7, 107.1, 89.2, 84.8, 75.1, 28.0, 27.3, 19.3, 0.2; IR (neat) 2175, 1957, 1249, 842 cm^{-1}; MS (GC/MS) *m/z* 163 (M^+-15), 147, 135, 118, 109.

4,4-Dimethyl-5-hydroxy-1-(trimethylsilyl)-6,7-octadien-1-yne (3): To a solution of 4,4-dimethyl-5-hydroxy-1-(trimethylsilyl)-1,6-diyne (66.5 mg, 0.32 mmol) in

dioxane (3 mL) were added copper (I) iodide (23.0 mg, 0.16 mmol), paraformaldehyde (24.0 mg, 0.80 mmol), diisopropylamine (90 μL., 0.64 mmol). The reaction mixture was refluxed for 3 h and cooled to rt, dioxane was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 (10 mL), washed with 10% ammonia in brine (2 x 5 mL), HCl solution (pH=2, 2 x 5mL) and water (5 mL). The organic layer was dried over $MgSO_4$, removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with 5% EtOAc/hexane) furnished the title compound (23 mg, 32%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.28 (q, *J* = 6.6 Hz, 1H), 4.87 (dd, *J* = 2.4, 6.7 Hz, 2H), 4.07-4.00 (m, 1H), 2.30 (d, *J* = 16.8 Hz, 1H), 2.18 (d, *J* = 16.8 Hz, 1H), 1.94 (d, *J* = 5.3 Hz, 1H), 0.99 (s, 3H), 0.98 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 207.5, 105.1, 91.4, 87.0, 77.5, 75.6, 38.6, 29.9, 23.1, 22.2, 0.1; IR (neat) 3449, 2174, 1956, 1037, 842 cm^{-1}; MS (GC/MS) *m/z* 207, 191, 167, 154, 139, 110; HRMS m/z (M^+) calcd 222.1440, obsd 222.1441.

4,4-Dimethyl-5-[(methoxymethyl)oxy]-1-(trimethylsilyl)-6,7-octadien-1-yne (5): To a solution of 4,4-dimethyl-5-hydroxy-1-(trimethylsilyl)-6,7-octadien-1-yne (46 mg, 0.21 mmol) and *N*,*N*-diisopropylethylamine (162 μL, 0.93 mmol) in CH_2Cl_2 (2 mL) at 0 °C, was added chloromethyl methylether (47 μL, 0.62 mmol) dropwise. The cooling bath was removed and the reaction was stirred at rt for 24 h. The reaction was diluted with CH_2Cl_2 (5 mL), washed with $NaHCO_3$, (2 x 5 mL), brine (5 mL), dried over Na_2SO_4. Removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with 3% EtOAc/hexane) afforded 4,4-dimethyl-5-[(methoxymethyl)oxy]-1-(trimethylsilyl)-6,7-octadien-1-yne (43.9 mg, 80%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.98 (dt, *J* = 6.6, 8.8 Hz, 1H), 4.79 (d, *J* = 6.6 Hz, 1H), 4.77-4.74 (m, 2H), 4.52 (d, *J* = 6.6 Hz, 1H), 3.96 (d, *J* = 8.8 Hz, 1H), 3.38 (s, 3H), 2.32 (d, *J* = 16.8 Hz, 1H), 2.21 (d, *J* = 16.8 Hz, 1H), 1.00 (s, 3H), 0.98 (s, 3H), 0.14 (s, 9H); ^{13}C NMR

(67.9 MHz, $CDCl_3$) δ 209.8, 105.2, 94.0, 87.6, 86.6, 80.1, 75.1, 55.9, 38.3, 30.1, 23.2, 22.2, 0.11; IR (neat) 2174, 1955, 1151, 1039, 844 cm^{-1}; MS (GC/MS) *m/z* 251, 221, 191, 189, 147, 113.

1-(Trimethylsilyl)-1,2-nonadien-8-yne (7): 6-Bromo-1-(trimethylsilyl)-1-hexyne was prepared according to a procedure described by Bailey and Aspris.[19] A solution of 6-bromo-1-(trimethylsilyl)-1-hexyne (1.05 g, 4.52 mmol) in Et_2O (20 mL) was added dropwise to a suspension of magnesium turnings (220 mg, 9.04 mmol) in Et_2O (20 mL). The reaction was initiated with slight heating then allowed to stir with frequent warming for 1 h. The Grignard reagent was added to a cooled (-5 °C) mixture of CuBr (7.0 mg, 0.05 mmol) and methyl propargyl ether (475 mg, 678 mmol) in Et_2O (15 mL). The reaction was stirred at -5 °C for 2 h then diluted with Et_2O (15 mL) and poured into an ice-cold 1:1 mixture of 1N HCl: sat'd NH_4Cl (30 mL). The aqueous layer was separated and washed with Et_2O (10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Chromatography (hexanes) afforded 264 mg (30%) of alkynyl allene **7** as a colorless oil. ^1H NMR (270 MHz, $CDCl_3$) δ 5.08 (quin, J = 6.7 Hz, 1H), 4.65 (dt, J = 6.7, 3.2 Hz, 2H), 2.21 (t, J =6.7 Hz, 2H), 2.00 (m, 2H), 1.61-1.44 (m, 4H), 0.13 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 208.6, 107.5, 89.8, 84.5, 74.8, 28.2, 28.1, 27.7, 19.7, 0.21; IR (neat) 2175, 1957, 1249, 841 cm^{-1}; MS (GC/MS) *m/z* 177.1 (M^+-15), 149, 135, 117, 109.

(A) Representative Procedure for the Preparation of the Alkynyl Allenes: **1-Trimethylsilyl-6,7-pentadecadien-1-yne (16)**: A flask was charged with anhydrous magnesium chloride (1.60 g, 16.8 mmol), THF (25 mL) and potassium (1.25 g, 32.0 mmol). The mixture was heated to reflux for 3 h and cooled to rt. 1-Chloro-5-(trimethylsilyl)-4-pentyne (2.20 g, 12.6 mmol) in THF (10 mL) was added slowly to the mixture and the reaction was stirred at rt for another 30 min. Into a 100 mL flask were

added copper(I)bromide (1.15 g, 8.0 mmol) and lithium bromide (0.70 g, 8.1 mmol). The combined solids were dried at 150-160 ºC/10-20 mmHg for 45 min or 120 ºC/0.06 mm Hg for 5 h and then cooled to rt under argon. THF (8 mL) was then added. The resulting solution was cooled to -50 ºC and the Grignard reagent prepared above was cannulated into this flask slowly. The mixture was stirred at -50 ºC for another 30 min and a solution of 3-(methylsulfonyloxy)-1-decyne (1.86 g, 8.0 mmol) in THF (10 mL) was added dropwise. After stirring for an additional 30 min at -50 ºC, the cooling bath was removed and the reaction mixture was stirred for 3 h at rt then poured into a solution of sodium cyanide (2 g) in a solution of sat'd NH_4Cl (50 mL). After vigorous shaking, the product was extracted with pentane (3 x 50 mL) and the combined organic layers were washed with water (50 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and purification of the residue by flash chromatography on silica gel (eluting with pentane) provided 1-(trimethylsilyl)-6,7-pentadecadien-1-yne (**16**) (2.1 g, 96%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.13-4.99 (m, 2H), 2.25 (t, *J* = 7.2 Hz, 2H), 2.10-1.91 (m, 4H), 1.61 (quin, *J* = 7.3 Hz, 2H), 1.40-1.25 (m, 10H), 0.87 (t, *J* = 6.6 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 204.0, 107.2, 91.3, 89.9, 84.5, 31.9, 29.2, 29.2, 29.1, 28.9, 28.1, 28.0, 22.7, 19.2, 14.1, 0.14; IR (neat) 2176, 1962, 1458, 1249, 840 cm^{-1}; MS (GC/MS) *m/z* 276 (M^+), 261, 233, 219, 203, 159, 145, 131; HRMS m/z (M^++1) calcd 277.2352, obsd 277.2356.

(B) Representative Procedure for Desilylation of Alkynyl Allenes

6,7-Pentadecadien-1-yne (**9**): To a solution of 1-trimethylsilyl-6,7-pentadecadien-1-yne (98 mg, 0.36 mmol) in THF (4 mL) at 0 ºC was added dropwise a solution of 1.0 M tetra-*n*-butylammonium fluoride (TBAF) in THF (0.43 mL, 0.43 mmol). The resulting solution was stirred at rt for 2 h then water (30 mL) was added. The mixture was extracted with pentane (3 x 30 mL) and the combined extracts were washed

with water (30 mL) and dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification of the residue by flash chromatography on silica gel (eluting with pentane) afforded 6,7-pentadecadien-1-yne (**9**) (66 mg, 90%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.13-5.01 (m, 2H), 2.23 (dt, *J* = 2.6, 7.1 Hz, 2H), 2.13-2.04 (m, 2H), 1.99-1.93 (m, 3H), 1.64 (quin, *J* = 7.1 Hz, 2H), 1.40-1.27 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 204.0, 91.4, 89.8, 84.3, 68.3, 31.9, 29.2, 29.1, 29.0, 28.9, 27.9, 22.7, 17.8, 14.1; IR (neat) 2120, 1962, 1457, 1252, 1070, 874 cm^{-1}; MS (GC/MS) *m/z* 189 (M-15), 175, 147, 133, 119, 105; HRMS m/z (M+) calcd 204.1878, obsd 204.1884.

8-Phenyl-6,7-octadien-1-yne (11): Using the standard procedure for the preparation of alkynyl allenes, method A, a flask was charged with anhydrous magnesium chloride (1.4 g, 14.7 mmol), (THF, 25 mL) and potassium (1.1 g, 28 mmol). The mixture was heated to reflux for 3 h then cooled to rt and 1-chloro-5-(trimethylsilyl)-4-pentyne (1.83 g, 10.5 mmol) in THF (10 mL) was added slowly. The mixture was stirred at rt for another 30 min.

Into a 100 mL flask, were added copper(I)bromide (1.0 g, 7.0 mmol) and lithium bromide (0.61 g, 7.0 mmol). The combined solids were dried at 150-160 ºC/10-20 mm Hg for 45 min or 120 ºC/0.06 mm Hg for 5 h and then cooled to rt under argon. (1-phenyl-1-(methylsulfonyloxy)-2-propyne can be prepared while drying the solids, *vide infra*). THF (15 mL) was then added and the resulting solution was cooled to -50 ºC. The Grignard reagent prepared above was cannulated into this flask over 20 min and the mixture was stirred at -50 ºC for 30 min.

To a solution of 1-phenyl-2-propyn-1-ol (0.85 mL, 7.0 mmol) and lithium bromide (0.61 g, 7.0 mmol) in THF (10 mL) was added *n*-butyllithium (4.4 mL of a 1.6 M solution in hexane, 7.0 mmol) at -50 ºC. After stirring for 30 min the alkoxide solution was

cannulated into a solution of methanesulfonyl chloride (0.54 mL, 7.0 mmol) in THF (10 mL) at -50 ºC over 10 min. The resulting solution was stirred for 1 h then the organocopper reagent prepared above was cannulated into this flask over 25 min. The reaction mixture was stirred for an additional 30 min at -50 ºC, then the cooling bath was removed and the reaction was stirred for 3 h. The reaction mixture was poured into a solution of sodium cyanide (2 g) and sat'd NH_4Cl (50 mL). After vigorous shaking, the product was extracted with pentane (3 x 50 mL) and the combined organic layers were washed with water (50 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and purification by flash chromatography on silica gel (eluting with pentane) provided **8-phenyl-1-(trimethylsilyl)-6,7-octadien-1-yne** (1.48 g, 83%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.37-7.20 (m, 5H), 6.20 (dt, *J* = 3.1, 6.3 Hz, 1H), 5.62 (q, *J* = 6.5 Hz, 1H), 2.36 (t, *J* =7.0 Hz, 2H), 2.28 (dt, *J* = 2.8, 7.1 Hz, 2H), 1.76 (quin, *J* = 7.1 Hz, 2H), 0.21 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.2, 134.8, 128.5, 126.7, 126.5, 106.8, 94.9, 94.1, 84.8, 27.8, 27.7, 19.3, 0.1; IR (neat) 2173, 1948, 1706, 1598, 1249, 1027; MS (GC/MS) *m/z* 239, 223, 195, 180, 141, 129, 115, 73.

Following the representative procedure for desilylation of alkynyl allenes Method B, **8-phenyl-1-(trimethylsilyl)-6,7-octadien-1-yne** (329 mg, 1.30 mmol) was treated with TBAF (1.55 mL, 1.55 mmol) to afford **8-phenyl-6,7-octadien-1-yne** (**11**) (170 mg, 72%) as an oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.36-7.18 (m, 5H), 6.18 (dt, *J* = 3.2, 6.3 Hz, 1H), 5.60 (q, *J* = 6.5 Hz, 1H), 2.33-2.23 (m, 4H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.81 (m, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.2, 134.8, 128.5, 126.7, 126.6, 95.0, 94.0, 84.0, 68.6, 27.7, 27.6, 17.9; IR (neat) 2116, 1948, 1597, 1495, 1458, 879; MS (GC/MS) *m/z* 181, 167, 154, 128, 115, 102.

1-Trimethylsilyl-6,7-pentadecadien-1-yne-hexacarbonyldicobalt complex (13): To a solution of 1-(trimethylsilyl)-6,7-pentadecadien-1-yne (**16**) (100 mg, 0.39 mmol) in benzene (4 mL) was added dicobalt octacarbonyl (146 mg, 0.43 mmol) at rt. After stirring 2 h, the solvent was removed *in vacuo* and the residue was subjected to flash chromatography using hexane as the eluent to give the title complex **13** (137 mg, 75%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.13 (quin, *J* = 4.7 Hz, 2H), 3.14-2.86 (m, 2H), 2.18-2.08 (m, 2H), 2.01-1.92 (m, 2H), 1.74 (quin, *J* = 7.6 Hz, 2H), 1.41-1.27 (m, 10 H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.30 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 204.0, 200.5, 112.5, 91.9, 90.0, 78.9, 34.8, 31.9, 31.7, 29.1, 28.9, 28.6, 22.7, 14.1, 0.7; IR (neat) 2929, 2857, 2012, 1853, 1659, 1587, 1037 cm^{-1}.

6-*n*-Butyl-1-(trimethylsilyl)-6,7-octadien-1-yne: This compound was prepared from 1-(methylsulfonyloxy)-2-heptyne (1.5 g, 7.9 mmol) using representative procedure **A** to provide 6-*n*-butyl-1-(trimethylsilyl)-6,7-octadien-1-yne (1.84 g, 100%) as a colorless oil**:** ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.65 (quin, *J* = 3.2 Hz, 2H), 2.23 (t, *J* = 7.1 Hz), 2.05-1.96 (m, 2H), 1.95-1.87 (m, 2H), 1.69 - 1.57 (m, 2H), 1.45-1.24 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.6, 107.2, 102.3, 84.5, 75.6, 31.9, 30.9, 29.7, 26.5, 22.4, 19.4, 13.9, 0.13; IR (neat) 2957, 2860, 2175, 1957, 1456, 1249, 1035, 844 cm^{-1}; MS (GC/MS) *m/z* 234, 219, 191, 163, 131, 109; HRMS m/z (M^+) calcd 234.1804, obsd 234.1805.

3-*n*-Butyl-1,2-octadien-7-yne (20): Following the experimental procedure for the desilylation of alkynyl allenes, method B, 3-*n*-butyl-8-(trimethylsilyl)-1,2-octadien-7-yne (0.57 g, 2.4 mmol) afforded 3-*n*-butyl-1,2-octadien-7-yne **20** (0.32 g, 82%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.65 (quin, *J* = 3.2 Hz, 2H), 2.21(dt, *J* = 2.6, 7.1 Hz, 2H), 2.06-1.99 (m, 2H), 1.94-1.90 (m, 3H), 1.71-1.60 (quin, *J* = 7.3 Hz,

2H), 1.43-1.25 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.5, 102.4, 84.3, 75.5, 68.3, 31.9, 30.9, 29.6, 26.3, 22.4, 18.0, 13.9; IR (neat) 2119, 1957, 1456, 846 cm^{-1}; MS (GC/MS) *m/z* 147 (M^+-15), 133, 119, 117, 105; HRMS m/z (M+) calcd 162.1409, obsd 162.1403.

3-*n*-Butyl-1-(trimethylsilyl)-1,2-octadien-7-yne (22): To a solution of 3-*n*-butyl-8-(trimethylsilyl)-1,2-octadien-7-yne (66 mg, 0.28 mmol) in THF (2 mL) at -30 ºC was added *n*-butyllithium (0.21 mL of a 1.6M solution in hexane, 0.34 mmol) dropwise. After stirring at -30 ºC for 30 min, the reaction was cooled to -78 ºC and TMSCl (45 µL, 0.35 mmol) was added. The reaction solution was allowed to warm to rt over 2 h and sat'd. NH_4Cl was added. The aqueous layer was extracted with pentane (3 x 10 mL) and the combined extracts were washed with water (10 mL) then dried over $MgSO_4$. After removal of the solvent *in vacuo* the residue was dissolved in CH_3OH/THF (4:1, 2.5 mL) and K_2CO_3 (72 mg, 0.52 mmol) was added. The reaction mixture was stirred for 12 h, then diluted with water and the mixture was extracted with pentane (3 x 10 mL). The combined extracts were washed with water (10 mL) then dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by flash chromatography (eluting with pentane) furnished 3-*n*-butyl-1-(trimethylsilyl)-1,2-octadien-7-yne **22** (44 mg, 67%) as a colorless oil. ^{1}H NMR (270 MHz, C_6D_6) δ 5.03 (quin, J = 3.8 Hz, 1H), 2.05 (dt, J = 2.6, 7.1 Hz, 2H), 1.99-1.90 (m, 2H), 1.88-1.81 (m, 2H), 1.77 (t, J = 2.7 Hz, 1H), 1.61 (quin, J =7.1 Hz, 2H), 1.45-1.22 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (67.9 MHz,

$CDCl_3$) δ 208.1, 95.9, 84.5, 84.0, 68.3, 31.5, 30.7, 30.0, 26.7, 22.5, 18.2, 14.0, −0.7; IR (neat) 1939, 1248, 840 cm^{-1}; MS (GC/MS) *m/z* 219 (M^+-15), 192, 177, 161, 131, 117, 105.

[*1R*,2R*,3R]-1-(*tert*-Butyldimethylsilyloxy)-2-(1-methylallenyl)-3-(2-propynyl)-5,5-dimethylcyclopentane (23):** This procedure was performed according to that reported by Inanaga.[20] To a solution of [*1R*,2S*,3R**]-1-(*tert*-butyldimethylsilyloxy)-2-(1-methyl-1-benzoyloxy-2-propyne)-3-(2-propynyl)-5,5-dimethylcyclopentane (42.5 mg, 0.097 mmol), tetrakis(triphenylphosphine)palladium (5.6 mg) and 2,4-dimethyl-3-pentanol (15 μL, 0.11 mmol) in THF (2 mL) at 40 ^{o}C, was added a 0.1 M solution of SmI_2 in THF (7.2 mL, 0.72 mmol). After stirring at this temperature for 3 h, the reaction mixture was poured into sat'd NH_4Cl (30 mL) and filtered through a pad of Celite® and Florisil. The filtrate was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with hexane) furnished the compound **23** (19 mg, 62%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.60 (q, *J* = 3.0 Hz, 2H), 3.5 (d, *J* = 8.1 Hz, 1H), 2.35-2.27 (m, 1H), 2.14-2.03 (m, 2H), 1.93-1.80 (m, 2H), 1.73-1.63 (m, 4H), 1.45 (dd, *J* = 9.2, 12.1 Hz, 1H), 0.96 (s, 3H), 0.91 (s, 3H), 0.87 (s, 9H), 0.14 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 207.2, 98.5, 84.4, 83.2, 74.3, 68.9, 55.9, 43.7, 40.2, 37.2, 28.9, 26.0, 24.9, 23.1, 18.2, 17.3, -4.1, -4.4; IR (neat) 2107, 1956, 1464, 1250, 1127, 875, 836 cm^{-1}; MS (GC/MS) *m/z* 303 (M^{+}-15), 261, 221, 187, 147, 129.

Representative Experimental Procedure for the Preparation of allenylcycloalkanes 25, 28 and 31. A flask was charged with anhydrous magnesium chloride (0.95 g, 10 mmol), THF (15 mL) and potassium (0.75 g, 19 mmol). The mixture was heated to reflux for 3 h and cooled to rt. 1-Bromo-4-(trimethylsilyl)-3-pentyne (1.64 g, 8.0 mmol) in THF (5 mL) was added over 15 min and the resulting mixture was stirred at rt for 30 min.

A 50 mL flask charged with $MnCl_2$ (150 mg, 1.2 mmol) and LiCl (102 mg, 2.4 mmol) was heated at 200 ^oC under vacuum (0.1 mm Hg) for 6 h then cooled to rt under argon. Copper(I)chloride (12 mg, 0.12 mmol), 1-acetyl-1-cyclopentene (440 mg, 4.0 mmol) and THF (8 mL) were added. The mixture was stirred at rt until dissolution was complete and then cooled to 0 ^oC. The Grignard reagent was cannulated to this solution over 25 min and stirring was continued for 1.5 h at 0 ^oC. Diethyl chlorophosphate (1.16 mL, 8.0 mmol) was added dropwise and the resulting reaction mixture was stirred at rt for 12 h. Sat'd NH_4Cl was added and the mixture was extracted with Et_2O (3 x 50 mL) and the combined extracts were dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with 25% EtOAc/hexane) afforded the enol phosphate (1.05 g, 70%) as a colorless oil.

To a solution of the enol phosphate (1.05 g, 2.82 mmol) in THF (10 mL) at -78 ^oC was added freshly prepared LDA (9.0 mmol) in THF (15 mL) slowly. The resulting solution was stirred at -78 ^oC for 3 h then poured onto pentane (40 mL) and ice-water (20 mL). The aqueous layer was extracted with pentane (3 x 20 mL) and the combined extracts were washed successively with cold 1M HCl, water, saturated $NaHCO_3$, water and brine then dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with pentane) afforded 1-vinylidenyl-2-[4-(trimethylsilyl)-3-butynyl]-cyclopentane (**28**) (0.39 g, 64%) as a colorless oil.

1-Vinylidenyl-2-[4-(trimethylsilyl)-3-butynyl]-cyclopentane (28): ^1H NMR (270 MHz, $CDCl_3$) δ 4.76-4.63 (m, 2H), 2.62-2.54 (m, 1H), 2.44-2.34 (m, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.96-1.66 (m, 3H), 1.64-1.44 (m, 2H), 1.32-1.17 (m, 1H), 0.12 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 202.2, 107.6, 106.7, 84.2, 76.7, 42.2, 34.4, 33.0, 30.8, 25.2, 18.5, 0.17; IR (neat) 2174, 1940, 1449, 1042, 842 cm^{-1}; MS (GC/MS) *m/z* 218, 203, 175, 159, 144, 129.

1-Vinylidenyl-2-(3-butynyl)-cyclopentane (25): Following the experimental procedure for desilylation of alkynyl allenes, method (B), 1-vinylidenyl-2-[4-(trimethylsilyl)-3-butynyl]-cyclopentane (**28**) (0.39 g, 1.8 mmol) was treated with TBAF to afford 1-vinylidenyl-2-(3-butynyl)-cyclopentane (**25**) (0.14 g, 53%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.77-4.64 (m, 2H), 2.70-2.55 (m, 1H), 2.46-2.36 (m, 2H), 2.30-2.22 (m, 2H), 1.98-1.68 (m, 4H), 1.65-1.46 (m, 2H), 1.32-1.19 (m, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 202.2, 106.6, 84.6, 76.7, 68.1, 41.9, 33.2, 33.0, 30.8, 25.2, 16.9; IR (neat) 3299, 2117, 1957, 1715, 1434 cm^{-1}; MS (GC/MS) *m/z* 145 (M^{+}-1), 131, 117, 105.

1-Vinylidenyl-2-(3-butynyl)-cyclohexane (31): Following the representative procedure for desilylation of alkynyl allenes, smethod (B), 1-vinylidenyl-2-[4-(trimethylsilyl)-3-butynyl]-cyclohexane (62 mg, 0.27 mmol) was treated with TBAF to give 1-vinylidenyl-2-(3-butynyl)-cyclohexane (**31**) (34 mg, 80%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.64 (dt, *J* = 0.8, 3.4 Hz, 2H), 2.29-2.12 (m, 3H), 2.07-1.95 (m, 2H), 1.91 (t, *J* = 2.7 Hz, 1H), 1.84-1.69 (m, 4H), 1.54-1.32 (m, 3H), 1.18-1.05 (m, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 202.7, 105.0, 84.8, 75.1, 68.0, 38.2, 33.3, 32.4, 31.4, 27.4, 25.5, 16.3; IR (neat) 3306, 2117, 1958, 1250, 844, cm^{-1}; MS (GC/MS) *m/z* 159 (M^{+}-1), 145, 131, 117.

1-Vinylidenyl-2-[3-(trimethylsilyl)-2-propynyl]-cyclopentane (34): A procedure reported by Inanaga[20] was followed for the preparation of compound **34**. To a solution of 1-ethynyl-1-acetoxy-2-[3-(trimethylsilyl)-2-propynyl]-cyclopentane (245 mg, 0.935 mmol), tetrakis(triphenylphosphine)palladium (54 mg, 0.05 μm) and 2,4-dimethylpentan-3-ol (0.144 mL, 1.03 mmol) in THF (5 mL) at 40 °C, was added SmI_2 (23.4 mL of a 0.1M solution in THF, 2.34 mmol). After stirring at this temperature for 9

h, the reaction mixture was poured into sat'd NH_4Cl (30 mL) and filtered through pads of Celite-Florisil. The filtrate was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with hexane) furnished the title compound (48 mg, 73% based on recovered starting material) as a colorless oil and 160 mg of recovered starting material. ^1H NMR (270 MHz, $CDCl_3$) δ 4.83 - 4.60 (m, 2H), 2.80 -2.64 (m, 1H), 2.51 -2.36 (m, 3H), 2.18 (dd, *J* = 8.9, 17.0 Hz, 1H), 2.05 -1.91 (m, 1H), 1.83 - 1.69 (m, 1H), 1.68 - 1,42 (m, 2H), 0.14 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 202.1, 106.3, 106.0, 84.7, 77.1, 41.9, 32.6, 30.9, 25.0, 24.5, 0.1; IR (neat) 2175, 1958, 1249, 1022, 842 cm^{-1}; MS (GC/MS) *m/z* 204, 189, 176, 161, 145, 130, 109.

8-Methyl-6,7-nonadien-1-yne (37): This compound was prepared using the same procedure for the preparation of the alkynyl allene **11**. Magnesium chloride (1.9 g, 20 mmol), THF (25 mL) and potassium (1.5 g, 38.4 mmol). 1-Chloro-5-(trimethylsilyl)-4-pentyne (2.09 g, 12.0 mmol) in THF (10 mL), copper(I)bromide (1.15 g, 8.02 mmol), lithium bromide (0.7 g, 8.1 mmol), 2-methyl-2-hydroxyl-1-butyne (0.78 mL, 8.0 mmol), lithium bromide (0.7 g, 8.1 mmol), *n*-butyl lithium (5.0 mL of a 1.6 M solution in hexane, 8.0 mmol) and methanesulfonyl chloride (0.62 mL, 8.0 mmol). Purification by flash chromatography on silica gel (eluting with pentane) provided 8-methyl-1-(trimethylsilyl)-6,7-nonadien-1-yne (1.44 g, 88%). ^1H NMR (270 MHz, $CDCl_3$) δ 4.96-4.86 (m, 1H), 2.25 (t, *J* = 7.2 Hz, 2H), 2.02 (dt, *J* =6.9, 7.1 Hz, 2H), 1.69-1.54 (m, 8H), 0.13 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 201.9, 107.4, 95.1, 87.8, 84.4, 28.3, 28.0, 20.7, 19.1, 0.16; IR (neat) 2936, 2857, 2175, 1445, 1249, 1049, 841, 760 cm^{-1}; MS (GC/MS) *m/z* 191, 173, 149, 132, 117, 109, 73, 67. Following the representative procedure for desilylation of alkynyl allenes, method (B), 8-methyl-1-(trimethylsilyl)-6,7-nonadien-1-yne

(0.412 g, 2.0 mmol) was treated with TBAF to afford 8-methyl-6,7-nonadien-1-yne (0.18 g, 67%) as a colorless oil. ^{1}H NMR ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.97-4.86 (m, 1H), 2.21 (dt, *J* = 2.6, 7.2 Hz, 2H), 2.04 (dt, *J* =6.7, 7.1 Hz, 2H), 1.92 (t, *J* = 2.7 Hz, 1H), 1.68-1.56 (m, 8H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 201.9, 95.3, 87.7, 84.4, 68.2, 28.1, 27.9, 20.6, 17.7; IR (neat) 3303, 2118, 1967, 1362, 1233 cm^{-1}; MS (GC/MS) *m/z* 133, 119, 105; HRMS m/z (M+) calcd 134.1096 obsd 134.1087.

7-[(Cyclohexa)methylidenyl]-6-hepten-1-yne (39): This compound was prepared using the same procedure for the preparation of the alkynyl allene **11**. Magnesium chloride (1.4 g, 14.7 mmol), THF (25 mL) and potassium (1.09 g, 27.9 mmol). 1-Chloro-5-(trimethylsilyl)-4-pentyne (1.95 g, 11.2 mmol) in THF (10 mL), copper(I)bromide (1.0 g, 7.0 mmol), 1-ethynyl-1-cyclohexanol (0.90 mL, 7.0 mmol), lithium bromide (0.61 g, 7.0 mmol), *n*-butyllithium (4.4 mL of a 1.6 M solution in hexane, 7.0 mmol) and methanesulfonyl chloride (0.54 mL, 7.0 mmol). Purification by flash chromatography on silica gel (eluting with pentane) provided 8-methyl-1-(trimethylsilyl)-6,7-nonadien-1-yne (1.46 g, 85%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.97-4.88 (m, 1H), 2.25 (t, *J* = 7.2, 2H), 2.16-1.98 (m, 6H), 1.67-1.46 (m, 8H), 0.13 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.5, 107.4, 102.7, 87.6, 84.3, 31.8, 28.3, 28.0, 27.5, 26.2, 19.1, 0.16; IR (neat) 2929, 2854, 2175, 1964, 1447, 1249, 840, 759 cm^{-1}; MS (GC/MS) *m/z* 231, 203, 187, 173, 144, 131, 107, 79, 73; HRMS m/z (M^+) calcd 246.1804, obsd 246.1810. Following the representative procedure for desilylation of alkynyl allenes, step (B), 7-[(cyclohexa)methylidenyl]-1-(trimethylsilyl)-6-hepten-1-yne (0.298 g, 1.21 mmol) was treated with TBAF to afford 7-[(cyclohexa)methylidenyl]-6-hepten-1-yne (0.189 g, 90%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.97-4.89 (m, 1H), 2.21 (dt, *J* = 2.6, 7.2, 2H), 2.12-1.99 (m, 6H), 1.92 (t, *J* = 2.6 Hz, 1H), 1.68-1.43 (m, 8H); ^{13}C

NMR (67.9 MHz, $CDCl_3$) δ 198.4, 102.8, 87.5, 84.4, 68.2, 31.7, 28.1, 27.7, 27.5, 26.2, 17.6; IR (neat) 3306, 2118, 1963, 1446, 1239 cm^{-1}; MS (GC/MS) *m/z* 173, 159, 145, 131, 117, 105.

Representative Procedure for the Allenic [2+2+1] Cycloaddition, Method (A). 4-Methylidenyl-2-(trimethylsilyl)-bicylco[3.3.0]oct-1-en-3-one (2): To a solution of alkynyl allene **1** (150 mg, 0.84 mmol) in toluene (11 mL) and DMSO (656 mg, 840 mmol) was added $Mo(CO)_6$ (266 mg, 1.01 mmol). The suspension was heated to 100 °C after which it became homogeneous. The reaction was stirred at 100 °C for 3 h then cooled to rt and filtered through a pad of silica gel, eluting with Et_2O (50 mL). The Et_2O was removed *in vacuo* and the crude reaction mixture was applied directly to a chromatography column. Chromatography (hexanes then 5% Et_2O/hex) gave 117 mg (68%) of cycloadduct **2** as a yellow oil. ^1H NMR (270MHz, $CDCl_3$) δ5.90 (dd, *J*=2.2, 1.8 Hz, 1H), 5.25 (br dd, *J*=1.5, 1.4 Hz, 1H), 3.31 (m, 1H), 2.64 (m, 1H), 2.58 (m, 1H), 2.29-2.14 (m, 1H), 2.11-2.01 (m, 2H), 1.23-1.07 (m, 1H), 0.20 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 201.7, 194.1, 147.5, 136.7, 113.6, 51.9, 28.8, 27.5, 26.1, -1.1; IR (neat) 2935, 1692, 1597, 1249 cm^{-1}; MS (GC/MS) m/e 206 (M^+), 191, 163, 135, 117.

7,7-Dimethyl-6-hydroxyl-4-methylidenyl-2-(trimethylsilyl)-bicyclo[3.3.0] oct-1-en-3-one (4): Following the representative procedure for the allenic [2+2+1] cycloaddition, Method A, after 20 h, cycloaddition of 4,4-dimethyl-5-hydroxy-1-(trimethylsilyl)-6,7-octadien-1-yne (3) (60 mg, 0.27 mmol) afforded the title compound (32 mg, 47%) as a colorless oil. **minor isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.34 (s, 1H), 3.89 (s, 2H), 2.54 (dd, *J* = 23.0, 19.0 Hz, 2H), 1.62 (s, 1H), 1.21 (s, 6H), 0.2 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 201.2, 191.4, 143.0, 139.0, 114.7, 77.2, 56.5, 45.9, 41.4, 29.2, 23.7, -1.3; IR (neat) 3431, 2174,

1682, 1647, 1591, 1092, 841 cm^{-1}; MS (GC/MS) *m/z* 250, 235, 222, 207, 180, 160, 145, 117; CI HRMS (M^+ + 1) calcd: 251.1467, obsd: 251.1478. **major isomer**: ^1H NMR (270 MHz, $CDCl_3$) δ 5.94 (dd, *J* = 1.7, 1.1 Hz, 1H), 5.51 (dd, *J* = 1.2, 1.2 Hz, 1H), 3.58 (d, *J* = 10.1 Hz, 1H), 3.41 (d, *J* = 10.1 Hz, 1H), 2.72 (d, *J* = 18.6 Hz, 1H), 2.47 (dd, *J* = 1.5, 18.7 Hz, 1H), 2.17 (s, 1H), 1.19 (s, 3H), 1.11 (s, 3H), 0.20 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 200.7, 185.7, 146.0, 139.2, 114.0, 82.0, 55.4, 43.4, 43.0, 28.2, 23.7, -1.2; IR (neat) 3431, 2174, 1682, 1647, 1591, 1092 cm^{-1}; MS (GC/MS) *m/z* 250, 235, 222, 207, 180, 160, 145.

7,7-Dimethyl-6-[(methoxymethyl)oxy]-4-methylidenyl-2-trimethylsilyl-bicyclo[3.3.0]oct-1-en-3-one (6): Following the representative procedures for the allenic [2+2+1] cycloaddition reactions, Method A, after 20 h, cycloaddition of 4,4-dimethyl-5-[(methoxymethyl)oxy]-1-(trimethylsilyl)-6,7-octadien-1-yne (32 mg, 0.12 mmol) gave 7,7-dimethyl-6-[(methoxymethyl)oxy]-4-methylidenyl-2-(trimethylsilyl)-bicyclo[3.3.0]oct-1-en-3-one as a mixture of two diastereomers (9.5 mg, 54% based on recovered starting material) together with 16 mg of starting material. **major isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 5.97 (dd, *J* =1,2, 1.8 Hz, 1H), 5.47 (t, *J* = 1.2 Hz, 1H), 4.74 (dd, *J* = 6.7, 10.9 Hz, 2H), 5.65 (d, *J* = 9.1 Hz, 1H), 3.42 (s, 3H), 3.35 (d, *J* = 9.1 Hz, 1H), 2.70 (d, *J* = 17.8, 1H), 2.46 (dd, *J* = 1.3, 17.7 Hz, 1H), 1.22 (s, 3H), 1.09 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 200.6, 185.9, 145.9, 138.7, 114.5, 96.9, 87.4, 55.8, 55.2, 43.6, 43.5, 28.9, 24.6, -1.1; IR (neat) 1692 1599, 1149, 1040 cm^{-1}; MS (GC/MS) *m/z* 294, 279, 249, 221, 219, 193, 147; HRMS (M^++1) calcd 295.1729 obsd 295.1740. **minor isomer:** ^1H NMR (270 MHz, $CDCl_3$) δ 5.91 (d, *J* = 3.8 Hz, 1H) 4.79 (d, *J* = 6.9 Hz, 1H), 4.69 (d, *J* = 6.7 Hz, 1H), 3.93 (d, *J* = 3.6 Hz, 1H), 3.42 (s, 3H), 2.90 (s, 2H), 2.70 (d, *J* = 16.8 Hz, 1H), 2.45 (d, *J* = 16.4 Hz, 1H),

1.03 (s, 3H), 0.99 (s, 3H), 0.24 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 209.0, 175.2, 141.6, 138.6, 123.6, 96.4, 78.9, 55.6, 39.0, 38.8, 36.6, 26.9, 22.8, -0.6; IR (neat) 1694, 1556, 1149, 1038 cm^{-1}; MS (GC/MS) *m/z* 294, 249, 233, 219, 190, 162, 134; HRMS m/z (M^++1) calcd 295.1729 obsd 295.1722.

4-Methylidenyl-2-(trimethylsilyl)-bicyclo[4.3.0]non-1-en-3-one (8): To a solution of alkynyl allene **7** (76 mg, 0.4 mmol) in benzene (7 mL) and DMSO (310 mg, 4.0 mmol) was added $Mo(CO)_6$ (125 mg, 0.48 mmol). The suspension was heated to 80 °C after which it became homogeneous. The reaction was stirred at 80 °C for 18 h then cooled to rt and filtered through a pad of silica gel eluting with Et_2O (25 mL). The ether was removed *in vacuo* and the crude reaction mixture applied directly to column chromatography. Chromatography (5% EtOAc/hex) gave 38.4 mg recovered alkynyl allene **7** and 13 mg (15%, 30% based upon recovered starting material) of cycloadduct **8** as a yellow oil. ^{1}H NMR (270MHz, $CDCl_3$) δ5.91 (dd, *J* =1.7, 1.0 Hz, 1H), 5.23 (t, *J* =1.2 Hz, 1H), 3.00 (m, 1H), 2.29-2.17 (m, 2H), 2.06-1.98 (m, 1H), 1.89-1.83 (m, 1H), 1.62-1.48 (m, 1H), 1.41-1.07 (m, 3H), 0.24 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 200.0, 186.2, 147.5, 137.2, 113.7,46.8, 33.7, 31.3, 27.0, 25.0, -0.3; IR (neat) 1690, 1647, 1579 cm^{-1}; MS (GC/MS) m/e 220 (M^+), 205, 189, 176, 161, 149.

Z*- and *E*-4-[(Heptyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (10):** Following the representative procedure for the allenic [2+2+1] cycloaddition, method A. A mixture of 6,7-pentadecadien-1-yne (**9**) (63 mg, 0.31 mmol), molybdenum carbonyl (122 mg, 0.46 mmol) and DMSO (219 μL, 3.1 mmol) in toluene (3 mL) was heated at 110 °C for 18 h to furnish *Z*-4-[(heptyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (18 mg, 25%) and *E*-4-[(heptyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (36 mg, 50%). The isomers **10-*E and **10-*Z*** were separated using column chromatography (3% ether/hexanes). ***Z*-4-[(Heptyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one**

(10): ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.98 (s, 1H), 5.90 (t, *J* = 7.5 Hz, 1H), 3.33-3.23 (m, 1H), 2.74 (q, *J* = 7.1 Hz, 2H), 2.67-2.43 (m, 2H), 2.18-2.01 (m, 3H), 1.41-1.10 (m, 11H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 199.3, 183.9, 138.7, 138.3, 127.4, 51.1, 31.8, 29.5, 29.4, 29.2, 29.1, 27.0, 26.3, 26.1, 22.6, 14.1; IR (neat) 1695, 1654, 1623, 1458, 1325 cm^{-1}; MS (GC/MS) *m/z* 232 (M^+), 203, 189, 161, 147, 134; HRMS *m/z* (M^++1) calcd 233.1905, obsd 233.1906. ***E*-4-[(Heptyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (10):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.49 (dt, *J* = 1.8, 7.7 Hz, 1H), 6.03 (s, 1H), 3.35 (t, *J* = 9.8 Hz, 1H), 2.70-2.46 (m, 2H), 2.33-2.04 (m, 5H), 1.50-1.10 (m, 11H), 0.86 (t, *J* = 6.7, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.2, 184.9, 139.2, 134.3, 126.0, 48.8, 31.7, 29.7, 29.4, 29.2, 29.1, 28.8, 25.9, 25.7, 22.6, 14.0; IR (neat) 1701, 1655, 1620, 1458 cm^{-1}; MS (GC/MS) *m/z* 232 (M^+), 203, 189, 161, 147, 134; HRMS *m/z* (M^++1) calcd 233.1905, obsd 233.1898.

***Z*- and *E*-4-[(Phenyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (12):** Following the representative procedure for the allenic [2+2+1] cycloaddition reaction Method A, after 11h, cycloaddition of 8-phenyl-6,7-octadien-1-yne (**11**) (55 mg, 0.30 mmol) gave *Z*-4-[(phenyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (7 mg, 12%) and *E*-4-[(phenyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (37 mg, 58%). ***Z*-4-[(Phenyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (12):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 1.7, 7.6 Hz, 2H), 7.41-7.18 (m, 3H), 6.66 (s, 1H), 6.07 (s, 1H), 3.59 - 3.48 (m, 1H), 2.76 - 2.48 (m, 2H), 2.32 - 2.06 (m, 3H), 1.40 - 1.23 (m, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 196.7, 183.3, 139.2, 134.8, 134.5, 130.7, 129.2, 128.0, 127.8, 52.8, 29.7, 26.3, 26.2; IR (neat) 1682, 1614, 1450, 1173 cm^{-1}; MS

(GC/MS) *m/z* 210, 181, 167, 154, 141; HRMS *m/z* (M^++1) calcd 211.1123, obsd 211.1123. ***E*-4-[(Phenyl)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (12):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57-7.52 (m, 2H), 7.43-7.30 (m, 4H), 6.14 (s, 1H), 3.76 (t, *J* = 9.7 Hz, 1H), 2.78 - 2.54 (m, 2H), 2.43 - 2.34 (m, 1H), 2.24 - 1.96 (m, 2H), 1.16 - 1.00 (m, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.8, 185.0, 137.7, 134.9, 130.5, 130.2, 129.0, 128.6, 125.7, 49.5, 28.0, 25.9, 24.9; IR (neat) 1694, 1614, 1449, 1181 cm^{-1}; MS (GC/MS) *m/z* 210, 181, 167, 154, 141; HRMS *m/z* (M^++1) calcd 211.1123, obsd 211.1122.

Representative Procedure for the Allenic [2+2+1] Cycloaddition, Method (B). 4-Heptyl-2-(trimethylsilyl)-bicyclo[4.3.0]nona-1,5-dien-3-one (14), *E- and Z*-4-[(heptyl)methylidenyl]-2-(trimethylsilyl)-bicyclo[3.3.0]oct-1-en-3-one (15): To a solution of 1-(trimethylsilyl)-6,7-pentadecadien-1-yne-hexacarbonyl dicobalt complex (**13**) (60 mg, 0.11 mmol) in CH_2Cl_2 (5 mmol) under air at 40 ºC was added DMSO (24 μL, 0.34 mmol). The reaction mixture was stirred at 40 ºC for 22 h and then passed through a small plug of silica gel, eluting with EtOAc/hexane (1:1). The solution was concentrated *in vacuo* and the residue purified by flash chromatography on silica gel, eluting with 2% EtOAc/hexane furnished the enone products (20 mg, 60%) as a mixture of three products (ratios based upon ^{1}H NMR). The separation of pure **14**, **15-*E* and 15-*Z*** was effected by HPLC using a silica column with 0.75 EtOAc/hexanes used as the eluent. ***Z*-4-[(Heptyl)methylidenyl]-2-(trimethylsilyl)-bicyclo[3.3.0]oct-1-en-3-one (15):** ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.86 (dt, *J* = 1.6, 7.5 Hz, 1H), 3.25 (dd, *J* = 6.9, 11.7 Hz, 1H), 2.83-2.43 (m, 4H), 2.16-1.94 (m, 3H), 1.42-1.03 (m, 11H), 0.85 (t, J=6.9 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 203.2, 192.4, 138.9, 138.3, 137.5, 53.1, 31.9, 31.7, 29.7, 29.4, 29.3, 27.6,

27.1, 26.5, 22.7, 14.2, -0.97; IR (neat) 1685, 1646, 1600, 1218 cm^{-1}; MS (GC/MS) *m/z* 304 (M^+), 289, 233, 220, 178, 161; HRMS *m/z* (M^++1) calcd 305.2301, obsd 305.2284. **4-Heptyl-2-(trimethylsilyl)-bicyclo[4.3.0]nona-1,5-dien-3-one (14):** ^1H NMR (270 MHz, $CDCl_3$) δ 5.97 (t, *J* = 4.0 Hz, 1H), 2.80-2.63 (m, 3H), 2.25 (q, *J* = 5.0 Hz, 2H), 1.87-1.72 (m, 2H), 1.70-1.56 (m, 2H), 1.15-1.23 (m, 10H), 0.84 (t, *J* = 6.9 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 212.6, 176.2, 142.7, 137.2, 125.1, 47.9, 31.9, 30.2, 29.9, 29.2, 27.5, 25.7, 25.2, 22.7, 22.6, 14.2, -0.4; IR (neat) 1687, 1553 cm^{-1}; MS (GC/MS) *m/z* 304 (M^+), 289, 206, 190, 147, 129. ***E*-4-[(Heptyl)methylidenyl]-2-(trimethylsilyl)-bicyclo[3.3.0]oct-1-en-3-one (15):** ^1H NMR (270 MHz, $CDCl_3$) δ 6.42 (dt, *J* = 2.0, 7.7 Hz, 1H), 3.28 (dd, *J* = 7.5, 12.1 Hz, 1H), 2.72-2.46 (m, 2H), 2.31-2.00 (m, 5H), 1.49-1.38 (m, 2H), 1.31-1.07 (m, 9H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 201.9, 192.8, 139.7, 136.7, 133.3, 50.7, 31.9, 29.9, 29.5, 29.2, 29.2, 29.0, 27.0, 26.2, 22.7, 14.2, -1.0; IR (neat) 1694, 1657, 1600, 839 cm^{-1}; MS (GC/MS) *m/z* 304 (M^+), 289, 233, 220, 189, 161, 131.

Representative Procedure for the Allenic [2+2+1] Cycloaddition, Method (C). To a solution of 1-(trimethylsilyl)-6,7-pentadecadien-1-yne-hexacarbonyldicobalt complex (**13**) (69 mg, 0.12 mmol) in CH_2Cl_2 (0.5 mL) was added trimethylamine *N*-oxide (56 mg, 0.75 mmol) at rt. The reaction mixture was stirred for 80 min and then passed through a small plug of silica gel, eluting with EtOAc/hexane (1:1). The solution was concentrated *in vacuo* and the residue purified by flash chromatography on silica gel, eluting with 2% EtOAc/hexane to furnish the enone (23 mg, 62%) as a mixture of isomers (see Table 2, entry 4).

Representative Procedure for the Allenic [2+2+1] Cycloaddition, Method (D). To a degassed solution of 1-(trimethylsilyl)-6,7-pentadecadien-1-yne (**16**) (30 mg, 0.11 mmol) in benzene (2 mL) was added dicobaltoctacarbonyl (45 mg, 0.13 mmol) at rt. After stirring for 3 h, the TLC showed complete complexation of the alkyne, DMSO (24 μL, 0.33 mmol) was then added and the mixture was stirred in air at 40 ^{o}C for 28 h. The reaction mixture was passed through a small plug of silica gel, eluting with EtOAc/hexane (1:1). The solution was concentrated *in vacuo* and flash chromatography on silica gel, eluting with 2% EtOAc/hexane furnished the enone (11 mg, 33%) as a mixture of isomers (see Table 2, entry 5).

Representative Procedure for the Allenic [2+2+1] Cycloaddition, Method (E): To a solution of Cp_2ZrCl_2 (53 mg, 0.18 mmol) in THF (2 mL) at -78 ^{o}C under argon was added *n*-butyllithium (0.23 mL of a 1.6M solution in hexane, 0.37 mmol). Upon completion of addition, stirring was continued at -78 ^{o}C for 1 h and 1-(trimethylsilyl)-6,7-pentadecadien-1-yne (**16**) (48 mg, 0.17 mmol) in THF (0.5 mL) was added. The reaction mixture was warmed to rt over 2 h then stirred for an additional 4 h, whereupon it was transferred to a sealed tube and cooled to 0 ^{o}C. The solution was degassed and flushed with CO, this process was repeated three times then the solution was placed under CO pressure (20 psi). The reaction mixture was stirred at 0 ^{o}C for 2 h and quenched with 3 M HCl (20 mL) and pentane (20 mL). The aqueous layer was extracted with pentane (3 x 20 mL) and the combined extracts were washed with $NaHCO_3$ (20 mL) and brine (20 mL), then dried over $MgSO_4$. Removal of the solvent *in vacuo* and purification by flash chromatography on silica gel (eluting with 2% EtOAc/hexane) afforded the enone products **14** and **15-*E*** (25 mg, 48%).

6-Butyl-bicyclo[4.3.0]-non-1,5-dien-3-one (21): Following the experimental procedure for the allenic [2+2+1] cycloaddition reaction, Method A, after 16 h, cycloaddition of 3-butyl-1,2-octadien-7-yne (**20**) (54 mg, 0.33 mmol) afforded the title

compound **21** (38 mg, 60%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.83 (s, 1H), 2.86 (s, 2H), 2.60 (t, *J* = 6.3 Hz, 2H), 2.21-2.08 (m, 4H), 1.80 (quin, *J*=6.2 Hz, 2H) 1.47-1.22 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.5, 172.3, 141.0, 131.1, 126.1, 37.6, 34.7, 29.6, 28.5, 26.1, 22.6, 22.4, 13.9; IR (neat) 2929, 2859, 1699, 1671, 1581, 1455, 1246, 841 cm^{-1}; MS (GC/MS) *m/z* 190 (M^+), 175, 161, 147, 119, 105, 91, 77, 65, 41; HRMS *m/z* (M^+) calcd 190.1358, obsd 190.1358.

6-Butyl-bicyclo[4.3.0]-non-1,5-dien-3-one (21): Following the experimental procedure for the allenic Pauson-Khand cycloaddition reaction, Method A, after 24h, cycloaddition of 3-butyl-1-(trimethylsilyl)-1,2-octadiene-7-yne (**22**) (23 mg, 0.098 mmol) afforded the title compound **21** (11 mg, 59%) as a colorless oil.

Enone 24: Following the experimental procedure for the allenic [2+2+1] cycloaddition Method A, after 19 h, cycloaddition of [*1R*,2R*,3R**]-1-(*tert*-butyldimethylsilyloxy)-2-(1-methylallenyl)-3-(2-propynyl)-5,5-dimethylcyclopentane (**23**) (19 mg, 0.06 mmol) gave the enone **24** (5 mg, 24%, 42% based on recovered starting material). ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.86 (s, 1H), 3.83 (d, *J* = 5.1 Hz, 1H), 2.86 (d, *J* = 4.6 Hz, 2H), 2.76-2.52 (m, 3H), 1.87 (s, 3H), 1.76-1.60 (m, 2H), 1.28-1.18 (m, 1H), 0.95 (s, 6H), 0.90 (s, 9H), 0.05 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.5, 170.7, 135.8, 131.7, 127.4, 85.0, 52.5, 44.5, 42.0, 38.1, 33.6, 30.2, 29.5, 26.1, 25.8, 20.0, 18.2, -3.7, -4.4; IR (neat) 1704, 1580, 1462, 1199, 1100, 1007 cm^{-1}; MS (GC/MS) *m/z* 346 (M^+), 331, 289, 233, 214, 172, 158, 118.

Table 3, entry 4: Following the experimental procedure for the allenic [2+2+1] cycloaddition reaction Method A, after 15 h, 1-vinylidenyl-2-(3-butynyl)-cyclopentane (41 mg, 0.28 mmol) gave two isomeric products (major isomer **26**: 31 mg, 64%; minor isomer **27**: 4.6 mg, 9%); Major isomer **26**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.78 (s, 1H), 2.83-

2.72 (m, 3H), 2.47-2.23 (m, 4H), 2.18-2.09 (m, 1H), 2.07-1.98 (m, 1H), 1.91-1.81 (m, 1H), 1.72-1.53 (m, 1H), 1.37-1.03 (m, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 206.1, 172.8, 148.2, 128.4, 125.0, 42.7, 37.4, 33.7, 29.4, 29.3, 26.4, 24.1; IR (neat) 1689, 1654, 1574, 1167, 922, 832 cm^{-1}; MS (GC/MS) *m/z* 174 (M^+), 159, 146, 131, 117; HRMS *m/z* (M^+) calcd 174.1045, obsd 174.1048. Minor isomer **27**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.96 (s, 1H), 5.81 (s, 1H), 5.17 (s, 1H), 2.62-2.52 (m, 2H), 2.41-2.31 (m, 1H), 2.12-1.97 (m, 2H), 1.90-1.62 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.5, 188.3, 154.4, 124.0, 111.4, 62.2, 46.2, 40.3, 36.2, 33.7, 27.5, 26.9; IR (neat) 1694, 1651, 1621, 1453, 1137 862 cm^{-1}; MS (GC/MS) *m/z* 174 (M^+), 159, 146, 131, 117; HRMS *m/z* (M^+) calcd 174.1045, obsd 174.1038.

Table 3, entry 5: Following the experimental procedure for the allenic [2+2+1] cycloaddition, Method A, after 12 h, 1-vinylidenyl-2-[4-(trimethylsilyl)-3-butynyl]-cyclopentane (**28**) (26 mg, 0.11 mmol) gave the enone **29** (15 mg, 50%); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.96 (dt, *J* = 17.0, 3.0 Hz, 1H), 2.77 (s, 2H), 2.50-2.25 (m, 4H), 2.22-2.01 (m, 2H), 1.94-1.80 (m, 1H), 1.74-1.56 (m, 1H), 1.41-1.06 (m, 2H), 0.22 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 210.1, 178.5, 147.2, 135.4, 130.0, 42.3, 38.0, 33.8, 29.7, 29.6, 27.4, 24.1, -0.4; IR (neat) 1957, 1889, 1664, 1542, 890 cm^{-1}; MS (GC/MS) *m/z* 246 (M^+), 231, 202, 187, 155, 129; HRMS *m/z* (M^+) calcd 246.1440, obsd 246.1442.

Table 3, entry 6: Following the experimental procedure for the allenic [2+2+1] cycloaddition, Method A, after 15 h, 2-(3-butynyl)-1-vinylidenyl-cyclohexane (**31**) (34 mg, 0.21 mmol) gave two isomeric products (major isomer **32**: 20 mg, 50%; minor isomer **33**: 5 mg, 12%); major isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.82 (s, 1H), 2.84 (s, 2H), 2.73 (dt, *J* = 4.3, 17.0 Hz, 1H), 2.49-2.37 (m, 2H), 2.22-2.12 (m, 1H), 2.04-1.74

(m, 5H), 1.48-1.20 (m, 3H), 1.05 (dq, J = 3.1, 12.5 Hz, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 205.7, 172.4, 142.5, 129.6, 126.4, 37.8, 37.3, 34.6, 31.1, 29.5, 26.6, 25.6, 25.3; IR (neat) 1698, 1673, 1579, 1210, 841 cm^{-1}; MS (GC/MS) *m/z* 188 (M^+), 173, 160, 132, 117; HRMS *m/z* (M^++1) calcd 188.1201, obsd 188.1200. minor isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.96 (s, 1H), 5.84 (s, 1H), 5.46 (s, 1H), 2.85-2.70 (m, 1H), 2.65-2.50 (m, 1H), 2.30-2.11 (m, 1H), 1.98-1.83 (m, 2H), 1.77-1.39 (m, 7H), 1.29-1.19 (m, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.3, 191.2, 152.2, 124.5, 112.2, 53.5, 39.4, 30.8, 27.0, 24.8, 24.4, 22.1, 19.5; IR (neat) 1701, 1618, 1118 cm^{-1}; MS (GC/MS) *m/z* 188 (M^+), 173, 160, 131, 117; HRMS *m/z* (M^++1) calcd 188.1201, obsd 188.1191.

Table 3, Entry 7 (35): Following the representative procedures for the allenic [2+2+1] cycloaddition reactions, Method A, after 5h, cycloaddition of 1-vinylidenyl-2-[3-(trimethylsilyl)-2-propynyl]-cyclopentane (**34**) (15.5 mg, 0.076 mmol) afforded the title compound **35** as a colorless oil (11.7 mg, 66%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.30 - 3.18 (m, 1H), 2.97 (dd, J = 6.3, 18.8 Hz, 1H), 2.76 (s, 2H), 2.42-2.22 (m, 3H), 2.17 - 1.99 (m, 3H), 1.25 -1.07 (m, 1H), 0.2 (s, 9H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 212.2, 199.3, 157.5, 135.7, 129.7, 55.7, 36.2, 32.8, 30.7, 27.7, 23.2, -1.1; IR (neat) 1697, 1676, 1559, 921 cm^{-1}; MS (GC/MS) *m/z* 232, 217, 189, 161, 143, 128.

4-[(1,1-Dimethyl)-methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (38): Following the representative procedures for the allenic [2+2+1] cycloaddition reaction, Method A, after 10h, cycloaddition of 8-methyl-6,7-nonadien-1-yne (**37**) (45 mg, 0.336 mmol) gave 4-[(1,1-dimethyl)-methylidenyl]-bicyclo[3,3,0]oct-1-en-3-one (**38**) (32 mg, 59%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.97(s, 1H), 3.33(t, J = 9.6 Hz, 1H), 2.66-2.40 (m, 2H), 2.32-2.20 (m, 4H), 2.12-2.01 (m, 2H), 1.89 (s, 3H), 1.24-1.06 (m, 1H); ^{13}C

NMR (67.9 MHz, $CDCl_3$) δ 198.7, 181.3, 145.1, 133.8, 127.5, 50.4, 29.6, 25.7, 25.4, 24.4, 19.6; IR (neat) 1682, 1632, 1446, 1067 cm^{-1}; MS (GC/MS) *m/z* 162, 147, 134, 119, 106; HRMS m/z (M+) calcd 162.1045 obsd 162.1047.

4-[(Cyclohexa)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (40): Following the representative procedures for the allenic [2+2+1] cycloaddition reactions, Method A, after 10h, cycloaddition of 8-phenyl-6,7-octadien-1-yne (**39**) (46 mg, 0.264 mmol) gave 4-[(cyclohexa)methylidenyl]-bicyclo[3.3.0]oct-1-en-3-one (**40**) (31 mg, 58% yield). ^1H NMR (270 MHz, $CDCl_3$) δ 5.98 (s, 1H), 3.34 (dd, *J* = 7.9, 11.1 Hz, 1H), 3.10-2.90 (m, 2H), 2.65-2.40 (m, 2H), 2.32-2.18 (m, 3H), 2.14-1.99 (m, 2H), 1.78-1.50 (M, 6H), 1.25-1.09 (M, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 199.3, 181.4, 153.2, 130.8, 127.9, 50.0, 34.4, 30.1, 28.5, 28.4, 28.2, 26.4, 25.7, 25.4; IR (neat) 1680, 1620,, 994 cm^{-1}; MS (GC/MS) *m/z* 202, 174, 160, 147, 131, 117; CI HRMS (M^++17) calcd: 219.1623 obsd: 219.1622

References and Notes:

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(8) Reaction conditions were systematically varied in the conversion of alkynyl allene **9** to dienone **10** in an effort to increase the overall efficiency of this cycloaddition process. The efficiency of these reactions were estimated by injecting aliquots of reaction mixtures on the GC-MS and by using tridecane as an internal standard. Initially the amount of dimethylsulfoxide (DMSO) was varied from 5 to 10 to 15 equivalents and the amount of molybdenum hexacarbonyl (1.2 equiv) and the temperature of the reaction (100 °C) were held constant. It was found that the best product/internal standard ratios were obtained when 10 equivalents of DMSO were used. Next the optimal amount of molybdenum hexacarbonyl was checked while holding the amount of DMSO (10 equiv) and reaction temperature (100 °C) constant. The amount of molybdenum hexacarbonyl was varied by 0.1 equivalents from 1.2 to 1.8 equivalents and it was found that 1.5 equivalents gave the best product/internal standard ratios. Finally reaction temperatures were varied by 10 degree increments from 90 to 130 degrees, while keeping the amount of molybdenum hexacarbonyl (1.5 equiv) and DMSO (10 equiv) constant. Increasing the reaction temperature shortened the reaction time and gave better product/internal standard ratios, but as the temperature was raised higher than 110 ℃ the product/internal standard ratio

dropped. Thus the optimal reaction conditions as evidenced by this study are $Mo(CO)_6$ (1.5 equiv), DMSO (10 equiv) in toluene at 110°C.

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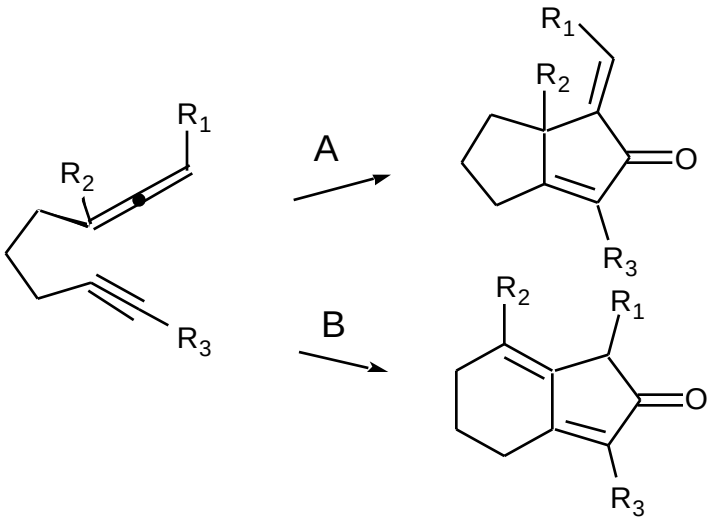
Scheme 1



Scheme 2

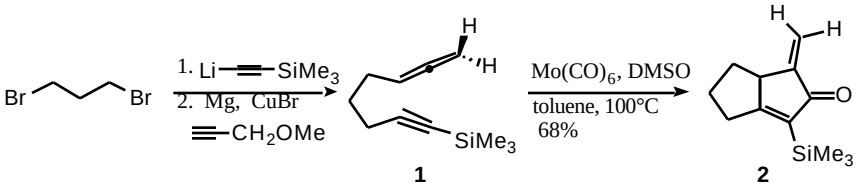
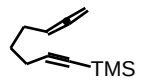
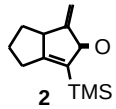
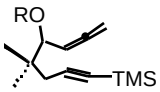
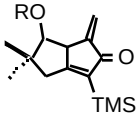
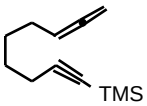
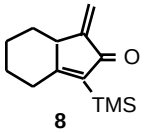


Table 1

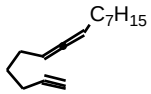
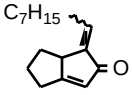
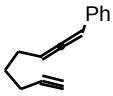
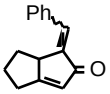
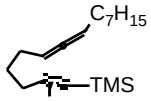
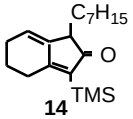
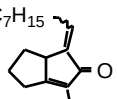
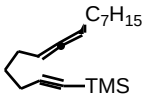
Table 1. Monosubstituted Allenes

Entry	Allenyne	Cyclopentenone	Conditions	Yield
1	 **1**	 **2**	A	68%
				
2	**3** R=H	**4**	A	47%
3	**5** R=MOM	**6**	A	54%
4	 **7**	 **8**	A	30%

Conditions A: $Mo(CO)_6$/DMSO/tol/Ar/100°C/10h

Table 2

Table 2. 1,3-Disubstituted Allenes

Entry	Allenyne	Cyclopentenone		Conditions	Yield
1	 **9**	 **10** E:Z 2:1		A	75%
2	 **11**	 **12** E:Z 5:1		A	70%
3	 **13**	 45%	 55% E:Z 10:1	B	60%
4		40%	60% E:Z 5:1	C	62%
5		55%	45% E:Z 3.5:1	D	33%
6	 **16**	5%	95% E only	E	48%

Conditions A: $Mo(CO)_6$/DMSO/tol/Ar/100°C/10h B: DMSO/air/CH_2Cl_2 40°C/22h C: Me_3NO/CH_2Cl_2/Ar/1.3h D: DMSO/air/benz/40°C/26h
E: 1. Cp_2ZrCl_2/n-buLi, 2. CO/2h

Scheme 3

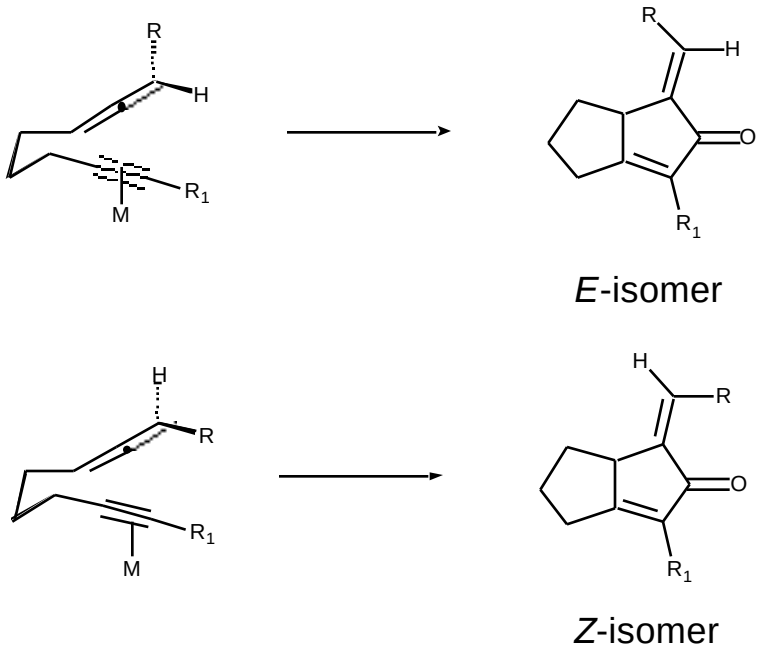
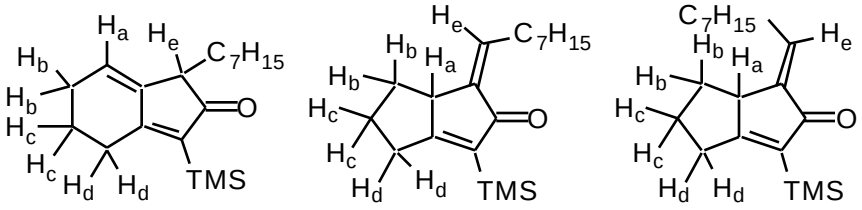
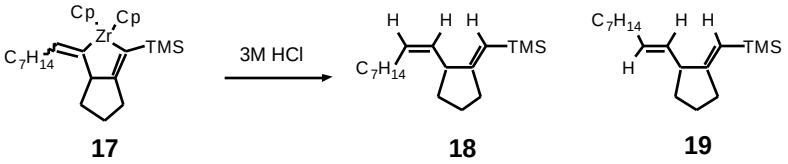


Figure 1



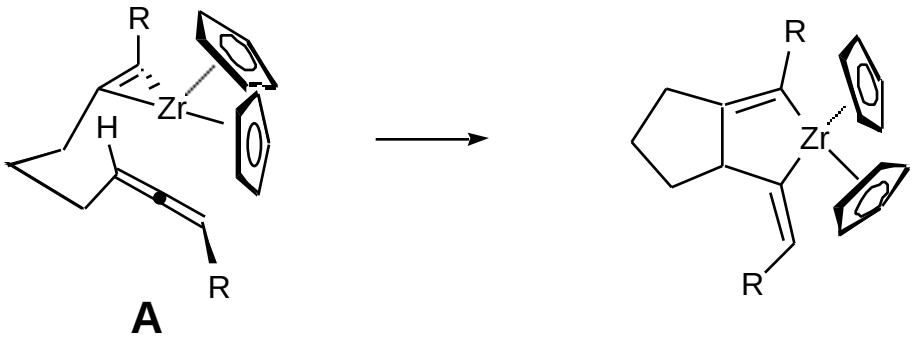
14 **15-*Z*** **15-*E***

Equation 1

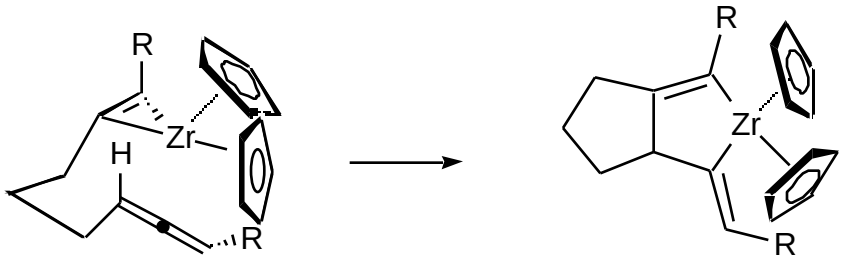


17 **18** **19** Eq. 1

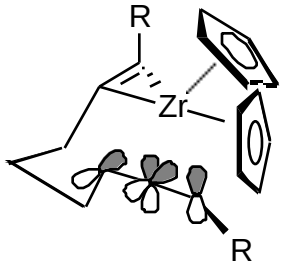
Scheme 4



A



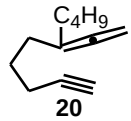
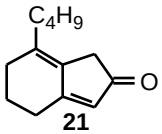
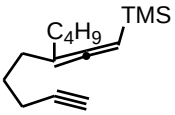
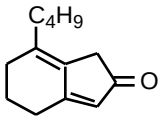
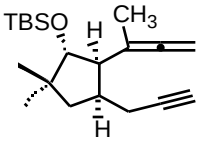
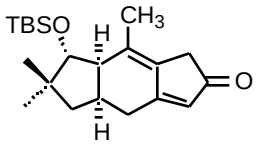
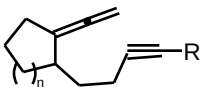
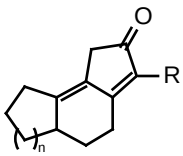
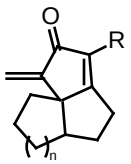
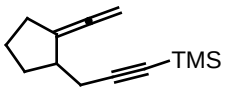
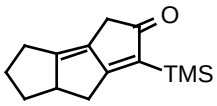
B



C

Table 3

Table 3. 3,3-Disubstituted Allenes

Entry	Allenyne	Cyclopentenone	Yield
1	 **20**	 **21**	60%
2	 **22**	 **21**	59%
3	 **23**	 **24**	42%[a]
4	 **25** n=1, R=H	 **26**	 **27**	73%[b]
5	**28** n=1, R=TMS	**29**	**30**	50%
6	**31** n=2, R=H	**32**	**33**	62%[c]
7	 **34**	 **35**	66%

All examples used conditions A: $Mo(CO)_6$/DMSO/tol/Ar/100°C
[a] Yield based upon recovered starting material [b] Product was a 7:1 ratio of β-methylene : α-methylene cyclopentenones [c] Product was a 4:1 ratio of β-methylene : α-methylene cyclopentenones

Scheme 5

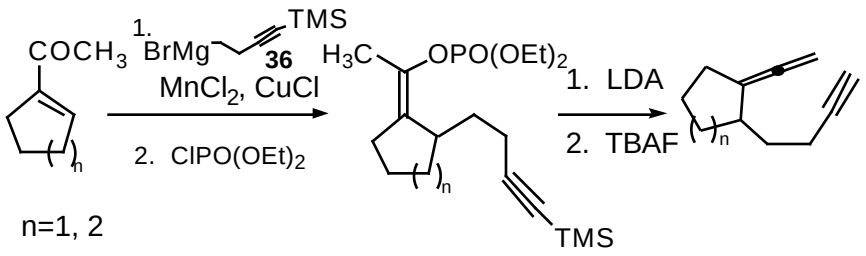
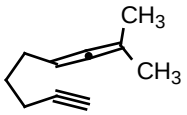
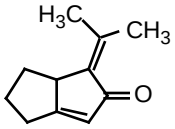
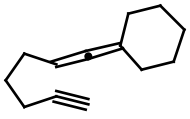
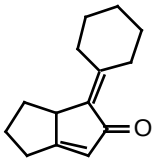


Table 4

Table 4. Trisubstituted Allenes

Entry	Allenyne	Cyclopentenone	Yield
1	 **37**	 **38**	59%
2	 **39**	 **40**	58%

All examples used conditions A: $Mo(CO)_6$/DMSO/tol/Ar/100°C