Polycyclic Cyclopropanes from Reactions of Alkene-Containing Fischer Carbene Complexes and Alkynes: A Formal Synthesis of (±)-Carabrone

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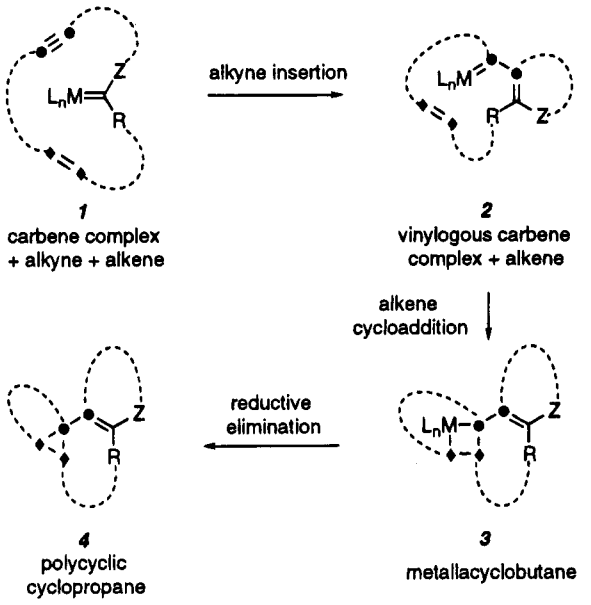
The polycyclic cyclopropanation reaction of several alkene-containing Fischer carbene complexes with various alkyne partners to provide bicyclo[4.1.0] enol ethers and ketones was examined. A number of features were probed, including the role of carbene donor substituent (amino vs alkoxy), the presence of one vs two pendant alkenes in the carbene complex, the level and sense of diastereoselectivity, and the impact of the substituents present on the alkyne partner. Relative configurations in cyclization products were established by ^{1}H NMR and difference NOE experiments. Using the above investigations as a guide, the tricyclic sesquiterpene lactone carabrone (**5**) was formally synthesized. The key cyclization of a symmetrical tetraene-containing carbene complex (**8**) with propyne provided ketone **42** in good yield as a single diastereomer. Six additional steps gave the tricyclic lactone **6**, thus constituting a formal total synthesis of carabrone (**5**). Notable features of the synthesis are that (i) the desymmetrizing cyclopropanation reaction between propyne and the symmetrical, tetraene-containing carbene complex is both efficient and highly diastereoselective, (ii) the alkenes remaining after the desymmetrizing cyclopropanation serve very effectively as protected carbonyl groups, and (iii) this work constitutes the first use of a Fischer carbene polycyclic cyclopropanation reaction in natural product synthesis.

Introduction

The Fischer carbene complex-mediated cyclopropanation of olefins with alkynes has been shown to proceed with facility on a variety of substrates in an inter-[1] or intramolecular[2–4] fashion. The overall process incorporates two atoms each from the alkyne (●) and alkene (◆) components and the carbene carbon in **1** (Z = donor atom) itself into the five-atom vinylcyclopropane moiety of the product **4**. The vinylogous Fischer carbene **2** and metallacyclobutane **3** are presumed to be intermediates in this powerful skeletal reorganization. The degree and nature of ring fusions in **4** follows from the extent of tethering in starting materials **1** (see dashed lines).

The version of this reaction where an alkene tethered to the carbene complex reacts intermolecularly with an alkyne is potentially quite valuable but has been explored only occasionally.[1a–c] Described here are bimolecular reactions of mono-and dialkene-containing carbene complexes with a variety of terminal alkynes to produce functionalized bicyclic cyclopropanes with high diastereoselectivity. Such transformations are valuable for the synthesis of cyclopropane-containing natural products.



Carabrone (**5**), a cyclopropane-containing sesquiterpene lactone, was first isolated from the fruits of *Carpesium abrotanoides*[5] and has been found subsequently in many other plant species.[6] An analgesic, local anesthetic, and antispasmodic, carabrone has an interesting skeletal

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(1) (a) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Organomet. Chem.* **1985**, *287*, C8. (b) Parlier, A.; Rudler, H.; Yefsah, R.; Alvarez, C. *J. Organomet. Chem.* **1987**, *328*, C21. (c) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041. (d) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1991**, *32*, 5223.

(2) (a) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676. (b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070. (c) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841. (d) Hoye, T. R.; Suriano, J. A. *Organometallics* **1992**, *11*, 2044.

(3) (a) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806. (b) Harvey, D. F.; Lund, K. P.; Neil, D. A. *Tetrahedron Lett.* **1991**, *32*, 6311. (c) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424. (d) Harvey, D. F.; Brown, M. F. *J. Org. Chem.* **1992**, *57*, 5559.

(4) (a) It should be noted that, in addition to the version of the Fischer carbene polycyclic cyclopropanation reaction that involves alkynes,[2,3] the version involving only an alkene has been well-studied.[5b–e] (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (c) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736. (d) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908. (e) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113.

(5) Minato, H.; Nosaka, S.; Horibe, I. *J. Chem. Soc.* **1964**, 5503.

(6) For examples: (a) Hernández, R.; Sandoval, A.; Setzer, A.; Romo, J. *Bol. Inst. Quim. Univ. Nac. Auton. Mex.* **1968**, *20*, 81. (b) Holub, M.; Samek, A.; Toman, J. *Phytochemistry* **1972**, *11*, 2627. (c) Bohlmann, F.; Mahanta, P. K.; Jakupovic, J.; Rastogi, R. C.; Natu, A. A. *Phytochemistry* **1978**, *17*, 1165. (d) Bohlmann, F.; Zdero, C.; King, R. M.; Robinson, H. *Phytochemistry* **1983**, *22*, 1288. (e) Spring, O.; Vargas, D.; Fischer, N. H. *Phytochemistry* **1991**, *30*, 1861. (f) Öksüz, S.; Topar, G. *Phytochemistry* **1992**, *31*, 195.

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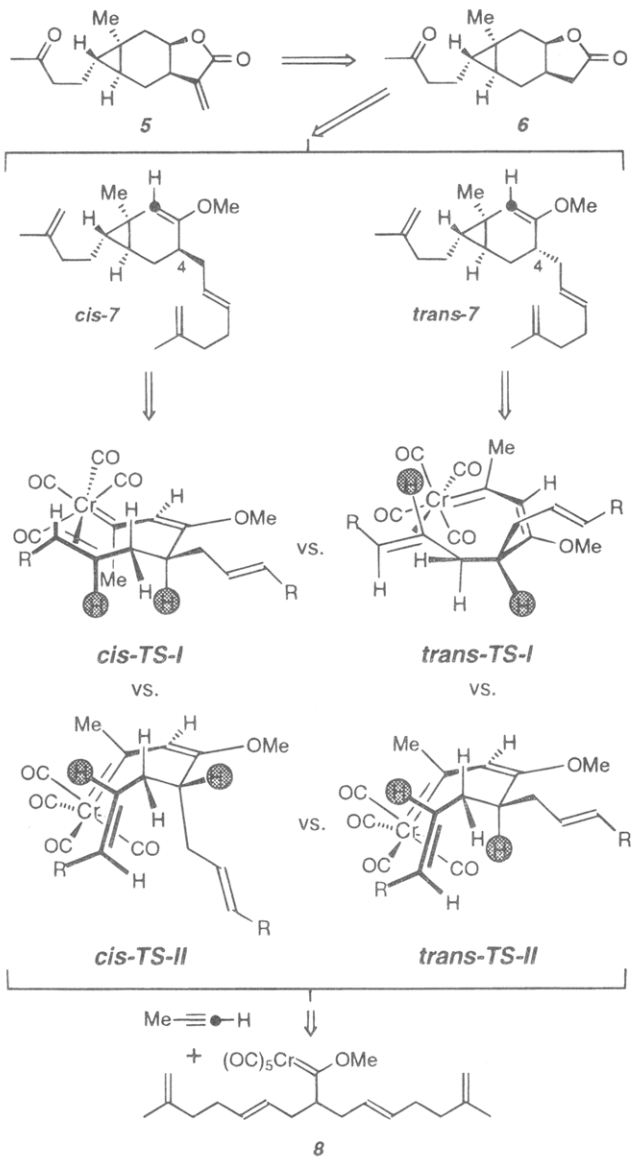
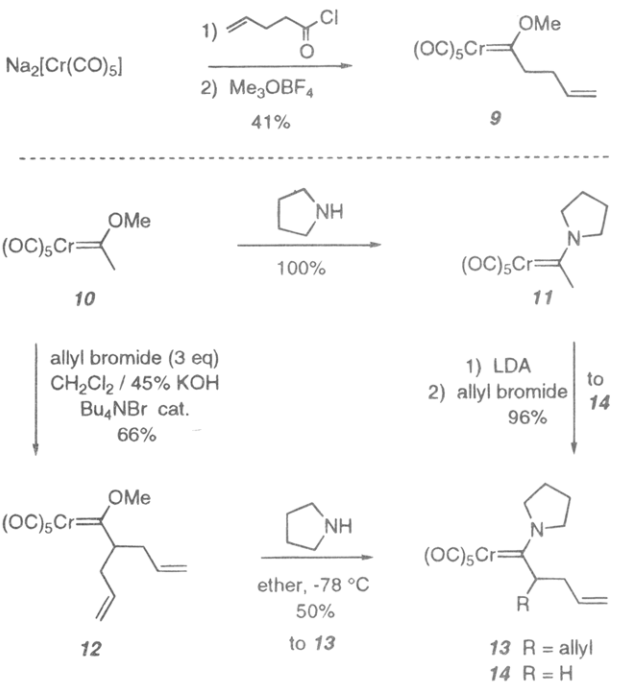
Scheme 1



Scheme 2



framework but has been synthesized only once.[7] Carabrone seemed to be an excellent target to demonstrate the utility of the Fischer carbene polycyclic cyclopropanation reaction[1-4] in the synthesis of natural products. We now report on a formal total synthesis of carabrone, which realizes that expectation.

In the retrosynthetic analysis, it was planned that the tricyclic keto lactone **6**, a late intermediate in Minato and Horibe's carabrone synthesis,[7] could be fashioned from bicyclic enol ether **7** (Scheme 1). Polycyclic cyclopropanation of the symmetrical carbene complex **8** with propyne was envisioned to provide **7** by a desymmetrizing process in which all of the carbon atoms and two of the three rings necessary for **6** were assembled in a single step from the acyclic precursors. The relative configuration of the three stereocenters in the cyclopropane ring is dictated by the *E*-olefin and the *cis*-fused nature of the norcarane moiety. It was of interest to learn the extent of selectivity for cyclization through presumed transition state geometries like ***cis***- and ***trans***-**TS-I** and ***cis***- and ***trans***-**TS-II** (Scheme 1),[8] which would lead to the β- and α-C(4)-epimers ***cis*-7** and ***trans*-7**, respectively. Note that, in this case, *cis* or *trans* refers to the relationship of the shaded hydrogens in the transition structures and products.

Results and Discussion

Preliminary Cyclization Studies. A series of cyclization reactions using substrates simpler than the ultimate **8** was explored. These studies provided experience in preparing diene carbene substrates like **8** and helped to define the nature of the alkyne and carbene (e.g. alkoxy vs amino substitution)[2b] that would be most compatible with the desired polycyclization. Toward this end, we prepared complexes **9**, **12**, **13**, and **14** (Scheme 2). The monoallyl methoxy complex **9** was made from the reaction of disodium pentacarbonyl chromate[9] with 4-pentenoyl chloride,[10] followed by alkylation of the acyl chromate with Meerwein's salt. Alkylation of (1-methoxyethylidene)pentacarbonylchromium(0) (**10**) with 1 equiv of LDA and allyl bromide typically gave ~4:1 mixtures of mono- and diallylated[11] complexes **9** and **12**, respectively, that could not be separated. The monoallylpyrrolidino complex **14** was prepared by deprotonation of the methylpyrrolidino complex **11** with LDA and alkylation with allyl bromide in 96% yield; diallyllation was not a problem with the amino-substituted complex.[11]

In the diallyl series, the methoxy complex was conveniently prepared by the phase transfer alkylation protocol of Sarkar.[12] Thus, **10** was treated in a two-phase

(7) (a) Minato, H.; Horibe, I. *J. Chem. Soc., Chem. Commun.* **1967**, 358. (b) Minato, H.; Horibe, I. *J. Chem. Soc. C* **1968**, 2131.

(8) (a) We have chosen to represent the parallel arrangement of the alkene and carbene ligands, although a perpendicular arrangement is possible.[4b-d,8b] (b) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574.

(9) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.

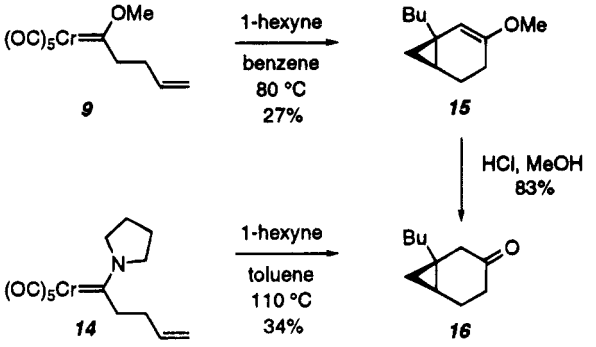
(10) Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.

(11) (a) Wulff, W. D.; Anderson, B. A.; Isaacs, L. D. *Tetrahedron Lett.* **1989**, *30*, 4061. (b) Wulff, W. D.; Xu, Y.-C. *J. Org. Chem.* **1987**, *52*, 3263 and references cited therein.

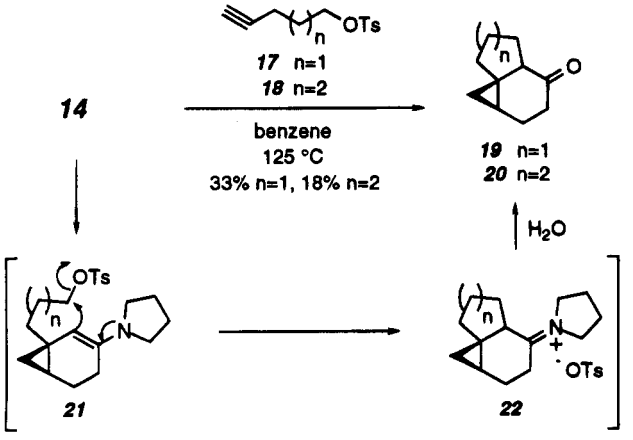
(12) Amin, S. R.; Sarkar, A. *Organometallics* **1995**, *14*, 547.

methylene chloride/aqueous hydroxide system in the presence of excess allyl bromide and 15 mol % of tetrabutylammonium bromide to give **12** in good yield. Exchange of pyrrolidino for methoxy in **12** generated **13** in acceptable yield, although long reaction times at low temperatures were required.[13] On one occasion, a solid byproduct having a ^{1}H NMR spectrum consistent with the complex $(CO)_5Cr$·pyrrolidine was isolated.[14] Complex **13** is a crystalline solid and was successfully stored under argon at −25 °C for weeks but is unstable in solution, especially at higher temperatures.

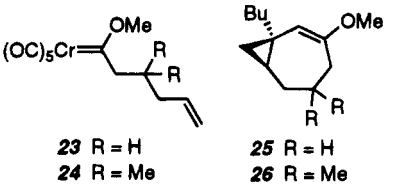
Participation of the monoallyl complexes **9** and **14** in the polycyclic cyclopropanation reaction was studied. Thermolysis of **9** with 1-hexyne gave the bicyclo[4.1.0] enol ether **15** as the only detected product. In contrast, the monoallylamino complex **14** produced the corresponding ketone **16**.[2b] Treatment of **15** with aqueous HCl



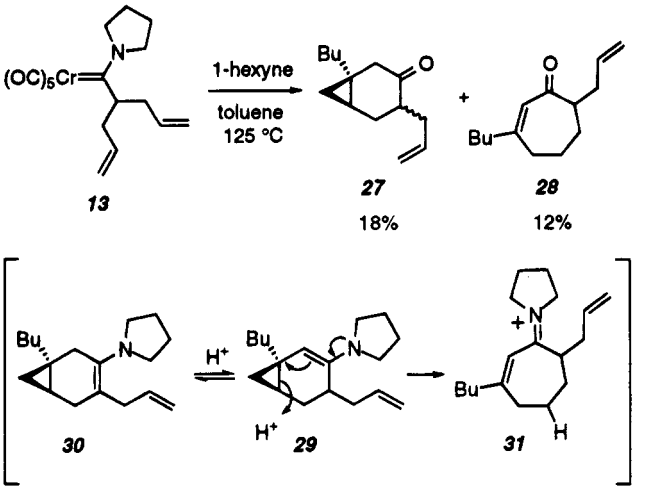
in methanol also provided **16** in good yield. In an effort to find evidence for and take advantage of the presumed intermediacy of the enamine **21**, the amino complex **14** was thermolyzed with the homologous ω-alkynyltosylates **17** and **18**. The tricyclic ketones **19** and **20** presumably arise via displacement of the tosyl group by the enamine in **21** and subsequent hydrolysis of the imminium salt **22**. The ketones **19** and **20** were isolated in modest yields



similar to those for **15** and **16**, implying that the enamine-trapping event was reasonably efficient. Note that four carbon−carbon bonds, three rings, and three stereogenic centers (one diastereomer of **19**, two (~85:15) of **20**) are created in this operation. Thermolysis of carbene complexes **23** and **24** with 1-hexyne failed to produce the bicyclo[5.1.0] derivatives **25** and **26**, suggesting that the rate of cyclization (cf. **2** to **3**) is quite sensitive to ring size. Alkyne oligomerization events apparently compete with the polycyclization pathway.[1c]



Polycyclic cyclopropanation of the carbene complexes bearing two equivalent alkenes (**12** and **13**) introduces the issue of diastereoselectivity. Substrates like **12** and **13** contain enantiotopic allyl groups; the alkene of each group possesses diastereotopic faces. Thermolysis of complex **13** with 1-hexyne gave bicyclic ketone **27** as an inseparable ~9:1 mixture of epimers at C(4) and the cycloheptenone **28**.[15] Opening of the cyclopropane ring (cf. **29** to **31**) followed by hydrolysis of the imminium species **31** would provide **28**. This mixture may reflect



the cyclization diastereoselectivity (cf. Scheme 1 and vide infra), although epimerization of C(4) through enamine isomerization (**29** to **30**) cannot be ruled out.

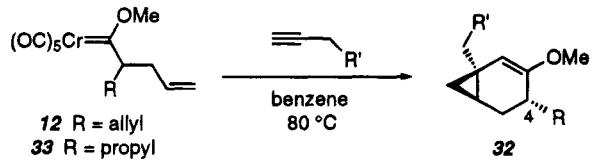
With the goal of improving the efficiency of generation of bicyclo[4.1.0] derivatives like **27**, as required for our planned synthesis of carabrone, we examined the cyclizations of diallyl methoxy complex **12** (Table 1). In contrast to the low yield of **27** from the pyrrolidino complex **13**, thermolysis of methoxy complex **12** with 1-hexyne gave enol ether **32a**, isolated as a single diastereomer (>97% by ^{1}H NMR analysis) in 71% yield (entry 1). Alkynes with propargylic oxygen substituents (entries 2 and 3) lowered the yields of **32** considerably, while a propargylic sulfur substituent (entry 4) resulted in a slightly higher yield. In each case, the relative configurations in the

(13) Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367.

(14) (a) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (b) Merlic, C. A.; Xu, D.; Gladstone, B. G. *J. Org. Chem.* **1993**, *58*, 538.

(15) This structure was assigned on the basis of the following data. (±)-7-(2-Propenyl)-3-butylcyclohept-2-en-1-one (**28**). R_f = 0.20 in 50:1 hexanes:ethyl acetate. IR ($CDCl_3$): 3075 (w), 1708 (s), and 1641 (w) cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.01 (s, 1H), 5.85 (dddd, J = 17.0, 10.2, 7.5, and 6.3 Hz, 1H), 5.05 (d, J = 17.0 Hz, 1H), 5.01 (d, J = 10.2 Hz, 1H), 2.75 (ddd, J = 14.5, 6.3, and 6.3 Hz, 1H), 2.44 (app dq, J = 12.6 and 6.3 Hz, 1H), 2.18 (ddd, J = 14.5, 7.5, and 7.5 Hz, 1H), 1.90 (m, 1H), 1.77 (br t, J = 7.2 Hz, 2H), 1.74 (m, 1H), 1.56 (m, 1H), 1.44 (m, 1H), 1.3−1.1 (m, 2H), 1.10 (m, 4H), and 0.79 (t, J = 7.0 Hz, 3H). ^{13}C NMR (C_6D_6, 125 MHz): δ 202.3 (C), 159.88 (C), 137.44, 129.84 (both CH), 116.17 (CH_2), 50.14 (CH), 40.50, 35.95, 32.52, 29.89, 28.76, 25.38, 22.61 (all CH_2), and 14.04 (CH_3); LRMS (EI): m/z (relative intensity) 206 ($M^{+\cdot}$, 14), 177 (25), 164 (63), 163 (29), 149 (31), 122 (46), 121 (58), 107 (52), 96 (28), 95 (82), 93 (40), 91 (44), 82 (68), 81 (90), 80 (33), 79 (76), 68 (35), 67 (100), and 41 (96).

Table 1. Cyclizations of α-Branched, α-Allylated Carbene Complexes with Alkyne Derivatives Bearing Different Propargylic Substituents

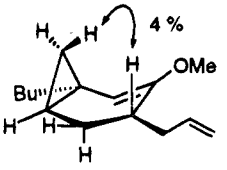


12 R = allyl
33 R = propyl

32

entry	carbene	R	R′	product	yield (%)
1	**12**	allyl	propyl	**32a**	71
2	**12**	allyl	OAc	**32b**	40
3	**12**	allyl	OTBS	**32c**	31
4	**12**	allyl	S^{t}Bu	**32d**	82
5	**33**	propyl	propyl	**32e**	56

product **32** between the allyl group at C(4) and the ring fusion atoms were the same. These relationships were established by ^{1}H NMR studies. Most convincing was the NOE between the *endo*-cyclopropyl proton and the methine proton at C(4) in **32a**.[16]

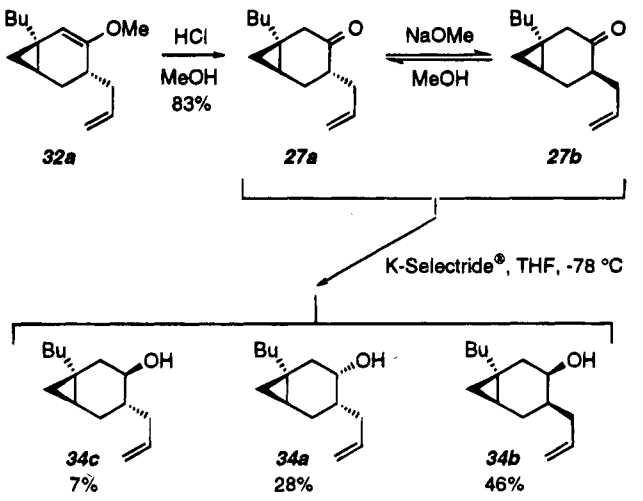


32a

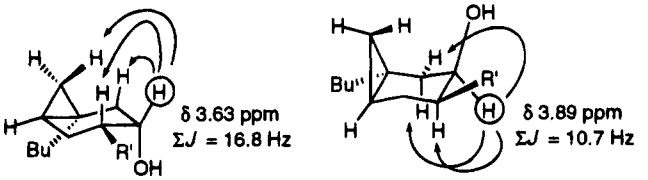
The highly diastereoselective formation of the *trans* isomers of **27** and **32** suggests the strong preference for reaction through transition state geometries ***trans*-TS-I** or ***trans*-TS-II**. Careful examination of models of each of the four transition state geometries indicated in Scheme 1 shows that very subtle changes in geometry around the metal center can impart significantly different interactions elsewhere in the molecule (e.g. between CO ligands and distal C_{sp^3}-substituents). One hypothesis for the high diastereoselectivity was that internal complexation of the alkene in the second allyl group with the chromium center in **12** might orient the spectator alkene substituent so as to favor formation of the *trans* diastereomer. We therefore prepared substrate **33** (entry 5) containing a saturated propyl substituent in lieu of the second allyl group. Thermolysis of **33** with 1-hexyne gave enol ether **32e**; again, only the *trans* diastereomer was observed.

Model Studies for Carabrone. Enol ether **32a** served as an excellent model system in which to work out experimental details for the synthesis of carabrone (**5**). The first order of business was to "correct" the stereochemistry at C(4) to match that present in the natural product (Scheme 3). Acidic hydrolysis of **32a** gave ketone **27a**. Treatment of **27a** with sodium methoxide set up an equilibrium with epimeric ketone **27b**. Reduction of the ketone mixture with K-Selectride (Aldrich) yielded alcohols **34a** and **34b** which were separated by chromatography in 28 and 46% yields, respectively,

Scheme 3



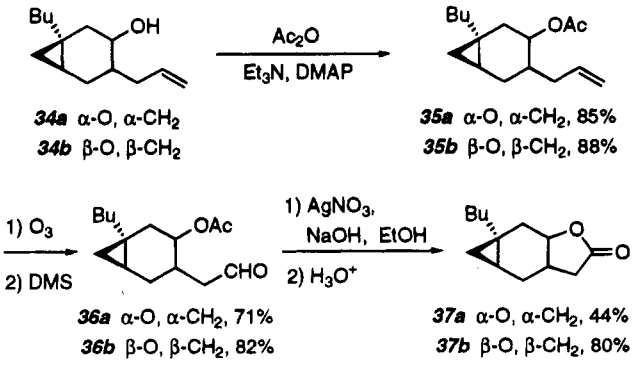
along with an isomeric *trans* alcohol (7%) tentatively assigned as **34c** which was not fully characterized.



34a Arrows show observed NOE's *34b*

Relative configurations of these alcohols were established through careful analysis of the ^{1}H NMR spectra along with NOE difference experiments. Namely, the C(3) methine of **34a** appears at 3.63 ppm with ΣJ's = 16.8 Hz while the C(3) methine of **34b** appears at 3.89 ppm and has ΣJ's = 10.7 Hz. The chemical shift difference is consistent with the shielding effect of the cyclopropane ring,[7b,17] and the sums of the coupling constants (ΣJ's)[18] are consistent with a *cis* relationship of the allyl and hydroxyl groups and with molecular modeling of the lowest energy conformers.

The alcohols **34a** and **34b** were carried on separately in the following sequence to model the remaining steps in the planned carabrone synthesis. Acetylation to **35a**



and **35b** followed by ozonolysis gave aldehydes **36a** and **36b**, respectively. Treatment with silver oxide in the

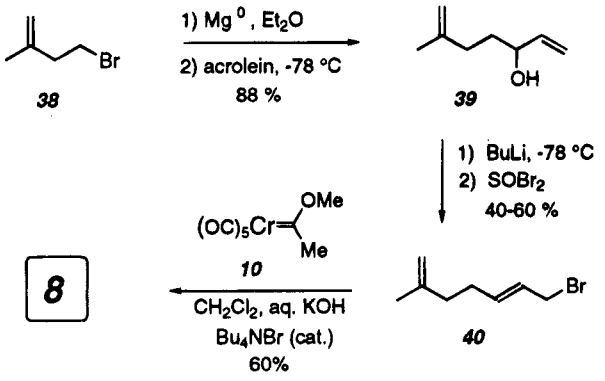
(16) The conformation shown for **32a** is the second lowest energy conformer (by 0.1 kcal mol^{-1}, MM2 with Monte Carlo minimization of the analog containing methyl groups in place of the butyl and allyl substituents). The presence of the cyclopropane fusion and two sp^2 centers flatten the cyclohexene ring, making the observed difference NOE small; NOEs of 6 and 5% for this interaction were measured for **32b** and **32d**, respectively. The ketones resulting from hydrolysis of these enol ethers have conformations that are more chairlike, and the NOE to H(4) is larger (e.g. **27a** showed a 9% NOE).

(17) Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Barton, D. H. R., Doering, W., Eds.; International Series of Monographs in Organic Chemistry; Pergamon: New York, 1969; Vol. 5, pp 98–101.

(18) Hoye, T. R.; Hanson, P. R.; Vyvyan, J. R. *J. Org. Chem.* **1994**, *59*, 4096.

presence of sodium hydroxide overnight, followed by acidification of the reaction mixture, afforded lactones **37a** and **37b** directly.

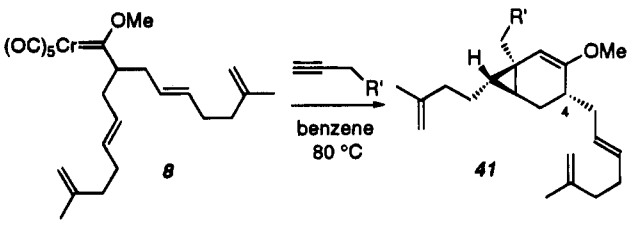
Carabrone Synthesis. With a procedure for functional group elaboration leading from a keto alkene like **27** or **42** (see below) to a *cis*-fused lactone like **37** or **6** developed, our proposed synthesis of carabrone now hinged only on preparing carbene complex **8** and successful polycyclization of this more complex substrate with propyne. Carbene **8** was synthesized in only three steps from 4-bromo-2-methyl-1-butene (**38**).[19] Thus, the Grignard reagent derived from **38** was added to acrolein to give allylic alcohol **39**, which was converted by the action of thionyl bromide with allylic rearrangement to the bromide **40**. Prior deprotonation of **39** was essential to prevent acid-promoted cyclization and/or HBr addition reactions. Dialkylation of **10** with excess **40** under phase transfer conditions[12] afforded carbene complex **8**.[20]



Three model cyclizations of complex **8** were examined. We wondered if the larger alkene-containing substituents in **8** would change the stereoselectivity observed earlier for complexes **12** and **33**. Thermolysis of **8** with 1-hexyne, propargyl acetate, and *tert*-butyl propargyl sulfide gave bicyclic enol ethers **41a**, **41b**, and **41c**, respectively, in good yield (Table 2). No other diastereomeric products were observed. Analysis of the NMR spectra of **41a–c**, as well as of the corresponding ketone from hydrolysis of **41a**, confirmed that the relative configurations within **41** were the same as those observed in **32**.

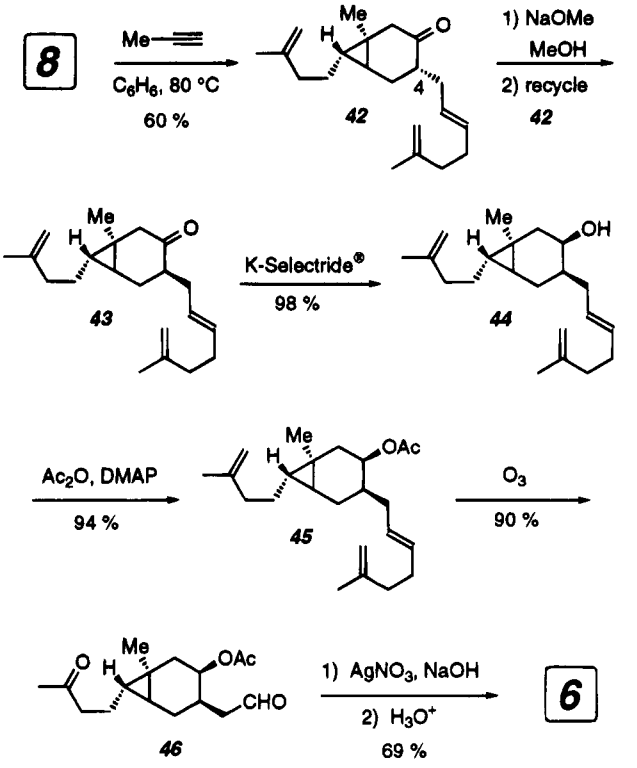
Thermolysis (80 °C, benzene) of complex **8** with excess propyne in a sealed tube gave a 60% yield of ketone **42**[21] as a single diastereomer with the same relative configuration at C(4) as observed for **32** and **41** (Scheme 4). The cyclization of **8** occurred exclusively from a single diastereotopic face (i.e. the *re*-face of the disubstituted alkene in the *pro-S* group and the *si*-face in the *pro-R* group). The unnatural configuration of C(4) in **42** made necessary an equilibration (NaOMe/MeOH; **42**:**43**, 1.4:1), separation (MPLC on SiO_2), and recycling strategy, which provided the epimeric ketone **43** with 60% efficiency. Ketone **43** was stereospecifically reduced with K-Selectride to give alcohol **44**. Ozonolysis of the alcohol

Table 2. Cyclizations of Carbene Complex 8 with Alkyne Derivatives Bearing Different Propargylic Substituents



entry	carbene	R′	product	yield (%)
1	**8**	propyl	**41a**	73
2	**8**	OAc	**41b**	34
3	**8**	S^{t}Bu	**41c**	59

Scheme 4



triene **44** gave a complex mixture. Therefore, **44** was acetylated, and subsequent ozonolysis of the acetate **45** cleanly cleaved all three olefins to give keto aldehyde **46**, which was oxidized under the same conditions used for the conversion of **36** to **37** to provide lactone **6** directly. The melting point and spectral data of **6** matched those previously reported,[7] thereby confirming this formal synthesis of carabrone (**5**).

Conclusions

We have demonstrated the Fischer carbene polycyclic cyclopropanation reaction of alkene-containing complexes with alkynes to be a highly efficient stereoselective route to functionalized bicyclo[4.1.0] derivatives. The forces that govern diastereoselectivity in reactions of this type of process are subtle and poorly understood. The utility of this reaction has been demonstrated in the formal synthesis of carabrone (**5**). The highly diastereofacially selective cyclopropanation reaction of the symmetrical tetraene-containing carbene complex **8** with propyne provides a one-step entry into the structurally elaborate

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(20) (a) In our hands, this convenient phase transfer protocol gave, as described,[12] reproducible yields of 66–85% with a variety of simple allylic bromides. However, for reasons that are unclear, alkylation with bromide **11** was sporadic (2× 50–60% and 3× <20%). An alternative preparation of complex **8** was achieved by two sequential deprotonation/alkylation steps in 30% yield.[11]

(21) An enol ether corresponding to **7** was observed by ^{1}H NMR and GC/MS analysis of the crude reaction mixture but hydrolyzed to ketone **42** before and/or during isolation.

bicyclic cyclopropane **42**, which contains all of the carbon atoms necessary for conversion to lactone **6**. The alkenes remaining after the desymmetrizing cyclopropanation serve very effectively as protected carbonyl groups. This work constitutes the first use of a Fischer carbene polycyclic cyclopropanation reaction in natural product synthesis.

Experimental Section

All reactions involving carbene complexes and other air-sensitive reagents were carried out under dry argon or nitrogen. Ether and THF were distilled from sodium and potassium benzophenone ketyl, respectively. Benzene and CH_2Cl_2 were distilled from CaH_2, and the benzene was stored under nitrogen over molecular sieves. Toluene was predried over $CaCl_2$ and distilled, discarding the first 10% of the material, and stored under nitrogen over molecular sieves. Melting points were determined either in sealed capillaries on a Mel-Temp apparatus or on a Bristoline hot stage microscope and are uncorrected. Where ^{13}C DEPT data were collected, carbon multiplicities are given in parentheses. The following compounds were prepared according to literature procedures: 4-pentenoyl chloride,[22] (1-methoxyethylidene)pentacarbonylchromium(0) (**10**),[23] (1-pyrrolidinoethylidene)pentacarbonylchromium(0) (**11**),[24] 4,4-dimethyl-5-iodo-1-pentene,[25] propargyl acetate,[3c] propargyl (dimethylethyl)dimethylsilyl ether,[26] *tert*-butylpropargyl sulfide,[27] (1-methoxypentylidene)-pentacarbonylchromium(0),[23] and 4-bromo-2-methyl-1-butene (**38**).[19] The alkynes 4-pentyn-1-ol, 4-methylbenzenesulfonate (**17**) and 5-hexyn-1-ol, 4-methylbenzenesulfonate (**18**) were prepared form the corresponding alcohols by standard procedures (TsCl, pyridine, 0 °C), and 5-iodo-1-pentene was prepared from the commercially available bromide (NaI, refluxing acetone).

(1-Methoxypent-4-enylidene)pentacarbonylchromium-(0) (9). To a solution of $Na_2[Cr(CO)_5]$[9] (2 mmol) at −78 °C was added 4-pentenoyl chloride (230 μL, 2 mmol) as a solution in THF (3 mL). After 15 min at −78 °C, the solvent was removed to leave a viscous orange-brown residue that was dissolved in cold water (30 mL). Meerwein's salt (357 mg, 2.4 mmol) was added, and the slurry was stirred for 15 min. The aqueous phase was extracted with hexanes (3 × 20 mL), dried over Na_2SO_4, and concentrated. Flash chromatography (hexanes) of the residue gave **9** as a bright orange oil (236 mg, 41%). TLC: R_f = 0.4 in 19:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3082, 2963, 2923, 2854 (all m), 2063 (s), 1920 (br vs), 1642 (m), 1256, 1035, and 917 (all s) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 5.46 (ddt, J = 17.1, 9.8, and 6.8 Hz, 1H), 4.85 (ddd, J = 17.1, 3.2, and 1.6 Hz, 1H), 4.83 (ddd, J = 9.8, 3.2, and 1.3 Hz, 1H), 3.88 (s, 3H), 3.02 (t, J = 7.5 Hz, 2H), and 1.85 (m, 2H). ^{13}C NMR (C_6D_6, 75 MHz): δ 361.73, 223.42, 216.69, 136.45, 115.69, 67.14, 61.89, and 30.31. Anal. Calcd for $C_{11}H_{10}CrO_6$: C, 45.53; H, 3.47. Found: C, 45.66; H, 3.54.

[1-Methoxy-2-(2-propenyl)pent-4-enylidene]pentacarbonylchromium(0) (12). To a 25 mL round-bottomed flask were charged **10** (253 mg, 1 mmol) and Bu_4NBr (49 mg, 0.15 mmol). Methylene chloride (15 mL) was added to give an orange solution, to which 45% aqueous KOH (2.5 mL) was added. Allyl bromide (0.25 mL, 3 mmol) was added, and the mixture was stirred at room temperature. When TLC analysis indicated that the starting carbene complex was consumed, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The extracts were dried over $MgSO_4$, concentrated, and purified by flash chromatography (50:1 hexanes: ethyl acetate) to give pure **12** as a bright orange oil (217 mg, 66%). R_f = 0.4 in 9:1 hexanes:ethyl acetate, and R_f = 0.63 in 3:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3080 (m), 3007 (w), 2980, 2960, 2914 (all m), 2852 (w), 2062, 2020 (both s), 1942 (br vs), 1641 (m), 1276, 1252, 1214, 1051, and 993 (all s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.74 (m, 2H), 4.98 (m, 4H), 4.79 (s, 3H), 4.16 (app pentet, J = 6.8 Hz, 1H), 2.24 (ddd, J = 13.7, 7.1, and 6.8 Hz, 2H), and 2.02 (ddd, J = 13.7, 7.2, and 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 367.74, 223.00, 216.21 (all C's), 135.28 (CH), 117.21 (CH_2), 69.91 (CH_3), 67.68 (CH), and 35.99 (CH_2). Anal. Calcd for $C_{14}H_{14}CrO_6$: C, 50.92; H, 4.27. Found: C, 50.96; H, 4.32.

[1-Pyrrolidino-2-(2-propenyl)pent-4-enylidene]pentacarbonyl chromium(0) (13). Methoxycarbene complex (**12**) (292 mg, 0.88 mmol) was dissolved in ether (5 mL), and the solution was cooled in a dry ice/acetone bath. Pyrrolidine (0.15 mL, 1.7 mmol, 2 equiv) was charged, and the reaction was monitored by TLC analysis. After 2 h, an additional 2 equiv of pyrrolidine was added, and the reaction mixture was stirred for 45 min. Solvent was removed on a rotary evaporator, and the yellow solid residue was washed five times with pentane (3 mL each) to remove traces of pyrrolidine and alkoxycarbene complex. Removal of solvent gave **3** as a yellow powder (mp 73−77 °C, 160 mg, 50%). The product was unstable in solution and gave a poor quality ^1H NMR spectrum with broad peaks. R_f = 0.40 in 3:1 hexanes:ethyl acetate. IR ($CDCl_3$): 3080 (w), 2980 (m), 2049 (vs), 2003 (s), 1898 (br vs), 1793 (m), 1639 (m), 1473, 1446, and 1095 (all s) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 5.6 (m, 2H), 4.9 (m, 4H), 3.75 (m, 3H), 2.80 (m, 2H), 2.48 (br s, 2H), 2.0 (m, 2H), and 1.08 (m, 4H). ^{13}C NMR (C_6D_6, 75 MHz): δ 276.63, 223.09, 219.48 (all C's), 136.36 (CH), 116.93 (CH_2), 62.66 (CH), 56.67, 54.65, 38.91, 24.58, and 24.30 (all CH_2). Anal. Calcd for $C_{17}H_{19}CrNO_5$: C, 55.28; H, 5.18; N, 3.79. Found: C, 55.02; H, 5.02; N, 3.86.

(1-Pyrrolidinopent-4-enylidene)pentacarbonylchromium(0) (14). A solution of (1-pyrrolidinoethylidene)pentacarbonylchromium(0) (**11**)[24] (1.44 g, 5 mmol) in THF (40 mL) under argon at −78 °C was treated with LDA in THF (5 mmol), at which time the pale yellow solution became more orange in color. After 45 min, allyl bromide (0.43 mL, 5.1 mmol) was added, the dry ice/acetone bath was replaced by an ice−water bath, and the solution gradually regained a yellow color. After 2.5 h, the reaction was quenched with 5% bicarbonate solution and the mixture diluted with ether (40 mL). The aqueous layer was discarded, and the organic phase was washed (saturated NH_4Cl (2 × 25 mL), Na_2CO_3 (2 × 25 mL), and brine (25 mL)), dried ($MgSO_4$), and concentrated to leave yellow crystals (mp 49.5−52.5 °C, 1.58 g, 96%). An analytical sample (mp 54−55.5 °C) was prepared by MPLC (9:1 hexanes:ethyl acetate). R_f = 0.47 in 2:1 hexanes:ethyl acetate and 0.25 in 9:1 hexanes:ethyl acetate. IR (neat, deposited on NaCl plates from CH_2Cl_2): 3081 (w), 2980, 2880 (both m), 2050 (s), 1993 (shoulder), 1896 (vs broad), 1641 (m), 1499, 1476, 1448, 1332, 1154, and 895 (all m) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 5.85 (ddt, J = 16.9, 10.1, and 6.6 Hz, 1H), 5.11 (dd, J = 16.9 and 1.5 Hz, 1H), 5.04 (dd, J = 10.1 and 1.5 Hz, 1H), 4.12 (t, J = 6.9 Hz, 2H), 3.67 (t, J = 7.1 Hz, 2H), 3.05 (distorted t, J = ~8.4 Hz, 2H), 2.22 (dt, J = 9.1 and 7.6 Hz, 2H), and 2.10 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 272.26, 223.16, 218.34 (all C's), 136.25 (CH), 115.66, 61.17, 52.35, 51.86, 29.11, 25.50, and 24.92 (all CH_2). Anal. Calcd for $C_{14}H_{15}CrNO_5$: C, 51.07; H, 4.59; N, 4.25. Found: C, 51.23; H, 4.93; N, 4.41.

General Procedure for Thermolysis of Carbene Complexes with Alkynes. (±)-(1α,6α)-1-Butyl-3-methoxybicyclo[4.1.0]hept-2-ene (15). Carbene complex **9** (1.08 mmol) and 1-hexyne (0.25 mL, 2.1 mmol) were placed in a screw-topped culture tube under argon and dissolved in benzene (15 mL). The tube was capped and heated in an oil bath (80−95 °C) overnight. After cooling, the reaction mixture was exposed to air for ~3 h, passed through a silica plug with petroleum ether, concentrated, and purified by MPLC (hexanes) to give enol ether **15** (52 mg, 27%). Prolonged exposure of **15** to $CDCl_3$ resulted in equilibration with a regioisomeric enol ether. R_f = 0.18 in hexanes. IR (neat, NaCl plates, mixture of isomers): 3060 (m), 1658, 1254, 1198, 1159 (all s), 1117, 1092, 1075, 1054, and 1019 (all m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.70 (s, 1H), 3.49 (s, 3H), 1.97−1.78 (m, 4H), 1.50

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(m, 1H), 1.30 (m, 4H), 1.10 (m, 1H), 0.92 (m, 1H), 0.88 (t, J = 6.9 Hz, 3H), and 0.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.15 (C), 97.68 (CH), 53.83 (CH_3), 38.98, 29.69, 23.87, 22.84, 20.75 (all CH_2), 20.33 (CH), 19.56 (C), 18.65 (CH_2), and 14.20 (CH_3). Anal. Calcd for $C_{12}H_{20}O$: C, 79.95; H, 11.18. Found: C, 79.96; H, 10.94.

(±)-(1α,6α)-1-Butylbicyclo[4.1.0]heptan-3-one (16). Using the general procedure, carbene complex **14** (112 mg, 0.34 mmol) and 1-hexyne (80 μL, 0.68 mmol) in toluene (4 mL) were heated (110 °C) for 2 h and stirred overnight at room temperature. A slurry of silica in hexanes was added, and the mixture was stirred, exposed to the air for 2 h, passed through silica (2:1 hexanes:ethyl acetate), and purified by MPLC (9:1 hexanes:ethyl acetate) to afford **16** as a colorless oil (19 mg, 34%). R_f = 0.12 in 9:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3060 (w), 1709 (s), 1458, 1438, 1420, 1348, 1195, and 895 (all m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.50 (s, 2H), 2.24 (m, 2H), 2.10 (m, 1H), 1.95 (m, 1H), 1.29 (m, 6H), 0.97 (m, 1H), 0.88 (br t, J = 7.4 Hz, 3H), 0.46 (dd, J = 8.5 and 4.9 Hz, 1H), and 0.42 (app t, J = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 212.68 (C), 43.58, 39.17, 35.63, 28.52, 22.75, 21.42 (all CH_2), 19.10 (C), 17.25 (CH), 14.15 (CH_2), and 14.08 (CH_3). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.77; H, 11.02.

(±)-Octahydrocycloprop[*h*]inden-4-one (19). Using the general procedure, carbene complex **14** (203 mg, 0.61 mmol) and **17** (220 mg, 0.93 mmol) in toluene (3 mL) were heated (125 °C) for 2 h. A slurry of silica in hexanes was added, and the mixture was stirred exposed to the air for 2 h, passed through silica (2:1 hexanes:ethyl acetate), and purified by MPLC (19:1 hexanes:ethyl acetate) to give **19** as a colorless oil (30 mg, 33%). R_f = 0.60 in 2:1 hexanes:ethyl acetate and 0.40 in 5:1 pentane:ether. IR (neat, NaCl plates): 3054 (w), 2949, 2864, 1710 (all s), 1451, 1349, 1308, 1201, 1173, 1135, and 1025 (all m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.54 (dd, J = 8.7 and 7.0 Hz, 1H), 2.27 (dddd, J = 13.7, 10.7, 5.5, and 5.5 Hz, 1H), 2.15 (m, 2H), 2.02 (app dq, J = 13.6 and 7.0 Hz, 1H), 1.99–1.91 (m, 2H), 1.73 (ddd, J = 12.0, 6.8, and 6.8 Hz, 1H), 1.65 (m, 2H), 1.54 (ddd, J = 12.0, 6.6, and 6.6 Hz, 1H), 0.99 (dddd, J = 8.8, 5.6, 5.4, and 3.2 Hz, 1H), 0.85 (dd, J = 8.8 and 5.0 Hz, 1H), and 0.74 (app t, J = 5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 214.50, 52.47, 37.42, 35.70, 29.30, 27.71, 25.44, 25.41, 18.56, and 17.23. HRMS Calcd for $C_{10}H_{14}O$ 150.1045, found 150.1042.

(±)-Decahydrocycloprop[*d*]naphthalen-1-one (20). Using the general procedure, carbene complex **14** (174 mg, 0.69 mmol) and **18** in toluene (3 mL) were heated (110–130 °C) for 2 h. A slurry of silica in hexanes was added, and the mixture was stirred exposed to the air for 2 h, passed through silica (2:1 hexanes:ethyl acetate), and purified by MPLC (19:1 hexanes:ethyl acetate) to give ketone **20** as a colorless oil (18 mg, 18%). R_f = 0.55 in 2:1 hexanes:ethyl acetate and 0.40 in 5:1 pentane:ether. IR (neat, NaCl plates): 3059 (w), 2997 (m), 2930, 2855, 1708 (all s), 1459, 1445, 1198, 1101, and 1017 (all m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.50 (m, 1H), 2.35–2.15 (m, 2H), 2.15–1.95 (m, 2H), 1.90–1.60 (m, 4H), 1.50–1.15 (m, 3H), 1.05–0.80 (m, 2H), 0.42 (app t, J = 5.6 Hz, 1H), and 0.30 (dd, J = 8.3 and 5.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 214.15 (C), 52.23 (CH), 35.59, 33.17, 29.17, 25.39, 24.86 (all CH_2), 20.34 (C), 19.64 (CH_2), 16.82 (CH), and 12.26 (CH_2). HRMS Calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

(1-Methoxyhex-5-enylidene)pentacarbonylchromium-(0) (23). A solution of 5-iodopentene (0.58 g, 2.9 mmol) in ether (15 mL) at −78 °C was treated with ^{t}BuLi (6.5 mmol, 2.2 equiv), and the clear solution was allowed to warm to room temperature. The solution of pentenyllithium was added to $Cr(CO)_6$ (0.58 g, 2.65 mmol), and the resulting dark brown solution was stirred for 1 h at room temperature. After removal of the ether, the residue was taken up in water (15 mL) and trimethyloxonium tetrafluoroborate was added until the yellow mixture was acidic (pH ~3). The aqueous mixture was extracted with hexanes, and the combined organic phases were washed (brine), dried ($MgSO_4$), and concentrated. Flash chromatography (hexanes) and collection of the orange band afforded **23** as a bright orange oil (209 mg, 26%). R_f = 0.45 in hexanes. IR (neat, NaCl plates): 3081 (w), 2062 (s), 1918 (vs broad), 1641 (m), 1453, 1249, and 1042 (all s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.74 (m, 1H), 5.00 (m, 2H), 4.76 (s, 3H), 3.31 (t, J = 7.6 Hz, 2H), 2.05 (br dt, ~q, J = 6.8 Hz, 2H), and 1.59 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 363.32, 223.13, 216.36, 137.53, 115.51, 67.59, 62.38, 33.13, and 25.37. Anal. Calcd for $C_{12}H_{12}CrO_6$: C, 47.38; H, 3.98. Found: C, 47.22; H, 4.07.

(1-Methoxy-3,3-dimethylhex-5-enylidene)pentacarbonylchromium(0) (24). Following a procedure analogous to that for the preparation of **23**, 4,4-dimethyl-5-iodo-1-hexene[25] (388 mg, 1.73 mmol), ^{t}BuLi (3.8 mmol, 2.2 equiv), $Cr(CO)_6$ (365 mg, 1.66 mmol), and Meerwein's salt, followed by flash chromatography (30:1 hexanes:ethyl acetate), provided **24** as a bright orange oil (212 mg, 37%). IR (neat, NaCl plates): 3078 (w), 2962, 2873 (both m), 2061 (s), 1921 (vs broad), 1640 (w), 1455, 1253, and 1029 (all s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.75 (ddt, J = 17.4, 11, and 7.4 Hz, 1H), 5.05 (br d, J = 11 Hz, 1H), 5.00 (br d, J = 17.4 Hz, 1H), 4.82 (s, 3H), 3.36 (s, 2H), 2.01 (d, J = 7.3 Hz, 2H), and 0.95 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 367.80, 223.26, 216.45, 134.80, 117.79, 72.85, 67.45, 47.55, 37.30, and 27.91. Anal. Calcd for $C_{14}H_{16}CrO_6$: C, 50.61; H, 4.85. Found: C, 50.49; H, 4.77.

(±)-(1α,4α,6α)-1-Butyl-3-methoxy-4-(2-propenyl)bicyclo-[4.1.0]hept-2-ene (32a). Following the general procedure, carbene complex **12** (369 mg, 1.12 mmol) and 1-hexyne (155 μL, 1.35 mmol) in benzene (30 mL) were heated (75 °C) for 14 h. The reaction mixture was passed through silica (2:1 hexanes:ethyl acetate), concentrated, and purified by MPLC (hexanes) to yield enol ether **32a** as a colorless oil (174 mg, 71%). R_f = 0.30 in hexanes. IR (neat, NaCl plates): 3060 (m), 1654, 1252, 1233, 1196, 1162, 1140, 1117, 1039, and 1025 (all m-s) cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz, assignments assisted by ^{1}H–^{1}H COSY at 300 MHz and by difference NOE experiments): δ 5.83 (ddt, J = 17.1, 10.1, and 7.1 Hz, 1H, CH=CH$_E$H$_Z$), 5.07 (ddt, J = 17.1, 2.5, and 1.5 Hz, 1H, CH=CH$_E$H$_Z$), 5.02 (ddt, J = 10.1, 2.5, and 1.5 Hz, 1H, CH=CH$_E$H$_Z$), 4.71 (s, 1H, CH=C(OMe)), 3.20 (s, 3H, OCH_3), 2.55 (ddddd, J = 13.3, 7.1, 4.9, 1.5, and 1.5 Hz, 1H, CH_aH$_b$-CH=CH$_2$), 2.35 (br ddd, J = 13.3, 7.1, and 6.3 Hz, 1H, CH$_a$H$_b$-CH=CH$_2$), 2.08 (m, 1H, CHC(OMe)), 1.88 (ddd, J = 13.7, 7.3, and 5.8 Hz, 1H, CHCH_αH$_\beta$CH), 1.82 (ddd, J = 13.7, 6.3, and 3.7 Hz, 1H, CHCH$_\alpha$H$_\beta$CH), 1.5–1.2 (m, 6H, $(CH_2)_3$), 0.92 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.83 (m, 1H, CHC(Bu)), 0.60 (dd, J = 8.5 and 3.8 Hz, 1H, CH$_{endo}$H$_{exo}$), and 0.45 (dd, J = 5.1 and 3.8 Hz, 1H, CH_{endo}H$_{exo}$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 157.40 (C), 137.71 (C), 115.56 (CH_2), 97.65 (CH), 53.91 (CH_3), 39.32, 36.70 (both CH_2), 35.30 (CH), 29.65, 29.45, 22.94, 22.37 (all CH_2), 20.08 (C), 17.08 (CH), and 14.17 (CH_3). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.82; H, 10.83.

Acetic Acid [(±)-(1α,4α,6α)-4-(2-Propenyl)-3-methoxybicyclo[4.1.0]hept-2-en-1-yl]methyl Ester (32b). Using the general procedure, carbene complex **12** (90 mg, 0.273 mmol) and propargyl acetate[3c] (46 mg, 0.469 mmol) in benzene (10 mL) were heated (80 °C) overnight. After the reaction mixture was passed through silica (6:1 hexanes:ethyl acetate), purification by MPLC (19:1 hexanes:ethyl acetate) provided **32b** as a colorless oil (29 mg, 40%). R_f = 0.44 in 6:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3072 (w), 1738, 1655, 1249, 1199, 1164, 1031 (all s), 996, 969, 913, and 802 (all m) cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 5.76 (dddd, J = 17.1, 10.0, 7.6, and 6.6 Hz, 1H), 5.04 (dddd, J = 17.1, 2.2, 1.3, and 1.1 Hz, 1H), 5.00 (dddd, J = 10.0, 2.2, 1.3, and 1.1 Hz, 1H), 4.75 (s, 1H), 4.15 (d, J = 11.2 Hz, 1H), 3.81 (d, J = 11.2 Hz, 1H), 3.17 (s, 3H), 2.49 (ddddd, J = 13.7, 6.6, 5.1, 1.3, and 1.1 Hz, 1H), 2.26 (ddddd, J = 13.7, 8.3, 7.6, 1.3, and 1.1 Hz, 1H), 1.99 (ddddd, J = 8.3, 6.3, 5.9, 5.1, and 1.0 Hz, 1H), 1.83 (ddd, J = 13.7, 6.6, and 6.3 Hz, 1H), 1.73 (s, 3H), 1.61 (ddd, J = 13.7, 5.9, and 4.2 Hz, 1H), 0.92 (ddddd, J = 8.6, 6.6, 5.3, 4.2, and 1.0 Hz, 1H), 0.69 (dd, J = 8.6 and 4.2 Hz, 1H), and 0.37 (dd, J = 5.3 and 4.2 Hz, 1H). ^{13}C NMR (C_6D_6, 50 MHz): δ 170.37 (C), 159.43 (C), 137.67 (CH), 115.97 (CH_2), 94.82 (CH), 71.72 (CH_2), 53.72 (CH_3), 37.06 (CH_2), 35.97 (CH), 29.35, 21.67 (both CH_2), 20.60 (CH_3), 20.54 (C), and 15.75 (CH). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.12; H, 8.39.

(±)-(1α,4α,6α)-4-(2-Propenyl)-1-[[(dimethylethyl)dimethylsiloxy]methyl]-3-methoxybicyclo[4.1.0]hept-2-ene (32c).

Using the general procedure, carbene complex **12** (274 mg, 0.83 mmol) and TBS-protected propargyl alcohol[26] (213 mg, 1.25 mmol) in benzene (25 mL) were heated (80 °C) for 2 h. After the reaction mixture was passed through silica (2:1 hexanes: ethyl acetate), purification by MPLC (hexanes) provided **32c** as a colorless oil (80 mg, 31%). R_f = 0.50 in 19:1 hexanes: ethyl acetate. IR (neat, NaCl plates): 3074 (w), 1656 (m), 1255, 1199, 1163, 1140, 1102, and 1005 (all m-s) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 5.82 (dddd, J = 17.1, 9.8, 8.1, and 6.3 Hz, 1H), 5.08 (d, J = 17.1 Hz, 1H), 5.02 (d, J = 9.8 Hz, 1H), 4.83 (s, 1H), 3.55 (d, J = 9.8 Hz, 1H), 3.51 (d, J = 9.8 Hz, 1H), 3.24 (s, 3H), 2.54 (ddd, J = 13.9, 6.3, and 5.8 Hz, 1H), 2.37 (ddd, J = 13.9, 8.3, and 8.1 Hz, 1H), 2.09 (dddd, J = 8.3, 6.5, 5.8, and 5.8 Hz, 1H), 1.94 (ddd, J = 13.7, 6.5, and 6.5 Hz, 1H), 1.72 (ddd, J = 13.7, 5.8, and 4.2 Hz, 1H), 1.0 (obscured m, 1H), 0.98 (s, 9H), 0.88 (dd, J = 8.5 and 4.2 Hz, 1H), 0.43 (dd, J = 4.7 and 4.2 Hz, 1H), 0.07 (s, 3H), and −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.01 (C), 137.64 (CH), 115.62 (CH_2), 95.04 (CH), 69.31 (CH_2), 53.90 (CH_3), 38.98 (CH_2), 36.21 (CH), 29.49 (CH_2), 26.00 (CH_3), 22.48 (C), 21.02 (CH_2), 18.44 (C), 13.68 (CH), −5.16 (CH_3), and −5.22 (CH_3). Anal. Calcd for $C_{18}H_{32}O_2Si$: C, 70.07; H, 10.45. Found: C, 69.87; H, 10.37.

(±)-(1α,4α,6α)-4-(2-Propenyl)-1-[[(1,1-dimethylethyl)-thio]methyl]-3-methoxybicyclo[4.1.0]hept-2-ene (32d). Using the general procedure, carbene complex **12** (200 mg, 0.61 mmol) and *tert*-butyl propargyl sulfide[27] (97 mg, 0.76 mmol) in benzene (7 mL) were heated (80 °C) overnight. After the reaction mixture was passed through silica (6:1 hexanes:ethyl acetate), purification by MPLC (99:1 hexanes:ethyl acetate) provided **32d** as a light yellow oil (133 mg, 82%). R_f = 0.20 in hexanes and 0.57 in 9:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3063 (m), 1651, 1376, 1363, 1229, 1197, 1163, 1141 (all s), 1040, 1025, 995, and 910 (all m) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 5.82 (ddt, J = 17.1, 10.2, and 7.1 Hz, 1H), 5.09 (dddd, J = 17.1, 2.4, 1.5, and 1.5 Hz, 1H), 5.02 (obscured m, 1H), 5.01 (s, 1H), 3.23 (s, 3H, OCH_3), 2.59 (d, J = 11.3 Hz, 1H), 2.56 (d, J = 11.3 Hz, 1H), 2.57 (obscured m, 1H), 2.38 (m, 1H), 2.06 (m, $\sum J$ = 25 Hz, 1H), 1.90 (ddd, J = 13.5, 7.4, and 6.0 Hz, 1H), 1.75 (ddd, J = 13.5, 6.1, and 3.7 Hz, 1H), 1.24 (s, 9H), 1.01 (m, 1H), 0.80 (dd, J = 8.6 and 4.0 Hz, 1H), and 0.54 (app t, J = 4.7 Hz, 1H). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.79 (ddt, J = 17.1, 10.1, and 6.9 Hz, 1H), 5.04 (br d, J = 17.1 Hz, 1H), 4.98 (br d, J = 10.1 Hz, 1H), 4.84 (s, 1H), 3.48 (s, 3H), 2.58 (s, 2H), 2.42 (m, 1H), 2.22 (m, 1H), 1.98 (m, $\sum J$ = 16 Hz, 1H), 1.92−1.75 (m, 2H), 1.30 (s, 9H), 1.06 (m, 1H), 0.76 (dd, J = 8.5 and 4.2 Hz, 1H), and 0.47 (app t, J = 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.79 (C), 137.58 (CH), 115.79 (CH_2), 96.54 (CH), 54.08 (CH_3), 41.38 (C), 38.96, 36.53 (both CH_2), 35.21 (CH), 31.01 (CH_3), 29.14, 22.86 (both CH_2), 19.41 (C), and 18.43 (CH). Anal. Calcd for $C_{16}H_{26}OS$: C, 72.12; H, 9.84. Found: C, 72.11; H, 9.69.

(±)-(1-Methoxy-2-propylpent-4-enylidene)pentacarbonylchromium(0) (33). Using a procedure analogous to that for the preparation of **12**, (1-methoxypentylidene)pentacarbonylchromium(0)[23] (360 mg, 1.23 mmol), tetrabutylammonium bromide (77 mg, 0.24 mmol), CH_2Cl_2 (15 mL), KOH (2 mL of a 45% solution), and allyl bromide (175 μL, 2.07 mmol), followed by flash chromatography (30:1 hexanes:ethyl acetate) and collection of the orange band, afforded **33** as a bright orange oil (246 mg, 60%). R_f = 0.50 in 19:1 hexanes: ethyl acetate. IR (neat, NaCl plates): 3081 (w), 2962 (m), 2935, 2874 (both w), 2061 (s), 1919 (vs br), 1641 (w), 1274, 1256, 1217, 1167, and 1110 (all m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.73 (m, 1H), 5.00 (br d, J = ~13 Hz, 2H), 4.78 (s, 3H), 4.08 (m, 1H), 2.25 (ddd, J = 13.6, 6.8, and 6.8 Hz, 1H), 1.98 (ddd, J = 13.6, 6.8, and 6.8 Hz, 1H), 1.45 (m, 2H), 1.24 (m, 2H), and 0.93 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 368.37, 223.05, 216.31, 135.63, 116.93, 70.68, 67.75, 36.34, 34.07, 20.92, and 14.53. Anal. Calcd for $C_{14}H_{16}CrO_6$: C, 50.61; H, 4.85. Found: C, 50.64; H, 4.76.

(±)-(1α,4α,6α)-1-Butyl-3-methoxy-4-propylbicyclo[4.1.0]-hept-2-ene (32e). Using the general procedure, carbene complex **33** (200 mg, 0.60 mmol) and 1-hexyne (120 μL, 1.05 mmol) in benzene (15 mL) were heated (85 °C) for 2 h. After the reaction mixture was passed through silica (6:1 hexanes: ethyl acetate), purification by MPLC (hexanes) provided **32e** as a colorless oil (75 mg, 56%). R_f = 0.50 in 19:1 hexanes: ethyl acetate. IR (neat, NaCl plates): 3058 (m), 1652 (s), 1252, 1231, 1196 (all m), and 1162 (s) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 4.70 (s, 1H), 3.24 (s, 3H), 2.05 (m, 1H), 1.94−1.78 (m, 3H), 1.53−1.40 (m, 5H), 1.37−1.20 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H), 0.84 (m, 1H), 0.67 (dd, J = 8.4 and 3.8 Hz, 1H), and 0.45 (br app t, J = 3.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.04 (C), 96.78 (CH), 53.80 (CH_3), 39.49 (CH_2), 35.83 (CH), 35.01, 30.54, 29.63, 23.38, 23.00, 20.78 (all CH_2), 20.26 (C), 16.87 (CH), 14.36, and 14.17 (both CH_3). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.03; H, 11.77.

(±)-(1α,4α,6α)-1-Butyl-4-(2-propenyl)bicyclo[4.1.0]heptan-3-one (27a) and Equilibration to (±)-(1α,4β,6α)-1-Butyl-4-(2-propenyl)bicyclo[4.1.0]heptan-3-one (27b). Enol ether **32a** (231 mg, 1.05 mmol) was dissolved in MeOH (5 mL), and 1 N HCl (0.5 mL) was added. TLC analysis after 15 min indicated complete consumption of the starting material. The reaction was quenched with saturated aqueous $NaHCO_3$ and the mixture extracted with ether. The combined ether layers were washed (brine), dried ($MgSO_4$), concentrated, and purified by MPLC (30:1 hexanes:ethyl acetate) to yield **27a** as a colorless oil (179 mg, 83%). R_f = 0.30 in 19:1 hexanes:ethyl acetate and 0.50 in 9:1 hexanes:ethyl acetate. IR (neat NaCl plates): 3075 (w), 1708 (s), 1641 (w), and 912 (m) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz, assignments assisted by $^1H-^1H$ COSY at 300 MHz): δ 5.66 (dddd, J = 16.9, 10.2, 7.7, and 6.2 Hz, 1H, $CH{=}CH_EH_Z$), 4.97 (m, 2H, $CH{=}CH_EH_Z$), 2.51 (ddddd, J = 13.8, 6.4, 4.8, 1.4, and 1.4 Hz, 1H, $CH_aH_bCH{=}CH_2$), 2.39 (d, J = 17.5 Hz, 1H, $CH_\alpha H_\beta C{=}O$), 2.30 (dd, J = 17.5 and 1.4 Hz, 1H, $CH_\alpha H_\beta C{=}O$), 2.04 (ddd, J = 13.8, 7.9, and 7.7 Hz, 1H, $CH_aH_bCH{=}CH_2$), 1.82 (ddd, J = 12.8, 6.2, and 3.1 Hz, 1H, $CHCH_\alpha H_\beta CH$), 1.78 (dddd, J = 11.0, 7.9, 6.2, and 4.8 Hz, 1H, CH(allyl)C=O), 1.64 (ddd, J = 12.8, 11.0, and 3.1 Hz, 1H, $CHCH_\alpha H_\beta CH$), 1.15−0.91 (m, 6H, $(CH_2)_3$), 0.83 (t, J = 6.9 Hz, 3H, CH_2CH_3), 0.61 (dddd, J = 8.7, 5.3, 3.4, and 3.4 Hz, 1H, CHC_{quat}), 0.22 (app t, J = 3.4 Hz, 1H, $CH_{endo}H_{exo}$), and 0.15 (ddd, J = 8.7, 5.3, and 1.4 Hz, 1H, $CH_{endo}H_{exo}$). ^{13}C NMR (C_6D_6, 125 MHz assignments assisted by partial HETCOR at 75 MHz): δ 210.08 (C), 136.51 (CH), 116.61 (CH_2), 43.85 (CH_2), 43.50 (CH), 39.74, 34.93 (both CH_2), 28.75 (butyl CH_2), 27.53 (CH_2), 23.10 (butyl CH_2), 19.43 (C), 17.74 (CH), 14.27 (CH_3), and 14.04 (CH). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.39; H, 10.53.

Sodium (26 mg, 1 mmol) was dissolved in methanol (10 mL) under nitrogen, and **27a** (179 mg, 0.87 mmol) in methanol (1 mL) was added. After the mixture was stirred at room temperature for 1.75 h, the reaction was quenched with water and 1 N HCl (1 mL each) and the mixture extracted twice with ether. The combined ether layers were washed ($NaHCO_3$), dried ($MgSO_4$), and concentrated to provide an inseparable mixture of epimeric ketones **27a** and **27b** as a colorless oil (143 mg, 80%). Integration of ^1H NMR signals showed the ratio of **27a**:**27b** to be 1.3:1. The NMR spectral data below for **27b** are extracted from spectra of the mixture. ^1H NMR (C_6D_6, 300 MHz): δ 5.68 (m, 1H), 4.97 (m, 2H), 2.50 (m, 1H), 2.27 (d, J = 15.5 Hz, 1H), 2.19 (d, J = 15.5 Hz, 1H), 2.2−1.6 (m, 4H), 1.2−0.95 (m, 6H), 0.83 (br t, J = 6.6 Hz, 3H), 0.55 (m, 1H), 0.44 (dd, J = 8.0 and 4.7 Hz, 1H), and −0.04 (dd, J = 4.7 and 4.7 Hz, 1H). ^{13}C NMR (C_6D_6, 75 MHz): δ 212.04 (C), 136.73 (CH), 116.33 (CH_2), 46.60 (CH), 45.13, 39.99, 34.55, 32.67, 29.03 (all CH_2), 23.47 (C), 23.08, 22.08 (both CH_2), 17.46 (CH), and 14.25 (CH_3).

(±)-(1α,3α,4α,6α)-1-Butyl-4-(2-propenyl)bicyclo[4.1.0]-heptan-3-ol (34a) and (±)-(1α,3β,4β,6α)-1-Butyl-4-(2-propenyl)bicyclo[4.1.0]heptan-3-ol (34b). A mixture of ketones **27a** and **27b** (135 mg, 0.655 mmol) was added as a solution in THF (3 mL) to K-Selectride (1.0 M in THF, 1.3 mmol, 2 equiv) at −78 °C. After 2 h, the mixture was allowed to warm to room temperature. Water (1 mL), ethanol (2 mL), 6 N KOH (1 mL), and 30% H_2O_2 (2 mL) were added sequentially. After 15 min, the aqueous layer was saturated with solid K_2CO_3 and extracted with ether (3×). The combined ether layers were washed (brine), dried ($MgSO_4$), and concentrated. MPLC (9:1 hexanes:ethyl acetate + 1% 2-propanol) gave, in order of elution, **34b** (63 mg, 46%), **34a** (38 mg, 28%), and 10 mg of an

alcohol with a *trans* relationship between the hydroxyl and allyl groups that was not characterized (**34c**). For **34b**, R_f = 0.30 in 9:1 hexanes:ethyl acetate. IR (neat, NaCl plates, mixture of alcohols): 3415 (br s), 3074, 1640, 1275, 1196 (all m), 1028, 993, 912 (all s), and 859 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz assignments assisted by $^1H-^1H$ COSY): δ 5.80 (dddd, J = 17.1, 10.4, 7.3, and 7.3 Hz, 1H, C*H*=CH_EH_Z), 5.03 (dddd, J = 17.1, 1.5, 1.5, and 1.5 Hz, 1H, CH=C*H*$_E$H$_Z$), 5.00 (m, 1H, CH=CH_E*H*$_Z$), 3.89 (br m, ΣJ's = 10.7 Hz, 1H, C*H*OH), 2.04 (dd, J = 14.7 and 2.7 Hz, 1H, C*H*$_\alpha$H$_\beta$CHOH), 2.05–1.87 (m, 4H, C*H*CHOH, CH_2CH=CH_2, and CHC*H*$_a$H$_b$CH), 1.74 (dd, J = 14.7 and 4.5 Hz, 1H, CH$_\alpha$*H*$_\beta$CHOH), 1.39 (m, 1H, CHCH$_a$*H*$_b$CH), 1.39–1.17 (m, 5H, $CH_3(CH_2)_2CH_aH_b$), 1.05 (m, 1H, $CH_3(CH_2)_2CH_a$*H*$_b$), 0.87 (t, J = 7.2 Hz, 3H, CH_2CH_3), 0.69 (m, 1H, C*H*C$_{quat}$), 0.59 (app t, J = 3.5 Hz, 1H, C*H*$_{endo}$H$_{exo}$), and 0.40 (dd, J = 8.8 and 3.5 Hz, 1H, CH$_{endo}$*H*$_{exo}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.24 (CH), 115.60 (CH_2), 68.65 (CH), 41.85 (CH_2), 38.31 (CH), 37.43, 35.70, 28.81, 25.58, 22.93, 20.24 (all CH_2), 17.86 (C), 17.12 (CH), and 14.16 (CH_3). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.57; H, 11.36. For **34a**, R_f = 0.22 in 9:1 hexanes:ethyl acetate. ^1H NMR ($CDCl_3$, 500 MHz, assignments assisted by $^1H-^1H$ COSY): δ 5.78 (dddd, J = 17.1, 10.1, 7.3, and 7.0 Hz, 1H, C*H*=CH_EH_Z), 5.04 (dddd, J = 17.1, 3.3, 1.5, and 1.5 Hz, 1H, CH=C*H*$_E$H$_Z$), 5.00 (dddd, J = 10.1, 3.3, 1.2, and 1.2 Hz, 1H, CH=CH_E*H*$_Z$), 3.63 (dddd, J = 5.4, 5.2, 4.3, and 1.9 Hz, 1H, C*H*OH), 2.17 (ddddd, J = 14.0, 7.3, 7.0, 1.5, and 1.2 Hz, 1H, C*H*$_a$H$_b$-CH=CH_2), 1.98 (ddddd, J = 14.0, 7.3, 7.0, 1.5, and 1.2 Hz, 1H, CH_a*H*$_b$CH=CH_2), 1.87 (dd, J = 14.8 and 4.3 Hz, 1H, C*H*$_\alpha$H$_\beta$-CHOH), 1.76 (dd, J = 14.8 and 4.2 Hz, 1H, CH_α*H*$_\beta$CHOH), 1.76 (m (obscured), 1H, CHC*H*$_a$H$_b$CH), 1.66 (ddd, J = 13.7, 5.2, and 1.2 Hz, 1H, CHC*H*$_a$H$_b$CH), 1.41–1.10 (m, 7H, $CH_3(CH_2)_3$ and C*H*CHOH), 0.89 (t, J = 7.3 Hz, 3H, CH_2CH_3), 0.76 (dddd, J = 9.2, 6.7, 4.9, and 1.2 Hz, 1H, C*H*C$_{quat}$), 0.40 (dd, J = 9.2 and 4.3 Hz, 1H, CH$_{endo}$*H*$_{exo}$), and 0.05 (dd, J = 4.9 and 4.3 Hz, 1H, C*H*$_{endo}$H$_{exo}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.40 (CH), 115.88 (CH_2), 67.72 (CH), 41.73, 36.70, 35.91 (all CH_2), 35.50 (CH), 28.97, 24.52, 22.89, 17.85 (all CH_2), 17.65 (CH), 17.07 (C), and 14.13 (CH_3). HRMS Calcd for $C_{14}H_{24}O$ $(M + H)^+$ 209.1905, found 209.1902.

Acetic Acid (±)-(1α,3α,4α,6α)-1-Butyl-4-(2-propenyl)-bicyclo[4.1.0]hept-3-yl Ester (35a). Alcohol **34a** (33 mg, 0.159 mmol) was dissolved in CH_2Cl_2 (1.5 mL), and triethylamine (75 μL, 0.54 mmol, 3.3 equiv) and acetic anhydride (30 μL, 0.317 mmol, 2 equiv) were added sequentially. After 2.5 h, TLC analysis indicated little reaction and a few milligrams of DMAP were added. After an additional 2 h, TLC analysis indicated complete consumption of the starting material. Saturated NH_4Cl was added, and the reaction mixture was extracted with ether (×2). The ether layers were washed (saturated NH_4Cl and brine) and dried ($MgSO_4$). Removal of the solvent gave acetate **35a** of sufficient purity to be used in subsequent reactions (33 mg, 85%). R_f = 0.50 in 9:1 hexanes: ethyl acetate. IR (neat, NaCl plates): 3062, 3055 (both m), 1736 (s), 1641 (m), 1242, 1190, 1019 (all m-s), 965, 913, and 837 (all m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.71 (ddt, J = 15.9, 11.1, and 7.2 Hz, 1H), 4.96 (d, J = 11.1 Hz, 1H), 4.94 (d, J = 15.9 Hz, 1H), 4.74 (br s, 1H), 2.02 (s, 3H), 2.0–1.6 (m, 6H), 1.24 (m, 6H), 1.05 (m, 1H), 0.85 (br t, J = 6.2 Hz, 3H), 0.73 (app dt, J = 9.1 and 5.6 Hz, 1H), 0.38 (dd, J = 9.1 and 4.3 Hz, 1H), and 0.05 (dd, J = 4.3 and 4.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.85 (C), 136.60 (CH), 116.17 (CH_2), 70.49 (CH), 41.44, 36.13 (both CH_2), 34.00 (CH), 33.35, 29.08, 25.12, 22.81 (all CH_2), 21.27 (CH_3), 18.05 (CH), 17.95 (CH_2), 16.98 (C), and 14.20 (CH_3). HRMS Calcd for $C_{16}H_{26}O_2$ $(M + H)^+$ 251.2011, found 251.2015.

Acetic Acid (±)-(1α,3β,4β,6α)-1-Butyl-4-(2-propenyl)-bicyclo[4.1.0]hept-3-yl Ester (35b). In a procedure analogous to that for **34a**, alcohol **34b** (48 mg, 0.231 mmol), CH_2Cl_2 (1.5 mL), triethylamine (100 μL, 0.72 mmol, 3.1 equiv), acetic anhydride (50 μL, 0.53 mmol, 2.3 equiv), and a few milligrams of DMAP gave acetate **35b** as a colorless oil (50 mg, 88%) of sufficient purity to be used in subsequent reactions. R_f = 0.50 in 9:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3073 (w), 2996, 2956 (both m), 2925 (s), 2860 (m), 1738 (s), 1641 (w), 1457, 1438, 1373 (all m), 1242 (s), 1125, 1024, 996, 947, and 913 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.70 (ddt, J = 17.5, 10.6, and 7.1 Hz, 1H), 4.93 (m, 3H), 2.11 (dd, J = 15.3 and 2.0 Hz, 1H), 2.05–1.77 (m, 3H), 1.99 (s, 3H), 1.70 (dd, J = 15.3 and 4.6 Hz, 1H), 1.40 (m, 1H), 1.30 (m, 1H), 1.25 (m, 5H), 1.05 (m, 1H), 0.84 (t, J = 6.9 Hz, 3H), 0.70 (m, 1H), and 0.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.41 (C), 136.44 (CH), 116.11 (CH_2), 71.25 (CH), 41.56, 37.12 (both CH_2), 36.99 (CH), 32.51, 28.73, 26.24, 22.89 (all CH_2), 21.26 (CH_3), 19.64 (CH_2), 17.70 (C), 16.81 (CH), and 14.11 (CH_3). Anal. Calcd for $C_{16}H_{26}O_2$: C, 80.71; H, 11.61. Found: C, 80.57; H, 11.36.

Acetic Acid (±)-(1α,3α,4α,6α)-1-Butyl-4-(2-oxoethyl)-bicyclo[4.1.0]hept-3-yl Ester (36a). Alkene acetate **35a** (25 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (1 mL), and methanol (1 mL) and a few crystals of $NaHCO_3$ were added to the flask. The solution was cooled in a dry ice/acetone bath, and a stream of ozone was bubbled through the solution for 5 min (the solution took on a blue color after 1 min). After the solution was purged with nitrogen for 10 min, dimethyl sulfide (0.1 mL) was added and the solution was allowed to warm to room temperature. After solvent removal, the residue was taken up in ether and washed (water (2×) and brine), dried ($MgSO_4$), and concentrated to yield aldehyde **36a** as a colorless oil (21 mg, 84%) of sufficient purity to be used in subsequent reactions. R_f = 0.13 in 9:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3054 (m), 2724 (w), 1732 (s), 1374 (m), 1242 (s), and 1019 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz assignments were assisted by $^1H-^1H$ COSY): δ 9.74 (t, J = 1.5 Hz, 1H, C*H*O), 4.75 (app td, J = 4.4 and 2.0 Hz, 1H, C*H*OAc), 2.49 (ddd, J = 17.6, 6.4, and 1.5 Hz, 1H, C*H*$_a$H$_b$CHO), 2.31 (ddd, J = 17.6, 6.8, and 1.5 Hz, 1H, CH$_a$*H*$_b$CHO), 2.05 (s, 3H, CH_3C=O), 2.1–1.7 (m, 5H), 1.26 (m, 5H), 1.10 (m, 1H), 0.87 (br t, J = 6.8 Hz, 3H, CH_2CH_3), 0.76 (m, 1H, C*H*C$_{quat}$), 0.45 (dd, J = 8.8 and 4.9 Hz, 1H, CH$_{endo}$*H*$_{exo}$), and 0.15 (app t, J = 4.9 Hz, 1H, C*H*$_{endo}$H$_{exo}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.48 (CH), 170.74 (C), 70.72 (CH), 45.69, 41.28, 32.50 (all CH_2), 28.96 (CH), 28.91, 25.78 (both CH_2), 22.77 (CH_3), 21.24, 17.97 (both CH_2), 17.32 (C), 17.03 (CH), and 14.18 (CH_3). LRMS (EI): m/z (relative intensity) 223 (M^+ − CHO, <1), 210 (M^+ − C_2H_2O, 3), 192 (M^+ − HOAc, 13), and 92 (100).

Acetic Acid (±)-(1α,3β,4β,6α)-1-butyl-4-(2-oxoethyl)-bicyclo[4.1.0]hept-3-yl Ester (36b). In a procedure identical to that for **36a,** alkene acetate **35b** (50 mg, 0.2 mmol) gave aldehyde **36b** as a colorless oil (47 mg, 93%) of sufficient purity to be used in subsequent reactions. R_f = 0.13 in 9:1 hexanes: ethyl acetate and 0.3 in 3:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3069 (w), 2723 (w), 1736 (s), 1242 (s), 1213 (m), 1130, 1108 (both w), 1047, and 1020 (both m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz assignments were assisted by $^1H-^1H$ COSY): δ 9.74 (t, J = 1.4 Hz, 1H, C*H*O), 4.98 (br m, ΣJ's = 9 Hz, 1H, C*H*OAc), 2.40 (ddd, J = 17.3, 6.0, and 1.4 Hz, 1H, C*H*$_a$H$_b$CHO), 2.20 (ddd, J = 17.3, 6.8, and 1.4 Hz, 1H, CH$_a$*H*$_b$-CHO), 2.12–1.98 (m, 3H, C*H*CHOAc, C*H*$_\alpha$H$_\beta$CHOAc, and CHC*H*$_a$H$_b$CH), 2.03 (s, 3H, CH_3C=O), 1.84 (dd, J = 15.3 and 4.6 Hz, 1H, CH$_\alpha$*H*$_\beta$CHOAc), 1.38 (m, 1H, CHCH$_a$*H*$_b$CH), 1.32–1.20 (m, 5H, $CH_3(CH_2)_2CH_aH_b$), 1.05 (m, 1H, $CH_3CH_2CH_2$-CH$_a$*H*$_b$), 0.87 (t, J = 6.9 Hz, 3H, CH_2CH_3), 0.77 (m, 1H, C*H*C$_{quat}$), and 0.42 (m, 2H, C_{quat}C*H*$_{endo}$H$_{exo}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.24 (CH), 170.46 (C), 71.64 (CH), 46.99, 41.45, 32.23 (all CH_2), 31.38 (CH), 28.70, 26.25, 22.88 (all CH_2), 21.25 (CH_3), 19.70 (CH_2), 17.46 (C), 16.49 (CH), and 14.12 (CH_3).

(±)-(3aβ,4aα,5aα,6aβ)-5a-Butylhexahydrocyclopropa-[f]benzofuran-2(3*H*)-one (37a). Aldehyde acetate **36a** (21 mg, 0.083 mmol) in absolute ethanol (1.5 mL) was treated with $AgNO_3$ (48 mg, 0.28 mmol, 3 equiv) as an aqueous solution (0.5 mL). NaOH (0.75 mL of a 1 N solution) was added dropwise, and a brown-black precipitate formed immediately. After stirring for 2 h, the mixture was filtered through a Celite plug, and the filter cake was rinsed with water (5 mL). The solution was washed with ether (2 × 10 mL), and the ether layers were discarded. The aqueous layer was acidified with 10% HCl and allowed to stand for 1 h. Extraction with CH_2Cl_2 (3 × 8 mL), drying of the organic layers ($MgSO_4$), and solvent removal gave 20 mg of a mixture of acetate–acid and lactone **37a**. The oil was dissolved in methanol, and NaOH (1 mL of a 1 N solution) was added. After 4 h, the mixture was acidified, extracted with ether, and concentrated. MPLC

of the residue (3:1 hexanes:ethyl acetate) gave pure **37a** as a viscous oil (7 mg, 44%), which was a solid at −20 °C but remelted as it was warmed to room temperature. R_f = 0.4 in 2:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3061 (w), 1773 (s), 1364, 1255 (both m-w), 1189, 1022 (both s), 969, and 949 (both m) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz assignments were assisted by $^1H-^1H$ COSY and difference NOE experiments): δ 4.69 (app dt, J = 8.2 and 5.8 Hz, 1H, C*H*OC=O), 2.75 (dd, J = 18.0 and 10.4 Hz, 1H, CH_aH$_b$C=O), 2.57 (ddddd, J = 10.4, 8.2, 7.6, 5.7, and 5.2 Hz, 1H, C*H*CH$_2$C=O), 2.35 (dd, J = 18.0 and 5.2 Hz, 1H, CH$_a$*H*$_b$C=O), 2.08 (dd, J = 15.0 and 5.8 Hz, 1H, CH_αH$_\beta$CHOC=O), 1.90 (ddd, J = 14.4, 7.6, and 4.6 Hz, 1H, CH_αH$_\beta$CHCH$_2$C=O), 1.76 (dd, J = 15.0 and 5.8 Hz, 1H, CH$_\alpha$*H*$_\beta$CHOC=O), 1.58 (ddd, J = 14.4, 5.7, and 5.7 Hz, 1H, CH$_\alpha$*H*$_\beta$CHCH$_2$C=O), 1.49 (ddd, J = 13.4, 10.1, and 4.9 Hz, 1H, H$_3$C(CH$_2$)$_2$C*H*$_a$H$_b$), 1.36 (m, 1H, H$_3$CCH$_2$C*H*$_a$H$_b$), 1.27 (m, 3H, CH$_3$C*H*$_2$CCH$_a$*H*$_b$), 1.01 (ddd, J = 13.4, 11.0, and 4.6 Hz, 1H, H$_3$CCH$_2$CH$_2$CH$_a$*H*$_b$), 0.88 (t, J = 6.7 Hz, 3H, CH$_2$C*H*$_3$), 0.78 (dddd, J = 8.2, 5.7, 4.8, and 4.6 Hz, 1H, C*H*C$_{quat}$), 0.41 (dd, J = 8.2 and 4.8 Hz, 1H, CH$_{endo}$*H*$_{exo}$), and 0.20 (dd, J = 4.8 and 4.8 Hz, 1H, C*H*$_{endo}$H$_{exo}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.81, 79.15, 39.16, 34.77, 30.59, 30.25, 28.75, 27.47, 22.77, 16.25, 15.98, 15.28, and 14.11. HRMS Calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1452.

(±)-(3aα,4aα,5aα,6aα)-5a-Butylhexahydrocyclopropa[f]benzofuran-2(3*H*)-one (37b). Aldehyde acetate **36b** (45 mg, 0.179 mmol) in absolute ethanol (1.5 mL) was treated with $AgNO_3$ (95 mg, 0.55 mmol) as an aqueous solution (0.5 mL). NaOH (1 mL of a 1 N solution) was added dropwise, and a brown-black precipitate formed immediately. After stirring for 16 h, the mixture was filtered through Celite, and the filter cake was rinsed with water (5 mL). The solution was washed with ether (2 × 10 mL), and the ether layers were discarded. The aqueous layer was acidified (10% HCl) and left to stir for 1 h. Extraction with CH_2Cl_2 (4 × 8 mL), washing with water and drying of the organic layers with $MgSO_4$, and solvent removal gave **37b** as a viscous oil (29 mg, 80%), which was pure by GC/MS analysis. An analytical sample was prepared by MPLC (3:1 hexanes:ethyl acetate), which was a solid at −20 °C but remelted as it was warmed to room temperature. R_f = 0.55 in 2:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3058 (w), 1774 (s), 1352 (m), 1182, 1030 (s), and 978 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz assignments were assisted by $^1H-^1H$ COSY and difference NOE experiments): δ 4.78 (ddd, J = 10.4, 8.2, and 7.0 Hz, 1H, C*H*OC=O), 2.78 (dd, J = 18.6 and 10.4 Hz, 1H, CH_aH$_b$C=O), 2.57 (ddddd, J = 13.1, 10.4, 8.2, 5.5, and 3.7 Hz, 1H, C*H*CH$_2$C=O), 2.44 (dd, J = 14.4 and 7.0 Hz, 1H, CH_αH$_\beta$CHOC=O), 2.19 (m, 1H, CH_αH$_\beta$CHCH$_2$C=O), 2.13 (dd, J = 18.6 and 3.7 Hz, 1H, CH$_a$*H*$_b$C=O), 1.27 (m, 5H, CH$_3$(C*H*$_2$)$_2$C*H*$_a$H$_b$), 1.13 (m, 1H, CH$_3$(CH$_2$)$_2$CH$_a$*H*$_b$), 1.04 (dd, J = 14.4 and 10.4 Hz, 1H, CH$_\alpha$*H*$_\beta$CHOC=O), 0.89 (t, J = 7.0 Hz, 3H, CH$_2$C*H*$_3$), 0.80 (m, 1H, CH$_\alpha$*H*$_\beta$CHCH$_2$C=O), 0.66 (m, 2H, C*H*C$_{quat}$ and CH$_{endo}$*H*$_{exo}$), and 0.21 (m, 1H, C*H*$_{endo}$H$_{exo}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.00 (C), 78.90 (CH), 37.97, 34.32 (both CH$_2$), 33.25 (CH), 33.12, 30.38, 29.41, 22.85, 22.76 (all CH$_2$), 17.19 (2 carbons, C and CH), and 14.05 (CH$_3$). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.81; H, 9.39.

(±)-6-Methyl-1,6-heptadien-3-ol (39). Magnesium turnings (9.44 g, 0.388 mol) and a magnetic stir bar were placed in a 1 L creased three-necked flask equipped with an addition funnel and a reflux condenser and flame-dried under N_2. Enough dry ether was added to cover the turnings, and a few crystals of I_2 were added. The mixture was stirred until colorless and then initiated with homoallylic bromide **38** (2.0 g in 2 mL of ether). Homoallylic bromide **38** (30.7 g, total bromide 0.215 mol) was added as a solution in ether (100 mL) at a rate sufficient to maintain reflux. The resulting solution was diluted with additional ether (150 mL) and cooled to −78 °C, at which time the solution became cloudy. Acrolein (15.0 mL, 0.224 mol, 1.04 equiv) was added dropwise, and the reaction mixture was allowed to warm to room temperature. A 10% HCl solution (125 mL) was added slowly to the clarified reaction mixture, the layers were separated, and the aqueous layer was extracted with ether. The combined ether layers were washed (water, saturated $NaHCO_3$, and brine) and dried over $MgSO_4$. Solvent removal via rotary evaporation gave crude alcohol **39** as a slightly yellow liquid (23.7 g, 88%). Analytically pure **39** was prepared by flash chromatography (5:1 pentane:ether). R_f = 0.25 in 5:1 pentane:ether. IR (neat, NaCl plates): 3355 (br s), 3077, 1648, 1121, 1064, and 994 (all s) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 5.88 (ddd, J = 16.8, 10.4, and 6.1 Hz, 1H), 5.23 (ddd, J = 16.8, 1.5, 1.5 Hz, 1H), 5.12 (ddd, J = 10.4, 1.5, and 1.5 Hz, 1H), 4.73 (br s, 1H), 4.71 (br s, 1H), 4.12 (app pentet, J = 6.1 Hz, 1H), 2.10 (m, 2H), 1.74 (s, 3H), and 1.68 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 145.42 (C), 141.03 (CH), 114.61 (CH$_2$), 110.04 (CH$_2$), 72.77 (CH), 34.79 (CH$_2$), 33.45 (CH$_2$), and 22.39 (CH$_3$). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.36; H, 11.37. A byproduct (<10% of product mass) from this reaction was 2,7-dimethyl-1,7-octadiene, whose characterization data is as follows. R_f = 0.95 in 5:1 pentane:ether. IR (neat, NaCl plates): 3074, 1649, 1450, 1374, and 886 (all s) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 4.69 (br s, 2H), 4.67 (br s, 2H), 2.02 (br t, J = 7.5 Hz, 4H), 1.71 (s, 6H), and 1.43 (app pentet, J = 7.5 Hz, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 146.00, 109.70, 37.69, 27.26, and 22.32. Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.99; H, 12.86.

(*E*)-7-Bromo-2-methylhepta-1,5-diene (40). Allylic alcohol **39** (635 mg, 5.03 mmol) was charged to a 100 mL round-bottomed flask under argon. Dry ether (50 mL) was introduced via cannula, and the solution was cooled with a dry ice/acetone bath. n-BuLi (2.45 mL (2.2 M in hexanes), 5.39 mmol, 1.06 equiv) was added dropwise. After the mixture was stirred 25 min, thionyl bromide (0.39 mL, 5.03 mmol, 1.0 equiv) was added dropwise, and the yellow solution was allowed to come to room temperature overnight. After the reaction mixture was quenched with "wet" ether (25 mL), the solvent was removed by distillation at atmospheric pressure and the residue was passed through silica with pentane eluent. Rotary evaporation yielded crude **40** (874 mg, 92%) that was reasonably pure by ^1H NMR. MPLC (hexanes) gave an analytical sample as a colorless liquid. Alternatively, the bromide could be distilled (bp 54−58 °C at 2.5 mmHg). R_f = 0.28 in hexanes. IR (neat, NaCl plates): 3074, 3032 (w), 1661, 1649, 1204, 964, and 889 (all s) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 5.75 (m, 2H), 4.73 (br s, 1H), 4.68 (br s, 1H), 3.95 (d, J = 7.4 Hz, 2H), 2.22 (dt, J = 8.4 and 6.1 Hz, 2H), 2.09 (t, J = 8.4 Hz, 2H), and 1.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.72 (C), 135.83, 126.53 (both CH), 110.34, 36.80, 33.36, 30.10 (all CH$_2$), and 22.38 (CH$_3$). Anal. Calcd for $C_8H_{13}Br$: C, 50.81; H, 6.93. Found: C, 50.52; H, 7.06.

[(*E*)-1-Methoxy-2-((*E*)-6-methyl-2,6-heptadienyl)-8-methyl-4,8-nonadienylidene]pentacarbonylchromium(0) (8). (1-Methoxyethylidene)pentacarbonylchromium (0)[23] (**10**) (513 mg, 2.05 mmol) and Bu_4NBr (134 mg, 0.416 mmol, 20 mol %) in methylene chloride (30 mL) were treated with N_2-purged 45% aqueous KOH solution (5 mL). Allylic bromide **40** (1.5 g, 7.9 mmol, 3.1 equiv) was introduced, and the reaction mixture was stirred vigorously at room temperature. The solution gradually became a dark orange-red. After 1.5 h, TLC indicated consumption of the starting carbene complex, and the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. Concentration of the solution on a rotary evaporator followed by flash chromatography (hexanes until color reached bottom of column, then 30:1 hexanes:ethyl acetate) afforded carbene complex **8** as a bright red-orange oil (576 mg, 60%). The carbene complex was always contaminated by a small amount of residual allylic bromide, precluding elemental analysis. R_f = 0.50 in 19:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3075, 2061 (s), 1930 (vs broad), 1649, 1274, 1242, 1205, 967, 888, 695, and 667 (all m-s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.42−5.29 (m, 4H), 4.79 (s, 3H), 4.69 (br s, 2H), 4.65 (br s, 2H), 4.09 (app pentet, J = 6.8 Hz, 1H), 2.22−1.85 (m, 12H), and 1.69 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 368.90 (C), 223.11 (C), 216.28 (C), 145.26 (C), 132.60, 126.98 (both CH), 110.01 (CH$_2$), 71.11 (CH$_3$), 67.70 (CH), 37.50, 34.92, 30.60 (all CH$_2$), and 22.33 (CH$_3$).

(±)-(1α,4α,6α,7α)-1-Butyl-7-(3-methyl-3-butenyl)-4-((*E*)-6-methyl-2,6-heptadienyl)-3-methoxybicyclo[4.1.0]hept-2-ene (41a). Using the general procedure, carbene complex

8 (203 mg, 0.435 mmol) and 1-hexyne (250 μL, 2.17 mmol) in benzene (10 mL) were heated (85 °C) overnight. After the reaction mixture was passed through silica (3:1 hexanes:ethyl acetate), purification by MPLC (50:1 hexanes:ethyl acetate) provided **41a** as a colorless oil (113 mg, 73%). R_f = 0.25 in 50:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3073 (m), 1649 (s), 1200, 1168, and 968 (all m) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz assignments assisted by $^1H-^1H$ COSY at 300 MHz): δ 5.51 (m, 2H, C*H*=C*H*), 4.84 (s, 1H, C=CH_aH_b), 4.83 (s, 1H, C=CH_aH_b), 4.79 (s, 1H, C=CH_cH_d), 4.78 (br s, 2H, C=CH_cH_d and C*H*=C(OMe)), 3.25 (s, 3H, OCH_3), 2.58 (m, 1H, CH_aH_bCH=CH), 2.34 (m, 1H, CH$_a$$H_b$CH=CH), 2.20–2.09 (m, 3H, CHCH$_\alpha$H$_\beta$C*H* and CH=CHCH_2CH$_2$), 2.11 (t, J = 7.3 Hz, 2H, CH_2CH$_2$CH$_{endo}$), 2.04 (t, J = 6.9 Hz, 2H, CH=CHCH$_2$CH_2), 1.97 (ddd, J = 13.7, 6.5, and 3.3 Hz, 1H, CHCH_aH$_b$CH), 1.92 (ddd, J = 13.7, 7.9, and 5.5 Hz, 1H, CHCH$_a$$H_b$CH), 1.67 (s, 3H, C$H_3$C=CH$_2$), 1.62 (s, 3H, C$H_3$C=CH$_2$), 1.7–1.4 (m, 4H, C$H_aH_bCH_{endo}$, C$H_aH_bC_{quat}$, and CH$_3CH_2CH_2$), 1.4–1.3 (m, 4H, CH$_a$$H_bCH_{endo}$, CH$_a$$H_bC_{quat}$, and CH$_3CH_2CH_2$), 0.96 (t, J = 7.3 Hz, 3H, CH_3CH$_2$), 0.70 (dt, J = 7.7 and 5.5 Hz, 1H, CHCH_{endo}), and 0.55 (br dt, app q, J = 5.5 Hz, 1H, CH$_\alpha$H$_\beta$C*H*CH$_{endo}$). ^{13}C NMR (C_6D_6, 75 MHz): δ 157.40 (C), 145.86, 145.36 (both C), 131.48, 129.53 (both CH), 110.41, 110.33 (both CH_2), 99.93 (CH), 53.64 (CH_3), 38.52, 38.20, 35.76 (all CH_2), 35.71, 33.98 (both CH), 33.93, 31.25, 30.58, 29.29, 28.25 (all CH_2), 24.50 (C), 24.47 (CH), 23.52 (CH_2), 22.55, 22.48, and 14.47 (all CH_3). Anal. Calcd for $C_{25}H_{40}O$: C, 84.21; H, 11.31. Found: C, 84.32; H, 11.14.

Acetic Acid [(±)-(1α,4α,6α,7α)-7-(3-Methyl-3-butenyl)-4-(*E*-6-methyl-2,6-heptadienyl)-3-methoxybicyclo[4.1.0]-hept-2-en-1-yl]methyl Ester (41b). Using the general procedure, carbene complex **8** (139 mg, 0.298 mmol) and propargyl acetate[3c] (103 mg, 1.05 mmol) in benzene (7 mL) were heated (85 °C) overnight. After the reaction mixture was passed through silica (3:1 hexanes:ethyl acetate), purification by MPLC (30:1 hexanes:ethyl acetate) provided **41b** as a colorless oil (38 mg, 34%). R_f = 0.19 in 30:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3072 (w), 1740, 1650, 1245 (all s), 1164, 1026, and 968 (all m) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz assignments assisted by $^1H-^1H$ COSY at 300 MHz): δ 5.47 (m, 2H, C*H*=C*H*), 4.94 (s, 1H, C*H*=C(OMe)), 4.80 (br s, 4H, C=CH_2 × 2), 4.25 (d, J = 12 Hz, 1H, CH_AH$_B$OAc), 4.20 (d, J = 12 Hz, 1H, CH$_A$$H_B$OAc), 3.22 (s, 3H, OC$H_3$), 2.51 (dt, J = 12.8 and 4.9 Hz, 1H, CHCH_aH$_b$CH=CH), 2.27 (m, 1H, CHCH$_a$$H_b$-CH=CH), 2.14 (m, 2H, CH=CHCH_2CH$_2$), 2.09 (m, 1H, CHCH$_\alpha$H$_\beta$C*H*), 2.05 (t, J = 8.2 Hz, 2H, CH_2CH$_2$CH$_{endo}$), 2.03 (t, J = 7.4 Hz, 2H, CH=CHCH$_2$CH_2), 1.92 (ddd, J = 13.5, 6.5, and 6.5 Hz, 1H, CHCH_aH$_b$CH), 1.79 (m, 1H, CHCH$_a$$H_b$CH), 1.77 (s, 3H, C$H_3CO_2$), 1.63 (s, 3H, C$H_3$C=CH$_2$), 1.62 (s, 3H, C$H_3$C=CH$_2$), 1.55 (app dq, J = 14.6 and 6.9 Hz, 1H, CH_aH$_b$-CH$_{endo}$), 1.35 (app dq, J = 14.6 and 7.3 Hz, 1H, CH$_a$$H_bCH_{endo}$), 0.76 (app br dt ~q, J = 5.8 Hz, 1H, CHCH_{endo}), and 0.67 (br app dt, ~q, J = 5.8 Hz, 1H, C*H*CH$_{endo}$). ^{13}C NMR (C_6D_6, 75 MHz): δ 170.35, 159.29, 145.45, 145.31 (all C), 131.66, 129.29 (both CH), 110.60, 110.49 (both CH_2), 96.82 (CH), 68.72 (CH_2), 53.72 (CH_3), 38.27, 38.15 (both CH_2), 36.39 (CH), 35.92 (CH_2), 35.23 (CH), 31.22, 29.24, 28.13 (all CH_2), 24.43 (C), 22.58, 22.44, 22.41 (CH and 2 CH_3), and 20.67 (CH_3). Anal. Calcd for $C_{24}H_{36}O_3$: C, 77.38; H, 9.74. Found: C, 77.51; H, 9.70.

(±)-(1α,4α,6α,7α)-7-(3-Methyl-3-butenyl)-1-[[(1,1-dimethylethyl)thio]methyl]-4-((*E*)-6-methyl-2,6-heptadienyl)-3-methoxybicyclo[4.1.0]hept-2-ene (41c). Using the general procedure, carbene complex **8** (192 mg, 0.411 mmol) and *tert*-butyl propargyl sulfide[27] (259 mg, 2.01 mmol) in benzene (10 mL) were heated (85 °C) overnight. After the reaction mixture was passed through silica (3:1 hexanes:ethyl acetate), purification by MPLC (50:1 hexanes:ethyl acetate) provided **41c** as a colorless oil (97 mg, 59%). R_f = 0.35 in 30:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3072 (m), 1652, 1374, 1363, 1199, 1162, 968, and 886 (all s) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz assignments assisted by $^1H-^1H$ COSY at 300 MHz): δ 5.51 (m, 2H, C*H*=C*H*), 5.20 (s, 1H, C*H*=C(OMe)), 4.85 (s, 1H, C=CH_aH_b), 4.82 (s, 1H, C=CH$_a$$H_b$), 4.79 (s, 1H, C=C$H_cH_d$), 4.78 (s, 1H, C=CH$_c$$H_d$), 3.27 (s, 3H, OC$H_3$), 2.80 (d, J = 11 Hz, 1H, CH_AH$_B$S), 2.64 (d, J = 11 Hz, 1H, CH$_A$$H_B$S), 2.58 (m, 1H, CHC$H_aH_b$CH=CH), 2.38 (m, 1H, CHCH$_a$$H_b$CH=CH), 2.20 (obscured, 1H, CH$_\alpha$H$_\beta$C*H*CH$_2$CH=CH), 2.17–2.10 (m, 4H, CH=CHCH_2CH$_2$ and CH_2CH$_2$CH$_{endo}$), 2.03 (br t, J = 7.1 Hz, 2H, CH=CHCH$_2$CH_2), 1.98 (m, 1H, CHCH_aH$_b$CH), 1.90 (ddd, J = 13.7, 6.3, and 3.5 Hz, 1H, CHCH$_a$$H_b$CH), 1.84 (m, 1H, C$H_aH_bCH_{endo}$), 1.67 (s, 3H, C$H_3$C=CH$_2$), 1.61 (s, 3H, C$H_3$C=CH$_2$), 1.39 (m, 1H, CH$_a$$H_bCH_{endo}$), 1.23 (s, 9H, C(C$H_3$)$_3$), 0.79 (dt, J = 7.7 and 5.8 Hz, 1H, CHCH_{endo}), and 0.69 (br app dt, ~q, J = 5.8 Hz, 1H, C*H*CH$_{endo}$). ^{13}C NMR (C_6D_6, 75 MHz): δ 157.94, 145.80, 145.33 (all C), 131.55, 129.44 (both CH), 110.43, 110.39 (both CH_2), 98.79 (CH), 53.72 (CH_3), 41.20 (C), 38.39, 38.16 (both CH_2), 36.02 (CH), 35.86 (CH_2), 35.07 (CH), 34.77, 31.25 (both CH_2), 31.03 (CH_3), 29.32, 28.29 (both CH_2), 25.54 (CH), 23.93 (C), 22.53, and 22.48 (both CH_3). Anal. Calcd for $C_{26}H_{42}OS$: C, 77.55; H, 10.51. Found: C, 77.26; H, 10.34.

(±)-(1α,4α,6α,7α)-7-(3-Methyl-3-butenyl)-4-((*E*)-6-methyl-2,6-heptadienyl)-1-methylbicyclo[4.1.0]heptan-3-one (42) and Epimerization to (±)-(1α,4β,6α,7α)-7-(3-Methyl-3-butenyl)-4-((*E*)-6-methyl-2,6-heptadienyl)-1-methylbicyclo[4.1.0]heptan-3-one (43). Carbene complex **8** (305 mg, 0.653 mmol) was charged to a screwcapped culture tube as a benzene solution and subjected to 5 freeze/pump/thaw cycles before an argon atmosphere was established. The tube was cooled in a dry ice/acetone slush, while propyne (approximately 2 mL, approximately 35 mmol) was condensed into the tube. The septum was replaced by a screwcap, and the tube was heated in a hot water bath with a magnetic stirring behind a blast shield. As the bath reached 65 °C, the golden orange solution started to turn an opaque brown. The bath temperature was held at 83 ± 5 °C for 3 h, then the heat was removed, and the tube was cooled to room temperature overnight. The tube was **cautiously** opened, at which time moderate outgassing occurred. An aliquot passed through a silica plug was analyzed by GC/MS and showed a dominant product whose molecular ion and fragmentation pattern corresponded to enol ether **7**. In addition, the ^1H NMR spectrum of this crude aliquot showed resonances consistent with the structure of **7**. The bulk reaction mixture was passed through silica (9:1 hexanes:ethyl acetate) and concentrated to a yellow-brown oil. MPLC (50:1 hexanes:ethyl acetate) of the crude product 36 h later did not give enol ether **7** but did give ketone **42** (131 mg, 64%) that was of sufficient purity to be used in the next reaction. R_f = 0.35 in 19:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3073 (m), 1707 (s), 1649 (m), 1208, 1161 (both w), 968 (m), and 886 (s) cm^{-1}. ^1H NMR (C_6D_6, 500 MHz assignments assisted by $^1H-^1H$ COSY): δ 5.39 (m, 2H, C*H*=C*H*), 4.80 (br s, 2H, C(Me)=CH_aH_b), 4.77 (br s, 2H, C(Me)=CH$_a$$H_b$), 2.51 (m, 1H, CHC$H_aH_b$CH=CH), 2.42 (d, J = 17.2 Hz, 1H, CH_aH$_b$C=O), 2.28 (d, J = 17.2 Hz, 1H, CH$_a$$H_b$C=O), 2.13 (m (obscured), 1H, CHCH$_a$$H_b$CH=CH), 2.09 (dt, J = 8.1 and 6.3 Hz, 2H, CH=CHCH_2CH$_2$), 2.01 (t, J = 8.1 Hz, 2H, CH=CHCH$_2$CH_2C(Me)=CH$_2$), 1.95 (t, J = 7.7 Hz, 2H, C$_{quat}$CH$_{endo}$CH$_2$CH_2C(Me)=CH$_2$), 1.90 (m, 1H, (CH$_2$)$_2$C*H*C=O), 1.87 (ddd, J = 13.4, 6.4, and 3.5 Hz, 1H, CHCH$_\alpha$H$_\beta$CH), 1.77 (ddd, J = 13.4, 9.9, and 3.3 Hz, 1H, CHCH_αH$_\beta$CH), 1.63 (s, 3H, H_3CC=CH$_2$), 1.61 (s, 3H, H_3CC=CH$_2$), 1.35 (m, 1H, CH$_{endo}$CH_aH$_b$CH$_2$C(Me)=CH$_2$), 1.27 (m, 1H, CH$_{endo}$CH$_a$$H_b$-CH$_2$C(Me)=CH$_2$), 0.86 (s, 3H, C$_{quat}CH_3$), 0.45 (app td, J = 7.0 and 5.1 Hz, 1H, C*H*$_{endo}$CH$_2$CH$_2$), and 0.31 (m, 1H, CH$_{endo}$C*H*-CH$_\alpha$H$_\beta$). ^{13}C NMR (C_6D_6, 125 MHz): δ 210.78, 145.60, 145.19, 132.34, 128.29, 110.55, 110.43, 47.76, 45.05, 38.38, 38.00, 34.24, 31.06, 27.83, 27.57, 25.76, 24.42, 22.47, 22.41, 19.70, and 19.15. LRMS (EI): m/z (relative intensity) 300 ($M^{\bullet+}$, 1), 285 (($M^{\bullet+}$ − CH_3), 3), 81 (100).

Sodium (15 mg, 0.65 mmol) was dissolved in methanol (4 mL) under an N_2 atmosphere. Ketone **42** (56.4 mg, 0.188 mmol) was added as a methanol solution and the mixture stirred for 1 h at room temperature. The solution was poured into 1 N HCl and extracted with ether (3 × 10mL). The combined extracts were washed with brine and dried over $MgSO_4$. After the solution was concentrated, MPLC (99:1 hexanes:ethyl acetate) afforded in order of elution **43** (17.4 mg, 31%) and recovered **42** (29.6 mg, 52%). This equilibration/separation protocol was repeated twice to give 33.6 mg (60%) of pure **43**. R_f = 0.20 in 30:1 hexanes:ethyl acetate and 0.13 in 99:1 hexanes:ethyl acetate. IR (neat, NaCl plates): 3073 (m), 1712 (s), 1649 (m), 1449, 1374, 970, and 886 (all m) cm^{-1}.

^{1}H NMR (C_6D_6, 500 MHz assignments assisted by ^{1}H–^{1}H COSY): δ 5.42 (m, 2H, C*H*=C*H*), 4.79 (m, 4H, C(Me)=CH_2), 2.54 (m, 1H, CHCH_aH$_b$CH=CH), 2.28 (m, 1H, CHCH_aH$_b$CH), 2.25 (d, J = 15.0 Hz, 1H, CH_aH$_b$C=O), 2.22 (d, J = 15.0 Hz, 1H, CH$_a$$H_b$C=O), 2.14–1.92 (m, 8H, remaining allylic H's and C*H*C=O), 1.62 (s, 6H, C(CH_3)=CH$_2$), 1.37–1.18 (m, 3H, CHCH$_a$$H_b$CH and CH$_{endo}CH_2CH_2$C(Me)=CH$_2$), 0.89 (s, 3H, C$_{quat}CH_3$), and 0.20 (m, 2H, C$H_{endo}$CHCH$_aH_b$CH). ^{13}C NMR ($C_6D_6$, 125 MHz): δ 212.32, 145.54, 145.25, 131.96, 128.29, 110.52, 110.46, 49.27, 46.80, 38.23, 38.06, 33.48, 33.19, 32.99, 31.15, 27.86 (2 carbons), 24.33, 23.34, 22.47, and 20.34. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 215.46, 145.67, 145.44, 131.94, 127.44, 109.99, 109.94, 49.35, 46.86, 37.91, 37.65, 33.29, 32.83, 32.70, 30.67, 27.84, 27.50, 24.07, 22.43, 22.38, and 20.31. LRMS (EI): m/z (relative intensity) 300 ($M^{\bullet+}$, 1), 285 (($M^{\bullet+}$ – CH_3), 1), 108 (100). HRMS Calcd for $C_{21}H_{32}O$ 300.2445, found 300.2445.

(±)-(1α,3β,4β,6α,7α)-7-(3-Methyl-3-butenyl)-4-((*E*)-6-methyl-2,6-heptadienyl)-1-methylbicyclo[4.1.0]heptan-3-ol (44). In a procedure analogous to that for the preparation of **34**, ketone **43** (8 mg, 0.027 mmol) was reduced to provide **44** as a colorless oil (8.1 mg, 100%). R_f = 0.47 in 6:1 hexanes:ethyl acetate. IR (neat, NaCl plates) 3453 (s, br), 3073, 1649, 1114, 1035, 968 (all m), and 885 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz assignments assisted by ^{1}H–^{1}H COSY): δ 5.42 (m, 2H, C*H*=C*H*), 4.68 (m, 4H, C(Me)=CH_2), 3.85 (m, ∑J's = 8.5 Hz, 1H, C*H*OH), 2.16–2.04 (m, 8H), 1.97–1.86 (m, 3H, CHC$H_a$$H_b$-CH and CHCH$_a$$H_b$CH=CH), 1.72 (s, 6H, H_3CC=CH$_2$), 1.65 (dd, J = 14.8 and 4.6 Hz, 1H, CH$_a$$H_b$CHOH), 1.47 (m, 1H, CH$_{endo}CH_aH_bCH_2$C(Me)), 1.35 (m, 2H, C*H*CHOH and CH$_{endo}$-CH$_a$$H_bCH_2$C(Me)), 1.26 (br s, 1H, O*H*), 1.03 (s, 3H, H_3CC$_{quat}$), 0.87 (m, 1H, C$_{quat}$CH_{endo}CH), and 0.37 (m, 1H, C$_{quat}$CH$_{endo}$C*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.55, 145.50, 131.34, 128.63, 109.98, 109.40, 68.93, 39.85, 38.37, 38.31, 37.75, 36.15, 30.70, 30.59, 28.43, 25.78, 24.35, 22.54, 22.43, 21.79, and 17.77. LRMS (EI): m/z (relative intensity) 302 ($M^{\bullet+}$, 2), 81 (100). HRMS Calcd for $C_{21}H_{34}O$ 302.2609, found 302.2600.

Acetic Acid (±)-(1α,3β,4β,6α,7α)-7-(3-Methyl-3-butenyl)-4-((*E*)-6-methyl-2,6-heptadienyl)-1-methylbicyclo[4.1.0]-hept-3-yl Ester (45). Alcohol **44** (7.8 mg, 0.026 mmol) was dissolved in CH_2Cl_2 (1 mL), and DMAP (17.4 mg, 0.142 mmol, 5.5 equiv) and acetic anhydride (25 μL, 0.26 mmol, 10 equiv) were added sequentially. The solution was gently swirled to ensure mixing and set aside overnight. The reaction mixture was diluted with ether (5 mL), washed with saturated NH_4Cl and brine, dried over $MgSO_4$, and concentrated to yield **45** as a light yellow oil (8.4 mg, 94%). R_f = 0.55 in 6:1 hexanes: ethyl acetate. IR (neat, NaCl plates): 3073 (w), 1738, 1648, 1239 (all s), 1158, 1129, 1107 (all m), and 1019 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.35 (m, 2H), 4.92 (m, ∑J's = 8.8 Hz, 1H), 4.70 (br s, 2H), 4.66 (br s, 2H), 2.17 (dd, J = 15.4 and 2.1 Hz, 1H), 2.13–1.97 (m, 8H), 2.00 (s, 3H), 1.80 (m, 1H), 1.72 (s, 3H), 1.71 (s, 3H), 1.64 (dd, J = 15.4 and 4.6 Hz, 1H), 1.45–1.30 (m, 4H), 1.02 (s, 3H), 0.67 (app td, J = 7.0 and 5.0 Hz, 1H), and 0.42 (ddd, J = 8.0, 5.0, and 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.46, 146.15, 145.55, 131.61, 127.92, 109.89, 109.83, 71.50, 38.23, 37.70, 37.05, 36.58, 35.84, 30.72, 29.54, 27.96, 26.40, 23.91, 22.46, 22.40, 21.50, 21.35, and 17.52. LRMS (EI): m/z (relative intensity) 284 (($M^{\bullet+}$ – HOAc), 2), 105 (100). HRMS Calcd for $C_{23}H_{36}O_2$ 344.2715, found 344.2721.

Acetic Acid (±)-(1α,3β,4β,6α,7α)-7-(3-Oxobutyl)-4-(2-oxoethyl)-1-methylbicyclo[4.1.0]hept-3-yl Ester (46). Triene acetate **45** (9.8 mg, 0.029 mmol) was dissolved in 1:1 MeOH:CH_2Cl_2, and solid $NaHCO_3$ (15 mg) was added. The flask was cooled in a dry ice/acetone slush, while a stream of ozone was bubbled through the solution. The solution turned blue after 30 s, and the ozone flow was stopped after 5 min. After the mixture was purged with nitrogen, dimethyl sulfide (0.3 mL) was added and the solution was allowed to warm to room temperature. After solvent removal, the residue was taken up in CH_2Cl_2, washed (water and brine), dried (Na_2SO_4), and concentrated to a light yellow oil, which was passed through a small silica plug (ethyl acetate) to yield **46** as a colorless oil (7.5 mg, 90%). R_f = 0.66 in 1:1 hexanes:ethyl acetate. IR (gas phase): 2990 (w), 2931 (m), 2875, 2815, 2715 (all w), 1758, 1736, 1228 (all s), 1156, 1089 (both w), 1017 (m), and 940 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.73 (s, 1H), 4.95 (m, ∑J's = 9 Hz, 1H), 2.49 (t, J = 7.3 Hz, 2H), 2.38 (dd, J = 17.0 and 5.5 Hz, 1H), 2.24–2.10 (m, 2H), 2.15 (s, 3H), 2.10–2.00 (m, 2H), 2.03 (s, 3H), 1.76 (dd, J = 15.5 and 4.5 Hz, 1H), 1.56 (m, 2H), 1.05 (s, 3H), 0.86 (m, 1H), 0.69 (app td, J = 7.3 and 5.2 Hz, 1H), and 0.47 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 209.12, 201.16, 170.44, 71.59, 46.97, 44.01, 36.15, 30.98, 30.01, 29.68, 29.45, 26.24, 24.12, 23.49, 21.28, and 17.41. LRMS (EI): m/z (relative intensity) 280 ($M^{\bullet+}$, 1), 252 (($M^{\bullet+}$ – CO), 1), 222 (($M^{\bullet+}$ – C_3H_6O), 3), 220 (($M^{\bullet+}$ – HOAc), 2), 118 (100). HRMS Calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1694. HRMS Calcd for $C_{16}H_{24}O_4$ (M – CO)$^+$ 252.1725, found 252.1725.

(±)-(3aα,4aα,5α,5aα,6aα)-5a-Methyl-5-(3-oxobutyl)hexahydrocyclopropa[*f*]benzofuran-2(3*H*)-one (6).[7] Aldehyde **46** (5.8 mg, 0.021 mmol) was dissolved in ethanol (1 mL). Silver nitrate (35 mg, 0.2 mmol, 9 equiv) was added as an aqueous solution (0.5 mL), followed by dropwise addition of 1 N NaOH (1 mL) with vigorous stirring. A brownish precipitate formed upon the addition of the first drop of NaOH; the volume of this precipitate increased during the addition and turned black. The suspension was stirred at room temperature overnight. The reaction mixture was filtered through Celite, and the filter cake was rinsed with water (2 mL). The filtrate was washed with ether (2 × 10 mL), and the ether washes were discarded. The aqueous layer was acidified with 10% HCl and extracted with CH_2Cl_2 (3 × 10 mL). The combined CH_2Cl_2 layers were dried over $MgSO_4$ and concentrated to give **6** as a viscous oil (3.4 mg, 69%). Chromatography (1:1 hexanes: ethyl acetate) provided a crystalline sample (mp 74–76 °C (lit.[7] 74–75 °C)). R_f = 0.25 in 1:1 hexanes:ethyl acetate. IR (gas phase): 2993 (w), 2946 (m), 2873 (w), 1807 (s), 1731 (m), 1361, 1163 (s), 1038, 1006, and 863 cm^{-1}. IR ($CDCl_3$): 2981, 2943, 2869 (w), 1768, 1712, 1465, 1380, 1187, 1097, 1033, and 992 (all m-s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz assignments assisted by ^{1}H–^{1}H COSY): δ 4.78 (ddd, J = 11.0, 8.5, and 6.4 Hz, 1H, C*H*O$_2$C), 2.75 (dd, J = 18.3 and 10.4 Hz, 1H, C$H_α$$H_β$-CO$_2$), 2.57 (ddddd, J = 10.4, 8.5, 8.2, 5.8, and 4.6 Hz, 1H, C*H*CH$_α$$H_βCO_2$), 2.52 (t, J = 7.3 Hz, 2H, H_3CC(=O)CH_2CH$_a$H$_b$-CH$_{endo}$), 2.31 (dd, J = 14.0 and 6.4 Hz, 1H, C$H_α$$H_βCHO_2$C), 2.15 (obscured, 1H, CHC$H_α$$H_β$CH), 2.15 (s, 3H, H_3CC(=O)CH$_2$-CH$_a$H$_b$CH$_{endo}$), 2.10 (dd, J = 18.3 and 4.6 Hz, 1H, CH$_α$$H_βCO_2$), 1.59 (app dq, J = 14.5 and 7.3 Hz, 1H, H_3CC(=O)CH$_2$CH_aH$_b$-CH$_{endo}$), 1.53 (app dq, J = 14.5 and 7.3 Hz, 1H, H_3CC(=O)-CH$_2$CH$_a$$H_bCH_{endo}$), 1.05 (s, 3H, H_3CC$_{quat}$), 0.98 (dd, J = 14.0 and 11.0 Hz, 1H, CH$_α$$H_βCHO_2$C), 0.78 (ddd, J = 14.0, 13.2, and 8.8 Hz, 1H, CHCH$_α$$H_β$CH), 0.44 (app td, J = 7.3 and 4.3 Hz, 1H, H_3CC(=O)CH$_2$CH$_a$H$_b$CH_{endo}), and 0.29 (ddd, J = 8.8, 8.2, and 4.3 Hz, 1H, CH$_{endo}$C*H*CH$_α$$H_β$CH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.71, 176.98, 78.11, 43.62, 37.26, 34.25, 34.18, 32.90, 30.16, 30.10, 23.68, 23.39, 18.53, and 16.75. LRMS (EI): m/z (relative intensity) 236 ($M^{\bullet+}$, 15), 221 (($M^{\bullet+}$ – CH_3), 9), 178 (56), 159 (36), 133 (85), 119 (100), 118 (86), 105 (56), 95 (36), 93 (49), 91 (52), 85 (27), 84 (85), and 79 (94).

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