Stereodefined Substituted Cyclopropyl Zinc Reagents from Gem-Bismetallics

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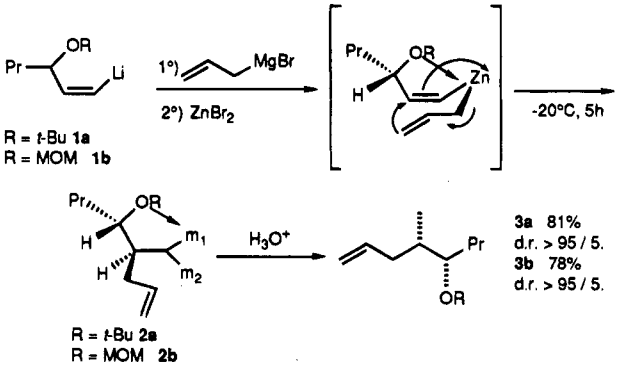
1,1- or *n,n*-Bismetallic reagents bearing a methoxymethyl ether in the γ position undergo cyclization at room temperature to give monometalated, diastereoselectively substituted cyclopropanes. The nature of the substituents is crucial for this diastereoselection, a π-chelation between one metal and a properly located unsaturation, as well as 1,2-strain, are proposed to explain the steric outcome of these reactions.

We have already reported on the high diastereoselections which operate when an allyl zinc reagent adds to a substituted vinyl metal, at low temperature in ether.[1] We interpreted this facial selectivity as a result of chelation between a heteroatom[2] (oxygen) and zinc, in a chairlike transition state (see Scheme 1) where the allyl moiety is delivered on the unshielded face of the five membered ring.

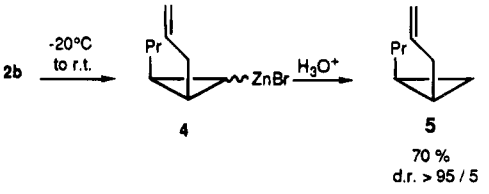
After hydrolysis of **2a** or **2b**, the corresponding *syn* 4-methyl-5-alkoxyalkenes **3a** and **3b** are obtained in high purity.[1b] However, when the chelating moiety is a methoxymethyl ether (OMOM) **1b**, the formed bismetallic species **2b** is not stabilized (as might be anticipated), but becomes thermally labile, and warming the mixture to room temperature promotes an internal nucleophilic substitution, leading to a metalated cyclopropane[3] **4** which is eventually hydrolyzed to a 1,2-*cis* disubstituted cyclopropane[4] **5** (Scheme 2).

Since the propyl and allyl groups in **3b** were *anti* to each other, this stereochemical outcome clearly shows that the internal nucleophilic substitution of the OMOM moiety by one of the C–M bonds, occurs with inversion of configuration at the electrophilic center, as is usual,[5] but also means that the chelation has to be broken for the reaction to proceed. In order to establish the relative configuration of the metalated carbon in **4**, we turned to a more simple substrate **6**, prepared according to the general scheme for this type of derivatives[6,7] (Scheme 3).

Scheme 1



Scheme 2



The same allylation–cyclization as above, performed with **6**, leads to **7** which is transmetalated to a copper reagent[8] and condensed with allyl iodide (Scheme 4). The bis allyl cyclopropane **8** shows a *trans* relationship between the two substituents, as evidenced by the ^{1}H NMR pattern of the cyclopropane CH_2 unit which appears as a doublet since both hydrogens are homotopic (C_2 symmetry).

We assume that the zinc to copper transmetalation occurs with retention of configuration as was shown for

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(2) (a) Hoftsee, H. K.; Boersma, J.; Van der Meulen, J. D.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *153*, 245. (b) Thiele, K. H.; Heinrich, M.; Brüser, W.; Schröder, S. Z. *Anorg. Allg. Chem.* **1977**, *432*, 221.

(3) Some secondary metalated cyclopropyl rings have been described. (a) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 5727 with a diastereomeric ratio of 70/30 in 92% yield. (b) Knochel, P.; Yeh, M. C. P. *Tetrahedron Lett.* **1988**, *29*, 6697 with a diastereomeric ratio of 95/5 and 48% yield. (c) Nakamura, E.; Isaka, M.; Matsuzawa, S. *J. Am. Chem. Soc.* **1988**, *110*, 1297. (d) Stoll, A. T.; Negishi, E. I. *Tetrahedron Lett.* **1985**, *26*, 5671. (e) Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1990**, *112*, 7428. (f) Kiyani, K.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1600. (g) Harada, T.; Katsuhira, T.; Hattori, K.; Oku, A. *J. Org. Chem.* **1993**, *58*, 2958 and references cited therein. (h) Fontani, P.; Carboni, B.; Vaultier, M.; Maas, G. *Synthesis* **1971**, 605. (i) Zweifel,G.; Clark, G. M.; Withney, J. *J. Am. Chem. Soc.* **1971**, *93*, 1305. (j) Lehmkuhl, H.; McLane, R. *J. Organomet. Chem.* **1981**, *221*, 123. (k) Kubota,K.; Nakamura, M.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 5867.

(4) Beruben, D.; Marek, I.; Normant, J. F. *Tetrahedron Lett.* **1993**, *34*, 7575.

(5) Walborsky, H. M., Murari, M. P. *J. Am. Chem. Soc.* **1980**, *102*, 426.

(6) (a) Ma, S, Lu, X. *J. Chem. Soc. Chem. Commun.* **1990**, 733 and 7653. (b) Ma, S; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709. (c) Meyer, C.; Marek, I.; Normant, J. F. *Synlett* **1993**, 386. (d) Marek, I.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1991**, *32*, 5329.

(7) Gras, J. L.; Kon win Chang, Y. Y.; Guerin, A. *Synthesis* **1985**, 74.

(8) (a) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 5727. (b) Knochel, P.; Yeh, M. C. P.; Berk, S. C. *J. Org. Chem.* **1988**, *53*, 5789. (c) Knochel, P.; Rozema, M. J.; Tucker, L. E.; Retherford, C.; Furlong, M.; Rao, A. S. *Pure Appl. Chem.* **1992**, *64*, 361 and references cited therein. (d) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *106*, 3368. (e) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056. (f) Ochiai, H.; Tamura, Y.; Tsubaki, K.; Yoshida, Z. *J. Org. Chem.* **1987**, *52*, 4418. (g) Tamaru, Y.; Tanijawa, H.; Yamamoto, T.; Yoshida, Z. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 351.

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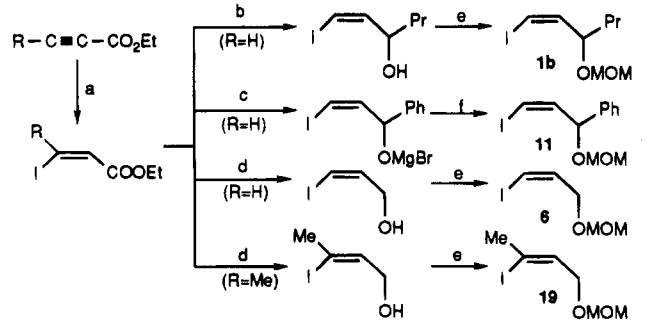
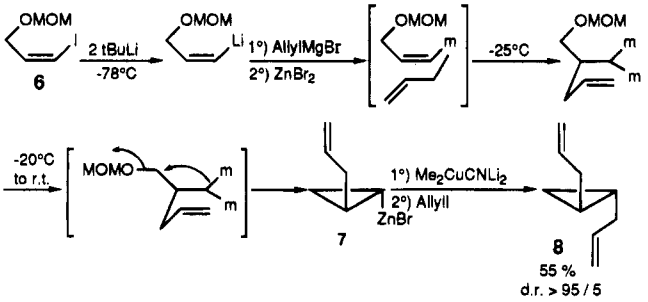
Scheme 3[a]

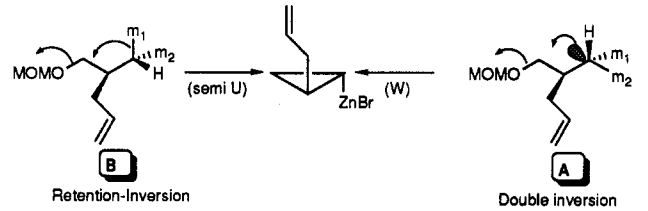


[a] Reagents: (a) NaI, AcOH 70 °C[6] R = H 92%; R = Me 87%, (b) 1 equiv of DIBAL-H, −78 °C, 30 min and then PrMgBr, −78 °C to rt 88%. (c) 1 equiv of DIBAL-H, −78 °C, 30 min and then PhMgBr, −78 °C to rt 85%; (d) 2 equiv of DIBAL-H, −78 °C, 1 h R = H 87%, R = Me 83%, (e) dimethoxymethane, LiBr, APTS, (f) CH_3OCH_2Br (path e cannot be used in this case).

Scheme 4

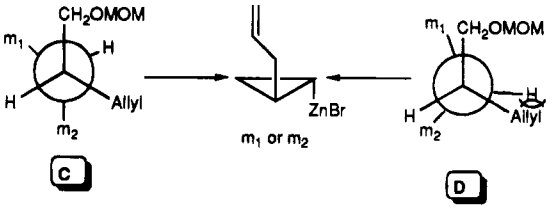


Scheme 5

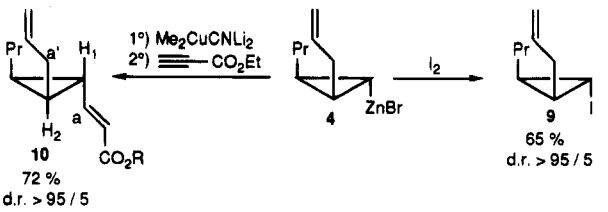


other transmetalations of this type.[9] Thus, one of the two C−M bonds has been involved in this internal nucleophilic substitution in a stereoselective way. It is however difficult to establish which one, since two mechanisms have been put forward to interpret the stereochemistry of 1,2-disubstituted cyclopropanes obtained by γ-elimination from *monometallic* species.[10] The most commonly adopted mechanism involves an inversion-inversion (at both centers) in a W shaped conformer[11-13] (**A** in Scheme 5). However, Hoppe *et al.* have recently shown that the retention−inversion mechanism, from a sickle shaped conformer (**B** in Scheme 5), was indeed possible.[14]

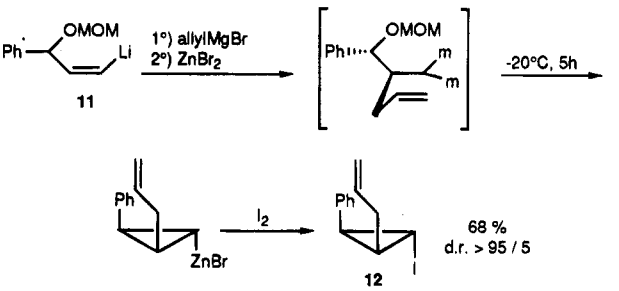
Scheme 6



Scheme 7



Scheme 8



In our case both mechanisms can be invoked to explain the formation of **7** since each of the two diastereotopic C−M bonds can be involved in either a W or a sickle transition state.

From here on, we shall consider that the double inversion mechanism is the more probable since in this case, a staggered transition state **C** should be prefered to the eclipsed one **D** deriving from a retention−inversion mechanism (Scheme 6).

If we now come back to the reaction depicted in Schemes 1 and 2, the intermediate **4** can be iodinolyzed to **9**, or transmetalated to the copper reagent, and added to ethyl propiolate to yield **10**; both are obtained as single isomers (see Scheme 7).

NOE effects on **10** show a proximity effect both between H_1 and Ha' and between H_2 and H_a. Thus, the C−M bond in **4** is anti to the propyl and allyl groups.

If the propyl group in **1b** is replaced by a phenyl, the same allylzincation−cyclization on **11** (prepared according to Scheme 3) also leads to a metalated cyclopropane which can be iodinolyzed to **12** in 68% yield (dr > 95/5) (Scheme 8). All three protons of the cyclopropane ring have chemical shifts sufficiently different to display a clear NOE effect which shows that, here again, the intermediate C−M bond was *anti* to the allyl and phenyl groups.

We then wondered whether a tetrasubstituted cyclopropane could be prepared diastereoselectively according to the same procedure. Our starting material was first an α-silylated vinyl metal prepared from the corresponding iodo derivatives **13** and **17** according to Scheme 9.[15]

(9) The configurational stability of cyclopropyllithiums has been established: (a) Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283. (b) Walborsky, H. M.; Banks, R. B. *Bull. Soc. Chim. Belg.* **1980**, 849. (c) Walborsky, H. M.; Zimmerman, C. *J. Am. Chem. Soc.* **1992**, *114*, 4996. (d) Walborsky, H. M.; Hamdouchi, C. *J. Org. Chem.* **1993**, *58*, 1187 and references cited therein.

(10) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914.

(11) Trost, B. M.; Schinski, W. L.; Chen, F.; Mantz, I. B. *J. Am. Chem. Soc.* **1971**, *93*, 676.

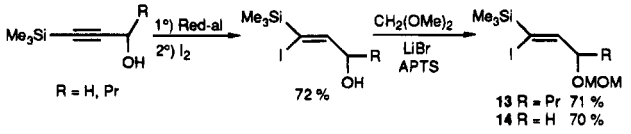
(12) Liu, Y.; Sorensen, T. S.; Sun, F. *Can. J. Chem.* **1993**, *71*, 258.

(13) (a) Krief, A.; Hobe, M.; Dumont, W.; Badaoui, E.; Guittet, E.; Evrard, G. *Tetrahedron Lett.* **1992**, *33*, 3381. (b) Krief, A.; Hobe, M. *Synlett* **1992**, 317. (c) Krief, A.; Hobe, M. *Tetrahedron Lett.* **1992**, 6527 and 6529.

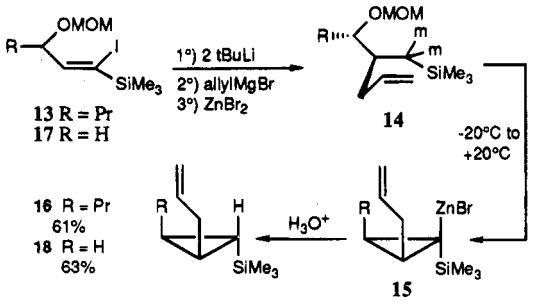
(14) (a) Hoppe, D.; Paetow, M.; Hintze, F. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 394. (b) Paetow, M., Kotthaus, M., Grehl, M.; Fröhlich, R.; Hoppe, D. *Synlett* **1994**, 1034.

(15) (a) Denmark S. E.; Jones T. K *J. Org. Chem.* **1982**, *47*, 4595. (b) .Jones T. K., Denmark S. E. *Org. Synth.* **1986**, *64*, 182.

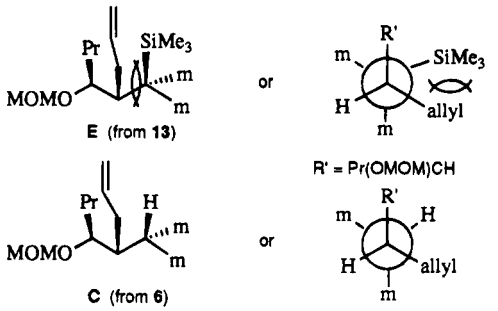
Scheme 9



Scheme 10



Scheme 11



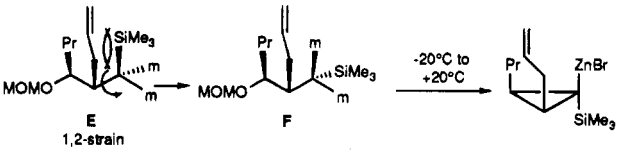
13 is subjected to the zinca allylation–cyclization reaction as above; but now, hydrolysis of the educt **15** delivers the silylated cyclopropane **16**[16] for which NOE effects show that the silyl group is located *anti* to the propyl and allyl groups.[16] Thus, in **15**, the remaining metal has to be *cis* to these substituents. An analogous result is obtained when we start from **17** (Scheme 10).

This change in the stereochemical outcome can be explained in two ways: first, the initial metalated species would be the epimer of **15** (analogous to **4**) which would experience epimerization, as is well documented for metalated cyclopropanes where the metal is geminal to a silyl group.[17] In such a case, **15** would represent the thermodynamic isomer.

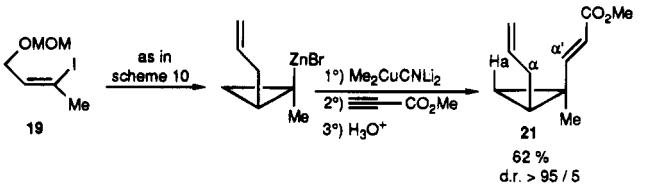
Another interpretation is to consider the W shaped transition state where a gauche interaction exists in **E** between the silyl and allyl groups, whereas such hindrance is absent in the nonsilylated compound **C** (see Scheme 11).

Considering that the C–Zn bond (21.5 nm) is less sterically demanding as compared to the C–Si bond (18.0 nm), free rotation from **E** to **F** would occur prior to cyclization[18] (Scheme 12).

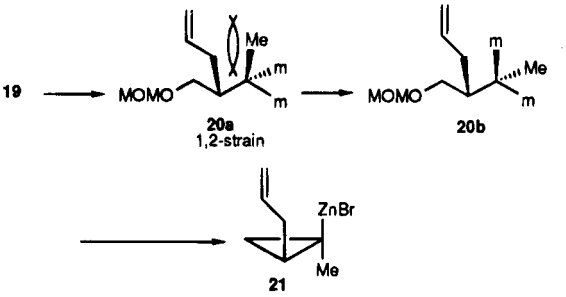
Scheme 12



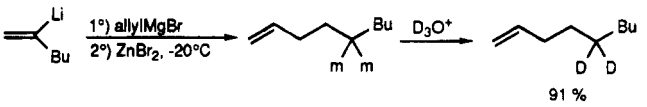
Scheme 13



Scheme 14



Scheme 15



In order to discriminate between these two hypothesis, we prepared the derivative **19** (see Scheme 3) where a methyl group replaces the silicon moiety of **17**.

19 is subjected to the metalation–allylzincation–cyclization sequence, and, due to its low molecular weight, a subsequent Zn to Cu transmetalation is performed, followed by 1,4-addition on methyl propynoate (Scheme 13).

Differential NOE effects between H_a and both the vinylic proton $H_{\alpha'}$ and the allylic protons H_α show that these two groups are *cis* to each other in **21**. It follows that the reaction can be depicted as in Scheme 14.

This result is in favor of our second interpretation for the formation of **16** (and **18**) and shows that in the case of **20** also, 1,2-steric strain between the methyl and allyl moieties is released when turning from **20a** to **20b**. In summary, the trimethylsilyl or methyl groups are bulkier than the metal, and these results represent a new way to prepare some tertiary cyclopropylzinc derivatives.

An alternative strategy would be to start from *n,n*-organogembismetallic reagents and we have already disclosed shortly[19] that 2-lithio-1-alkenes also undergo the allylzincation in ether, to give an "internal" bis metallic species (Scheme 15).

If one starts with such a substrate bearing a methoxymethyl ether in the homoallylic position, one may anticipate a ring closure analogous to the preceding ones where a *tertiary* metalated cyclopropane would ensue

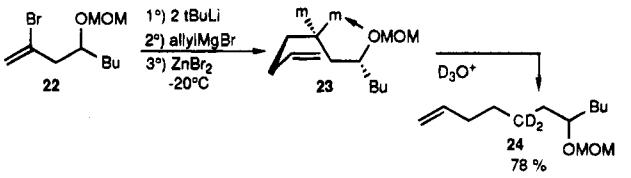
(16) (a) Grignon-Dubois, M.; Dunogués; J.; Calas, R. *Synthesis* **1976**, 737. (b) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Petraud, M. *Organometallics* **1984**, *3*, 1060. In fact NOE effects only show the *cis* relationship of the propyl and allyl groups; the *trans* relationship between the allyl group and the $SiMe_3$ group was detected in **18**.

(17) (a) Hiyama, T.; Kanamura, A.; Motizawa, Y.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 1279. (b) Nakajima, T.; Tanabe, M.; Ohno, K.; Segi, M.; Suga, S. *Chem. Lett.*, **1986**, 177. (c) Stoll, A. T.; Negishi, E. I. *Tetrahedron Lett.* **1985**, *26*, 5671.

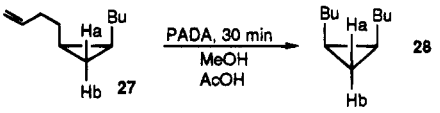
(18) We have not developed further this result, but it may be anticipated that a subsequent attack of **14** by an electrophile followed by a diastereoselective desilylation would give access to the 1,2,3-*cis* trisubstituted cyclopropanes.

(19) (a) Beruben, D.; Marek, I.; Labaudinière, L.; Normant, J. F. *Tetrahedron Lett.*, **1993**, *34*, 2303. (b) For gem bismetals in benzylic position, see Knochel P.; Yeh, M. C. P.; Xiao, C. *Organometallics* **1989**, *8*, 2831.

Scheme 16



Scheme 17



(Scheme 16). The starting alcohol is obtained[20] in 89% yield from the corresponding aldehyde, and 2,3-dibromopropene and is protected[7] as a MOM ether **22** in 92% yield.

22 is submitted to the usual carbometalation reaction (at −20 °C) and the organogembismetallic can be deuterolyzed at this temperature to afford **24** in 78% yield. Raising the temperature to + 20 °C before hydrolysis furnishes **27** as a single isomer by a diastereoselective 1,3-elimination, in which the butyl and butenyl groups end up *cis* to each other.

This was ascertained by reduction[21] of **27** with diimide, prepared from potassium azodicarboxylate (PADA)[22] (see Scheme 17).

28 was compared to the two isomers resulting from cyclopropanation[23] ($Et_2Zn + CH_2I_2$) of (*Z*) and (*E*) 5-decene (obtained respectively in 70 and 65% yield). **28** shows the same ^1H NMR pattern as the *cis* isomer thus prepared, where H_a displays a typical negative shift (−0.32 ppm), as compared to H_b (+ 0.55 ppm). It is interesting to note that **27** also exhibits such a negative δ value for H_a.

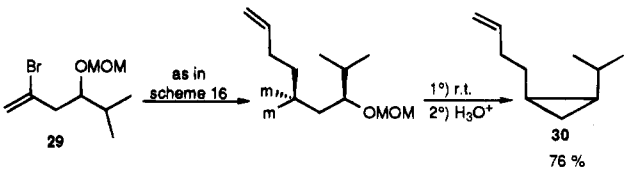
If we consider a W shaped transition state where the reacting C−M bond and the C−OMOM bond are coplanar (breakage of the initial chelation), one now faces a new problem, since the n-butyl and butenyl residues experience a 1,3 steric interaction (see **25** in Scheme 16).

In order to get more information about this steric hindrance, we prepared the starting material **29** where a bulkier group (isopropyl) replaces the n-butyl group.

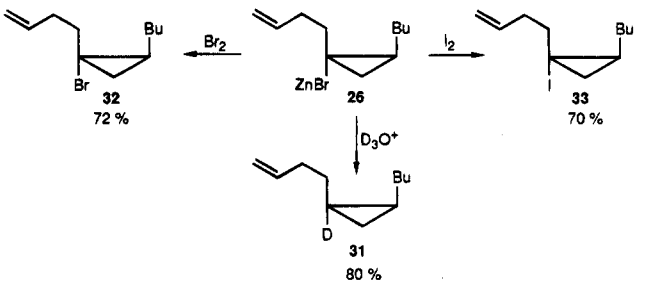
29 is prepared, as **22**, from dibromopropene and isobutyraldehyde[20] (90%) followed by etherification (75%). The same reaction sequence as in Scheme 16 is then applied and leads to 1-isopropyl-2-(4-butenyl)cyclopropane (**30**) in 76% yield as a single isomer (Scheme 18).

NMR study shows the two substituents are, again in a *cis* relationship. It must be noted that in other intramolecular nucleophilic substitution cyclopropanation reactions described in the literature,[24] the *cis* isomer is

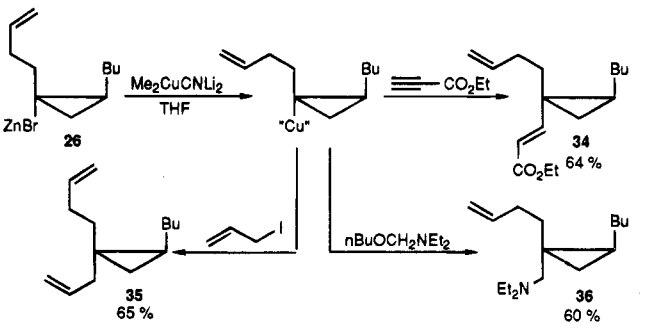
Scheme 18



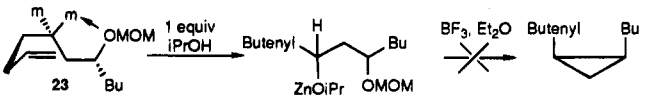
Scheme 19



Scheme 20



Scheme 21



kinetically obtained, although no comments are presented for this peculiar aspect.

The tertiary zinc reagent **26** has been deuterated, brominated, and iodinated according to Scheme 19. In every case a single isomer is found.

26 can also be transmetalated to copper and then reacted with ethyl propiolate, allyl iodide, or an amino ether to give respectively **34**, **35**, or **36** in 60−65% yield (Scheme 20).

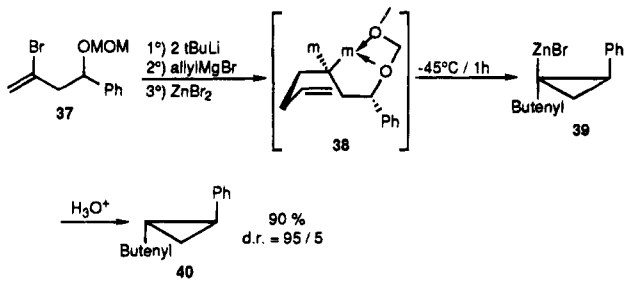
These derivatives can find interesting applications for further spiro annulations; their yields are modest but correspond to the "one pot" creation of three carbon−carbon bonds stereoselectively.

Worthy of note is the fact that selective monohydrolysis of **23**, by 1 equiv of 2-propanol, leads to the corresponding monometallic derivative, which is totally unable to cyclize after warming up to room temperature for hours. In this case, the methoxy methyl ether does not exhibit leaving group properties any more (Scheme 21).

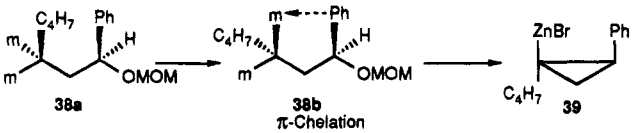
We have seen in Scheme 8 that changing the propyl group of **1b** to a phenyl group (**11**) did not change the steric outcome of the cyclization reactions. Such is not the case if we switch from **22** (Scheme 16) to its phenylated counterpart **37** (prepared in the same way[20,7]).

(20) Mandai, T.; Nokami, J.; Yano, T.; Yoshinaga, Y.; Otera, J. *J. Org. Chem.* **1984**, *49*, 172.
(21) Hamersma, J. W.; Snyder, E. I. *J. Org. Chem.* **1965**, *30*, 3985.
(22) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.
(23) (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* **1969**, *24*, 53. (b) Kawabata, N.; Nakagawa, T.; Nakao, T.; Yamashita, S. *J. Org. Chem.* **1977**, *42*, 3031. (c) Denmark, S. E.; Edwards, J. P. *J. Org. Chem.* **1991**, *56*, 6974.
(24) (a) Dechoux, L.; Ebel, M.; Jung, L.; Stambach, J. F. *Tetrahedron Lett.* **1993**, *34*, 7405. (b) Dechoux, L.; Doris, E. *Tetrahedron Lett.* **1994**, *35*, 2017.

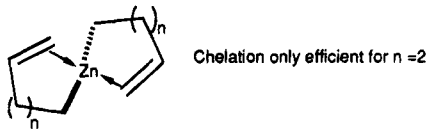
Scheme 22



Scheme 23



Scheme 24



The carbometalation of **37** is performed at −45 °C, but the intermediate bismetallic reagent **38** cannot be trapped and cyclizes immediately to the cyclopropane **39** which is hydrolyzed to **40** in 90% yield with a diastereomeric ratio of 95/5 (Scheme 22).

The intermediate **39** has a *cis* relationship between the metal and the phenyl group (deduced from the analysis of the NMR spectra of **40**) as opposed to **26** (in Scheme 16). The corresponding W shaped transition state should be depicted as **38b** (Scheme 23).

We cannot invoke a 1,3-steric interaction to explain this result as it should be present for **25** as well (Scheme 16). We are thus led to consider a π-chelation between one metal and the phenyl group. Such interactions have been established by Oliver et al,[25] between zinc and a C=C double bond, in bis ω-alkenyl zincs. A dipole interaction between $Zn^{+\delta}-C^{-\delta}$ and the negative charge of the terminal sp_2 carbon was postulated to interpret the spiro structure of di-4-pentenyl zinc (Scheme 24).

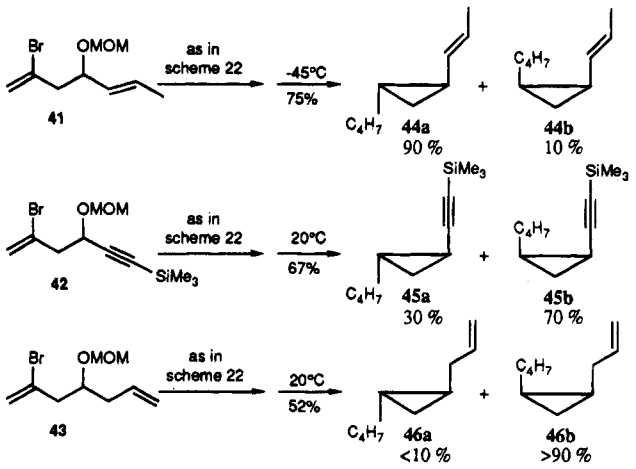
Such interaction is evidenced by NMR when $n = 2$, but does not occur for $n = 1$ or 3. More recently Posner et al.[26] used this concept to explain the stereochemistry of a cyclic product derived from an organocopper reagent.

In our case, such a π-chelation would divert the W shaped conformed from **38a** to **38b** (Scheme 23).

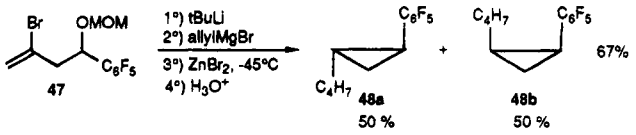
In order to assess this hypothesis, we have considered cases where the phenyl moiety is replaced by other unsaturated residues. Namely we prepared compounds **41**−**43** in the same way as **22**.[20,7]

These derivatives, when lithiated and allylzincated at −45 °C, as above, gave the corresponding cyclopropanes after warming to + 20 °C for **42** and **43** and directly at −45 °C for **41** (Scheme 25).

Scheme 25



Scheme 26



The stereochemistry of the major products has been established by differential NOE effects in each case.

It thus appears, that the influence of the propenyl group in **41**, exactly parallels the one displayed by a phenyl group in **37**, π-chelation promoting the predominant formation of the *trans* product **44a**.

For **42** the ethynyl group is farther away from the metal than is an ethenyl group, but nevertheless, a 30% ratio of the *trans* compound **45a** is formed. In **43** however, where the C=C double bond of the allyl moiety should interact with one metal in a seven-membered ring, almost no interaction occurs, and the *cis* compound **46b** is predominant (as it was for a n-butyl group). This behavior is reminiscent of the absence of chelation observed by Oliver in bis-5-hexenyl zinc cited above (Scheme 24).

Another way to back up the π-chelation interaction is to consider that this donation of electrons from a π system toward a metal should be lessened if one introduces electron-withdrawing groups on the π system. Along those lines we prepared the pentafluorophenyl derivative **47**[20,7] and submitted it to the addition−cyclization sequence (Scheme 26).

Contrary to **40** obtained as a (95/5) *cis* isomer, **48** is obtained as a 50/50 mixture of *cis* and *trans* isomers. This result can be interpreted in terms of a diminished ability of the C_6F_5 residue to undergo π chelation.

The analogous experiment performed with a monofluorinated phenyl derivative **49**, led to no change, as compared with the phenyl group, yielding the *trans* cyclopropane in 79% with a 90/10 dr.

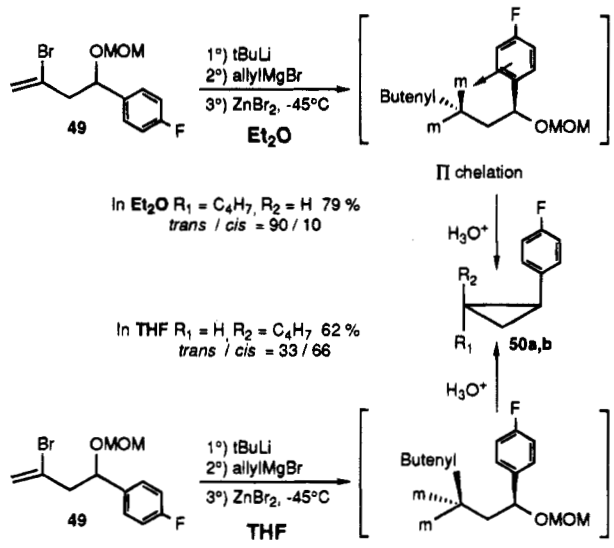
At this point, we also considered that using a solvent which coordinates to the zinc atoms, more efficiently than does ether, would override the π electron donation of the phenyl ring. We thus compared the reactions described in Scheme 27.

In ether, a 90/10 ratio in favor of the *trans* isomer is obtained whereas in THF (which requires a higher temperature of 0 °C for the carbometalation), the major isomer is now *cis* (66/33). This result can be interpreted as a result of weakening π-chelation by favoring solvation of the metal by a more donating solvent.

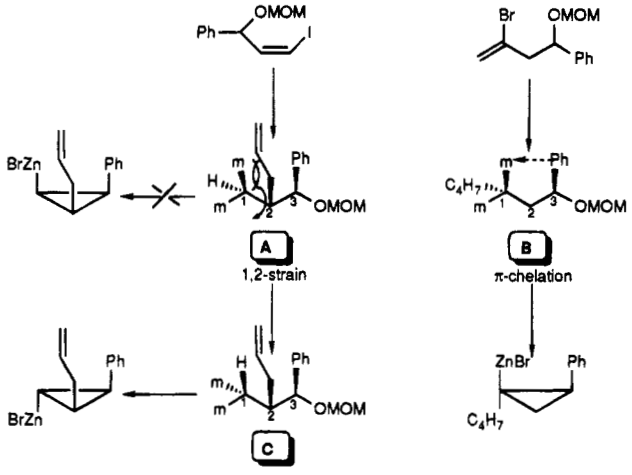
(25) (a) St Denis, J.; Oliver, J. P.; Smart, J. B. *J. Organomet. Chem.* **1972**, *44*, C32. (b) St Denis, J.; Oliver, J. P.; Dolzine, T. *J. Am. Chem. Soc.* **1972**, *94*, 8260. (c) St Denis, J.; Oliver, J. P.; Dolzine, T.; Smart, J. B. *J. Organomet. Chem.* **1974**, *71*, 315. (d) Albright, M. G.; St Denis, J.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *125*, 1. (e) Haaland, A.; Lehmkuhl, H.; Nehl, H. *Acta. Chem. Scand.* **1984**, *38*, 547.

(26) (a) Posner, G. H.; Lentz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934. (b) For a general discussion of π stacking see: Maddaluno, J. F.; Giessner-Pretre, C. *J. Org. Chem.* **1994**, *59*, 793 and references cited therein.

Scheme 27



Scheme 28



If we compare the cyclopropanations discussed thus far, originating from either 1,1-bismetallic reagents or *n,n*-bismetallic reagents, we see that the influence of a phenyl group is totally different in both cases (compare Scheme 8 and Scheme 22). In the former case, the W-shaped transiton state corresponds to **A** and in the latter case to **B** (see Scheme 28).

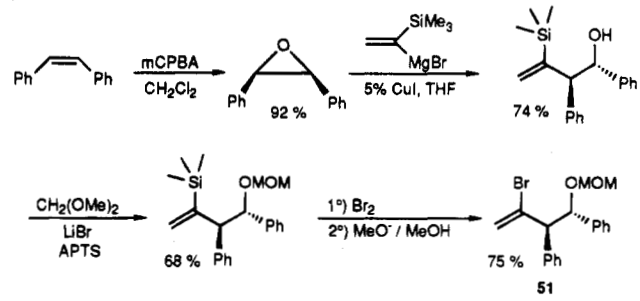
Both differ by the degree of substitution on carbons 1 and 2. We considered π chelation in **B** to explain our results, but it might be present as well in **A** between the phenyl (and the allyl moiety) toward the metal which does not participate in the elimination reaction. We must then suspect that the 1,2-steric interaction (as was developed in Scheme 14), between this metal and the allyl group (eclipsed in **A**) is strong enough to override these π chelations. We then decided to compare transition state **B**, with a similar one where carbon 2 would be also substituted.

The starting product was prepared according to Scheme 29.

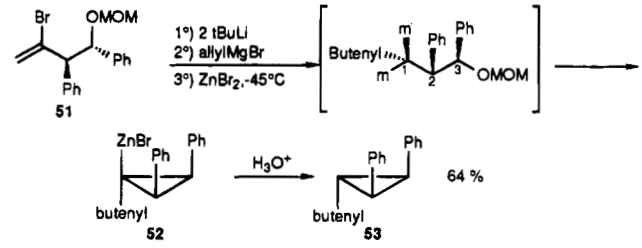
51 is submitted to the metalation–allylzincation–cyclization as above and leads to a unique isomer **53** in 64% yield (Scheme 30).

One may consider three hypothesis to explain this result: (i) the phenyl group in C_2 coordinates to the metal but this is contrary to the results observed by Oliver for bis-3-butenyl zinc (Scheme 24); (ii) the phenyl group on

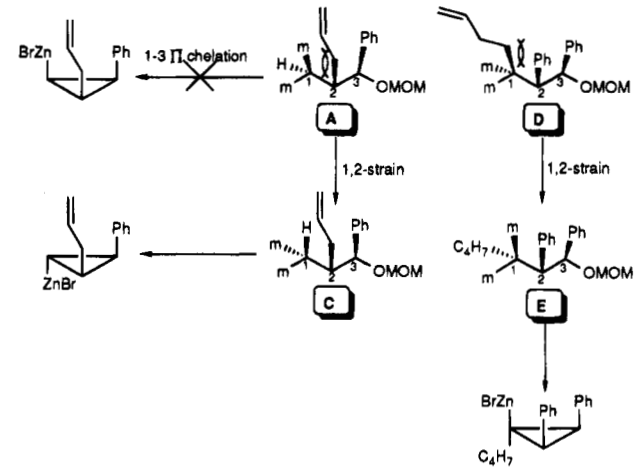
Scheme 29



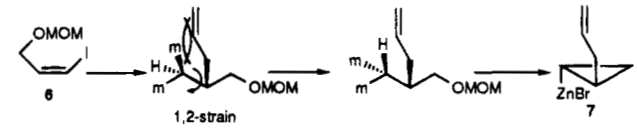
Scheme 30



Scheme 31



Scheme 32



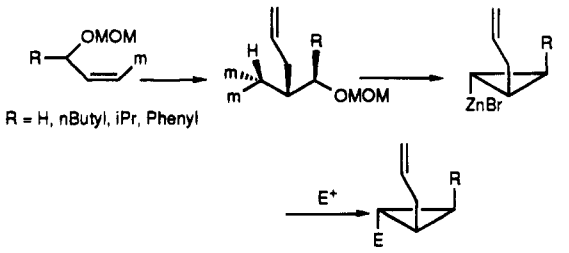
C_3 coordinates to the metal, but this π chelation is not found in **A** (Scheme 28); (iii) a steric 1,2-interaction between the phenyl on C_2 and the butenyl residue (see **D** Scheme 31). This strain, responsible for the conversion of **A** to **C** would be responsible now for the conversion of **D** to **E**, analogous to the conversion of **20a** to **20b** (Scheme 14).

This implies that the relative bulkiness of the substituents follows a sequence H < M < butenyl, and is in agreement with the fact that when a primary allylic ether **6** was used (see Scheme 4) the only possible steric interaction was the one between H/allyl versus M/allyl, in which the former is preferred (Scheme 32).

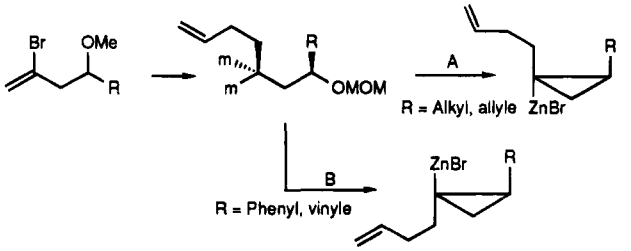
In summary, the steric result of these cyclopropanations depends on the nature of the gem bismetallic species, either terminal ($RCHM_2$) or internal (RCM_2R').

In the first case, the carbometalation introduces an allyl moiety on carbon 2, which is *syn* to the R group in the bismetallic in a W shaped transition state, and 1,2-

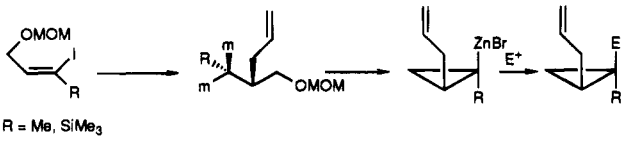
Scheme 33



Scheme 34



Scheme 35



strain then leads to a *cis* relationship between allyl and R (whatever the nature of R: aliphatic or aromatic) and a trans relationship between the metal and these two groups. (Scheme 33).

In the second case, the internal bismetallics undergoes cyclization (Scheme 34), to yield also a disubstituted cyclopropane (after hydrolysis of the tertiary C–M bond). The latter is *cis* if R is an alkyl, or allyl moiety (path A), or *trans* if R is a phenyl or vinyl group (path B), due to π chelation of the remaining metal with these groups.

In the case of an internal gembismetallic of type **14** or **20b** (Scheme 35). The cyclopropane obtained after hydrolysis is also *trans*, and we attribute this steric outcome to a 1,2-strain between the R group (Me, Me_3Si) and the allyl moiety.

In conclusion, we have shown that 1,1- or *n,n*-organogembismetallics, bearing a MOM ether in γ position, easily cyclize to give a large array of metalated cyclopropanes. The cyclization requires only warming up the mixture at room temperature, after the initial carbometalation step has been performed at −40 °C to −20 °C. Several factors govern the stereochemistry: π chelation with appropriate vinyl or phenyl groups completely inverses the stereochemistry which is obtained with alkyl or even allyl groups, unless we introduce 1,2-strain, which is then predominant. The order of steric interaction follows the sequence: butenyl, Me_3Si, methyl > metal > H. It must be emphasized that when these different factors compete, the overall outcome is largely in favor of one distinct isomer.

Experimental Procedure

Synthesis of (*Z*) β-Iodo ethyl acrylate (R = H) and (*Z*) β-iodo-β-methyl ethyl acrylate (R = Me) (Scheme 3). A 250 mL round-bottomed flask equipped with a magnetic stirring bar and a nitrogen gas inlet is charged with 22.5 g (0.15 mol) of dry sodium iodide and 100 mL of glacial acetic acid. To the stirred solution is added in one 10.1 mL portion (0.1 mol) of ethyl propiolate (or β−methyl methyl propiolate), and the resulting mixture is heated with an oil-bath at +70 °C (external temperature) during 12 h. The brown solution is cooled to room temperature, and 100 mL of water and 100 mL of ether are added. The organic layer is separated and the aqueous layer extracted twice with 20 mL of ether. The combined organic layers are treated with 3 M aqueous potassium hydroxide (ca. 150 mL per portions of 50 mL) until the aqueous phase becomes neutral (pH = 7), washed with 50 mL of brine, and dried over anhydrous magnesium sulfate. After rotary evaporation of the solvent, the residual brown oil is distilled to give 20.8 g (92% yield) of (*Z*)-β-iodo ethyl acrylate as a pale yellow liquid: bp 57 °C (0.1 mmHg) and 19.6 g (87% yield) of (*Z*) β-iodo-β-methyl ethyl acrylate as a pale yellow liquid: bp 62 °C (0.1 mmHg).

(*Z*)-β-iodo ethyl acrylate: IR (film) 3080, 2940, 1735, 1640, 1425, 1365, 1230, 1170, 1020, 925, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, J = 9.34 Hz, 1H, =C(*H*)I), 6.89 (d, J = 9.34 Hz, 1H, CH=), 4.25 (q, J = 7.14 Hz, 2H, OCH_2), 1.32 (t, J = 7.14 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.57 (CO_2Et), 129.92 (HC=), 94.60 (=CHI), 60.78 (OCH_2), 14.17 (CH_3). Anal. Calcd for $C_5H_7IO_2$: C, 26.57; H, 3.12. Found: C, 26.34; H, 3.14.

(*Z*) β-Iodo-β-methyl ethyl acrylate: IR (film): 3080, 2940, 1735, 1640, 1425, 1365, 1230, 1170, 1020, 925, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.84 (q, ^4J = 1.45 Hz, 1H, CH=), 3.75 (s, 3H, OCH_3), 2.75 (d, ^4J = 1.45 Hz, =CCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.73 (CO_2Me), 125.24 (=CCO_2), 113.65 (IC=), 55.53 (OCH_3), 36.55 (=CCH_3). Anal. Calcd for $C_5H_7IO_2$: C, 26.57; H, 3.12. Found: C, 26.58; H, 3.15.

(*Z*)-1-Iodohex-1-en-3-ol. A 100 mL, dry four-necked, round bottomed flask equipped with a mechanical stirrer, an internal thermometer, a rubber septum, and a nitrogen gas inlet was charged with 11.3 g (50 mmol) of (*Z*) β-iodo ethyl acrylate and 100 mL of anhydrous dichloromethane . The stirred solution was cooled to −78 °C by mean of a liquid nitrogen bath and 50 mL (50 mmol) of a 1 M solution of diisobutyl aluminium hydride in hexane were added dropwise via a syringe at such a rate that the temperature does not exceed −75 °C. After stirring for 30 min at −78 °C, 40.26 mL (60 mmol, 1.49 M solution in Et_2O) of n-propylmagnesium bromide in ether was added dropwise with a syringe at −78 °C, through the septum. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. The hydrolysis was carried out at −20 °C by dropwise addition of 50 mL of 1 M aqueous solution of hydrochloric acid, followed by addition of 100 mL of ether. The organic layer was separated, the aqueous one extracted with two portions of 20 mL of ether, and the combined extracts were dried over magnesium sulfate. After rotary evaporation of the solvents, the residual pale yellow oil was purified by chromatography (cyclohexane/ether: 95/5) yielding 10.4 g of (*Z*)-1-iodohex-1-en-3-ol (92% yield) as a pale yellow liquid: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.33 (d, J = 7.69 Hz, 1H, =CHI), 6.20 (t, J = 7.69 Hz, 1H, =CH), 4.40 (m, 1H, CHOH), 1.70 (s, 1H, OH), 1.51–1.31 (m, 4H, CH_2CH_2), 0.90 (t, J = 7.15 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4 (=CH), 82.2 (=CI), 74.4 (CHOH), 35.6, 20.6, 14.0.

(*Z*)-1-Iodo-3-phenylprop-1-en-3-ol. A pale yellow oil (4.94 g, 95%) was obtained after flash chromatography on basic alumina (cyclohexane/ethyl acetate: 95/5) from the reduction of (*Z*)-β-iodo ethyl acrylate (4.52 g, 20 mmol) by 1 equiv of DIBAL (1 M in hexane) and addition of phenylmagnesium bromide (14.45 mL, 24 mmol, 1.66 M) in Et_2O as described above for (*Z*)-1-iodohexen-3-ol: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.3–7.5 (m, 5H, Ar H), 6.45 (m, 2H, HC=CH), 5.55 (m, 1H, CHOH), 2.2 (br. s, 1H, OH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.25, 128.68, 128.04, 126.00 (Ar C), 141.46 (**HC**=), 127.15 (**CI**=), 83.05 (**CHOH**).

(*Z*)-1-Iodoprop-1-en-3-ol. A 100 mL, dry four-necked, round bottomed flask equipped with a mechanical stirrer, an internal thermometer, a rubber septum, and a nitrogen gas inlet was charged with 11.3 g (50 mmol) of (*Z*) β-iodo ethyl acrylate and 100 mL of anhydrous dichloromethane. The stirred solution was cooled to −78 °C by mean of a liquid nitrogen bath, and 100 mL (100 mmol) of a 1 M solution of

diisobutyl aluminium hydride in hexane was added dropwise via a syringe at such a rate that the temperature did not exceed −75 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. The hydrolysis was carried out at −20 °C by dropwise addition of 50 mL of 1 M aqueous solution of hydrochloric acid, followed by addition of 100 mL of ether. The organic layer was separated, the aqueous one extracted with two portions of 20 mL of ether, and the combined extracts were dried over magnesium sulfate. After rotary evaporation of the solvents, the residual pale yellow oil was purified by chromatography (cyclohexane/ether: 90/10) yielding 2.26 g (10 mmol) of the title compound: IR (film) 3400, 2910, 2860, 1610, 1445, 1270, 1040, 1005 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.50 (dt, J = 7.7 Hz, J = 5.6 Hz, 1H, =CH), 6.36 (d, J = 7.7 Hz, 1H, =CHI), 4.25 (m, 2H, CH_2O), 1.60 (t, J = 5.5 Hz, 1H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.0 (=CH), 82.7 (=CI), 65.7 (CH_2OH).

(*Z*)-2-Iodobut-2-en-4-ol. The same procedure as described for the preparation of (*Z*)-1-iodoprop-1-en-3-ol. The title compound (3.28 g, 83%) was obtained from (*Z*) β-iodo-β-methyl methyl acrylate (4.52 g, 20 mmol).^1H NMR ($CDCl_3$, 400 MHz) δ 5.78 (t, J = 4.4 Hz, HC=), 4.17 (m, 2H,CH_2OH), 2.54 (s, 3H, $=CCH_3$), 1.54 (m, 1H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.07 (HC=), 101.38 (=CMe), 66.96 (CH_2OH), 33.44 ($=CCH_3$).

General Procedure for Protection Using Dimethoxymethane. (*Z*)-1-Iodo-3-(methoxymethoxy)-hex-1-ene, 1b. To a stirred solution of (*Z*)-1-iodohex-1-en-3-ol (10.4 g, 46 mmol) in dimethoxymethane (50 mL) were added at room temperature lithium bromide (0.8 g, 9.2 mmol) and then *p*-toluenesulfonic acid (0.8 g, 0.46 mmol), and the resulting mixture was stirred during 12 h. The mixture was hydrolyzed with a saturated sodium chloride solution (50 mL) and extracted with ether. The organic layer was dried with sodium sulfate. The solvent was evaporated, and the product **1b** is purified by column chromatography on silica gel using cyclohexane/ethyl acetate (90/10) given 8.94 g (72%) as a pale yellow liquid: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.42 (d, J = 7.7 Hz, 1H, =C(*H*)I), 6.14 (t, J = 7.7 Hz, 1H, CH=), 4.66 (d, J = 6.6 Hz, 2H, 1H, OCH_2O), 4.55 (d, J = 6.6 Hz, 2H, 1H, OCH_2O), 4.36 (m, 1H, CHOR), 3.39 (s, 3H, OCH_3), 1.7−1.3 (m, 4H, $(CH_2)_2$), 0.95 (t, J = 7.15 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.14 (HC=), 94.4 (OCH_2O), 83.39 (I(*H*)C=), 77.9 (CHOR), 55.48 (OCH_3), 36.45, 18.32, 14.08 (*n*-propyl). Anal. Calcd for $C_8H_{15}IO_2$: C, 35.57; H, 5.60. Found: C, 35.75; H, 5.80.

(*Z*)-1-Iodo-3-(methoxymethoxy)-prop-1-ene, 6. A pale yellow oil was obtained (1.6 g, 81%) from (*Z*)-1-iodoprop-1-en-3-ol (1.6 g, 8.7 mmol), LiBr (0.15 g, 1.74 mmol), and APTS (0.15 g, 0.87 mmol) in dimethoxymethane (50 mL), after the usual workup as described for **1b**: ^1H NMR ($CDCl_3$, 200 MHz) δ 6.45 (m, 2H, HC=CH), 4.65 (s, 2H, OCH_2O), 4.15 (d, J = 4.3 Hz, 2H, $=CCH_2O$), 3.40 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.92 (CH=), 96.18 (OCH_2O), 83.25 (=CHI), 70.17 (CH_2-OR), 55.43 (OCH_3).

(*Z*)-1-Iodo-3-phenylprop-1-en-3-ol, 11. To a solution of (*Z*)-1-iodo-3-phenylprop-1-en-3-ol (3.44 g, 13.23 mmol) in Et_2O (20 mL) was added at 0 °C ethylmagnesium bromide (52 mL, 14.56 mmol, 0.28 N in ether), and the mixture was stirred for 30 min at room temperature. Methoxymethyl bromide (2.48 g, 19.84 mmol, 1.5 equiv) was then added, and the solution was stirred 1 h at this temperature. The mixture was hydrolyzed with hydrochoric acid, and sodium hydroxide was added until pH = 14. The aqueous layer was separated and extracted twice more with ether (20 mL); the organic layers were combined and dried over $MgSO_4$. Purification very quickly by flash chromatography (cyclohexane/ethyl acetate: 98/2) afforded the product **11** (3.34 g, 83%). The product was stored as an ethereal solution: ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.45 (m, 5H, Ar H), 6.50 (d, J = 7.70 Hz, 1H, =CHI), 6.43 (dd, J = 8.25 Hz, J = 7.70 Hz, 1H, HC=), 5.46 (d, J = 8.25 Hz, 1H, CHOR), 4.70 and 4.50 (dd, AB syst, J = 6.60 Hz, 2H, OCH_2O), 3.20 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 140.96, 128.61, 128.03, 126.73 (Ar C), 139.48 (HC=), 93.85 (OCH_2O), 83.88 (=CHI), 79.17 (CHOR), 55.70 (OCH_3).

2(*Z*)-Iodo-4-(methoxymethoxy)-but-2-ene, 19. The same procedure as described for the protection of **1b** was utilized. The compound **19** (2.67 g, 67%) was obtained from the preceding alcohol (3.28 g, 16.56 mmol): ^1H NMR ($CDCl_3$, 200 MHz) δ 5.57 (m, 1H, HC=), 4.65 (s, 2H, OCH_2O), 4.10 (m, 2H, CH_2OR), 3.41 (s, 3H, OCH_3), 2.67 (s, 3H, $=CCH_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 131.94 (HC=), 102.68 (=CMe), 96.06 (OCH_2O), 71.85 (CH_2OR), 55.37 (OCH_3), 33.72 ($=CCH_3$). Anal. Calcd for $C_6H_{11}IO_2$: C, 29.77; H, 4.58. Found: C, 29.79; H, 4.59.

Typical Procedure for Carbometalation. (4(*S),5(*S**)) 5-(Methoxymethoxy)-4-methyloct-1-ene, 3b.** To a solution of (*Z*)-1-iodo-3-(methoxymethoxy)-hex-1-ene (**1b**) (594 mg, 2.2 mmol) in Et_2O (30 mL) was added, at −78 °C, 2 equiv of *t*-BuLi (1.6 M solution in hexane, 2.8 mL, 4.4 mmol). This solution was warmed to −65 °C for 10 min to complete the lithium−iodine exchange, and then, at −65 °C, 2 equiv of allylmagnesium bromide was added (1 M solution in Et_2O, 4.4 mL, 4.4 mmol) followed by 2 equiv of $ZnBr_2$ in Et_2O at −40 °C (1 M solution in Et_2O, 4.4 mL, 4.4 mmol). The reaction mixture was stirred at −20 °C for 5 h. The hydrolysis was carried out with an aqueous solution of hydrochloric acid (1 N solution, 20 mL). The aqueous phase was extracted twice with ether (2 × 20 mL), and the combined organic phases were washed with 1 N HCl (2 × 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, washed with $NaHCO_3$ (2 × 20 mL), and then dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on SiO_2 (cyclohexane/ether: 95/5) to give **3b** as a pale yellow liquid: 78% (319 mg); IR (film) 3060, 2900, 1640, 1460, 1375, 1150−1030; ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.05 Hz, J = 9.34 Hz, J = 7.15 Hz, 1H, CH=), 5.00 (m, 2H, CH_2=), 4.65 (s, 2H, OCH_2O), 3.43 (m, 1H, CHOR), 3.38 (s, 3H, OCH_3), 2.30 (m, 1H, =CCH), 1.90 (m, 1H, =CCH), 1.70 (m, 1H, CH-Me), 1.20−1.50 (m, 4H, $(CH_2)_2$), 0.95 (t, J = 7.15 Hz, 3H, $-(CH_2)_2CH_3$), 0.87 (d, J = 6.6 Hz, 3H, $CHCH_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.88 (HC=), 115.68 (H_2C=), 96.21 (OCH_2O), 81.24 (CHOR), 55.56 (OCH_3), 37.04 (CH_2-C=C), 36.06, 33.33 ($(CH_2)_2$), 19.20 (CH), 14.47, 14.26 (2 × CH_3); Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 71.05; H, 12.01.

Typical Procedure for Cyclopropanation. 1(*S)-(Prop-2-enyl)-2(*S**)-propylcyclopropane, 5.** To a solution of (Z)-1-iodo-3-(methoxymethoxy)hex-1-ene (**1b**) (1.35 g, 5 mmol) in Et_2O (30 mL) were added, at −78 °C, 2 equiv of *t*-BuLi (1.6 M solution in hexane, 6.25 mL, 10 mmol). This solution was warmed to −65 °C for 10 min to complete the lithium−iodine exchange, and then, at −65 °C, 2 equiv of allylmagnesium bromide were added (1 M solution in Et_2O, 10 mL, 10 mmol) followed by 2 equiv of $ZnBr_2$ in Et_2O at −40 °C (1 M solution in Et_2O, 10 mL, 10 mmol). The reaction mixture was stirred at −20 °C for 5 h and was then allowed to warm to room temperature. After one night, the reaction was worked up as described above for the preparation of **3b**, and purification by flash chromatography afforded the product **5** (434 mg, 70%) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddt, J = 17.15 Hz, J = 10.25 Hz, J = 7.15 Hz, 1H, CH=), 5.00 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.25 Hz, J_{gem} = 1.62 Hz, 2H, CH_2=), 2.15 (m, 2H, CH_2C=), 1.40 (m, 4H, $(CH_2)_2$), 0.70−0.80 (m, 2H, CH_2), 0.55−0.60 (dd, J = 4.4 Hz, J = 3.75 Hz, 1H, CH), −0.30 (dd, J = 5.50 Hz, J = 4.40 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.20 (HC=), 114.50 ($=CH_2$), 34.40 (CH_2C=), 28.70, 22.70 ($(CH_2)_2$), 15.78, 15.31, 10.92, ($C_{cyclopr}$), 14.14 (CH_3).

***Trans*-1,2-Di-(2-propenyl)cyclopropane, 8.** To a suspension of CuCN (394 mg, 4.4 mmol) in THF was added, at −20 °C ,MeLi (4.63 mL, 8.8 mmol, 1.9 N), and the reaction was stirred until the suspension disappeared (20 min). Then, this solution was transferred via syringe at −30 °C to the solution of cyclopropyl metal **4** prepared as described above by the tandem "carbometalation−cyclopropanation" reaction of **6** (594 mg, 2.2 mmol). The reaction mixture was stirred 1 h at −30 °C and then was warmed to 0 °C during 10 min. The reaction was cooled back to −30 °C, and 2 equiv of allyl iodide were added (739 mg, 4.4 mmol). This reaction mixture was allowed to warm to 0 °C, stirred at this temperature for 1 h, and then was hydrolyzed with aqueous NH_3/NH_4Cl (1/3:2/3). The aqueous layer was extracted with ether, and the combined organic layers were dried over $MgSO_4$. After purification by flash chromatography (eluent, pentane), the desired product **8** (147 mg, 55%) was isolated as a liquid: ^1H NMR ($CDCl_3$,

400 MHz) δ 5.85 (ddt, J = 17.05 Hz, J = 10.45 Hz, J = 6.60 Hz, 2H, HC=), 5.05 (ddd, J_{trans} = 17.05 Hz, J_{cis} = 10.45 Hz, J_{gem} = 1.70 Hz, 4H, H_2C=), 1.97 (m, 4H, CH_2C=), 0.55 (dd, J = 6.60 Hz, J = 5.50 Hz, 2H, $CH_{cycloprop}$), 0.28 (dd, J = 6.60 Hz, J = 5.50 Hz, 2H, $CH_{2cycloprop}$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 140.20 (HC=), 114.70 (=CH_2), 35.10 (CH_2C=), 15.78, 11.05, ($C_{cyclopr}$).

1(S*)-Iodo-2(S*)-(2-propenyl)-3((R*))-propylcyclopropane, 9. After the tandem "carbometalation–cyclopropanation" reaction of **1b** (594 mg, 2.2 mmol), the cyclopropyl metal **4** was cooled back to −20 °C, and a solution of iodine (1.12 g, 4.4 mmol) in THF (5 mL) was added. The reaction mixture was warmed to room temperature, stirred 10 min, and then hydrolyzed with HCl (1 N). The two layers were separated, and the aqueous layer was extracted with ether (2 × 50 mL). The organic layers were combined and washed with sodium thiosulfate. The organic layer was separated and dried over $MgSO_4$. After purification by flash chromatography (cyclohexane/ethyl acetate: 98/2) on silica gel, the title product **9** (357 mg, 65%) was obtained: ^1H NMR (C_6D_6, 400 MHz) δ 5.80 (ddt, J = 17.05 Hz, J = 9.90 Hz, J = 6.05 Hz, 1H, HC=), 5.05 (ddd, J_{trans} = 17.05 Hz, J_{cis} = 9.9 Hz, J_{gem} = 1.6 Hz, H_2C=), 1.80 (m, 2H, CH_2C=), 1.60 (m, 1H, CHI), 1.25 (m, 2H, CH_3-CH_2), 1.00–1.20 (m, 2H, 2 × $H_{cyclopr}$), 1.10 to 0.90 (m, 2H, CH_2), 0.90 (m, 3H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz) δ 136.87 (HC=), 115.31 (H_2C=),31.91 (CH_2C=), 30.01, 22.57, 14.08 (C_{propyl}), 28.09, 26.81 ($CH_{cyclopr}$), −9.0 (CHI).

1(S*)-[2(E)-Carbethoxyvinyl]-2(S*)-(2-propenyl)-3(R*)-propylcyclopropane, 10. To a suspension of CuCN (394 mg, 4.4 mmol) in THF was added, at −20 °C, MeLi (4.63 mL, 8.8 mmol, 1.9 N), and the reaction was stirred until the suspension disappeared (20 min). The resulting solution was transferred via syringe at −30 °C to the solution of cyclopropyl metal **4** prepared as described above by the tandem "carbometalation–cyclopropanation" reaction of **1b** (594 mg, 2.2 mmol). The reaction mixture was stirred 1 h at −30 °C, and then was warmed to 0 °C during 10 min. The reaction was cooled back to −30 °C and methyl propiolate was added. This reaction mixture was allowed to warm to 0 °C, stirred at this temperature for 1 h, and then hydrolyzed with NH_3/NH_4Cl (1/3: 2/3). The aqueous layer was extracted with ether, and the combined organic layers were dried over $MgSO_4$. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **10** was obtained (351 mg, 72%) as a oil: ^1H NMR ($CDCl_3$) δ 6.56 (dd, J = 15.41 Hz, J = 9.90 Hz, 1H, CH=CCO), 5.85 (ddt, J = 17.15 Hz, J = 10.26 Hz, J = 6.11 Hz, 1H, HC=), 5.81 (d, J = 15.41 Hz, 1H, =CHCO), 5.05 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.26 Hz, J_{gem} = 1.70 Hz, 2H, H_2C=), 4.17 (q, J = 7.14 Hz, 2H, OCH_2), 2.25–2.05 (m, 2H, CH_2), 1.55–1.40 (m, 4H, $(CH_2)_2$), 1.27 (t, J = 7.14 Hz, 3H, OCH_2CH_3), 1.25 (m, 1H, $CH_{cycloprop}$-$(CH_2)_2$), 1.17 (m, 1H, $CH_{cycloprop}$-allyl), 1.06 (dt, J = 9.90 Hz, J = 4.50 Hz, 1H, $CH_{cycloprop}C$=), 0.91 (t, J = 7.27 Hz, 3H, CH_3); ^{13}C NMR δ 166.95 (CO_2), 153.78 (CH=CCO), 137.28 (HC=), 117.24 (=CHCO), 114.94 (=CH_2), 59.96 (OCH_2), 31.76 (CH_2C=), 29.86, 22.78 ($(CH_2)_2$), 14.38 (OCH_2CH_3), 13.95 (CH_3), 28.73, 28.05, 26.88 ($C_{cycloprop}$).

1(R*)-Iodo-2(S*)-phenyl-3-(2-propenyl)cyclopropane, 12. The same procedure as described for **9** was utilized. The cyclopropyl metal obtained from the tandem "carbometalation–cyclopropanation" reaction of **11** (608 mg, 2 mmol) was treated with a solution of iodine (762 mg, 3 mmol) in THF (5 mL) at −20 °C. After usual workup, the residual oil was purified by flash chromatography (cyclohexane/ethyl acetate: 95/5) affording **12** (386 mg, 68%): ^1H NMR ($CDCl_3$, 200 MHz) δ 7.50–7.00 (m, 5H, Ar, H), 5.65 (m, 1H, HC=), 4.95 (m, 2H, =CH_2), 2.60 (t, J = 4.80 Hz, 1H, $ICH_{cycloprop}$), 2.60 (dd, J = 9.80 Hz, J = 4.80 Hz, 1H, $PhCH_{cyclprop}$), 1.80 (m, 2H, CH_2C=), 1.65 (m, 1H, $CH_{cycloprop}$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 136.38, 128.78, 128.47, 127.2, 126.63 (Ar C), 135.96 (HC=), 115.60 (CH_2=), 77.25, 32.97, 31.94, 29.86.

3(Z)-Iodo-3-(trimethylsilyl)-2-propen-1-ol. A three-necked flask equipped with a thermometer, mechanical stirring, addition funnel, and nitrogen inlet was charged with 3-(trimethylsilyl)prop-2-yn-1-ol (3.84 g, 30 mmol) and Et_2O (60 mL). A solution of Red-Al (8.57 mL, 30 mmol, 3.5 M in toluene) was added at 0 °C. The reaction was stirred 1 h at this temperature and then allowed to warm to room temperature. After 30 min, the reaction mixture was cooled back to −20 °C, and iodine was added (11.43 g, 45 mmol). The solution was warmed to room temperature and stirred for 30 min. The mixture was cooled to 0 °C and then quenched by the addition of an aqueous solution of sodium potassium tartrate. It was then filtered through a pad of Celite and extracted with ether (2 × 30 mL). The organic layers were combined and dried over $MgSO_4$. The solvents were then removed; the residual brown oil was distilled (50–60 °C/15 mmHg) yielding 5.68 g (74%) of the desired compound: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.50 (m, 1H, HC=), 4.27 (m, 2H, CH_2OH), 1.63 (m, 1H, OH), 0.19 (s, 9H, Me_3Si); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.97 (HC=), 113.58 (=CI), 70.80 (CH_2OH), 0.0 (Me_3Si).

1(Z)-Iodo-1-(trimethylsilyl)-1-hexen-3-ol. The same procedure as described for the preparation of 3(Z)-iodo-3-(trimethylsilyl)-2-propen-1-ol previously described but from 1-(trimethylsilyl)-1-hexyn-3-ol was utilized. Distillation (80–90 °C/15 mmHg) afforded the title compound (6.35 g, 72%): ^1H NMR ($CDCl_3$, 200 MHz) δ 6.20 (d, J = 7.30 Hz, 1H, HC=), 4.45 (m, 1H, CHOH), 1.81 (s, 1H, OH), 1.6–1.4 (m, 4H, $(CH_2)_2$), 0.95 (t, J = 7.15 Hz, 3H, CH_3), 0.19 (s, 9H, Me_3Si); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 149.55 (HC=), 97.58 (=CI), 74.20 (CHOH), 38.50, 20.60, 13.95 (C_{propyl}), 0.00 (Me_3Si).

3(Z)-Iodo-1-(methoxymethoxy)-3-(trimethylsilyl)-2-propene, 17. The same procedure as described for **1b** was utilized. The title compound **17** (4.66 g, 70%) was obtained from 3(Z)-iodo-3-(trimethylsilyl)-2-propen-1-ol (5.68 g, 22.2 mmol): ^1H NMR ($CDCl_3$, 200 MHz) δ 6.50 (t, J = 4.75 Hz, 1H, HC=), 4.68 (s, 2H, OCH_2O), 4.19 (d, J = 4.75 Hz, 2H, CHOR), 3.40 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 144.41 (HC=), 112.75 (CI=), 96.37, (OCH_2O), 74.28 (CHOR), 55.42 (OCH_3).

1(Z)-Iodo-3-(methoxymethoxy)-1-(trimethylsilyl)-1-hexene, 13. The same procedure as described for **1b** was utilized. The title compound **13** (5.17 g, 71%) was obtained from 1(Z)-iodo-1-(trimethylsilyl)-1-hexen-3-ol (6.35 g, 21.3 mmol): ^1H NMR ($CDCl_3$, 200 MHz) δ 6.10 (d, J = 7.30 Hz, 1H, HC=), 4.64 (d, J = 6.95 Hz, 1H, OCH_2O), 4.48 (d, J = 6.95 Hz, 1H, OCH_2O), 4.45 (m, 1H, CHOR), 3.40 (s, 3H, OCH_3), 1.70–1.30 (m, 4H, $(CH_2)_2$), 0.95 (t, J = 7.15 Hz, 3H, CH_3), 0.19 (s, 9H, Me_3Si); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.92 (HC=), 114.12 (CI=), 94.76 (OCH_2O), 81.69 (CHOR), 55.42 (OCH_3), 36.24, 18.42, 14.11 (C_{propyl}). Anal. Calcd for $C_{11}H_{23}IO_2Si$: C, 38.60; H, 6.77. Found: C, 38.65; H, 6.82.

1(S*)-(Trimethylsilyl)-2(S*)-(2-propenyl)cyclopropane, 18. The same procedure as described for **5** was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 98/2), **18** (194 mg, 63%) was obtained from **17** (600 mg, 2 mmol): ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddt, J = 17.15 Hz, J = 10.25 Hz, J = 7.15 Hz, 1H, CH=), 5.00 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.25 Hz, J_{gem} = 1.62 Hz, 2H, CH_2=), 2.15–1.95 (m, 2H, CH_2C=), 0.70 (m, 1H, $CH_2CH_{cycloprop}$), 0.45 (ddd, J_{cis} = 7.1 Hz, J_{trans} = 6.60 Hz, J_{gem} = 3.60 Hz, 1H, $CH_{2cycloprop}$ same side of silicium), 0.37 (ddd, J_{cis} = 10.00 Hz, J_{trans} = 4.20 Hz, J_{gem} = 3.60 Hz, 1H, $CH_{2cycloprop}$ same side as propenyl), −0.62 (dt, J_{cis} = 10.00 Hz, J_{trans} = 6.60 Hz, 1H, Me_3-$SiCH_{cycloprop}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.40 (HC=), 114.41 (=CH_2), 39.90 (CH_2C=), 14.81 ($CH_2CH_{cycloprop}$), 8.59 ($CH_{2cycloprop}$), 4.28 ($SiCH_{cycloprop}$), −2.23 (Me_3Si).

1(S*)-(Trimethylsilyl)-2(S*)-(2-propenyl)-3(R*)-propylcyclopropane, 16. The same procedure as described for **5** was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 98/2), **16** (239 mg, 61%) was obtained from **13** (684 mg, 2 mmol): ^1H NMR (200 MHz, $CDCl_3$) δ 5.85 (m, 1H, HC=), 5.00 (m, 2H, =CH_2), 2.30–1.90 (m, 2H, CH_2C=), 1.70–1.00 (m, 6H, $(CH_2)_2$-, 2 × $CH_{cycloprop}$), 0.95 (t, J = 7.15 Hz, 3H, CH_3), 0.50 (m, 1H, $CH_{cycloprop}$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 139.25 (HC=), 115.65 (=CH_2), 39.90 (CH_2C=), 29.85, 20.55, 13.95 (C_{propyl}), 14.81 ($CH_2CH_{cycloprop}$), 8.75 ($CH_{2cycloprop}$), 5.02 ($SiCH_{cycloprop}$). Anal. Calcd for $C_{12}H_{24}$-Si: C, 73.38; H, 12.31. Found: C, 73.39; H, 12.33.

1(R*)-[2(E)-Carbomethoxyvinyl]-1-methyl-2(R*)-(2-propenyl)cyclopropane, 21. To a solution of (Z)-2-iodo-4-(methoxymethoxy)-but-2-ene (**19**) (482 mg, 2 mmol) in Et_2O (30 mL) was added, at −78 °C, 2 equiv of t-BuLi (1.6 M solution

in hexane, 2.6 mL, 4 mmol). This solution was warmed to −65 °C for 10 min to complete the lithium−iodine exchange, and then, at −65 °C, 2 equiv of allylmagnesium bromide was added (1 M solution in Et_2O, 4 mL, 4 mmol) followed by 2 equiv of $ZnBr_2$ in Et_2O at −40 °C (1 M solution in Et_2O, 4 mL, 4 mmol). The reaction mixture was stirred at −20 °C for 5 h. The solution was then allowed to warm to room temperature. After one night a solution of cuprate, prepared by the reaction of CuCN (358 mg, 4 mmol) and MeLi (4.18 mL, 8 mmol, 1.9 N) in THF (20 mL), was added at −30 °C as described for the synthesis of **10**. The reaction mixture was stirred 1 h at −30 °C and then was warmed to 0 °C during 10 min. The reaction was cooled back to −30 °C and methyl propiolate was added. This reaction mixture was allowed to warm to 0 °C and stirred at this temperature for 1 h. The reaction was hydrolyzed with NH_3/NH_4Cl. The aqueous phase was extracted twice with ether (2 × 20 mL), and the combined organic phases were washed with 1 N HCl (2 × 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, washed with $NaHCO_3$ (2 × 20 mL), and then dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (eluent, cyclohexane/ethyl acetate: 98/2) afforded the pure product **21** (223 mg, 62%) as an oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 6.81 (d, J_{trans} = 15.60 Hz, 1H, HC=), 5.93−5.71 (m, 1H, HC=), 5.83 (d, J_{trans} = 15.60 Hz, 1H, HC=), 5.00 (m, 2H, $=CH_2$), 3.72 (s, 3H, CO_2CH_3), 2.2 (m, 2H, $=CCH_2$), 1.23 (s, 3H, CH_3), 1.15 (m, 1H, $CH_2CH_{cycloprop}$), 0.97 (dd, J_{cis} = 8.11 Hz, J_{gem} = 4.52 Hz, 1H, $CH_{cycloprop}$ same side as C=C CO_2Me), 0.75 (dd, J_{trans} = 5.01 Hz, J_{gem} = 4.52 Hz, 1H, $CH_{cycloprop}$ same side as methyl); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 167.30 (CO_2Me), 154.44 (HC=), 137.16 (HC=), 117.96 (HC=), 114.92 (HC=), 51.34 (CO_2CH_3), 33.75 ($=CCH_2$), 30.17, 29.12 ($CH_{cycloprop}$), 22.41 (C_{quat}), 22.24 (CH_3). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.3; H, 8.95. Found: C, 73.21; H, 9.07.

2-Bromooct-1-en-4-ol. To a suspension of tin powder (7.12 g, 60 mmol) and 2,3-dibromopropene (24 g, 120 mmol) in an ether−water (each 20 mL) mixture were added a few drops of a 1 M HBr solution and pentanal (3.44 g, 40 mmol). The mixture was stirred at 20 °C overnight, then filtered through Celite, and extracted with 3 × 20 mL of Et_2O. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel (cyclohexane/ethyl acetate: 90/10) to give the corresponding alcohol (7.37 g, 89%): ^1H NMR ($CDCl_3$, 400 MHz) δ 5.68 (br s, 1H, =CH), 5.52 (d, J =1.65 Hz, 1H, =CH), 3.95 (m, 1H, CHOH), 2.55 (dd, J = 14.3 Hz, J = 3.85 Hz, 1H, =CCH) 2.48 (dd, J =14.3 Hz, J = 8.24 Hz, 1H, =CCH), 1.65 (d, J = 3.85 Hz, 1H, -OH), 1.5−1.35 (m, 6H, $(CH_2)_3$), 0.9 (t, J = 7.15 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 130.75 (=C(Br)), 119.15 (H_2C=), 68.8 (CH(OH)), 49.17 (=C(Br)CH_2), 35.89, 27.57, 22.46, 13.87 (nBu) Anal. Calcd for $C_8H_{15}BrO$: C, 43.06; H, 6.77. Found: C, 43.15; H, 6.75.

2-Bromo-5-methylhex-1-en-4-ol. The same procedure as described for 2-bromooct-1-en-4-ol using isobutyraldehyde (1.44 g, 20 mmol) was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10) the title compound (3.47 g, 90%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 5.57 (br s, 1H, =CH), 5.55 (d, J = 1.65 Hz, 1H,=CH), 3.70 (ddd, J = 8.8 Hz, J = 5.3 Hz, J = 3.5 Hz, 1H, CHOH), 2.55 (dd, J = 14.3 Hz, J = 3.5 Hz, 1H, =CCH), 2.48 (dd, J = 14.3 Hz, J = 8.8 Hz, 1H, =CCH), 1.8 (qd, J = 6.8 Hz, J = 5.3 Hz, 1H, $CH(CH_3)_2$), 1.7 (s, 1H, OH), 0.96 (d 3H, J = 6.8 Hz, 3H, $(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.66 (=C(Br)), 119.52 (H_2C=), 73.8 (CH(OH)), 46.68 ($=CCH_2$), 33.12 ($CH(CH_3)_2$), 18.8 ($(CH_3)_2$) Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 43.43; H, 6.93.

2-Bromo-4-phenylprop-1-en-4-ol. The same procedure as described for 2-bromooct-1-en-4-ol using benzaldehyde (2.12 g, 20 mmol) was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10) the corresponding alcohol (4.26 g, 90%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38 (Ar. H), 5.68 (br s, 1H, =CH), 5.54 (d, J = 1.65 Hz, 1H,=CH), 5.04 (dd, J = 8.8 Hz, J = 4.4 Hz, 1H, CHOH), 2.85 (dd, J = 14.3 Hz, J = 8.8 Hz, 1H, =CCH), 2.75 (dd, J = 14.3 Hz, J = 4.4 Hz, 1H, =CCH), 2.05 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.21, 128.3, 127.64, 125.7 (Ar C), 129.81 (=C(Br)), 119.77 (H_2C=), 71.42 (CH(OH)), 50.86 ($=CCH_2$). Anal. Calcd for $C_{10}H_{11}BrO$: C, 52.88; H, 4.88. Found: C, 52.73; H, 4.99.

2-Bromo-2,5-heptadien-4-ol. The same procedure as described for 2-bromooct-1-en-4-ol using 2-butenal (1.4 g, 20 mmol) was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), the corresponding alcohol (3.13 g, 82%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.8 (dd, J = 15.28 Hz, J = 6.4 Hz, 1H, CH=), 5.7 (br s, 1H, HC=CBr), 5.56−5.44 (m, 1H, CH=), 5.52 (d, J = 1.42 Hz, 1H, CH=), 4.4 (m, 1H, CH-OH), 2.6 (m, 2H, $=CCH_2$), 1.74 (s, 1H, OH), 1.72 (d, J = 6.28 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 132.34 (=CCH(OH)), 130.36 (=C-(Br)), 127.98 (MeC=), 119.8 (H_2C=), 70.35 (CH(OH)), 49.46 ($=CCH_2$), 17.85 ($=CCH_3$). Anal. Calcd for $C_7H_{11}BrO$: C, 44,-83; H, 5.87. Found: C, 45.91; H, 6.16.

5-Bromo-1-(trimethylsilyl)hex-5-en-1-yn-3-ol. The same procedure as described for 2-bromooct-1-en-4-ol using 3-(trimethylsilyl)propynal (2.52 g, 20 mmol) was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), the corresponding alcohol (3.70 g, 75%) was obtained as a pale yellow oil: IR (film): 3600−3200, 3850, 1630, 1400, 1250, 1100, 840 (cm^{-1}); ^1H NMR ($CDCl_3$, 200 MHz) δ 5.75 (br s, 1H, HC=CBr), 5.56 (d, J = 1.71 Hz, 1H, CH=), 4.67 (dd, J = 8.08 Hz, J = 5.9 Hz, 1H, CH(OH)), 2.85 (dd, J = 14.50 Hz, J = 8.08 Hz, 1H, =CCH), 2.76 (dd, J = 14.50 Hz, J = 5.90 Hz, 1H, =CCH), 2.1 (s, 1H, OH), 0.17 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 128.48 (=C(Br)), 120.62 (H_2C=), 104.97, 90.80 (quaternary C), 60.92 (CH(OH)), 49.70 (=C(Br)-CH_2), 0 ($SiMe_3$). Anal. Calcd for $C_9H_{15}BrOSi$: C, 43.72; H, 6.11. Found: C, 43.75; H, 6.12.

2-Bromo-1,6-heptadien-4-ol. To a solution of dimethylformamide (1.46 g, 20 mmol) in ether (20 mL) at −60 °C was added 1.2 equiv of allylmagnesium bromide (24 mL, 24 mmol, 1 N in ether). The reaction mixture was warmed to 0 °C and stirred 2 h at this temperature. Then, the reaction was cooled back to −60 °C and hydrolyzed with hydrochloric acid (1 N). The organic layer was separated and the aqueous layer was extracted with ether (2 × 20 mL). The organic layers were combined and dried over $MgSO_4$. The resulting 3-butenal (1.4 g, 20mmol) was converted to the title compound by reaction with 2,3-dibromopropene according to the experimental procedure described for 2-bromooct-1-en-4-ol. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10) the corresponding alcohol (2.83 g, 75%) was isolated (1.4 g, 20 mmol). ^1H NMR ($CDCl_3$, 400 MHz) δ 5.86 (ddt, J = 14.30 Hz, J = 9.90 Hz, J = 7.15 Hz, 1H, =CH), 5.70 (br s, 1H, HC=CBr), 5.54 (d, J = 1.65 Hz, 1H, CH=), 5.16 (ddd, J = 14.30 Hz, J = 9.90 Hz, J = 1.65 Hz, 2H, $=CH_2$), 4.01 (m, 1H, CHOH), 2.56 (m, 2H, $=CCH_2$), 2.37−2.20 (m, 2H, CH_2C=), 1.82 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 134.08 (HC=), 130.48 (=C(Br)), 119.64 (H_2C=), 118.47 (CH_2=), 68.14 (CHOH), 48.53 ($=CCH_2$), 40.76 (CH_2C=). Anal. Calcd for $C_7H_{11}BrO$: C, 44.00; H, 5.80. Found: C, 44.25; H, 5.85.

2-Bromo-4-(4-fluorophenyl)but-1-en-4-ol. The same procedure as described for 2-bromooct-1-en-4-ol using p-fluorobenzaldehyde (2.48 g, 20 mmol) was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), the corresponding alcohol (4.85 g, 99%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.4−7.0 (m, 4H, Ar H), 5.65 (br s, 1H, CH=), 5.53 (d, J = 1.65 Hz, 1H, CH=), 5.01 (m, 1H, CHOH), 2.81 (dd, J = 14.25 Hz, J = 8.8 Hz, 1H, $=CCH_2$), 2.71 (dd, J = 14.25 Hz, J = 4.85 Hz, 1H, $=CCH_2$), 2.17 (d, J = 2.97 Hz, 1H, OH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.68 (CF), 159.9, 138.59, 127.61, 115.6, 115.16 (Ar C), 129.8 (=C(Br)), 121.19 (H_2C=), 71.04 (CHOH), 51.14 ($=CCH_2$). Anal. Calcd for $C_{10}H_{10}BrFO$: C, 49.00; H, 4.11. Found: C, 49.05; H, 4.15.

2-Bromo-4-(pentafluorophenyl)but-1-en-4-ol. The same procedure as described for 2-bromooct-1-en-4-ol using pentafluorobenzaldehyde (3.92 g, 20 mmol) was utilized. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), the corresponding alcohol (5.05 g, 80%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.73 (br s, 1H, CH=), 5.53 (br s, 1H, CH=), 5.45 (dd, J = 8.22 Hz, J = 6.05, 1H, CHOH), 3.17 (dd, J = 14.25 Hz, J = 8.22

Hz, 1H, =CCH$_2$), 2.91 (dd, J = 14.25 Hz, J = 6.05 Hz, 1H, =CCH$_2$), 2.04 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 127.90 (=C(Br)), 120.78 (H_2C=), 64.03 (CHOH), 47.90(=CCH$_2$). Anal. Calcd for $C_{10}H_8BrF_5O$: C, 37.64; H, 2.52. Found: C, 37.65; H, 2.52.

2-Bromo-4-(methoxymethoxy)-oct-1-ene, 22. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), **22** (8.22 g, 92%) was obtained from the corresponding alcohol (7.37 g, 35.6 mmol) following the procedure described for **1b**: IR (film) 2920, 1630, 1140, 1100, 1040 (cm^{-1}), ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.66 (br s, 1H, =CH), 5.47 (d, J = 1.65 Hz, 1H, =CH), 4.69 (d, J = 6.6 Hz, 1H, OCH$_2$O), 4.67 (d, J = 6.6 Hz, 1H, OCH$_2$O), 3.95 (m, 1H, CHOMOM), 3.40 (s, 3H, OCH$_3$), 2.67 (dd, J = 14.3 Hz, J = 8.24 Hz, 1H, =CCH$_2$), 2.52 (dd, J = 14.3 Hz, J = 3.85 Hz, 1H, =CCH$_2$), 1.53–1.2 (m, 6H, (CH$_2$)$_3$), 0.9 (t, J = 7.15 Hz, 3H, CH$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 130.90 (=C(Br)), 118.61 (H_2C=), 95.55 (OCH$_2$O), 74.87 (CHOR), 55.25 (OCH$_3$), 46.82 (=CCH$_2$), 33.6, 27.03, 22.54, 13.81 (nBu). Anal. Calcd for $C_{10}H_{19}BrO_2$: C, 47.82; H, 7.62. Found: C, 47.82; H, 7.64.

2-Bromo-4-(methoxymethoxy)-5-methylhex-1-ene, 29. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **29** (3.19 g, 90%) was obtained from the corresponding alcohol (3.47 g, 17.98 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.68 (br s, 1H, =CH), 5.47 (d, J = 1.10 Hz, 1H, =CH), 4.69 (d, J = 6.6 Hz, 1H, OCH$_2$O), 4.65 (d, J = 6.6 Hz, 1H, OCH$_2$O), 3.75 (dd, J = 8.8 Hz, J = 3.5 Hz, 1H, CHOR), 3.38 (s, 3H, OCH$_3$), 2.61 (dd, J = 14.1 Hz, J = 8.8 Hz, 1H, =CCH$_2$), 2.51 (dd, J = 14.1 Hz, J = 3.5 Hz, 1H, =CCH$_2$), 1.90 (m, 1H, CH(CH$_3$)$_2$), 0.95 (d, J = 7.15 Hz, 3H, CH$_3$), 0.91 (t, J = 7.15 Hz, 3H, CH$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.64 (=C(Br)), 118.86 (H_2C=), 96.3 (OCH$_2$O), 79.61 (CHOMOM), 55.60 (OCH$_3$), 43.42 (=CCH$_2$), 30.8 (CH(CH$_3$)$_2$), 17.85 (CH$_3$), 17.3 (CH$_3$). Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.58; H, 7.22. Found: C, 45.60; H, 7.23.

2-Bromo-4-(methoxymethoxy)-4-phenylprop-1-ene, 37. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **37** (4.47 g, 88%) was obtained from the corresponding alcohol (4.26 g, 18.76 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.4–7.3 (Ar. H), 5.63 (br s, 1H, =CH), 5.47 (d, J = 1.65 Hz, 1H, =CH), 4.95 (dd, J = 8.8 Hz, J = 4.7 Hz, 1H, CHOR), 4.55 (s, 2H, OCH$_2$O), 3.37 (s, 3H, OCH$_3$), 2.90 (dd, J = 14.3 Hz, J = 8.8 Hz, 1H, =CCH$_2$), 2.71 (dd, J = 14.3 Hz, J = 4.7 Hz, 1H, =CCH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 141.06, 130.88, 128.19, 127.12 (Ar C), 128.72 (=C(Br)), 119.60 (H_2C=), 94.67 (OCH$_2$O), 75.86 (CHOR), 55.92 (OCH$_3$), 50.33 (=CCH$_2$). Anal. Calcd for $C_{12}H_{15}BrO_2$: C, 53.15; H, 5.57. Found: C, 53.14; H, 5.58.

2-Bromo-4-(methoxymethoxy)-2,5-heptadiene, 41. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **41** (3.27 g, 85%) was obtained from the corresponding alcohol (3.13 g, 16.38 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.8 (dd, 1H, J = 15.34 Hz, J = 6.5 Hz, CH=), 5.66 (br s, 1H, HC=CBr), 5.47 (d, J = 1.47 Hz, 1H, CH=), 5.30 (qd, J = 15.34, J = 8.10 Hz, 1H, CH=), 4.72 (d, J = 6.6 Hz, 1H, OCH$_2$O), 4.51 (d, J = 6.6 Hz, 1H, OCH$_2$O), 4.3 (dd, J = 8.10 Hz, J = 6.50 Hz, 1H, CHOR), 3.37 (s, 3H, OCH$_3$), 2.73 (dd, J = 14.48 Hz, J = 8.10 Hz, 1H, =CCH$_2$), 2.54 (dd, J = 14.48 Hz, J = 6.50 Hz, 1H, =CCH$_2$), 1.7 (d, 3H, CH$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 131.5 (=CH), 130.13 (=C(Br)), 129.88 (MeC=), 119.06 (H_2C=), 93.48 (OCH$_2$O), 74.20 (CHOH), 55.50 (OCH$_3$), 47.75 (=CCH$_2$), 17.68 (=CCH$_3$). Anal. Calcd for $C_9H_{15}BrO_2$: C, 39.83; H, 7.16. Found: C, 39.85; H, 7.15.

5-Bromo-1-(trimethylsilyl)-3-(methoxymethoxy)hex-5-en-1-yne, 42. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **42** (3.66 g, 84%) was obtained from the corresponding alcohol (3.70 g, 14.98 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.57 (br s, 1H, HC=CBr), 5.36 (d, 1H, J = 1.65 Hz, CH=), 4.78 (d, J = 7.00 Hz, 1H, OCH$_2$O), 4.48 (dd, J = 8.24 Hz, J = 4.95 Hz, 1H, CHOR), 4.44 (d, J = 7.00 Hz, OCH$_2$O), 2.70 (dd, J = 14.50 Hz, J = 8.24 Hz, 1H, =CCH$_2$), 2.61 (dd, J = 14.25 Hz, J = 4.95 Hz, 1H, =CCH$_2$), 0.17 (s, 9H, SiMe$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 128.78 (=C(Br)), 120.09 (H_2C=), 102.94, (quaternary C), 94.31 (OCH$_2$O), 63.93 (CHOR), 55.94 (OCH$_3$), 47.84 (=CCH$_2$), 0 (SiMe$_3$). Anal. Calcd for $C_{11}H_{19}BrO_2Si$: C, 45.36; H, 6.57. Found: C, 45.43; H, 6.75.

2-Bromo-4-(methoxymethoxy)-1,6-heptadiene, 43. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), **43** (3.13 g, 90%) was obtained from the corresponding alcohol (2.83 g, 14.81 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.8 (ddt, J = 14.30 Hz, J = 9.90 Hz, J = 7.15 Hz, 1H, =CH), 5.70 (br s, 1H, HC=CBr), 5.5 (d, J = 1.65 Hz, 1H, CH=), 5.1 (ddd, J = 14.30 Hz, J = 9.90 Hz, J = 1.65 Hz, 2H, =CH$_2$), 4.7 (s, 2H, OCH$_2$O), 4.01 (m, 1H, CHOR), 3.5 (s, 3H, OCH$_3$), 2.6 (m, 2H, =CCH$_2$), 2.35 (m, 2H, CH$_2$C=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.33 (HC=), 131 (=C(Br)), 119.54 (H_2C=), 118.08 (CH$_2$=), 96 (OCH$_2$O), 74.41 (CHOR), 55.75 (OCH$_3$), 46.62 (=CCH$_2$), 38.20 (CH$_2$C=).

2-Bromo-4-(methoxymethoxy)-4-(pentafluorophenyl)-but-1-ene, 47. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **47** (3.62 g, 63%) was isolated from the corresponding alcohol (5.05 g, 15.98 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.73 (br s, 1H, CH=), 5.53 (br s, 1H, CH=), 5.37 (m, 1H, CHOR), 4.65 (d, J = 6.6 Hz, 1H, OCH$_2$O), 4.55 (d, J = 6.6 Hz, 1H, OCH$_2$O), 3.31 (s, 3H, OCH$_3$), 3.10 (m, 2H, =CCH$_2$), 2.90 (m, 2H, =CCH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 127.90 (=C-(Br)), 120.78 (H_2C=), 95.55 (OCH$_2$O), 74.03 (CHOR), 55.55 (OCH$_3$), 48.95 (=CCH$_2$). Anal. Calcd for $C_{12}H_{10}BrF_5O_2$: C, 39.91; H, 2.79. Found: C, 39.90; H, 2.75.

2-Bromo-4-(methoxymethoxy)-4-(4-fluorophenyl)but-1-ene, 49. After purification by flash chromatography (cyclohexane/ethyl acetate: 90/10), **49** (4.46 g, 78%) was obtained from from the corresponding alcohol (4.85 g, 19.80 mmol) following the procedure described for **1b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.5–7.0 (m, 4H, Ar H), 5.70 (br s, 1H, CH=), 5.60 (d, J = 1.65 Hz, 1H, CH=), 5.03 (dd, J = 8.4 Hz, J = 5.15 Hz, 1H, CHOR), 4.62 (s, 2H, OCH$_2$O), 3.45 (s, 3H, OCH$_3$), 3.02 (dd, J = 14.25 Hz, J = 8.4 Hz, 1H, =CCH$_2$), 2.71 (dd, J = 14.25 Hz, J = 5.15 Hz, 1H, =CCH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.89 (CF), 159.9, 136.50, 128.62, 115.6, 115.20 (Ar C), 129.82 (=C-(Br)), 119.60 (H_2C=), 94.27 (OCH$_2$O), 74.81 (CHOR), 55.13 (OCH$_3$), 50.05 (=CCH$_2$). Anal. Calcd for $C_{12}H_{14}BrO_2F$: C, 49.85; H, 4.88. Found: C, 49.85; H, 4.89.

5,5-d$_2$-7-(Methoxymethoxy)undec-1-ene, 24. To a solution of **22** (502 mg, 2 mmol) in Et_2O (30 mL) was added, at −78 °C, 2 equiv of t-BuLi (1.6 M solution in hexane, 2.5 mL, 4 mmol). This solution was warmed to −65 °C for 10 min to complete the lithium−iodine exchange, and then, at −65 °C, 2 equiv of allylmagnesium bromide was added (1 M solution in Et_2O, 4 mL, 4 mmol) followed 2 equiv of $ZnBr_2$ in Et_2O at −40 °C (1 M solution in Et_2O, 4 mL, 4 mmol). The reaction mixture was stirred at −20 °C for 5 h. The bismetallic **23** was deuterolyzed by D_2O (3 equiv, 6 mmol), and the hydrolysis was carried out with an aqueous solution of hydrochloric acid (1 N solution, 20 mL). The aqueous phase was extracted twice with ether (2 × 20 mL), and the combined organic phases were washed with 1 N HCl (2 × 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, washed with $NaHCO_3$ (2 × 20 mL), and then dried over $MgSO_4$ and concentrated in vacuo. The product **24** was obtained (337 mg, 78%) as an oil after flash chromatography (eluent cyclohexane/ether 95/5): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.01 Hz, J = 10.21 Hz, J = 6.60 Hz, 1H, CH=), 4.95 (m, 2H, CH$_2$=), 4.65 (s, 2H, OCH$_2$O), 3.52 (m, 1H, CHOR), 3.38 (s, 3H, OCH$_3$), 2.05 (m, 2H, =CCH$_2$), 1.6–1.2 (m, 10H, (CH$_2$)$_5$), 0.95 (t, J = 7.15 Hz, 3H, CH$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.97 (HC=), 114.32 (H_2C=), 95.39 (OCH$_2$O), 76.43 (CHOR), 55.47 (OCH$_3$), 34.04 (CH$_2$C=C), 33.74, 28.93, 28.68, 27.54, 22.90, 23.03, ((CH$_2$)$_5$), 24.22 (quint, CD$_2$), 14.05 (CH$_3$).

1(*R)-(3-Butenyl)-2(*S**)-butylcyclopropane, 27.** To a solution of **22** (502 mg, 2 mmol) in Et_2O (30 mL) was added, at −78 °C, 2 equiv of t-BuLi (1.6 M solution in hexane, 2.5 mL, 4 mmol). This solution was warmed to −65 °C for 10 min to complete the lithium−iodine exchange, and then, at −65 °C, 2 equiv of allylmagnesium bromide was added (1 M solution in Et_2O, 4 mL, 4 mmol) followed by 2 equiv of $ZnBr_2$ in Et_2O at −40 °C (1 M solution in Et_2O, 4 mL, 4 mmol). The reaction mixture was stirred at −20 °C for 5 h. The solution

was then allowed to warm to room temperature. After one night, the hydrolysis was carried out with an aqueous solution of hydrochloric acid (1 N solution, 20 mL). The aqueous phase was extracted twice with ether (2 × 20 mL), and the combined organic phases were washed with 1 N HCl (2 × 20 mL). The organic layer was treated with an aqueous solution of Na_2S, washed with $NaHCO_3$ (2 × 20 mL), and then dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (cyclohexane) afforded the pure product **27** (274 mg, 90%) as a *unique* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddt, J = 17.15 Hz, J = 10.25 Hz, J = 7.15 Hz, 1H, CH=), 5 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.25 Hz, J_{gem} = 1.62 Hz, 2H, CH_2=), 2.15 (m, 2H, CH_2C=), 1.4 (m, 8H, $(CH_2)_4$), 0.95 (t, J = 7.15 Hz, 3H, CH_3), 0.68–0.67 (dd, J_{cis} = 5.5 Hz, J_{trans} = 4.74 Hz, 2H, 2 × CH), 0.6–0.55 (dd, J_{trans} = 4.74 Hz, J_{gem} = 3.75 Hz, 1H, CH_2), −0.30 (dd, J_{cis} = 5.5 Hz, J_{gem} = 3.75 Hz, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.19 (HC=), 114.07 (=CH_2), 34.40 (CH_2C=), 32.45, 28.41, 28.34, 22.70 (4 × CH_2), 15.82, 15.38 ($CH_{cycloprop}$), 10.92 ($CH_{2cyclopr}$), 14.14 (CH_3).

Preparation of Dipotassium Azodicarboxylate (PADA). The title product was prepared by adding 11.68 g (0.1 mol) of azodicarbonamide to a mechanically stirred 40% aqueous potassium hydroxide solution (35.06 mL) and cooled by an external acetone–ice bath at a rate such that the temperature of the reaction mixture did not exceed 10 °C (15 min). After the addition, the mixture was stirred for 1 h at this temperature and then filtered and washed with 300 mL of cold methanol to afford PADA as a yellow powder (19.4 g, 100%).

Reduction of 1(*R)-(3-Butenyl)-2(*S**)-butylcyclopropane, 27, with PADA.** To a solution of **27** (100 mg, 0.66 mmol) in MeOH (5 mL) was added the solid potassium salt (194 mg, 2 mmol). The mixture was stirred magnetically while a solution of AcOH (0.2 mL) in MeOH (3 mL) was added at such a rate that caused a gentle boiling. After the addition, the reaction mixture was hydrolyzed with water, and the aqueous layer was separated and extracted with pentane (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and purified by column chromatography to afford dibutylcyclopropane **28** (101.64 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.4–1.1 (m, 12H, $(CH_2)_6$), 0.95 (t, J = 7.15 Hz, 6H, 2 × CH_3), 0.68–0.67 (m, 2H, 2 × CH), 0.6–0.55 (dd, J_{trans} = 4.74 Hz, J_{gem} = 3.75 Hz, 1H, CH_2), −0.30 (dd, J_{cis} = 5.5 Hz, J_{gem} = 3.75 Hz, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ, 32.47, 28.41, 22.70 (CH_2), 15.73 ($CH_{cycloprop}$), 10.91 ($CH_{2cyclopr}$), 14.16 (CH_3).

1(*R)-(3-Butenyl)-2(*R**)-isopropylcyclopropane, 30.** The same procedure as described for the synthesis of the cyclopropane **27** was utilized. The cyclopropane **30** (209 mg, 76%) was obtained from **29** (474 mg, 2 mmol) as an oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.85 (m, 1H, HC=), 5.0 (m, 2H, =CH_2), 2.2 (m, 2H, =CCH_2),1.6–1.1 (m, 3H, CH_2, CH), 0.95 (m, 6H, $(CH_3)_2$), 0.8 (m, 2H, 2 × $CH_{cycloprop}$), 0.5 (m, 1H, $CH_{cycloprop}$), −0.3 (m, 1H, $CH_{cycloprop}$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 139.20 (HC=), 114.07 (=CH_2), 34.50 (=CCH_2), 29.95 (CH), 15.85, 15.25 ($CH_{cycloprop}$), 14.50, 14.15 (2 × CH_3), 10.85 ($CH_{cycloprop}$).

1(*R)-*d*-1-(3-Butenyl)-2(*S**)-butylcyclopropane, 31.** The same procedure as described for **27** was utilized. The cyclopropyl metal **26** obtained from the tandem "carbometalation–cyclopropanation" reaction of **22** (502 mg, 2 mmol) was submitted to the addition of D_2O (0.5 mL, 10 mmol). The hydrolysis was carried out with an aqueous solution of hydrochloric acid (1 N solution, 20 mL). The aqueous phase was extracted twice with ether (2 × 20 mL), and the combined organic phases were washed with 1 N HCl (2 x 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, washed with $NaHCO_3$ (2 × 20 mL), and then dried over $MgSO_4$ and concentrated in vacuo. The residual oil was purified by flash chromatography (cyclohexane/ethyl acetate: 95/5) to afford **31** (245 mg, 80%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 (ddt, J = 17.15 Hz, J = 10.25 Hz, J = 7.15 Hz, 1H, CH=), 5 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.25 Hz, J_{gem} = 1.62 Hz, 2H, CH_2=), 2.15 (m, 2H, =CCH_2), 1.5–1.1 (m, 8H, 4 × CH_2), 0.95 (t, J = 7.15 Hz, 3H, CH_3), 0.67 (m, 1H, $CH_{cycloprop}$), 0.57 (dd, J_{cis} = 8.25 Hz, J_{gem} = 4.4 Hz, 1H, $CH_{2cycloprop}$), −0.15 (dd, J_{trans} = 5.5 Hz, J_{gem} = 4.4 Hz, 1H, $CH_{2cycloprop}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.24 (HC=), 114.10 (=CH_2), 34.40 (=CCH_2CH_2), 32.48, 28.42, 28.22, 22.71, (4 × CH_2), 15.72 ($CH_{2cycloprop}$), 15.02 (t, CD), 14.17 ($CH_{cycloprop}$), 10.82 (CH_3).

1(*R)-Bromo-1-(3-butenyl)-2(*S**)-butylcyclopropane, 32.** The same procedure as described for **27** was utilized. The cyclopropyl metal **26** obtained from the tandem "carbometalation–cyclopropanation" reaction of **22** (502 mg, 2 mmol) was submitted to the addition of bromine (480 mg, 3 mmol, in THF). After workup as described for **22**, the residual oil was purified by flash chromatography (cyclohexane/ethyl acetate: 95/5) to afford **32** (332 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 (ddt, J = 17.15 Hz, J = 10.25 Hz, J = 7.15 Hz, 1H, CH=), 5 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.25 Hz, J_{gem} = 1.62 Hz, 2H, CH_2=), 2.35 (m, 2H, =CCH_2), 1.85 and 1.70 (m, 2H, =CCH_2CH_2), 1.50 and 1.07 (m, 2H, $CH_{cycloprop}CH_2R$), 1.37 and 1.2 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.30 (m, 1H, $CH_{cycloprop}$), 1.15 and 0.35 (m, 2H, $CH_{2cycloprop}$), 0.85 (t, J = 7.15 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.77 (HC=), 114.91 (=CH_2), 40.02 (CBr), 36.62 (=CCH_2CH_2), 32.38 (=CCH_2), 31.46 (CH_2CH_3), 28.75, 28.55 (($CH_2)_2$), 22.42 ($CH_{cycloprop}$), 22.15 ($CH_{2cycloprop}$), 14.05 (CH_3).

1(*S)-Iodo-(3-butenyl)-2(*S**)-butylcyclopropane, 33.** The same procedure as described for **27** was utilized. The cyclopropyl metal **26** obtained from the tandem "carbometalation–cyclopropanation" reaction of **22** (502 mg, 2 mmol) was submitted to the addition of a solution of iodine (762 mg, 3 mmol) in THF (5 mL). After workup as described for **22**, the residual oil was purified by flash chromatography (cyclohexane/ethyl acetate: 95/5) to afford **33** (389 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 (ddt, J = 17.15 Hz, J = 10.25 Hz, J = 7.15 Hz, 1H, CH=), 5 (ddd, J_{trans} = 17.15 Hz, J_{cis} = 10.25 Hz, J_{gem} = 1.62 Hz, 2H, CH_2=), 2.5 (m, 2H, =CCH_2), 1.70 (m, 2H, =CCH_2CH_2), 1.59 and 1.1 (m, 2H, $CH_{cycloprop}CH_2R$), 1.45–1.20 (m, 4H, $(CH_2)_2$), 1.35 (m, 1H, $CH_{cycloprop}$), 1.15 (m, 2H, CH_2), 1.12 and 0.4 (m, 2H, $CH_{2cycloprop}$), 0.85 (t, J = 7.15 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.48 (HC=), 115.00 (=CH_2), 38.92 (=CCH_2CH_2), 38.41 (CI), 34.64 (=CCH_2), 31.43, 30.24 (($CH_2)_2$), 28.48 ($CH_2CH_{cycloprop}$), 23.74 ($CH_{2cycloprop}$), 22.48 ($CH_{cycloprop}$), 14.05 (CH_3). Anal. Calcd for $C_{11}H_{19}I$: C, 47.49; H, 6.88. Found: C, 47.53; H, 7.05.

1(*R)-(3-Butenyl)-2(*S**)-[2(*E*)-carbethoxyvinyl]-butyl-1-cyclopropane, 34.** The same procedure as described for **27** was utilized. The cyclopropyl metal **26**, obtained from **22** (502 mg, 2 mmol), reacted after transmetalation (see experimental procedure of **10** for transmetalation) with 2 equiv of ethyl propiolate (392 mg, 4 mmol) at −20 °C. The reaction mixture was allowed to warm to 0 °C, stirred at this temperature for 1 h, and then hydrolyzed with NH_3/NH_4Cl (1/3:2/3). The aqueous layer was extracted with ether, and the combined organic layers were dried over $MgSO_4$. After purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), **34** was isolated as an oil (320 mg, 64%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.60 (d, J = 15.95 Hz, 1H, HC=), 5.90 (ddt, J = 17.05 Hz, J = 10.45 Hz, J = 6.60 Hz, 1H, CH=), 5.65 (d, J = 15.95 Hz, 1H, HC=), 5 (ddd, J_{trans} = 17.05 Hz, J_{cis} = 10.45 Hz, J_{gem} = 1.65 Hz, 2H, CH_2=), 4.16 (q, J = 7.15 Hz, 2H, OCH_2), 2.2 (m, 2H, =CCH_2), 1.6–1.4 (m, 8H, 4 × CH_2), 1.28 (t, J = 7.15 Hz, OCH_2CH_3), 1.01 (m, 1H, $CH_{cycloprop}$), 0.89 (t, J = 7.15 Hz, CH_3), 0.42 (m, 2H, $CH_{2cycloprop}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.23 (CO_2), 157.30 (HC=), 138.50 (HC=,) 115.71 (=CH_2), 114.47 (CH=), 60.06 (OCH_2), 31.88 (CH_2), 31.41 (=CCH_2), 29.34 (2 × CH_2), 28.72 (CH_2), 22.46 ($CH_{cycloprop}$), 21.86 ($CH_{2cycloprop}$), 14.36 (OCH_2CH_3), 14.05 (CH_3). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.46. Found: C, 76.85; H, 10.35.

1(*S)-(3-Butenyl)-1-(2-propenyl)-2(*S**)-butylcyclopropane, 35.** The same procedure as described for **27** was utilized. The cyclopropyl metal **26**, obtained from **22** (502 mg, 2 mmol), reacted after transmetalation (see experimental procedure of **10** for transmetalation) with 2 equiv of allyl iodide (504 mg, 4 mmol) at −20 °C. After workup as described for **34**, purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), afforded **35** as an oil (250 mg, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.80 (m, 2H, 2 × CH=), 5 (m, 4H, 2 × CH_2=), 2.15–1.90 (m, 4H, 2 × =CCH_2), 1.6–1.4 (m, 8H, 4 × CH_2), 0.95 (t, J = 7.15 Hz, 3H, CH_3), 0.55 (m, 1H, $CH_{cycloprop}$), 0.4 (dd, J_{cis} = 7.14 Hz, J_{gem} = 4.4 Hz, 1H, $CH_{2cycloprop}$), −0.1 (dd, J_{trans} = 5.5 Hz, J_{gem} = 4.4 Hz, 1H, $CH_{2cycloprop}$); ^{13}C NMR

($CDCl_3$, 100 MHz) δ 140.45 (=CH), 137.78 (HC=), 116.67 ($=CH_2$), 114.88 ($CH_2=$), 43.08 (2 × $=CCH_2$), 33.41 (CH_2), 32.20 (C_{quat}), 31.29 (CH_2), 30.72 (CH_2), 24.90 ($CH_{cycloprop}$), 23.66 (CH_2), 18.83 ($CH_{cycloprop}$), 15.16 (CH_3). Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.65; H, 12.78.

1(S*)-(3-Butenyl)-1-[(diethylamino)methyl]-2(S*)-butylcyclopropane, 36. The same procedure as described for **27** was utilized. The cyclopropyl metal **26**, obtained from **22** (502 mg, 2 mmol), reacted after transmetalation (see experimental procedure of **10** for transmetalation) with 2 equiv of amino ether (636 mg, 4 mmol) at −20 °C. After workup as described for **34**, purification by flash chromatography (cyclohexane/ethyl acetate: 95/5), afforded **36** as an oil (285 mg, 60%). ^1H NMR ($CDCl_3$, 400 MHz) δ 5.90 (ddt, J = 17.05 Hz, J = 10.45 Hz, J = 6.60 Hz, 1H, CH=), 5 (m, 2H, $CH_2=$), 2.6 (m, 4H, NCH_2CH_3), 2.5 and 1.95 (m, 2H, NCH_2), 2.25 (m, 2H, $=CCH_2$), 1.7−1.2 (m, 8H, 4 × CH_2), 1.1 (t, J = 7.15 Hz, 6H, NCH_2CH_3), 0.95 (t, J = 7.15 Hz, CH_3), 0.65 (m,1H, $CH_{cycloprop}$), 0.4 (dd, J_{cis} = 7.14 Hz, J_{gem} = 4.4 Hz, 1H, $CH_{2cycloprop}$), −0.1 (dd, J_{trans} = 5.5 Hz, J_{gem} = 4.4 Hz, 1H, $CH_{2cycloprop}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.90 (=CH), 113.50 ($=CH_2$), 60.02 (CH_2N), 46.40 (NCH_2CH_3), 32.26 (CH_2), 31.22 ($=CCH_2$), 29.31 (CH_2), 28.76 (CH_2), 24.00 ($CH_{cycloprop}$), 22.66 (CH_2), 21.60 (C_{quat}), 16.22 ($CH_{2cycloprop}$), 14.06 (CH_3), 11.32 (NCH_2CH_3). Anal. Calcd for $C_{16}H_{31}N$: C, 80.94; H, 13.16. Found: C, 81.02; H, 13.25.

1(S*)-(3-Butenyl)-2(S*)-phenylcyclopropane, 40. The same procedure as described for **27** was utilized. The cyclopropane **40** (310 mg, 90%, de = 90%) was obtained from **37** (542 mg, 2 mmol) as an oil. Major diastereoisomer: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.5−7.4 (m, 5H, Ar H), 5.90 (ddt, J = 17.05 Hz, J = 10.25 Hz, J = 6.60 Hz, 1H, HC=), 4.98 (m, 2H, $=CH_2$), 2.26 (m 2H, $=CCH_2$), 1.65 (ddd, J_{cis} = 8.5 Hz, J_{trans} = 5.2 Hz, J_{trans} = 4.81 Hz, 1H, $PhCH_{cycloprop}$), 1.47 (m, 2H, $=CCH_2CH_2$), 1.07 (m, 1H, $CH_{cycloprop}$), 0.90 (ddd, J_{cis} = 8.5 Hz, J_{trans} = 4.8 Hz, J_{gem} = 5.2 Hz, 1H, $CH_{2cycloprop}$ same side as phenyl), 0.75 (ddd, J_{cis} = 8 5 Hz, J_{trans} = 5.1 Hz, J_{gem} = 5.2 Hz, 1H, $CH_{2cycloprop}$ same side as butenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.80 (HC=), 129.16, 128.34, 125.76, 125.32 (Ar C), 114.65 ($=CH_2$), 34.06 ($=CCH_2CH_2$), 33.79 ($=CCH_2$), 23.44 (2 × $CH_{cycloprop}$), 16.30 ($CH_{2cycloprop}$).

1(S*)-(3-Butenyl)-2(S*)-[1(E)-propenyl]cyclopropane, 44a. The same procedure as described for **27** was utilized. The cyclopropane **44** (204 mg, 75%, de = 80%) was obtained from **41** (470 mg, 2 mmol) as an oil. Major diastereoisomer: ^1H NMR ($CDCl_3$, 400 MHz) δ 5.85 (ddt, J = 17.05 Hz, J = 10.22 Hz, J = 6.67 Hz, 1H, HC=), 5.47 (dq, J = 15.18 Hz, J = 6.42 Hz, =C(*H*)Me), 5.1−4.8 (m, 3H, $=CH_2$, HC=), 2.15 (m, 2H, $=CCH_2$), 1.70 (dd, J = 6.42 Hz, ^4J = 1.57 Hz, 3H, CH_3), 1.3 (m, 2H, $=CCH_2CH_2$), 1.10 (m, 1H, $=CCH_{cycloprop}$), 0.7 (m, 1H, $CH_{cycloprop}$), 0.47 (ddd, J_{cis} = 8.3 Hz, J_{trans} = J_{gem} = 4.6 Hz, 1H, $CH_{2cycloprop}$ same side as propenyl), 0.43 (ddd, J_{cis} = 8.3 Hz, J_{trans} = 5.1 Hz, J_{gem} = 4.6 Hz, 1H, $CH_{2cycloprop}$ same side as butenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.80 (HC=), 134.44 (HC=), 122.16 (=CHMe), 114.34 ($=CH_2$), 33.96, 33.68 ($(CH_2)_2$), 21.33 ($=CHCH_{cycloprop}$), 20.10 ($CH_{cycloprop}$), 17.81 ($=CCH_3$), 13.44 ($CH_{2cycloprop}$).

1(R*)-(3-Butenyl)-2(S*)-[(trimethylsilyl)ethynyl]cyclopropane, 45b. The same procedure as described for **27** was utilized. The cyclopropane **45** (204 mg, 75%) was obtained from **42** (470 mg, 2 mmol) as an oil. Major diastereoisomer: ^1H NMR ($CDCl_3$, 400 MHz) δ 5.75 (ddt, J = 17.05 Hz, J = 10.22 Hz, J = 6.67 Hz, 1H, =CH), 4.95 (m, 2H, $=CH_2$), 2.10−2.0 (m, 2H, $=CCH_2$), 1.55 (m, 2H, $=CHCH_2CH_2$), 1.38 (ddd, J_{cis} = 8.3 Hz, J_{cis} = 8.3 Hz, J_{trans} = 5.6 Hz, 1H, $CH_{cycloprop}$), 1.0 (m, 1H, $RCH_{cycloprop}$), 0.92 (ddd, J_{cis} = 8.3 Hz, J_{cis} = 8.3 Hz, J_{gem} = 4.1 Hz, 1H, $CH_{2cycloprop}$), 0.4 (ddd, J_{trans} = 5.7 Hz, J_{trans} = 5.6 Hz, J_{gem} = 4.1 Hz, 1H, $CH_{2cycloprop}$ same side as substituents); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.95 (HC=), 114.22 ($=CH_2$), 33.05 ($=CCH_2$), 29.31, 26.70, 22.34, 18.03, 14.83, 6.02, 0.0 ($SiMe_3$).

2(R*)-(3-Butenyl)-1(S*)-(2-propenyl)cyclopropane, 46b. The same procedure as described for **27** was utilized. The cyclopropane **45** (141 mg, 52%) was obtained from **43** (470 mg, 2 mmol) as an oil. Major diastereoisomer: ^1H NMR ($CDCl_3$, 400 MHz) δ 5.80 (m, 2H, 2 × CH=), 5 (m, 4H, 2 × $CH_2=$), 2.15 to 1.90 (m, 4H, 4 × $=CCH_2$), 1.6−1.4 (m, 6H, 3 x CH_2), 0.55 (m,1H, $CH_{cycloprop}$), 0.4 (m, 1H, $CH_{2cycloprop}$), −0.3 (m, 1H, $CH_{2cycloprop}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.45 (=CH), 137.78 (HC=), 116.67 ($=CH_2$), 114.88 ($CH_2=$), 43.08 (2 × $=CCH_2$), 33.41 (CH_2), 32.20 (C_{quat}), 30.72 (CH_2), 24.90 ($CH_{cycloprop}$), 18.83 ($CH_{2cycloprop}$).

1-(3-Butenyl)-2-(pentafluorophenyl)cyclopropane, 48. The same procedure as described for **27** was utilized. The cyclopropane **48** (283 mg, 54%) was obtained in Et_2O from **47** (720 mg, 2 mmol) in a dr = 1/1: ^1H NMR ($CDCl_3$, 400 MHz) δ 5.9−5.72, m, 2H, HC= cis + trans), 5.06−4.90 (m, 4H, $=CH_2$ cis + trans), 2.23 and 2.15 (m, 4H, $=CCH_2$ cis + trans), 1.80 (m, 2H, $PhCH_{cycloprop}$ cis + trans), 1.6−1.2 (m, 6H, cis + trans), 1.2 (m, 1H, $CH_{2cycloprop}$ trans), 1.15 (m, 1H, $CH_{2cycloprop}$ cis), 0.9 (m, 1H, $CH_{2cycloprop}$ trans), 0.8 (m, 1H, $CH_{2cycloprop}$ cis); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.43 (HC= trans + cis), 114.65(=CH_2 trans + cis) 33.88, 33.29, 33.48, 29.36, 19.98, 16.96, 13.50, 12.95, 10.96, 10.75 Anal. Calcd for $C_{13}H_{11}F_5$: C, 59.54; H, 4.23. Found: C, 59.72; H, 4.35.

1(S*)-(3-Butenyl)-2(S*)-(p-fluorophenyl)cyclopropane, 50. The same procedure as described for **27** was utilized. The cyclopropane **50** (300 mg, 79%, de = 80%) was obtained from **49** (578 mg, 2 mmol) as an oil. Major isomer (trans): ^1H NMR ($CDCl_3$, 400 MHz) δ 7.02−6.90 (m, 4H, Ar H), 5.80 (ddt, J = 17.05 Hz, J = 9.9 Hz, J = 6.6 Hz, HC=), 4.90 (ddd, J = 17.05 Hz, J = 9.9 Hz, J = 1.65 Hz, $=CH_2$), 2.20 (m, 2H, $=CCH_2$), 1.60 (ddd, J_{cis} = 8.5 Hz, J_{trans} = 5.2 Hz, J_{trans} = 4.81 Hz, 1H, $PhCH_{cycloprop}$), 1.45 (m, 2H, $=CCH_2CH_2$), 0.95 (m, 1H, $CH_{cycloprop}$), 0.82 (ddd, J_{cis} = 8.5 Hz, J_{trans} = 4.8 Hz, J_{gem} = 5.2 Hz, 1H, $CH_{2cycloprop}$ same side as phenyl), 0.75 (ddd, J_{cis} = 8 5 Hz, J_{trans} = 5.1 Hz, J_{gem} = 5.2 Hz, 1H, $CH_{2cycloprop}$ same side as butenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.57 (HC=), 130.45, 127.02, 115.12, 114.60 (Ar C), 114.65 ($=CH_2$), 34.36 ($=CCH_2CH_2$), 33.98 ($=CCH_2$), 23.39, 23.09 (2 × $CH_{cycloprop}$), 15.83 ($CH_{2cycloprop}$); ^{19}F NMR ($CFCl_3$, 90MHz) δ −118.9 ppm.

Minor isomer (cis): ^1H NMR ($CDCl_3$, 400 MHz) δ 7.10−7.0 (m, 4H, Ar H), 5.70 (ddt, J = 17.05 Hz, J = 9.9 Hz, J = 6.6 Hz, 1H, HC=), 4.85 (m, 2H, $=CH_2$), 2.10 (m, 2H, $=CCH_2$), 0.6 (ddd, J_{trans} = 5.5 Hz, J_{trans} = 4.95, J_{gem} = 5.2 Hz, 1H, $CH_{2cycloprop}$ same side as butenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.72 (HC=), 130.30, 127.18, 114.82, 114.70 (Ar C), 114.65 ($=CH_2$), 33.51 ($=CCH_2CH_2$), 28.26 ($=CCH_2$), 20.25, 18.31 (2 × $CH_{cycloprop}$), 9.88 ($CH_{2cycloprop}$); ^{19}F NMR ($CFCl_3$, 90MHz) δ −118.3 ppm. Anal. Calcd for $C_{13}H_{15}F$: C, 82.07; H, 7.95. Found: C, 82.08; H, 7.95.

***(cis)*-1(R*)-(3-butenyl)-2(S*)-(p-fluorophenyl)cyclopropane, 50, in THF.** The same procedure as described for **27** was utilized. The cyclopropane was obtained in THF (30 mL) in 2 h at +35 °C from **49**. After usual workup, the cyclopropane *(cis)* **50** was isolated (266 mg, 70%), dr = 2/1) as an oil.

3(R*),4(R*)-Diphenyl-2-(trimethylsilyl)but-1-en-4-ol. Magnesium turnings (1.2 g, 50 mmol) covered with THF (10 mL) were activated by 1,2-dibromoethane (0.55 g,3 mmol) in THF (3 mL). The reaction mixture was cooled to 0 °C by an acetone−ice bath, and 1-bromo-1-(trimethylsilyl)ethene (3.25 g, 18.18 mmol) was added. An exothermic reaction occurred, and the reaction was stirred 1 h at room temperature. The reaction was then diluted with THF (10 mL) and was poured, via a syringe, in a suspension of CuI (60 mg, 3 mmol), in Et_2O (50 mL) at −78 °C. The reaction mixture was stirred 1 h at −78 °C, and then *cis*-stilbene oxide (2.97 g, 15.15 mmol) in Et_2O (15 mL) was added. The reaction was allowed to warm slowly to room temperature. The completion of the reaction was followed by performing the GC analysis of hydrolyzed reaction aliquots (2 h). The reaction mixture was hydrolyzed with an aqueous solution of hydrochloric acid (1 N) and neutralized by a solution of Na_2CO_3, and the organic layer was separated. The aqueous layer was extracted with Et_2O (2 × 30 mL). The organic layers were combined and dried over Na_2SO_4. Purification by chromatography on silica gel (cyclohexane/ethyl acetate: 85/15) afforded the title compound (3.32 g, 74%): ^1H NMR ($CDCl_3$, 200 MHz) δ 7.2−6.9 (m, 10H, Ar H), 6.24 (br s, 1H, HC=), 5.87 (d, J = 1.78 Hz, 1H, HC=), 5.1 (d, J = 9.70 Hz, 1H, PhCHOH), 3.76 (d, J = 9.70 Hz, 1H, PhCHC=), 2.58 (s, 1H, OH), −0.1 (Me_3Si); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.30, 142.00, 139.54, 129.37, 127.98, 127.79,

127.11, 126.34, 124.64, 76.58 (PhCHOH), 59.25 (PhCHC=), −1.32 (Me_3Si). Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.98; H, 8.16. Found: C, 77.01; H, 8.25.

3(*R),4(*R**)-Diphenyl-4-(methoxymethoxy)-2-(trimethylsilyl)but-1-ene.** To a stirred solution of the preceding alcohol (3.32 g, 11.21 mmol) in dimethoxymethane (30 mL) were added lithium bromide (210, 2.24 mmol) and then *p*-toluenesulfonic acid (210 mg, 1.21 mmol) at room temperature. The mixture was stirred overnight and hydrolyzed with a saturated sodium chloride solution (40 mL) and extracted with ether (2 × 20 mL). The organic layers were combined and dried with sodium sulfate. The solvent was evaporated, and the title product (2.58 g, 68%) was purified by column chromatography on silica gel (cyclohexane/ethyl acetate: 95/5): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.17−6.99 (m, 10H, Ar H), 6.26 (br s, 1H, HC=), 5.80 (br s, 1H, HC=), 5.13 (d, J = 9.35 Hz, 1H, PhCHOR), 4.55 (d, J = 7.15 Hz, 1H, OCH_2O), 4.52 (d, J = 7.15 Hz, 1H, OCH_2O), 3.90 (d, J = 9.35 Hz, 1H, PhCHC=), 3.36 (s, 3H, OCH_3), 0.0 (Me_3Si); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.65, 141.78, 141.38, 130.54, 128.91, 128.85, 128.32, 127.26, 125.40, 95.62 (OCH_2O), 81.60 (PhCHOR), 57.53 (PhCHC=), 57.37 (OCH_3), −0.25 (Me_3Si). Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.08; H, 8.28. Found: C, 74.10; H, 8.23.

2-Bromo-3(*R),4(*R**)-diphenyl-4-(methoxymethoxy)-but-1-ene, 51.** To a solution of the preceding ether (2.58 g, 7.6 mmol) in CH_2Cl_2, cooled to −78 °C, was slowly added bromine (1.51 g, 9.48 mmol) in CH_2Cl_2 (10 mL). To the red-orange solution was added 25 mL of MeOH and 0.5 g of sodium sulfite, and the resulting mixture was vigorously stirred until the mixture became yellow. While still cold (−78 °C), the reaction mixture was poured into a separatory funnel containing a 10% sodium sulfite solution and shaken until all the color had disappeared. After separation, the aqueous layer was extracted with pentane, and the combined organic layers were dried over Na_2SO_4. The solvent was removed by rotary evaporation to afford the crude dibromide which was dissolved in MeOH and treated with 1 M sodium methoxide (11.5 mL, 1 M in methanol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, allowed to warm to room temperature and then stirred for an additional 2 h. Then, the reaction mixture was partitioned between pentane and water and separated. The aqueous layer was extracted with pentane, and the combined organic layers were dried over Na_2SO_4. Purification by flash chromatography on silica gel afforded the title compound **51** (1.98 g, 75%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.2 (m, 10H, Ar H), 6.08 (d, J = 1.90 Hz, 1H, HC=), 5.66 (d, J = 1.90 Hz, 1H, HC=), 4.84 (d, J = 10.10 Hz, 1H, PhCHOR), 4.53 (d, J = 7.15 Hz, 1H, OCH_2O), 4.50 (d, J = 7.15 Hz, 1H, OCH_2O), 3.99 (d, J = 10.10 Hz, 1H, PhCHC=), 3.39 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.63, 137.53, 135.06, 128.7, 127.99, 127.93, 127.69, 126.98, 118.07, 94.34 (OCH_2O), 79.14 (PhCHOR), 62.35 (PhCHC=), 53.31 (OCH_3). Anal. Calcd for $C_{18}H_{19}BrO_2$: C, 62.26; H, 5.51. Found: C, 62.26; H, 5.51.

1-(3-Butenyl)-2(*R),3(*S**)-diphenylcyclopropane, 53.** See typical procedure for the preparation of the cyclopropane **27**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.5−6.88 (m, 10H, Ar H), 5.95 (ddt, J = 17.05 Hz, J = 10.21 Hz, J = 6.65 Hz, 1H, HC=), 5.10 (m, 2H, $=CH_2$), 2.35 (m, 2H, $=CCH_2$), 2.24 (d, J_{trans} = 4.94 Hz, 2H, 2 × $PhCH_{cycloprop}$), 1.7 (m, 3H, $CH_2CH_{cycloprop}$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.52 (HC=), 128.90, 127.65, 125.50 (Ar C), 114.89 ($=CH_2$), 33.76 ($=CCH_2$), 33.61 ($CH_{cycloprop}$), 32.00 ($PhCH_{cycloprop}$), 25.36 (CH_2). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.62; H, 8.38.

Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra (and some 2-D spectra) of all compounds (130 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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