5c, 137332-64-0; 5d, 137332-65-1; L-alaninamide hydrochloride, 33208-99-0; 2,6-dichloro-3-nitrobenzoic acid, 55775-97-8; 2,6-difluoro-3-nitrobenzoic acid, 83141-10-0; 2,5-dichloro-3-nitrobenzoic acid, 88-86-8; prenyl bromide, 870-63-3.

Supplementary Material Available: ^1H spectra for compounds 1b, 3b–5b, 1c, 3c–5c, 1d, and 5d; ^{13}C spectra for 3b–5b, 1c, 4c, 5c, 1d, and 5d (20 pages). Ordering information is given on any current masthead page.

Vinylcyclopentane Synthesis via Phenylthio Radical Catalyzed Alkenylation of Vinylcyclopropanes: Preparative and Mechanistic Studies

Ken S. Feldman,* Anthony L. Romanelli, Robert E. Ruckle, Jr., and Ginette Jean

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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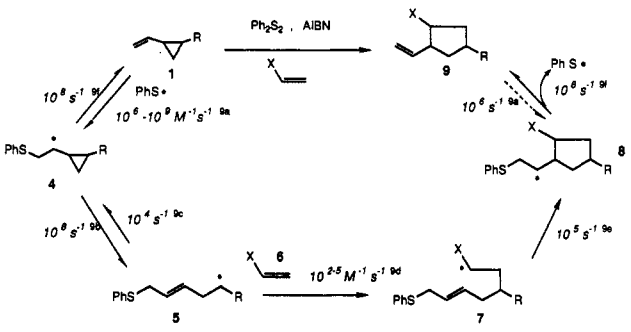
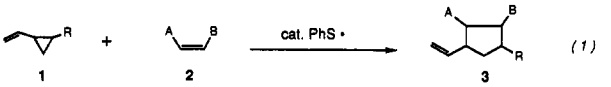
1-Vinylcyclopropanes bearing ether or ester substituents at C(2) of the cyclopropyl ring or alkyl groups at other ring (or alkenyl) positions were subjected to PhS• catalyzed olefination with ester- or oxygen-functionalized alkenes. In some instances, variations in reaction conditions (low temperature, Lewis acids) led to levels of stereoselectivity unprecedented in such simple, unbiased substrates. In general, the stereochemical outcome of these transformations can be rationalized by citing existing models for selectivity upon cyclization of substituted 5-hexenyl radicals. However, in a few specific instances, results obtained with alkylated vinylcyclopropyl substrates are not consistent with some of the predictions of these models.

The development of methodology for the regio- and stereocontrolled synthesis of highly functionalized five-membered carbocycles has enabled efficient construction of a host of cyclopentanoid target molecules. Two distinct approaches, acyclic closure of five carbon chains and [3 + 2] addition, have emerged as the most versatile strategies in this regard. The roster of addition reactions which utilize a [3 + 2] bond construction strategy includes the combination of alkenes or alkynes with three-atom synthons such as trimethylene methane equivalents,[1] substituted allyl or allenyl fragments,[2] and functionalized cyclopropanes.[3] Each approach has characteristic strengths and weakness, typically involving issues of functional group compatibility, stereoselectivity, and/or regioselectivity.

We[4] and others[5] have recognized that [3 + 2] strategies for cyclopentanoid synthesis which are based on free radical transformations have the decided advantages of functional group tolerance and regiochemical predictability relative to many dipolar approaches. However, often modest stereoselectivity accompanies these radical reactions. Our approach to free radical based cyclopentanoid synthesis relies on the phenylthio radical catalyzed combination of substituted vinylcyclopropanes 1 with functionalized alkenes 2 to afford the vinylcyclopentane derivatives 3 eq 1. Although this reaction proceeds through

Scheme I





(1)

a complex multistep mechanism, product stereochemistry is set in a single step—the cyclization of a substituted 5-hexenyl radical (vide infra, Scheme I, 7 → 8). Substituent/stereoselectivity relationships have been documented for a variety of 5-hexenyl radical cyclizations, and general guidelines with predictive value have emerged.[6] Nevertheless, some subtle issues remain unresolved, including (1) ranking the relative importance of specific steric interactions in cyclization transition states and (2) identifying which of two possible transition states precedes a

(1) (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1 and references cited therein. (b) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371. (c) Little, R. D.; Bode, H.; Stone, K. J.; Wallquist, O.; Dannecker, R. *J. Org. Chem.* **1985**, *50*, 2400.

(2) (a) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935 and references cited therein. (b) Danheiser, R. L.; Kwasigrouch, C. A.; Tsai, Y. M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (c) Curran, D. P.; Chen, M.-H. *J. Am. Chem. Soc.* **1987**, *109*, 6558. (d) Clive, D. L. J.; Angoh, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 980. (e) Cekovic, Z.; Saicic, R. *Tetrahedron Lett.* **1986**, *27*, 5893. (f) Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165. (g) Bunce, R. A.; Wamsley, E. J.; Pierce, J. D.; Shellhammer, A. J., Jr.; Drumright, R. E. *J. Org. Chem.* **1987**, *52*, 464. (h) Beak, P.; Wilson, K. D. *J. Org. Chem.* **1987**, *52*, 218.

(3) (a) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1984**, *106*, 805. (b) Binger, P.; Schäfer, B. *Tetrahedron Lett.* **1988**, *29*, 4539 and references cited therein. (c) Demuth, M.; Wietfeld, B.; Pandey, B.; Schaffner, K. *Angew Chem.* **1985**, *97*, 777. (d) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 3825. (e) Snider, B. B.; Beal, R. B.; Dombroski, M. A. *J. Org. Chem.* **1986**, *51*, 4391.

(4) (a) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. (b) Feldman, K. S.; Ruckle, R. E., Jr.; Romanelli, A. L. *Tetrahedron Lett.* **1989**, *30*, 5843.

(5) (a) Saicic, R.; Cekovic, Z. *Tetrahedron* **1990**, *46*, 3627. (b) Curran, D. P., Chen, M.-H. *J. Am. Chem. Soc.* **1987**, *109*, 6558. (c) Miura, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett* **1988**, *29*, 5135. (d) Singleton, D. A.; Church, K. M. *J. Org. Chem.* **1990**, *55*, 4780.

(6) (a) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959. (b) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, *482*, 484. (c) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

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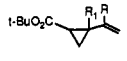
given cyclopentane product. We felt that within the context of this project we would have the opportunity to systematically explore, and possibly exploit, these steric effects and hence increase both stereoselectivity and understanding in simple 5-hexenyl radical cyclizations (and therefore vinylcyclopentane synthesis) beyond existing levels.

The olefination of vinylcyclopropanes (eq 1) was developed in direct analogy to our earlier work on the oxygenation of these same substrates.[7] We believe that the mechanistic course of this transformation, shown in Scheme I, closely parallels that established in the oxygenation case. However, in the alkene additions, the crucial bimolecular addition (**5** + **6**) occurs at a rate 10^4–10^7 slower than the corresponding oxygen addition. Hence, judicious pairing of substituents R and X is necessary for alkene trapping of **5** to compete with other unwanted processes (Ph_2S_2 trapping,[8] addition of **5** to **1** and subsequent polymerization). In a preliminary communication, vinylcyclopentane synthesis through a series of successful alkene/vinylcyclopropane pairings was described.[4a] In this full account of our work, we expand upon this original subset of representative addends. These new experiments help define the scope and limitations of this process and illuminate some of the interactions which contribute to stereoselectivity upon 5-hexenyl radical cyclization.

Results

In the course of these studies, we have examined the efficiency and stereoselectivity of vinylcyclopentane formation from the alkoxy-substituted substrates **10a–g** and the ester-substituted species **11a–d**. Two atom addends in these addition reactions included both ester-bearing and oxygen-bearing alkenes. In several instances (vide infra), the possibility of thermodynamic control of product stereochemistry was checked by appropriate control (resubmission) experiments. In no case, however, was any evidence obtained which supported this possibility. Thus, we believe that product formation is under kinetic control, and as such is reflective of the relative conformational energetics attending substituted 5-hexenyl radical cyclization. The alkyl substituted vinylcyclopropanes **11b-11d** serve as useful steric probes of mechanism and help delineate prominent steric interactions during this key cyclization.

10a R=CH_2Ph, R_1=H
10b R=t-$BuMe_2Si$, R_1=H
10c R=Ac, R_1=H
10d R=$CH_2C_6H_4$(p-OCH_3), R_1=H
10e R=$CH_2C_6H_4$(p-CF_3), R_1=H
10f R=CH_2CH_3, R_1=H
10g R=CH_3, R_1=OCH_3



11a R=R_1=H
11b R=CH_3, R_1=H
11c R=t-Bu, R_1=H
11d R=H, R_1=CH_3

In an effort to maximize both yield and stereoselectivity, various experimental parameters were examined in a systematic manner. In general, reactions run with the ester-bearing species **11** at low temperature (−50 to 0 °C) in the presence of $AlMe_3$ proceeded with higher stereoselectivity and with no loss of yield when compared to the same reactions run in refluxing benzene. Unfortunately, the oxygen-substituted series **10** did not benefit from these low-temperature/Lewis acid conditions, despite the fact that control experiments indicated that both starting cyclopropane and product cyclopentane were stable to the reaction conditions. In several cases, use of near stoichiometric ratios of alkene to vinylcyclopropane led to higher yields (although slightly lower selectivity) than similar reactions run with a large excess (10–15 equiv) of alkene. This observation is consistent with a process in which excess alkene siphons off an intermediate 5-hexenyl radical **7** in competition with cyclization to form cyclopentyl radical **8**. Other parameters, such as concentration (11–130 mM), initiator ratio (0.05–1.0 equiv), or solvent (benzene, toluene, acetonitrile, methanol, hexane) did not have pronounced effects upon either yield or stereoselectivity for the test case reaction of **10a** with methyl acrylate (vide infra).

Studies with Vinylcyclopropyl Alcohol Derivatives 10. The vinylcyclopentanes formed upon combination of the prototype oxygenated vinylcyclopropane 1-(benzyloxy)-2-ethenylcyclopropane (**10a**) and the electronically dissimilar alkenes methyl (and *tert*-butyl) acrylate and vinyl acetate (and pivalate) are shown in entries a–d of Table I. In these transformations, all four possible diastereomeric products are formed. Those species with the original OBn and CH=CH_2 units syn disposed (**12** and **13**) are formed in approximately equal amounts with the vinylcyclopentanes (**14** and **15**) that have the corresponding anti arrangement. Within the syn series, a slight preference for the trans relationship (e.g., **12**) between vinyl appendage and X (X = CO_2R or OCOR) over the cis relationship (**13**) is seen in each case. In the anti series **14/15**, a slight preference for the cis relationship between these two groups is seen. Interestingly, increasing the steric bulk in the acrylate alkene addend (i.e., (b) CO_2-*t*-Bu vs (a) CO_2CH_3) enhances these preferences slightly, while a corresponding increase in the isosteric vinyl ester series ((d) OCO-*t*-Bu vs (c) $OCOCH_3$) diminishes these preferences. Taken together, these and related observations will permit identification of salient steric interactions which determine product ratios in the cyclization of the intermediate substituted 5-hexenyl radicals (vide infra).

That the stereoisomers shown in entry a were not formed under thermodynamic control was ascertained by base-mediated equilibration studies. Thus, independent treatment of either syn-trans cyclopentane **12a** with CH_3ONa/CH_3OH or the syn-cis isomer **13a** led to the same equilibrium mixture of 10:1 **12a**:**13a** (88%) after 10 days at room temperature.

Efforts to improve these disappointing syn/anti stereoselectivities focused on variation in the group attached to oxygen. Thus, the use of the *p*-CH_3O (entry e) and *p*-CF_3 (entry f) substituted benzyl ethers **10d** and **10e**, respectively, were part of an attempt to probe for the effects of electron demand on cyclization selectivity. We had hoped that through either indirect (dipole magnitude and direction) or direct (radical complexation (cf. **16a**)) interaction,[10] these substituted aromatic moieties might influence the conformational preferences of the 5-hexenyl radical. However, neither yield nor stereoselectivity was responsive to these substituent variations. Furthermore, the *alkoxy*-substituted vinylcyclopropane **10f** provided

(7) (a) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. (b) Feldman, K. S.; Simpson, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 4878. (c) Feldman, K. S.; Simpson, R. E. *Tetrahedron Lett* **1989**, *30*, 6985.

(8) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398. The rate constant for Ph_2S_2 addition to the 5-hexenyl radical is reported to be 7.6×10^4 s^{-1} M^{-1} (25 °C).

(9) The rate constants shown in Scheme I are for simpler model systems. (a) Sivertz, C. *J. Phys. Chem.* **1959**, *63*, 34. (b) Matthew, L.; Warketin, J. *J. Am. Chem. Soc.* **1980**, *108*, 7981. See also: Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662. (c) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (d) Brandrop, J.; Immergut, E. H. "*Polymer Handbook*", 3rd ed.; J. H. Wiley and Sons: New York, 1989. (e) Park, S.-V.; Chung, S.-K.; Newcomb, M. *J. Am. Chem. Soc.* **1980**, *108*, 240. (f) Wagner, P. J.; Sedon, J. H., Lindstrom, M. J. *J. Am. Chem. Soc.* **1990**, *100*, 2579.

(10) For another attempt to detect aromatic association (between Ar and a diene), see Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.

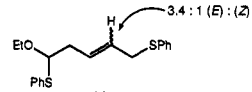
Table I. Alkene Addition to Vinylcyclopropyl Ethers

entry		(no. of equiv)	condns[a]	% yield[b] overall (syn:anti)	12 trans	13 cis	14 trans	15 cis
a	CH_2Ph, **10a**	CO_2CH_3 (1)	A (80 °C)	70 (1:1)	2.9	1.9	1.0	3.8
		(15)	A (110 °C)	63 (1:1)	2.8	1.6	1.0	3.5
		(15)	A (−25 °C)	65 (1:1.3)	4.8	4.3	1.0	11.0
b	CH_2Ph, **10a**	CO_2-*t*-Bu (15)	A	60 (1.6:1)	4.2	1.1	1.0	2.4
c	CH_2Ph, **10a**	$OCOCH_3$ (15)	A	39 (1:1)	2.3	1.9	1.0	3.4
d	CH_2Ph, **10a**	OCO-*t*-Bu (15)	A	43 (1.1:1)	2.0	1.3	1.0	2.1
			B	49 (1.2:1)	2.4	2.1	1.0	3.5
e	$CH_2C_6H_4$(*p*-OCH_3), **10d**	CO_2CH_3 (15)	A	74 (1:1.1)	1.8	1.3	1.0	2.6
f	$CH_2C_6H_4$(*p*-CF_3), **10e**	CO_2CH_3 (15)	A	80 (1:1)	3.1	1.8	1.0	3.7
g	CH_2CH_3, **10f**	CO_2CH_3 (15)	A	50 (1:1)	3.3	2.0	1.0	4.2
h	CH_2CH_3, **10f**		A	42 (1:1.5)	not observed	4.4	1.0	5.5
i	Si-*t*-$BuMe_2$, **10b**	CO_2CH_3 (10)	A	78 (1:1)	3.8	2.3	5.1	1.0
			B		8.1	7.1	17.9	1.0
j	Ac, **10c**	CO_2CH_3 (5)	A	22[c]				

[a] See Experimental Section for a description of conditions. [b] Yields reported are for chromatographically isolated pure products. Stereoisomer ratios were determined by GC analysis of the crude reaction mixture. [c] Four isomers (2.4:1.7:1.5:1); not further characterized

cyclopentane products in almost identical ratios to the *aryl*oxyl precursor **10a** (Table I, compare entries a and g). Finally, the silyloxy and acetoxy vinylcyclopropanes **10b** and **10c** in combination with methyl acrylate were examined. In both cases, overall syn/anti selectivity did not vary much from the benzyloxy species. However, a strong preference (~18:1) for the trans **14i** over the cis **15i** product in the anti series for **10b**, relative to the opposite preference (1:2–4) in every other substrate examined, is noteworthy. In general, however, for no case investigated were satisfactory levels of 1,3 (syn/anti) stereoselectivity detected for the vinylcyclopentanol-derived class of substrates.

16a



16b

The successful addition of the sluggishly reactive disubstituted alkene vinylene carbonate (entry h) to cyclopropane **10f** defines a lower boundary of olefin reactivity. Thus, addition of radical **5** (R = OEt) to vinylene carbonate (note: k = 500 s^{-1} M^{-1} (80 °C) for CH_2CH·(OAc) + vinylene carbonate[9d]) is scarcely able to compete with trapping of **5** by Ph_2S_2 ($k \sim 10^5$ s^{-1} M^{-1}),[8] as the 42% yield of vinylcyclopentane adducts **12f–15f** is accompanied by a 37% yield of the formal Ph_2S_2 1,5 adduct **16b**. Bisthio ether **16b** has primarily *E* alkene geometry, a point of some mechanistic consequence (vide infra). It should be noted that in other similar systems[7b,11] trapping of homoallylic radicals related to **5** with *H*SPh, O_2, or Ph_2S_2 led to allylic phenylsulfide products with strictly *E* alkene geometry. Unfortunately, stereochemical control in this more geometrically restricted (entry h) system was only marginally better than in any system described in Table I.

Studies with Vinylcyclopropyl Ester Derivatives 11. As in the prior vinylcyclopropanol derived series **10a–g**, the vinylcyclopropyl esters **11a–d** afforded the expected vinylcyclopentane products **17–20** upon PhS· catalyzed combination with both oxygenated alkenes (butyl vinyl ether, vinyl pivalate) and ester-substituted alkenes (*tert*-butyl acrylate). In most cases, all four of the possible diastereomeric vinylcyclopentane products could be isolated and structurally characterized (Table II; for a notable exception, see entry g). However, unlike the corresponding vinylcyclopentanol derivatives **12–15**, a general preference for syn (**17** + **18**) over anti (**19** + **20**) product stereochemistry was detected. Furthermore, this stereochemical preference was enhanced under specific reaction conditions, viz. low temperature in the presence of the Lewis acid $AlMe_3$, leading ultimately to product ratios in favorable cases (>5:1 syn: anti, Table II, entries a–c, e, g) that may be potentially useful in organic synthesis. The role of the Lewis acid in these reactions plausibly stems from its ability to complex the ester functionality in either the cyclopropyl moiety or the alkene partner (if applicable), thus rendering the intermediate radical **5** or the (acrylate) radical acceptor **6** more reactive.[12] Unfortunately, cyclopentanylations with **11** did not proceed at low temperature without the Lewis acid present, and at higher temperatures only intractable tars resulted from Lewis acid mediated reactions. Thus, the influence of acid cannot be factored from the effects of lower temperature in evaluating the improvements in stereoselectivity in these cases. Resubmission experiments confirmed that the Lewis acid did not alter the product diastereomer ratios. Finally, the well-documented role that the Lewis acid triethyl boron (in the presence of adventitious oxygen) plays in initiation of free-radical chain reactions suggests that a similar role for $AlMe_3$ in our process may be possible.[13]

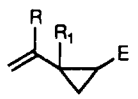
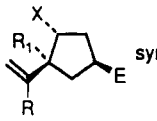
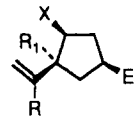
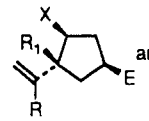
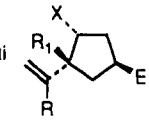
Comparison of entries a–c reveals that the alkene substituent (O-*n*-Bu, OCO-*t*-Bu, CO_2-*t*-Bu, respectively) does not significantly influence the syn/anti ratio. Furthermore, replacement of the hydrogen at C(1) of the vinyl appendage (R in **11**) with CH_3 or *t*-Bu seems to suppress only

(11) Feldman, K. S.; Fisher, T. E. *Tetrahedron* **1989**, *45*, 2969.

(12) Hirai, H. *J. Polym. Sci. Macromol. Rev.* **1976**, *11*, 47.

(13) (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron Lett* **1990**, *31*, 4681. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett* **1988**, *29*, 6125, 6127. (c) Brown, H. C. In *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, New York, 1972.

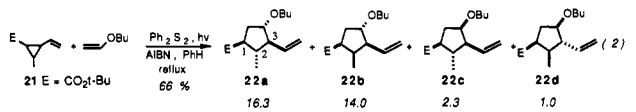
Table II. Alkene Addition to Vinylcyclopropyl Esters

entry	 E = CO_2-*t*-Bu	 (no. of equiv)	condns[a]	% yield[b] overall (syn:anti)	 17 trans	 18 cis	 19 trans	 20 cis
a	R = R_1 = H, **11a**	O-*n*-Bu (15)	A	94 (3.3:1)	6.1	1.4	1.3	1.0
			B	75 (5.1:1)	14.2	2.0	2.2	1.0
b	R = R_1 = H, **11a**	OCO-*t*-Bu (15)	A	55 (6.2:1)	4.0	2.2		1.0
			B	52 (4.4:1)	12.8	10.9	1.0	4.4
c	R = R_1 = H, **11a**	CO_2-*t*-Bu (15)	A	53 (1.9:1)	4.4	1.2	1.0	1.9
			B (−50 °C)	52 (6.2:1)	10.3	4.0	1.0	1.3
d	R = CH_3, R_1 = H, **11b**	O-*n*-Bu (15)	A	96 (2.7:1)	4.2	1.4	1.0	1.1
			B	70 (4.4:1)	7.0	2.6	1.0	1.2
e	R = CH_3, R_1 = H, **11b**	CO_2-*t*-Bu (15)	A	44 (6.7:1)	3.7	3.0	1.0	
			B	48 (5.3:1)	3.6	1.7	1.0	
f	R = *t*-Bu, R_1 = H, **11c**	O-*n*-Bu (15)	A	33 (3:1)	4.7	1.2	1.0	1.0
			B	21 (3.8:1)	7.0	1.3	1.2	1.0
g	R = H, R_1 = CH_3, **11d**	O-*n*-Bu (15)	A	66 (>10:1)	1.0	1.0		
			B	69 (>10:1)	1.8	1.0		

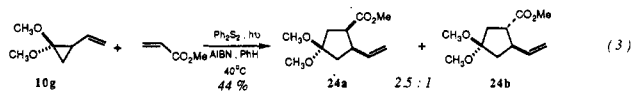
[a] See Experimental Section for a description of conditions. [b] Yields reported are for chromatographically isolated pure products. Stereoisomer ratios were determined by GC analysis of the crude reaction mixture. syn anti

slightly this syn preference (entries d–f). However, the situation is very different with the ring methyl substituted isomer **11d** (entry g). In this instance, syn selectivity is complete—anti substituted product could not be detected. Taken together, these examples (entries a and d–g) provide critical evidence for the identity of the 5-hexenyl radical conformation (chair or boat?) which precedes anti product (**19/20**) (vide infra).

Miscellaneous Cyclopentanylations. Combination of ring-methylated vinylcyclopropyl ester **21** with butyl-vinyl ether (eq 2) probes the issue of relative asymmetric induction upon alkene addition to a simple *acyclic* radical bearing an adjacent stereogenic center. Surprisingly, only a very few characterized examples of this type of radical addition have been reported,[14] and with the exception of one series[14g] the observed selectivities have been quite modest (~65:35). Apparently, 1,2 relative asymmetric induction upon formation of cyclopentane **22** is no better—a 1.1:1 ratio of the 1,2 trans (**22a** + **22c**) to 1,2 cis (**22b** + **22b**) products were isolated.



Phenylthio radical catalyzed addition of methyl acrylate to the vinylcyclopropyl ketal **10g** provides the cyclopentanone derivative **24a/b** as a mixture of isomers (eq 3). Presumably, the now trisubstituted intermediate



radical (cf. **5**) suffers no untoward steric interactions and remains competent in this transformation. In addition, the more highly functionalized cyclopentanone derivative **24** may permit access to stereoisomerically homogeneous cyclopentanol species (after appropriate manipulation) which currently can only be formed as components of complex mixtures from the vinylcyclopropyl ethers **10**.

Stereochemical Elucidation. The structures and stereochemistry of vinylcyclopentanes **12a–15a, 12d–15d, 12g–15g, 12h–15h, 12i–15i, 17a–20a, 17b–20b, 17c–20c, 17d–20d, 17e–20e, 17f–20f, 17g–20g, 22a–d,** and **24a,b** were determined by analysis of a combination of ^{1}H decoupling and DNOE data (supplementary material). The structure and stereochemistry of the vinyl acetate adducts **12c–15c** and the *tert*-butyl ester adducts **12b–15b** were ascertained by chemical correlation. Thus, independent reduction ($LiAlH_4$) of each stereoisomer **12c–15c** led to a single alcohol product whose retention time by GC matched that of the alcohol derived from reduction of the appropriate vinyl pivalate adducts **12d–15d** whose structures were secure. In a similar manner, the structures of *tert*-butyl acrylate adducts **12b–15b** were determined by correlation with the known methylacrylate adducts **12a–15a** (see supplementary material for retention times). The structure and stereochemistry of the substituted benzyloxy vinylcyclopropane adducts **12e–15e** and **12f–15f** were deduced by comparison of key ^{1}H NMR signals with those of the unsubstituted benzyloxy series **12a–15a** whose structures have been determined already (see supplementary material for data).

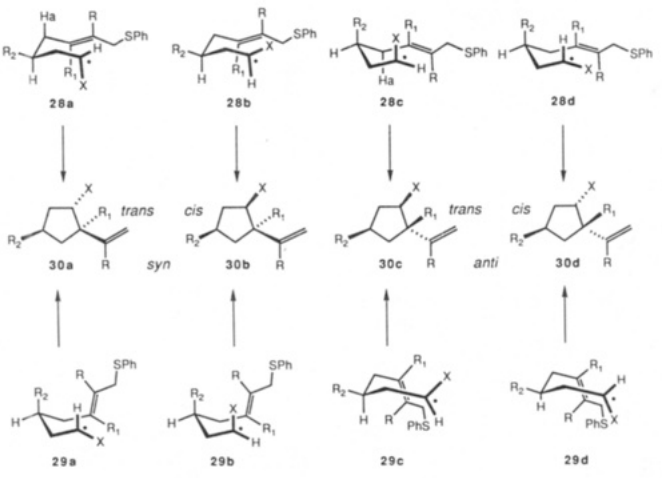
Discussion

Vinylcyclopentane synthesis proceeds from a wide range of electronically disparate vinylcyclopropane and alkene precursors. In essence, two criteria must be met to achieve successful reaction: (1) The vinylcyclopropane must be substituted with a radical-stabilizing group to permit formation of useful quantities of the key homoallylic radical **5**. For example, alkyl-substituted vinylcyclopropanes do not participate in this reaction—in this instance, it is likely that **4** → **5** does not compete with **4** → **1** (Scheme 1). (2) The alkene partner must be sufficiently reactive to intercept radical **4** in competition with trapping by the starting material vinylcyclopropane **1** (→polymerization) or Ph_2S_2 (**5** → **16b**). Models for predicting alkene/radical reactivity which rely on analysis of both steric and frontier orbital interactions have been developed,[15]

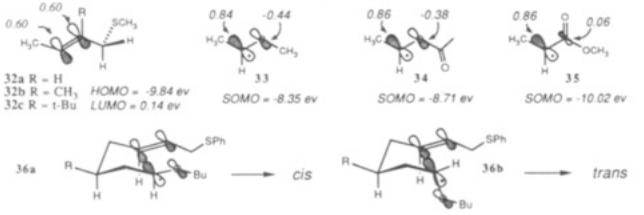
(14) (a) Geise, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969. (b) Geise, B.; Harnisch, H.; Lüning, U. *Chem. Ber.* **1985**, *118*, 1345. (c) Adlington, R. M.; Baldwin, J. E.; Basak, A.; Kozyrod, R. P. *J. Chem. Soc., Chem. Commun.* **1983**, 944. (d) Henning, R.; Urbach, H. *Tetrahedron Lett* **1983**, *24*, 5343. (e) Barluenga, J.; Lopez-Prado, J.; Campos, P. J.; Arsensio, G. *Tetrahedron* **1983**, *39*, 2663. (f) Kozikowski, A. P.; Scripto, J. *Tetrahedron Lett* **1983**, *24*, 2051. (g) Guindon, Y.; Lavallee, J.-F.; Boisvert, L.; Chabot, C.; Delorme, D.; Yoakim, C.; Hall, D.; Lemieux, R.; Simon, B. *Tetrahedron Lett* **1991**, *32*, 27.

(15) (a) Problet, J. M.; Canadell, E.; Sordo, T. *Can. J. Chem.* **1983**, *61*, 2068. (b) Geise, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.

Scheme II



Scheme III



although alternative approaches have been proposed.[16] Among the transformations reported herein, a useful lower limit for reactivity seems to be reached with **10f** and vinylene carbonate, where equal amounts of the Ph_2S_2 trapping product and vinylcyclopentane are produced.

Any analysis of the stereochemical outcome of 5-hexenyl radical cyclizations must be predicated upon establishing whether kinetic or thermodynamic control of observed selectivity prevails. That kinetic control of bond formation operates in our system was established by conducting the resubmission experiments described above. In earlier studies,[7c] we have shown that PhS• radical addition to vinyl-appended dioxolanes is facile under these conditions (e.g., **8** rapidly generated from **9**, Scheme I). Apparently, PhS• ejection from **8** ($k \approx 10^8$ s^{-1}[9f]) is much faster than reversion to **7** ($k < 10^5$ s^{-1}).

The stereochemical profiles which result from cyclization of many acyclic-substituted 5-hexenyl radical systems have been recorded.[17] Both qualitative and quantitative models have been developed, and applied with good success, toward rationalizing these observations.[6] Extension of the structural basis of these models to the systems **10** and **11** is shown in Scheme II—the four diastereomeric products **30a–30d** are derived from eight possible transition states which resemble chairlike (**28a–28d**) or boatlike conformations (**29a–29d**). To the extent that the critical geometric parameters of these constructs are cognate with chair and boat cyclohexanes, energy evaluations can be made based on familiar steric (1,3-diaxial, $A^{1,3}$) considerations. In general, the stereochemical results reported herein are in accord with these models. However, in certain instances, these results are not consistent with predictions made by Houk[6a] based on his computational (ab initio/molecular mechanics) model for substituted 5-hexenyl radical cyclization.

Syn/Anti Stereoselectivity. The cyclization of 3-substituted (but otherwise unadorned) 5-hexenyl radicals is expected to provide syn product (e.g., **30a** or **30b** vs **30c** or **30d**) preferentially based on these models and much precedent. Thus, it is no surprise that in the C(3) ester substituted series (R_2 = CO_2-*t*-Bu), a moderate (≤6.1:1) preference for syn product is observed, presumably as a consequence of cyclization through the lowest energy chairlike (equatorial-R_2) arrangement **28a/b**. However, it is surprising that in the vinylcyclopropyl ether series (R_2 = OCH_2Ar) no particular syn/anti preference was detected. Inspection of *A* values for related groups suggests a role for steric interactions in these disparate selectivities, although other unidentified factors may also intervene—CO_2Et (*A* value = 1.20 kcal/mol (80 °C)),[18] OEt (*A* value = 0.98 kcal/mol (100 °C)),[18] compare CH_3 (*A* value = 1.70 kcal/mol (30 °C)),[18] syn/anti = 2.9:1 upon 5-hexenyl radical cyclization[17a]).

However, does anti product derive from the chairlike/axial-R_2 conformers **28c/d** or the boat-like/equatorial R_2 conformers **29c/d**? Conformers **28c/d** are implicated by the *A* value data, yet Houk and Spellmeyer[6a] predict that the boatlike/R_2-equatorial alternatives **29c/d** are lower in energy for simple systems (e.g., R_n = CH_3). The vinylcyclopropyl substrates **11a–d** (Table II) provide experimental probes of Houk's predictions. Thus, increasing the size of the vinyl substituent R (R = H, entry a; R = CH_3, entry d, R = *t*-Bu, entry f) should lead to a corresponding decrease in anti product **30c/d** if conformers **29c/d** precede product. However, if conformations **28c/d** are precursors to cyclopentane product, no such trend is expected (to a first approximation, the R–H_a steric interaction in **28c/d** should be countered by the similar interaction in **28a/b**). Inspection of the data in Table II reveals that no significant attenuation of anti product accompanies alkyl substitution; in fact, just the opposite trend is observed. Furthermore, substitution of CH_3 for H at C(5) (R_1 in **28c/d**) should lead to the complementary prediction (decrease in anti product) if the chairlike/R_2-axial species **28c/28d** are participants. Comparison of the stereochemical outcome of entries a and g (Table II) provides data consistent with this latter hypothesis. Thus, in the case of C(3) ester-substituted 5-hexenyl radicals, our experimental results lend no support to Houk and Spellmeyer's model which predicts that anti product formation occurs through a boatlike transition state. Furthermore, Houk and Spellmeyer predict that alkyl substitution at C(5) (R_1 in **28/29**) should enforce an anti preference upon cyclization of a 3-alkyl substituted 5-hexenyl radical.[6a] In our system (Table II, entries a vs g), the opposite effect (enhanced syn preference) is observed. Whether these transition-state preferences can be extended to other substit-

(16) Shaik, S. S.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 1446.

(17) For representative examples of 1,2 relative asymmetric induction between C(1) and C(5) upon cyclization of substituted 5-hexenyl radicals, see (a) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925. (b) RajanBabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759. (c) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911. (d) Curran, D. P.; Kim, D.; Liu, H. T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900. (e) Bradney, M. A. M.; Forbes, A. D.; Wood, J. *J. Chem. Soc., Perkin Trans. II* **1973**, 1655. (f) Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711. (g) Kuehne, M. E.; Damon, R. E. *J. Org. Chem.* **1977**, *42*, 1825. (h) Julia, M.; Maumy, M.; *Bull. Chem. Soc. Fr.* **1966**, 434. (i) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561. (j) Ziegler, F. E.; Zheng, Z.-L. *Tetrahedron Lett.* **1987**, *28*, 5973. (k) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003. (l) Enholm, E. J.; Prasad, G. *Tetrahedron Lett* **1989**, *30*, 4939. (m) Curran, D. P.; Chen, M.-H; Spletzer, E.; Seong, C. M.; Chung, C.-T. *J. Am. Chem. Soc.* **1989**, *111*, 8872. (n) Curran, D. P.; Snieckus, V.; Cuevas, J.-C.; Sloan, C. P.; Liu, H. *J. Am. Chem. Soc.* **1990**, *112*, 896. (o) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. (p) Kilburn, J. D. *Tetrahedron Lett.* **1990**, *31*, 2193. (q) Porter, N. A.; Wujek, D. G. *Tetrahedron* **1985**, *41*, 3973. (r) Willing, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6064. (s) Beckwith, A. L. J. *Tetrahedron*, **1981**, *37*, 3073. (t) Keck, G. E.; Tafesh, A. M. *Synthesis Lett.* **1990**, 257. (u) Arya, P.; Samson, C.; Lesage, M.; Griller, D. *J. Org. Chem.* **1990**, *55*, 6248.

(18) Hirsch, J. D. *Top. Stereochem.* **1967**, 199.

uent patterns remains to be seen.

Cis/Trans [3,4] Stereoselectivity. Analysis of the second stereochemical issue which arises upon 5-hexenyl radical cyclization, the cis/trans (e.g., **30b** vs **30a**) ratio further defines the germane transition-state steric interactions, but also raises the possibility of mitigating stereoelectronic factors as well. Specifically, the strong preference for a trans disposition of the OBu substituent and vinyl moiety (Table II, entry a, **17a:18a** = 7:1) relative to the pivalate (Table II, entry b, **17b:18b** = 1.2:1) or *tert*-butyl ester (Table II, entry c, **17c:18c** = 2.6:1) may result from the interplay between putative *secondary orbital interactions* and the usual steric interactions.[19]

Thus, the intervention of unfavorable secondary orbital interactions (Scheme III) may contribute to the preference for trans product **17a** when butyl vinyl ether is used. The unfavorable secondary orbital interactions cited here are related to the *attractive* interactions proposed by Beckwith to rationalize the cis stereochemical preference observed upon cyclization of simple 1-methyl substituted 5-hexenyl radicals.[20] However, Houk and Spellmeyer's computational analysis of relevant transition states did not detect any such attractive "hyperconjugative" interaction.[6a] In our case, semiempirical molecular orbital calculations (PM3 Hamiltonian[21]) reveal that, to the extent that a frontier orbital model[16] is an appropriate predictor of reactivity, the dominant interaction will be between the HOMO of the alkene (cf. **32**) and the radical SOMO (cf. **33–35**)(Beckwith utilizes the alkene LUMO in his analysis). In this scenario, a net antibonding interaction for **33** and **34** accompanies the eclipsing disposition of substituents in the cis precursor transition state **36a**, while in the alternative trans precursor transition state **36b**, this unfavorable interaction is absent. Inspection of the SOMO orbital coefficients in **33–35** suggests that this interaction would be correspondingly more severe in the alkoxy case **33** relative to the pivalate or ester case (which actually would have a slightly favorable interaction in the cis related transition state). While this *qualitative* stereoelectronic rationalization is open to dispute, it is not apparent that this unusually high stereoselectivity (Table II, entry a) can be readily addressed by simple steric arguments.

In the substituted vinyl cases (Table II, entries d and f), this strong trans preference is slightly attenuated, again perhaps as a consequence of this electronic effect—analogous calculations on the methyl and *tert*-butyl analogues of **32** (**32b**, R = CH_3, **32c**, R = *t*-Bu) reveal that alkyl substitution lessens the HOMO coefficient on C(2) relative to a hydrogen at this position (for both alkyl substituents, C(1) $\simeq$ 0.65, C(2) $\simeq$ 0.54) and hence may lessen the impact of the unfavorable secondary interaction shown in **36a**. It should be noted that reaction through alternative boatlike cyclization transition states (cf. **29c/d**) instead of **36a/b** is contraindicated by the results from the substituted vinylcyclopropanes **11a–d** discussed earlier.

Conclusion

The PhS$^{\bullet}$ mediated addition/cyclization reaction of substituted vinylcyclopropanes with electronically activated alkenes is, under favorable circumstances, a useful method for the preparation of highly functionalized vinylcyclopentane derivatives. High levels of stereoselectivity could not be achieved upon reaction of vinylcyclopropyl *ether* derivatives. However, vinylcyclopropyl *esters* did engage in cyclopentannelation with good diastereoselectivity under low-temperature/Lewis acid reaction conditions. Alkyl-substituted variants of the vinylcyclopropyl ester substrates, which served as steric probes of mechanism, revealed that while Beckwith's[6b,c] and Houk's[6a] generally accepted models for diastereoselectivity upon substituted 5-hexenyl radical cyclization provided adequate rationalization of the observed selectivites, some specific predictions of the model were not borne out experimentally. Thus, our results (1) are consistent with 1,3 anti vinylcyclopentane formation through a chairlike transition state with an axial C(3) substituent rather than the predicted boatlike equatorial C(3) substituent alternative and (2) challenge the prediction that 1,3 anti cyclopentane product will be preferred upon alkyl substitution at C(5).

Experimental Section

Gas–liquid chromatography (GLC) was performed with a capillary cross-linked methyl silicone column (25 m; id. 0.20 mm; film thickness 0.33 mm) and a flame ionization detector. Liquid (flash)[22] chromatography was carried out with 32–63-μm silica gel and the indicated solvent. Analytical thin-layer chromatography was performed with precoated silica gel (60 F_{254}) plates (E Merck). High-pressure liquid chromatography (HPLC) was performed on a Waters 6000A semipreparative instrument equipped with an R-401 refractometer and 440 UV detector, using a ZORBAX-SIL column (25 cm × 20 mm, DuPont). The preparation of vinylcyclopropanes **10a**,[23a] **10c**,[23a] **10f**,[23a] **11a**, **11b**,[7b] and **11c**[7b] have been described.

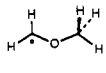
Vinylcyclopentane Synthesis. General Procedure A. A deoxygenated solution of phenyl disulfide (1 equiv, 100 mM) and AIBN (0.2 equiv, 20 mM) in the indicated solvent (Table I or II) was added dropwise via motor driven syringe to a stirring deoxygenated solution of vinylcyclopropane substrate (100 mM) and substituted alkene (number of equivalents indicated in Table I or II) in the indicated solvent and temperature, under an inert atmosphere (N_2 or Ar), with concomitant sunlamp irradiation. Reaction progress was monitored by TLC or GLC, and when the vinylcyclopropane was consumed, the reaction solution was concentrated in vacuo. The pure cyclopentane diastereomers were isolated by flash chromatography of the crude reaction mixture and, if necessary, HPLC.

Vinylcyclopentane Synthesis. General Procedure B. To a solution of alkene (number of equivalents indicated in Table I or II) in the indicated solvent and temperature was added $AlMe_3$ (0.8 equiv relative to cyclopropane), and the solution was allowed to stir for 5 min. A solution of the vinylcyclopropane (100 mM) in the indicated solvent was added and the resulting solution deoxygenated and placed under an inert atmosphere (N_2). A deoxygenated solution of phenyl disulfide (1 equiv, 100 mM) and

(19) Recently, Keck and Tafesh[17t] have observed similar stereoselectivity in a 1-OSi-substituted 5-hexenyl radical. Their rationalization for the selectivity appears related to the one proposed herein.

(20) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, *26*, 2251.

(21) A reviewer cautions us on the use and interpretation of a low-level calculational technique (MOPAC 5.0 with the PM3 Hamitonian) for this analysis. Higher level theory (fully geometry optimized UHF and ROHF 4-31G level. Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062) has been applied to structures similar to **33–35** leading to SOMO valves which differ from our computed valves by ~10–15%:



Nevertheless, the *trends* observed in our calculations are born out by the higher level entries. In any event, it is clear that for either calculational approach, application of FMO theory[16] to the cyclization of **36** suggests that interactions between the radical SOMO and alkene HOMO will dominate the addition process. For further analysis (with caveats) of the applicability of FMO theory to radical addition reactions, see: (a) Canadell, E.; Eisenstein, O.; Ohanession, G.; Poblet, J. M.; *J. Phys. Chem.* **1985**, *98*, 4856. (b) Canadell, E.; Poblet, J. M.; Sordo, T. *Can. J. Chem.* **1983**, *61* 2068. (c) Elliot, R. J.; Richards, W. G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 943. (d) Ref. 16.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(23) Romanelli, A. L. Ph.D. Thesis, Pennsylvania State University, 1989.

AIBN (0.2 equiv 20 mM) in the indicated solvent was added dropwise via motor-driven syringe to the reaction mixture with concomitant sunlamp irradiation. Reaction progress was monitored by TLC or GLC, and when the vinylcyclopropane was consumed, 1 mL of H_2O was added and the reaction solution subsequently concentrated in vacuo. The residue was taken up in CH_2Cl_2, washed with 1 M H_3PO_4 and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The pure cyclopentane diastereomers were isolated from the crude reaction mixture by flash chromatography, and if necessary, HPLC.

Reaction of 1-(Benzyloxy)-2-ethenylcyclopropane (10a) with Methyl Acrylate. Following general procedure A, a solution containing 1-(benzyloxy)-2-ethenylcyclopropane (**10a**) (50 mg, 0.29 mmol), methyl acrylate (372 mg, 4.32 mmol), phenyl disulfide (63 mg, 0.29 mmol), and AIBN (9 mg, 0.06 mmol) in refluxing benzene was irradiated for 45 min. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 48 mg (64%) of cyclopentane product (diastereomer ratio: 3.8 (**15a**):2.9 (**12a**):1.9 (**13a**):1.0 (**14a**)) as a yellow oil. **12a**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (m, 5 H), 5.76 (ddd, J = 17.3, 10.1, 7.4 Hz, 1 H), 4.97 (ddd, J = 17.1, 1.7, 1.0 Hz, 1 H), 4.90 (ddd, J = 10.2, 1.7, 0.7 Hz, 1 H), 4.40 (s, 2 H), 4.03 (m, 1 H), 3.60 (s, 3 H), 2.70 (m, 1 H), 2.64 (m, 1 H), 2.22 (ddd, J = 13.7, 7,8, 6.2 Hz, 1 H), 2.02 (m, 2 H), 1.57 (ddd, J = 13.4, 9.2, 5.0 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.7, 140.4, 138.4, 128.4, 127.6, 127.5, 114.6, 79.0, 70.9, 51.6, 48.2, 46.6, 39.1, 36.6; MS m/z (relative intensity) 260 (M^+, 4), 169 (6), 154 (13), 91 (100); HRMS calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1400; GLC with a Carbowax 20M capillary column 12.12 min. **13a**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.22 (m, 5H), 5.88 (ddd, J = 17.3, 10.1, 8.4 Hz, 1 H), 5.06 (ddd, J = 17.0, 1.8, 0.9 Hz, 1 H), 5.00 (ddd, J = 10.2, 1.9, 0.6 Hz, 1 H), 4.52 (s, 2 H), 4.04 (pentet, J = 7.1 Hz, 1 H), 3.65 (s, 3 H), 2.91 (q, J = 8.2 Hz, 1 H), 2.83 (m, 1 H), 2.25 (m, 1 H), 2.14 (m, 2 H), 1.84 (dt, J = 13.2, 6.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 138.6, 138.4, 128.4, 127.6, 127.5, 115.5, 78.9, 71.3, 51.4, 46.9, 44.4, 37.7, 34.1; MS m/z (relatively intensity) 260 (M^+, 5), 169 (4), 154 (24), 107 (10), 91 (100); HRMS calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1417; GLC with a Carbowax 20M capillary column 15.75 min. **14a**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 5 H), 5.78 (ddd, J = 17.3, 10.2, 7.4 Hz, 1 H) 5.08 (dt, J = 17.0, 1.5 Hz, 1 H), 5.00 (dt, J = 10.4, 1.0 Hz, 1 H), 4.48 (s, 2 H), 4.06 (m, 1 H), 3.69 (s, 3 H), 3.09 (m, 1 H), 2.77 (m, 1 H), 2.52 (q, J = 9.1 Hz, 1 H), 2.30 (ddd, J = 13.7, 9.0, 6.0 Hz, 1 H), 2.12 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 140.0, 138.6, 128.4, 127.6, 127.5, 114.7, 78.6, 70.6, 51.7, 48.8, 45.4, 38.9, 36.3; MS m/z (relative intensity) 260 (M^+, 4), 169 (2), 154 (24), 107 (10) 91 (100); HRMS calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1417; GLC with a Carbowax 20M capillary column 12.98 min. **15a**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 7.14 (m, 5 H), 5.78 (ddd, J = 17.4, 10.1, 7.8 Hz, 1 H), 4.96 (m, 2 H), 4.16 (s, 2 H), 3.94 (m, 1 H), 3.32 (s, 3 H), 3.08 (m, 1 H), 3.04 (m, 1 H), 2.24 (dt, J = 12.7, 6.3 Hz, 1 H), 1.92 (m, 2 H), 1.76 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 138.6, 138.0, 128.4, 127.6, 127.5, 115.6, 79.6, 70.7, 51.3, 47.0, 44.8, 37.6, 35.2; MS m/z (relative intensity) 260 (M^+, 1), 169 (23), 154 (2), 91 (100); HRMS calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1401; GLC with a Carbowax 20M capillary column 12.70 min.

Reaction of 1-(Benzyloxy)-2-ethenylcyclopropane (10a) with *tert*-Butyl Acrylate. Following general procedure A, a solution of 1-(benzyloxy)-2-ethenylcyclopropane (**10a**) (50 mg, 0.29 mmol), *tert*-butyl acrylate (553 mg, 4.32 mmol), phenyl disulfide (63 mg, 0.29 mmol), and AIBN (9 mg, 0.06 mmol) in refluxing benzene was irradiated for 45 min. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 52 mg (60%) of 1,1-dimethylethyl 3-(benzyloxy)-5-ethenyl-1-cyclopentanecarboxylates (diastereomer ratio: 4.2 (**12b**):2.4 (**15b**):1.1 (**13b**):1.0 (**14b**) as a yellow oil. The structure and stereochemistry of the diastereomers were ascertained by correlation of the gas chromatography retention times of the derived alcohols ($LiA1H_4$,) with the alcohols derived from the reduction of the diastereomerically pure methyl acrylate derivatives (**12a–15a**).

Reaction of 1-(Benzyloxy)-2-ethenylcyclopropane (10a) with Vinyl Pivalate. Following general procedure B, a solution of 1-(benzyloxy)-2-ethenylcyclopropane (**10a**) (50 mg, 0.29 mmol), vinyl pivalate (553 mg, 4.32 mmol), phenyl disulfide (163 mg, 0.29 mmol), AIBN (9 mg, 0.06 mmol), and trimethylaluminum (120 μL of a 2 M solution in hexane, 0.23 mmol) in benzene, at 0 °C, was irradiated for 12 h. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 42.9 mg (49%) of cyclopentane product (diastereomer ratio: 3.5 (**15d**):2.4 (**12d**):2.1 (**13d**):1.0 (**14d**)) as a yellow oil. **12d**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.26 (m, 5 H), 5.76 (ddd, J = 17.3, 10.2, 7.7 Hz, 1 H), 5.16 (q, J = 6.9 Hz, 1 H), 5.05 (ddd, J = 17.2, 1.6, 1.2 Hz, 1 H), 4.92 (ddd, J = 10.2, 1.7, 1.2 Hz, 1 H), 4.20 (d, J = 2.5 Hz, 2 H), 3.81 (m, 1 H), 2.41 (pentet, J = 8.0 Hz, 1 H), 2.25 (ddd, J = 13.8, 7.4, 4.5 Hz, 1 H), 2.01 (m, 1 H), 1.68 (m, 1 H), 1.54 (ddd, J = 13.4, 9.4, 5.8 Hz, 1 H), 1.14 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 139.1, 138.4, 128.4, 127.6, 127.5, 115.1, 77.7, 77.3, 71.0, 47.7, 38.6, 38.0, 36.5, 27.1; MS m/z (relative intensity) 302 (M^+, 1), 196 (15), 91 (78), 57 (100); HRMS calcd for $C_{19}H_{26}O_3$ 302.1882, found 302.1898. **13d**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 5 H), 5.82 (ddd, J = 17.4, 7.3 Hz, 1 H), 5.04 (m, 1 H), 4.98 (m, 2 H), 4.43 (s, 2 H), 4.01 (m, 1 H), 2.54 (m, 1 H), 2.26 (ddd, J = 14.7, 8.2, 5.9 Hz, 1 H), 2.15 (dt, J = 12.9, 6.9 Hz, 1 H), 1.83 (m, 2 H), 1.12 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 138.5, 136.4, 128.3, 127.6, 127.5, 115.9, 77.8, 75.7, 71.1, 46.4, 39.0, 38.8, 36.4, 27.1; MS m/z (relative intensity) 302 (M^+, 1), 196 (10), 107 (4), 91 (100), 57 (72); HRMS calcd for $C_{19}H_{26}O_3$ 302.1882, found 302.1874. **14d**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 5 H), 5.68 (ddd, J = 17.3, 10.3, 7.2 Hz, 1 H), 5.00 (dt, J = 17.2, 1.5 Hz, 1 H), 4.94 (dt, J = 10.3, 1.5 Hz, 1 H), 4.75 (m, 1 H), 4.40 (s, 2 H), 3.95 (m, 1 H), 2.83 (m, 1 H,), 2.42 (ddd, J = 14.6, 7.9, 6.8, Hz, 1 H), 2.03 (ddt, J = 13.7, 7.4 2.0 Hz, 1 H), 1.66 (m, 1 H), 1.58 (m, 1 H), 1.12 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 138.7, 138.5, 128.4, 127.5, 115.3, 77.7, 70.6, 47.0, 38.6, 38.3, 36.3, 27.1; MS m/z (relative intensity) 302 (M^+, 1), 196 (10), 107 (6), 91 (51), 57 (100); HRMS calcd for $C_{19}H_{26}O_3$ 302.1882, found 302.1864. **15d**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 7.22 (m, 5 H), 5.83 (ddd, J = 17.4, 10.7, 7.1 Hz, 1 H), 5.35 (dt, J = 5.5, 2.5 Hz, 1 H), 4.98 (m, 2 H), 4.18 (d, J = 2.3 Hz, 2 H), 3.88 (m, 1 H), 2.84 (m, 1 H), 2.04 (dddd, J = 15.0, 4.6, 3.4, 1.0 Hz, 1 H), 1.91 (m, 2 H), 1.74 (ddd, J = 17.7, 11.3, 6.3 Hz, 1 H), 1.12 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 138.4, 136.3, 128.4, 127.6, 116.0, 78.1, 76.7, 70.8, 45.8, 40.4, 38.8, 35.9, 27.1; MS m/z (relative intensity) 302 (M^+, 2), 196 (15), 91 (92), 57 (100); HRMS calcd for $C_{19}H_{26}O_3$ 302.1882 found 302.1857.

Reaction of 1-(Benzyloxy)-2-ethenylcyclopropane (10a) and Vinyl Acetate. Following general procedure A, a solution of 1-(benzyloxy)-2-ethenylcyclopropane (**10a**) (50 mg, 0.29 mmol), vinyl acetate (371 mg, 4.32 mmol), phenyl disulfide (63 mg, 0.29 mmol), and AIBN (9 mg, 0.06 mmol) in refluxing benzene was irradiated for 4.5 h. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 29 mg (39%) of 3-(benzyloxy)-5-ethenyl-1-cyclopentenyl acetates (diastereomer ratio: 3.4 (**15c**):2.3 (**12c**):1.9 (**13c**):1.0 (**14c**)) as a yellow oil. The structure and stereochemistry of the diastereomers were ascertained by correlation of the gas chromatography retention times of the derived alcohols ($LiAlH_4$) with the alcohols formed upon reduction of the diastereomerically pure vinyl pivalate derivatives (**12d–15d**).

Reaction of 2-Ethenyl-1-[(*p*-methoxybenzyl)oxy]cyclopropane (10d) with Methyl Acrylate. Following general procedure B, a solution of 2-ethenyl-1-[(*p*-methoxybenzyl)oxy]-cyclopropane (**10d**) (150 mg, 0.735 mmol), methyl acrylate (950 mg, 11.0 mmol), phenyl disulfide (160 mg, 0.735 mmol), and AIBN (24 mg, 0.147 mmol) in refluxing benzene was irradiated for 1 h. Purification of the residue by flash chromatography using 7% Et_2O in hexane as eluent yielded 157 mg (74%) of cyclopentane products (diastereomer ratio: 2.6 (**15e**):1.8 (**12e**):1.3 (**13e**):1.0 (**14e**)) as a yellow oil. The structure and stereochemistry of the diastereomers were ascertained by correlation of the ^1H NMR spectra (chemical shift and multiplicity) with those of the diastereomerically pure benzyloxy series (**12a–15a**). **12e**: IR (CCl_4) 1750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 5.70 (ddd, J = 17.2, 10.2, 7.9 Hz, 1 H), 5.05 (ddd, J = 17.0, 1.8, 0.9 Hz, 1 H), 5.00 (ddd, J = 10.1, 1.8, 0.6 Hz, 1 H), 4.40 (s, 2 H), 4.20 (m, 1 H), 3.81 (s, 3 H), 3.63 (s, 3 H), 3.16 (m, 2 H), 1.88 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.8, 159.0, 137.9, 130.5, 129.1, 115.5, 113.7, 79.3, 70.4, 55.3, 51.3, 47.1, 44.9, 37.7, 35.2; MS m/z (relative intensity) 290 (M^+, 5), 169 (2), 137

(3), 121 (58), 49 (100); HRMS calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1521. **13e**: IR (CCl_4) 1750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 8.8 Hz, 2 H), 6.79 (d, J = 8.7 Hz, 2 H), 5.79 (ddd, J = 17.1, 10.1, 8.4 Hz, 1 H), 4.95 (ddd, J = 16.9, 1.8, 1.0 Hz, 1 H), 4.88 (ddd, J = 10.1, 1.8, 0.6 Hz, 1 H), 4.37 (s, 2 H), 3.94 (pentet, J = 6.9 Hz, 1 H), 3.72 (s, 3 H), 3.56 (s, 3 H), 2.84 (q, J = 8.2 Hz, 1 H), 2.76 (m, 1 H), 2.20–1.98 (m, 3 H), 1.74 (dt, J = 12.9, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 159.1, 138.4, 130.6, 129.2, 115.4, 113.7, 78.6, 71.0, 55.2, 51.4, 46.8, 44.4, 37.7, 34.1; MS m/z (relative intensity) 290 (M^+, 2), 137 (92), 121 (100); HRMS calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1524. **14e**: IR (CCl_4) 1750 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.19 (d, J = 8.7 Hz, 2 H), 6.80 (d, J = 8.8 Hz, 2 H), 5.77 (ddd, J = 17.4, 10.2, 7.4 Hz, 1 H), 5.07 (ddd, J = 17.0, 1.4, 0.6 Hz, 1 H), 4.99 (ddd, J = 10.1, 1.0, 0.5 Hz, 1 H), 4.45 (s, 2 H), 4.07 (m, 1 H), 3.82 (s, 3 H), 3.68 (s, 3 H), 3.08 (m, 1 H), 2.72 (m, 1 H), 2.50 (q, J = 9.4 Hz, 1 H), 2.25 (dt, J = 13.1, 7.6 Hz, 1 H), 2.10 (m, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.1, 159.1, 140.0, 132.0, 130.6, 115.8, 114.7, 78.3, 68.2, 55.3, 51.7, 48.7, 45.4, 38.9, 36.3; MS m/z (relative intensity) 290 (M^+, 4), 169 (2), 137 (3), 121 (100); HRMS calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1526. **15e**: IR (CCl_4) 1750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 5.80 (ddd, J = 17.3, 10.1, 7.4 Hz, 1 H), 5.05 (ddd, J = 17.1, 1.5, 0.9 Hz, 1 H), 4.97 (ddd, J = 10.1, 1.7, 0.5 Hz, 1 H), 4.40 (s, 2 H), 4.10 (m, 1 H), 3.81 (s, 3 H), 3.68 (s, 3 H), 2.74 (m, 2 H), 2.29 (ddd, J = 13.7, 7.7, 6.2 Hz, 1 H), 2.06 (m, 2 H), 1.62 (ddd, J = 14.3, 9.3, 5.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 159.1, 140.4, 130.5, 129.2, 114.7, 113.8, 78.7, 70.6, 55.3, 51.7, 48.2, 39.2, 36.6; MS m/z (relative intensity) 290 (M^+, 7), 169 (2), 137 (4), 121 (100); HRMS calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1516.

Reaction of 2-Ethenyl-1-[[(*p*-trifluoromethyl)benzyl]oxy]cyclopropane (10e) with Methyl Acrylate. Following general procedure A, a solution of 2-ethenyl-1-[[(*p*-trifluoromethyl)benzyl]oxy]cyclopropane (**10e**) (50 mg, 0.21 mmol), methyl acrylate (276 mg, 3.10 mmol), phenyl disulfide (45 mg, 0.21 mmol), and AIBN (7 mg, 0.04 mmol) in refluxing benzene was irradiated for 45 min. Purification of the residue by flash chromatography using 5% Et_2O in hexane was eluent yielded 54.6 mg (80%) of methyl 3-[[(*p*-trifluoromethyl)benzyl]oxy]-5-ethenyl-1-cyclopentanecarboxylates (**12f–15f**) (diastereomer ratio: 3.7 (**15f**):3.1 (**12f**):1.8 (**13f**):1.0 (**14f**)) as a yellow oil. The structure and stereochemistry of the diastereomers were ascertained by correlation of the ^1H NMR spectra (chemical shift and multiplicity) with those of the diastereomerically pure benzyloxy series **12a–15a**.

Reaction of 2-Ethenyl-1-ethoxycyclopropane (10f) with Methyl Acrylate. Following general procedure A, a solution of 2-ethenyl-1-ethoxycyclopropane (**10f**) (100 mg, 0.892 mmol), methyl acrylate (1.15 g, 13.4 mmol), phenyl disulfide (194 mg, 0.892 mmol), and AIBN (30 mg, 0.18 mmol) in refluxing benzene was irradiated for 1 h. Purification of the residue by flash chromatography using 5% Et_2O in pentane as eluent yielded 89 mg (50%) of cyclopentane products (diastereomer ratio: 4.2 (**15g**):3.3 (**12g**):2.0 (**13g**):1.0 (**14g**)) as a yellow oil. **12g**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddd, J = 17.3, 10.2, 7.3 Hz, 1 H), 5.02 (ddd, J = 17.2, 1.6, 1.1 Hz, 1 H), 4.95 (ddd, J = 10.3, 1.7, 0.6 Hz, 1 H), 4.00 (m, 1 H), 3.67 (s, 3 H), 3.43 (q, J = 7.0 Hz, 2 H), 2.71 (m), 2.67 (m, 1 H), 2.26 (ddd, J = 13.7, 7.6, 6.2 Hz, 1 H), 2.03 (m, 2 H), 1.54 (m, 1 H), 1.18 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 140.4, 114.5, 79.2, 64.2, 51.6, 48.2, 46.5, 39.3, 36.6, 15.4; MS m/z (relative intensity) 198 (M^+, 7), 169 (22), 139 (11), 49 (100); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1249. **13g**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (ddd, J = 17.1, 10.2, 8.6 Hz, 1 H), 5.02 (ddd, J = 17.0, 1.9, 1.0 Hz, 1 H), 4.96 (ddd, J = 10.0, 1.8, 0.7 Hz, 1 H), 3.93 (pentet, J = 7.1 Hz, 1 H), 3.63 (s, 3 H), 3.47 (dq, J = 7.0, 3.0 Hz, 2 H), 2.90 (m, 1 H), 2.82 (m, 1 H,), 2.22 (dt, J = 13.4, 7.6 Hz, 1 H), 2.11 (m, 1 H), 2.05 (m, 1 H), 1.74 (m, 1 H), 1.20 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 138.5, 115.3, 79.3, 64.7, 51.4, 46.7, 44.2, 37.7, 34.2, 15.5; MS m/z (relative intensity) 198 (M^+, 2), 169 (10), 139 (13), 49 (100); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1312. **14g**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.4, 10.3, 7.5 Hz, 1 H), 5.07 (dt, 1 H, J = 17.2, 1.4 Hz), 5.00 (ddd, J = 10.3, 1.6, 1.0 Hz, 1 H), 3.95 (m, 1 H), 3.68 (s, 3 H,), 3.43 (m, 2 H), 3.02 (m, 1 H), 2.49 (q, J = 9.4 Hz, 1 H), 2.28 (ddd, J = 13.7, 9.0, 4.7 Hz, 1 H), 2.00 (m, 2 H), 1.60 (m, 1 H), 1.19 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 140.1, 114.7, 78.8, 64.0, 51.7, 48.8, 45.4, 39.0, 36.4, 15.4; MS m/z (relative intensity) 198 (M^+, 2), 169 (5), 139 (3), 49 (100); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1251. **15g**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.69 (ddd, J = 17.1, 10.2, 8.0 Hz, 1 H), 5.04 (dt, J = 17.1, 1.5, Hz, 1 H), 4.98 (ddd, J = 10.2, 1.7, 1.0 Hz, 1 H), 4.09 (m, 1 H), 3.62 (s, 3 H), 3.42 (dq, J = 7.0, 1.3 Hz, 2 H), 3.14 (m, 1 H), 3.08 (m, 1 H), 2.22 (dt, J = 14.1, 6.5 Hz, 1 H), 1.92 (m, 2 H), 1.85 (m, 1 H), 1.18 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 138.1, 115.5, 79,7, 64.0, 51.3, 47.0, 44.8, 37.7, 35.2, 15.5; MS m/z (relative intensity) 198 ($M^+ - C_2H_5$, 8) 139 (14), 49 (100); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1249.

Reaction of 2-Ethenyl-1-ethoxycyclopropane (10f) with Vinylene Carbonate. Following general procedure A, a solution of 2-ethenyl-1-ethoxycyclopropane (**10f**) (50 mg, 0.45 mmol), vinylene carbonate (384 mg, 4.46 mmol), phenyl disulfide (97 mg, 0.45 mmol), and AIBN (15 mg, 0.089 mmol) in refluxing benzene was irradiated for 2 h. Purification of the residue by flash chromatography using 30% Et_2O in hexane as eluent yielded 55 mg (37%) of 1,5-bis(phenylthio)-1-ethoxypent-3-ene (**16b**) as a 3.4:1 mixture of olefin isomers and 37 mg (42%) of cyclopentane products (diastereomer ratio: 5.5 (**15h**):4.4 (**13h**):1.0 (**14h**)) as a yellow oil. **16b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.5–7.1 (m, 10 H (M + m)), 5.59 (m, 2 H (M + m)), 4.48 (t, J = 6.7 Hz, 1 H (M)), 4.43 (t, J = 6.8 Hz, 1 H (m)), 3.44 (d, J = 5.6 Hz, 2 H (M + m)), 3.36 (m, 2 H (M + m)), 2.34 (m, 2 H (M + m)), 1.13 (t, J = 7.0 Hz, 3 H (m)), 1.11 (t, J = 7.0 Hz, 3 H (M)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 135.9, 133.9, 133.8, 132.8, 130.4, 129.8, 129.3, 128.7, 128.2, 128.1, 127.6, 127.0, 126.4, 126.1, 88.4, 63.8, 63.6, 38.9, 36.3, 33.8, 31.5, 14.8; MS m/z (relative intensity) 221 (M^+ – SPh, 12), 111 (100), 109 (16); HRMS calcd for $C_{13}H_{17}OS_2$ 221.1000, found 221.0992. **13h**: IR (CCl_4) 1830 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (ddd, J = 17.6, 10.6, 7.2 Hz, 1 H), 5.22 (m, 1 H), 5.17 (dt, J = 9.0, 1.2 Hz, 1 H), 5.01 (t, J = 5.5 Hz, 1 H), 4.94 (t, J = 5.5 Hz, 1 H), 3.84 (ddd, J = 11.1, 5.9, 5.0 Hz, 1 H), 3.61 (m, 2 H), 2.56 (m, 1 H), 2.13 (m, 1 H), 1.83 (dt, J = 12.9, 11.5 Hz), 1.26 (t, J = 7.0 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 132.9, 118.2, 81.4, 79.1, 78.1, 65.7, 43.7, 31.9, 15.2; MS m/z (relative intensity) 198 (M^+, 14) 152 (4), 111 (100), 44 (31); HRMS calcd for $C_{10}H_{14}O_4$ 198.0982, found 198.0892. **14h**: IR (CCl_4) 1830 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.5, 10.1, 6.5 Hz, 1 H), 5.19 (m, 1 H), 5.14 (m, 1 H), 4.94 (dd, J = 7.4, 4.6 Hz, 1 H), 4.77 (dd, J = 7.4, 2.8 Hz, 1 H), 3.97 (m, 1 H), 3.61 (m, 2 H), 3.06 (m, 1 H), 2.10 (dt, J = 13.8, 7.0 Hz, 1 H), 1.76 (ddd, J = 12.0, 6.7, 5.0 Hz, 1 H), 1.23 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 136.4, 116.7, 83.7, 79.0, 78.0, 66.4, 45.2, 32.9, 15.3; MS m/z (relative intensity) 198 (M^+, 2), 152 (2), 111 (100), 44 (41); HRMS calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0896. **15h**: IR (CCl_4) 1830 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.88 (ddd, J = 17.6, 10.0, 7.6 Hz, 1 H), 5.22 (m, 2 H), 5.02 (m, 1 H), 4.87 (dd, J = 6.4, 1.4 Hz), 3.94 (d, J = 4.2 Hz, 1 H), 3.50 (m, 2 H), 2.98 (m, 1 H), 2.04 (dd, J = 13.8, 6.0 Hz, 1 H), 1.77 (dt, J = 13.8, 4.3 Hz, 1 H), 1.25 (t, J = 7.0 Hz, 3 H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 133.5, 118.1, 83.6, 82.8, 81.5, 64.8, 45.9, 33.0, 15.2; MS m/z (relative intensity) 198 (M^+, 20), 152 (4), 111 (100), 44 (24); HRMS calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0900.

Reaction of 1-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-ethenylcyclopropane (10b) with Methyl Acrylate. Following general procedure A, a solution of 1[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2-ethenylcyclopropane (**10b**) (40 mg, 0.20 mmol), methyl acrylate (174 mg, 2.02 mmol), phenyl disulfide (22 mg, 0.10 mmol), and AIBN (6 mg, 0.04 mmol) in refluxing benzene was irradiated for 1 h. Purification of the residue by flash chromatography using 4% Et_2O in hexane as eluent yielded 45 mg (78%) of cyclopentane products (diastereomer ratio: 5.1 (**14i**):3.8 (**12i**):2.3 (**13i**):1.0 (**15i**)) as a clear oil. The stereochemistry of the minor diastereomer (**15i**) was confirmed by gas chromatography retention time correlation of the epimerization (NaOMe/MeOH) products of pure anti diastereomer **14i** (a 1.3:1 mixture of **14i**:**15i**). **12i**: IR (CCl_4) 1745 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82 (ddd, J = 17.6, 10.1, 7.6 Hz, 1 H), 5.02 (ddd, J = 17.1, 1.6, 1.0 Hz, 1 H), 4.96 (ddd, J = 10.1, 1.7, 0.6 Hz, 1 H), 4.35 (m, 1 H), 3.68 (s, 3 H), 2.80 (q, J = 8.8 Hz, 1 H), 2.74 (m, 1 H), 2.19 (ddd, J = 13.7, 8.3, 5.6 Hz, 1 H), 2.01 (td, J = 13.1, 6.1 Hz, 1 H), 1.92 (m, 1 H), 1.50 (dddd, J = 13.4, 8.5, 4.9, 1.2 Hz, 1 H), 0.88 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.9,

141.1, 114.1, 72.9, 51.7, 48.2, 46.3, 42.5, 40.1, 25.9, 18.1, −4.7; MS m/z (relative intensity) 284 (M^+, 8), 227 (100), 153 (57); HRMS calcd for $C_{15}H_{28}O_3Si$ 284.1808, found 284.1802. **13i**: IR (CCl_4) 1745 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 6.00 (ddd, J = 17.1, 10.1, 8.7 Hz, 1 H), 5.01 (ddd, J = 17.0, 2.0, 1.0 Hz, 1 H), 4.92 (ddd, J = 10.1, 2.1, 0.5, Hz, 1 H), 3.96 (pentet, J = 7.0 Hz, 1 H), 3.34 (s, 3 H), 2.65 (q, J = 8.6 Hz, 1 H), 2.56 (m, 1 H), 2.24 (ddd, J = 13.2, 9.3, 7.5 Hz, 1 H), 1.94 (dt, J = 13.3, 7.4 Hz, 1 H), 1.79 (m, 2 H), 0.95 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.1, 138.8, 115.1, 72.8, 51.3, 46.6, 44.1, 41.1, 37.4, 25.8, 18.1, −4.7; MS m/z (relative intensity) 269 ($M^+ - CH_3$, 3), 227 (100), 153 (8); HRMS calcd for $C_{11}H_{19}O_3Si$ ($M^+ - C_4H_9$) 227.1103, found 227.1100. **14i**: IR (CCl_4) 1745 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.69 (ddd, J = 17.3, 10.2, 7.9 Hz, 1 H), 5.04 (ddd, J = 17.0, 1.9, 1.0 Hz, 1 H), 4.96 (ddd, J = 10.0, 1.8, 0.8 Hz, 1 H), 4.45 (m, 1 H), 3.63 (s, 3 H), 3.20 (m, 1 H), 3.16 (m, 1 H,), 2.20 (ddd, J = 13.6, 7.3, 5.5 Hz, 1 H), 1.80 (m, 3 H), 0.88 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.1, 138.4, 115.3, 73.1, 51.3, 46.9, 44.5, 41.5, 38.8, 25.8, 18.1, −4.8; MS m/z (relative intensity) 284 (M^+, 2), 227 (100), 153 (64); HRMS calcd for $C_{15}H_{28}O_3Si$ 284.1808, found 284.1822. **15i**: IR (CCl_4) 1745 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (ddd, J = 17.1, 10.2, 7.8 Hz, 1 H), 5.06 (dt, J = 17.3, 1.7 Hz, 1 H), 4.94 (ddd, J = 10.1, 1.8, 0.8 Hz, 1 H), 4.30 (m, 1 H), 3.67 (s, 3 H), 3.17 (m, 1 H), 2.48 (q, J = 8.8 Hz, 1 H), 2.20 (m, 1 H), 1.91 (m, 2 H), 1.79 (ddd, J = 13.0, 10.3, 6.0 Hz, 1 H), 0.87 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 140.6, 114.2, 72.4, 51.6, 48.5, 44.8, 42.2, 39.9, 25.8, 18.0, −4.7; MS m/z (relative intensity) 284 (M^+, 4), 269 (3), 277 (100), 153 (43); HRMS calcd for $C_{15}H_{28}O_3Si$ 284.1808, found 284.1824.

Reaction of 1,1-Dimethylethyl 2-Ethenylcyclopropanecarboxylate (11a) with *n*-Butyl Vinyl Ether. Following general procedure B, a solution of cyclopropyl ester **11a** (50 mg, 0.30 mmol), *n*-butyl vinyl ether (449 mg, 4.5 mmol), trimethylaluminum (240 μL of a 1.0 M solution in toluene, 0.24 mmol), phenyl disulfide (65 mg, 0.3 mmol), and AIBN (10 mg, 0.06 mmol) in toluene at −25 °C was irradiated for 5 h. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 61 mg (76%) of cyclopentane products (diastereomer ratio: 14.2 (**17a**):2.0 (**18a**):2.2 (**19a**):1.0 (**20a**). Individual diastereomers were isolated following HPLC with 3% Et_2O in hexane as eluent. **17a**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (ddd, J = 17.4, 10.3, 7.4 Hz, 1 H), 5.08 (dt, J = 17.4, 1.5 Hz, 1 H), 5.00 (dt, J = 10.4, 1.4 Hz, 1 H), 3.63 (dd, J = 11.4, 6.3 Hz, 1 H), 3.41 (d, J = 6.5 Hz, 2 H), 2.87 (pentet, J = 8.9 Hz, 1 H), 2.53 (pentet, J = 7.4 Hz, 1 H), 2.14–2.04 (m, 2 H), 1.86 (ddd, J = 13.6, 9.0, 5.0 Hz, 1 H), 1.65–1.28 (m, 5 H), 1.44 (s, 9 H), 0.90 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 140.2, 114.5, 84.8, 80.0, 69.3, 50.0, 42.1, 34.9, 32.1, 28.1, 19.3, 13.9; MS m/z (relative intensity) 268 (M^+, 0.2), 212 (18); HRMS calcd for $C_{12}H_{20}O_3$ ($M^+ - CH_2{=}C(CH_3)_2$) 212.1412, found 212.1415. **18a**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 6.20 (ddd, J = 17.4, 11.9, 7.9 Hz, 1 H), 5.07 (d, J = 17.5 Hz, 1 H), 5.03 (d, J = 11.5 Hz, 1 H); 3.45 (dt, J = 3.0, 4.8 Hz, 1 H), 3.38 (dt, J = 9.0, 6.4 Hz, 1 H), 3.12 (dt, J = 9.0, 6.4, Hz, 1 H), 2.59 (m, 1 H), 2.35 (ddd, J = 13.9, 5.9, 2.8 Hz, 1 H), 2.3–2.0 (m, 2 H), 1.93 (m, 1 H,), 1.70 (ddd, J = 14.0, 10.3, 5.0 Hz, 1 H), 1.5–1.3 (m, 4 H), 1.38 (s, 9 H), 0.86 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 174.8, 138.2, 114.8, 81.1, 79.9, 68.7, 48.8, 42.3, 34.3, 33.3, 31.9, 28.1, 19.4, 13.9; MS m/z (relative intensity) 212 ($M^+ - CH_2{=}C(CH_3)_2$, 24). **19a**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.3, 10.3, 7.2 Hz, 1 H), 5.08 (dt, J = 17.2, 1.5 Hz, 1 H), 5.00 (dt, J = 10.4, 1.4 Hz, 1 H), 3.55 (quartet, J = 6.8 Hz, 1 H), 3.4 (m, 2 H,), 2.72 (m, 1 H), 2.62 (pentet, J = 7.6 Hz, 1 H), 2.26 (m, 1 H), 2.17 (m, 1 H), 1.83 (dt, J = 13.0, 7.9 Hz, 1 H), 1.68 (m, 1 H), 1.54–1.29 (m, 4 H), 1.44 (s, 9 H), 0.90 (t, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 140.2, 114.5, 84.8, 80.0, 69.4, 48.4, 40.8, 35.0, 32.1, 28.3, 19.3, 13.9; MS m/z (relative intensity) 212 ($M^+ - CH_2{=}C(CH_3)_2$); HRMS calcd for $C_{12}H_{20}O_3$ ($M^+ - CH_2{=}C(CH_3)_2$); 212.1412, found 212.1429. **20a**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.92 (ddd, J = 17.7, 10.4, 8.1 Hz, 1 H), 5.05 (dd, J = 17.6 Hz, 1 H), 5.00 (d, J = 10.0 Hz, 1 H), 3.79 (dt, J = 2.8, 4.6 Hz, 1 H), 3.39 (dt, J = 9.3, 6.6 Hz, 1 H), 3.30 (dt, J = 9.3, 6.6 Hz, 1 H), 2.90 (pentet, J = 7.6 Hz, 1 H), 2.6 (m, 1 H), 2.03 (ddd, J = 13.7, 9.3, 2.8 Hz, 1 H), 1.93 (t, J = 8.2 Hz, 2 H), 1.89 (ddd, J = 13.5, 7.7, 5.0 Hz, 1 H), 1.54–1.30 (m, 4 H), 1.42 (s, 9 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 138.0, 115.0, 83.3, 80.0, 69.0, 48.1, 41.4, 34.9, 33.1, 32.0, 28.1, 19.4, 13.9; MS m/z (relative intensity) 212 ($M^+ - CH_2{=}C(CH_3)_2$, 22); HRMS calcd for $C_{12}H_{20}O_3$ ($M^+ - CH_2{=}C(CH_3)_2$) 212.1412, found 212.1417.

Reaction of 1,1-Dimethylethyl 2-Ethenylcyclopropanecarboxylate (11a) with Vinyl Pivalate. Following a general procedure A, a solution containing cyclopropyl ester **11a** (50 mg, 0.30 mmol), vinyl pivalate (575 mg, 4.5 mmol), phenyl disulfide (65 mg, 0.30 mmol), and AIBN (10 mg, 0.06 mmol) in refluxing benzene was irradiated for 50 min. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent afforded 49 mg (55%) of cyclopentanes as a 4.0 (**17b**):2.2 (**18b**):1.0 (**20b**) ratio of diastereomers. Individual isomers could be obtained in pure form by rechromatography with 4% Et_2O in hexane as eluent. **17b**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.80 (ddd, J = 17.3, 10.0, 7.3 Hz, 1 H), 5.08 (dd, J = 17.2, 1.4 Hz, 1 H), 5.02 (dd, J = 10.3, 1.4 Hz, 1 H), 4.91 (q, J = 6.0 Hz, 1 H), 2.90 (pentet, J = 8.8 Hz, 1 H), 2.61 (ddd, J = 15, 7.6, 7.4 Hz, 1 H), 2.2 (m, 2 H), 1.84 (ddd, J = 13.7, 9.1, 4.4 Hz, 1 H), 1.71 (m, 1 H), 1.44 (s, 9 H), 1.18 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 174.4, 138.6, 115.3, 80.4, 79.0, 49.4, 42.4, 38.6, 34.8, 33.3, 28.0, 27.1; MS m/z (relative intensity) 296 (M^+, 0.1,), 240 (8); HRMS calcd for $C_{13}H_{20}O_4$ 240.1362, found 240.1348. **18b**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.81 (ddd, J = 17.4, 10.4, 7.1 Hz, 1 H), 5.1 (m, 3 H), 2.8 (m, 1 H), 2.61 (dt, J = 11.8, 6.8 Hz, 1 H), 2.26 (ddd, J = 16.1, 10.7, 5.4 Hz, 1 H), 2.0 (m, 3 H), 1.43 (s, 9 H), 1.16 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 174.3, 136.0, 116.2, 80.2, 76.6, 48.4, 42.1, 38.8, 35.6, 32.9, 28.1, 27.1; MS m/z (relative intensity) 296 (M^+, 0.3), 240 (14); HRMS calcd for $C_{13}H_{20}O_4$ 240.1362, found 240.1366. **20b**: IR (CCl_4) 1725 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.77 (ddd, J = 17.4, 10.3, 7.2 Hz, 1 H), 5.23 (m, 1 H), 5.05 (m, 2 H), 2.95 (dq, J = 8.6, 4.4 Hz, 1 H), 2.78 (m, 1 H), 2.15 (ddd, J = 14.5, 7.9, 4.8 Hz, 1 H), 2.0 (m, 2 H), 1.45 (s, 9 H), 1.17 (s, 9 H); ^{13}C NMR (75 (MHz, $CDCl_3$) δ 177.7, 175.5, 136.1, 116.2, 80.3, 78.0, 47.4, 41.6, 36.2, 32.7, 28.0, 27.2; MS m/z (relative intensity) 240 ($M^+ - C_4H_8$, 7); HRMS calcd for $C_{17}H_{28}O_4$ 296.1988, found 296.199.

Reaction of 1,1-Dimethylethyl 2-Ethenylcyclopropanecarboxylate (11a) with 1,1-Dimethylethyl Acrylate. Following general procedure B, a solution of cyclopropyl ester **11a** (50 mg, 0.30 mmol), *tert*-butyl acrylate (569 mg, 4.4 mmol), trimethylaluminum (120 μL of a 2.0 M solution in toluene, 0.24 mmol), phenyl disulfide (65 mg, 0.30 mmol), and AIBN (10 mg, 0.06 mmol) in toluene at −50 °C was irradiated for 52 h. Purification of the crude product by flash chromatography with 5% Et_2O in hexane furnished 46 mg (52%) of cyclopentane products as a 10.3 (**17c**):4.0 (**18c**):1.3 (**20c**):1.0 (**19c**) mixture of diastereomers. Individual stereoisomers could be obtained via HPLC with 3% Et_2O in hexane as eluent. **17c**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.78 (dd, J = 17.4, 10.1, 7.6 Hz, 1 H), 5.06 (d, J = 17.1 Hz, 1 H), 4.99 (d, J = 10.4 Hz, 1 H), 2.85 (pentet, J = 7.2 Hz, 1 H), 2.70 (m, 1 H), 2.54 (q, J = 9.1 Hz, 1 H), 2.14 (m, 3 H), 1.67 (ddd, J = 21.0, 11.1, 10.9 Hz, 1 H), 1.45 (s, 9 H), 1.44 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 174.2, 139.8, 114.8, 80.3, 80.2, 50.3, 48.8, 43.5, 36.6, 32.7, 28.1, 28.0; MS m/z (relative intensity) 223 ($M^+ - C_4H_9O$, 15). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 69.08; H, 9.85. **18c**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.81 (ddd, J = 17.3, 10.0, 7.9 Hz, 1 H), 5.05 (dd, J = 17.7, 1.6 Hz, 1 H), 4.99 (dd, J = 10.3, 1.6 Hz, 1 H), 2.82 (m, 2 H), 2.72 (pentet, J = 9.1 Hz, 1 H), 2.25 (m, 1 H), 2.1 (m, 2 H), 1.92 (ddd, J = 13.1, 9.2, 7.5 Hz, 1 H), 1.45 (s, 9 H)$_3$, 1.41 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 172.8, 138.1, 115.4, 80.4, 80.1, 49.1, 46.5, 44.0, 34.8, 31.5, 28.2, 28.1; MS m/z (relative intensity) 223 ($M^+ - C_4H_9O$, 5), HRMS calcd for $C_{13}H_{19}O_3$ 223.1334, found 223.1318. **19c**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.74 (ddd, J = 17.5, 10.1, 7.5 Hz, 1 H), 5.05 (d, J = 17.0 Hz, 1 H), 4.98 (d, J = 10.6 Hz, 1 H), 2.81 (m, 2 H), 2.41 (dt, J = 10.0, 7.4 Hz, 1 H), 2.3–2.0 (m, 2 H), 2.05 (ddd, J = 12.9, 10.6, 8.9 Hz, 1 H), 1.7 (m, 1 H), 1.45 (s, 9 H), 1.43 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 173.5, 140.0, 114.6, 80.4, 80.3, 51.5, 47.3, 43.1, 35.1, 33.7, 28.1, 28.0; MS m/z (relative intensity) 223 ($M^+ - C_4H_9O$, 5); HRMS calcd for $C_{13}H_{19}O$ 223.1334, found 223.1340. **20c**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.76 (ddd, J = 17.5, 10.3, 7.7 Hz, 1 H), 5.06 (d, J = 17.0 Hz, 1 H), 5.01 (d, J = 9.1 Hz, 1 H), 3.01 (m, 1 H), 2.93 (m, 2 H,), 2.19 (m, 1 H), 2.01 (m, 3 H), 1.44 (s, 9 H), 1.41 (s, 9 H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 175.8, 173.2, 137.7, 115.5, 80.3, 80.1, 49.4, 46.7, 42.8, 34.9, 31.4, 28.2, 28.1; MS *m/z* (relative intensity) 223 ($M^+ - C_4H_9O$, 7); HRMS calcd for $C_{13}H_{19}O_3$ 223.1334, found 223.1331.

Reaction of 1,1-Dimethylethyl 2-(1-Methylethenyl)cyclopropanecarboxylate (11b) with *n*-Butyl Vinyl Ether. Following general procedure B, a solution of cyclopropyl ester **11b** (46 mg, 0.25 mmol), *n*-butyl vinyl ether (380 mg, 3.8 mmol), trimethylaluminum (100 μL of a 2.0 M solution in toluene, 0.2 mmol), phenyl disulfide (55 mg, 0.25 mmol), and AIBN (8 mg, 0.05 mmol) in toluene at −30 °C was irradiated for 5 h. Purification of the crude product by flash chromatography with 5% Et_2O in hexane yielded 50 mg (70%) of the cyclopentane products as a 7.0 (**17d**):2.6 (**18d**):1.2 (**20d**):1.0 (**19d**) mixture of diastereomers. **17d**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.80 (s, 1 H), 4.77 (s, 1 H), 3.76 (dt, *J* = 4.6, 6.6 Hz, 1 H), 3.42 (dt, *J* = 9.2, 6.5 Hz, 1 H), 3.37 (dt, *J* = 9.2, 6.6 Hz, 1 H), 2.86 (pentet, *J* = 8.7 Hz, 1 H), 2.51 (dt, *J* = 11.2, 6.8 Hz, 1 H), 2.14–2.01 (m, 2 H), 1.88 (ddd, *J* = 13.5, 8.5, 4.3 Hz, 1 H), 1.76 (s, 3 H), 1.70 (m, 1 H,), 1.57–1.29 (m, 4 H), 1.44 (s, 9 H), 0.91 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.2, 146.0, 110.3, 83.0, 80.1, 69.2, 53.2, 42.2, 35.1, 33.3, 32.1, 28.1, 21.0, 19.4, 13.9; MS *m/z* (relative intensity) 282 (M^+, 1), 226 (12); HRMS calcd for $C_{13}H_{22}O_3$ ($M^+ - CH_2{=}C(CH_3)_2$), 226.1768, found 226.1572. **18d**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.82 (s, 1 H), 4.75 (s, 1 H), 3.84 (dt, *J* = 1.9, 5.0 Hz, 1 H), 3.45 (dt, *J* = 9.3, 6.6 Hz, 1 H), 3.21 (dt, *J* = 9.3, 6.6 Hz, 1 H), 2.72 (m, 1 H), 2.36 (pentet, *J* = 5.8 Hz, 1 H), 2.18–2.08 (m, 2 H), 2.04–1.94 (m, 2 H), 1.80 (s, 3 H), 1.53–1.28 (m, 4 H), 1.45 (s, 9 H), 0.88 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 144.5, 110.9, 80.4, 79.9, 68.3, 51.9, 42.5, 34.1, 31.9, 31.3, 28.1, 22.4, 19.4, 13.9; MS *m/z* (relative intensity) 226 ($M^+ - CH_2{=}C(CH_3)_2$).**19d**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 4.77 (s, 2 H), 3.71 (q, *J* = 7.0 Hz, 1 H), 3.45 (dt, *J* = 9.2, 6.5 Hz, 1 H), 3.39 (dt, *J* = 9.2, 6.7 Hz, 1 H), 2.70 (dq, *J* = 6.2, 8.8 Hz, 1 H), 2.60 (q, *J* = 8.0 Hz, 1 H), 2.27 (dq, *J* = 8.3, 6.4 Hz, 1 H), 2.15 (ddd, *J* = 13.5, 9.1, 6.2 Hz, 1 H), 1.84 (m, 1 H), 1.76 (s, 3 H), 1.71 (m, 1 H), 1.57–1.30 (m, 4 H), 1.46 (s, 9 H), 0.91 (t, *J* = 7.7 Hz, 3 H), ^{13}C NMR (90 MHz, $CDCl_3$) δ 174.9, 146.1, 110.1, 83.1, 69.3, 51.2, 40.9, 35.2, 32.1, 30.4, 28.1, 21.1, 19.4, 13.9; MS *m/z* (relative intensity) 282 (M^+, 0.5), 226 (12); HRMS calcd for $C_{13}H_{21}O_2$ ($M^+ - OC(CH_3)_3$) 209.1541, found 209.1545. **20d**: IR (CCl_4) 1725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.83 (s, 1 H), 4.73 (s, 1 H), 3.93 (t, *J* = 4.0 Hz, 1 H), 3.45 (dt, *J* = 9.4, 6.4 Hz, 1 H), 3.25 (dt, *J* = 9.4, 6.5 Hz, 1 H), 2.94 (m, 1 H), 2.53 (m, 1 H), 2.14 (m, 2 H), 1.94 (ddd, *J* = 11.5, 8.0, 3.5 Hz, 1 H), 1.89 (ddd, *J* = 13.9, 7.8, 4.4 Hz, 1 H), 1.80 (s, 3 H), 1.53–1.28 (m, 4 H), 1.44 (s, 9 H), 0.89 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 144.4, 110.8, 81.7, 79.9, 68.7, 50.6, 41.4, 34.8, 32.0, 30.7, 28.1, 22.8, 19.7, 13.9; MS *m/z* (relative intensity) 282 (M^+, 2), 226 (13); HRMS calcd for $C_{17}H_{30}O_3$ 282.2195, found 282.2175.

Reaction of 1,1-Dimethylethyl 2-(1-Methylethenyl)cyclopropanecarboxylate (11b) with 1,1-Dimethylethyl Acrylate. Following general procedure A, a solution of cyclopropyl ester **11b** (200 mg, 1.1 mmol), *tert*-butyl acrylate (2.1 g, 17 mmol), phenyl disulfide (240 mg, 1.1 mmol), and AIBN (36 mg, .22 mmol) in benzene at reflux was irradiated for 4 h. The residue was purified by flash chromatography with 4% Et_2O in hexane as eluent to furnish 150 mg (44%) of cyclopentane products as a 3.7 (**17e**):3.0 (**18e**):1.0 (**19e**) mixture of diastereomers. Pure isomers could be obtained via HPLC with 3% Et_2O in hexane as eluent. **17e**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.78 (s, 1 H), 4.75 (s, 1 H), 2.86–2.63 (m, 3 H), 2.2–2.0 (m, 3 H), 1.73 (s, 3 H), 1.7 (m, 1 H), 1.44 (s, 9 H), 1.42 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 174.6, 145.2, 111.1, 80.2, 51.9, 48.2, 43.3, 35.5, 33.0, 28.1, 19.7; MS *m/z* (relative intensity) 237 ($M^+ - C_4H_9O$, 8); HRMS calcd for $C_{14}H_{21}O_3$ ($M^+ - C_4H_9O$): 237.1491, found 237.1489. **18e**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.79 (s, 1 H), 4.77 (s, 1 H), 2.92 (dt, *J* = 8.0, 5.0 Hz, 1 H), 2.73 (pentet, *J* = 8.2 Hz, 1 H), 2.65 (m, 1 H), 2.27 (ddd, *J* = 13.8, 8.6, 5.2, 1 H), 2.14 (m, 2 H), 1.95 (m, 1 H), 1.79 (s, 3 H), 1.45 (s, 9 H), 1.38 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 173.5, 114.1, 111.2, 80.2, 80.0, 50.0, 47.1, 43.7, 32.5, 31.7, 28.1, 28.0, 22.9; MS *m/z* (relative intensity) 310 (M^+, 0.5), 254 (7), 237 (2). Anal. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74, found C, 69.80; H, 9.83. **19e**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 4.76 (s, 1 H), 4.74 (s, 1 H), 2.85 (pentet, *J* = 9.4 Hz, 1 H), 2.7 (m, 1 H), 2.58 (dt, *J* = 10.4, 7.4 Hz, 1 H), 2.25 (dt, *J* = 12.8, 7.8 Hz, 1 H), 2.13 (m, 1 H), 2.04 (ddd, *J* = 12.8, 10.7, 9.4 Hz, 1 H), 1.75 (m, 1 H), 1.72 (s, 3 H), 1.44, (s, 9 H), 1.42 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 173.7, 145.6, 110.6, 80.2, 50.3, 49.6, 43.2, 34.0, 28.1, 19.9; MS *m/z* (relative intensity) 310 (M^+, 0.1), 254 (2), 237 (5); HRMS calcd for $C_{18}H_{30}O_4$ 310.2145, found 310.2165.

Reaction of 1,1-Dimethylethyl 2-(3,3-Dimethylbut-1-en-2-yl)-1-cyclopropanecarboxylate (11c) with Butyl Vinyl Ether. Following general procedure B, a solution containing 1,1-dimethylethyl 2-(3,3-dimethylbut-1-en-2-yl)-1-cyclopropanecarboxylate (**11c**) (50 mg, 0.22 mmol), butyl vinyl ether (335 mg, 3.4 mmol), trimethylaluminum (13 mg, 0.22 mmol), phenyl disulfide (60 mg, 0.22 mmol), and AIBN (9 mg, 0.05 mmol) was irradiated for 40 h. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 15 mg (21%) of cyclopentanes (diastereomer ratio: 7.0 (**17f**):1.3 (**18f**):1.2 (**19f**):1.0 (**20f**)) as a clear oil. **19f**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.91 (s, 1 H), 4.74 (s, 1 H), 3.75 (dd, *J* = 14.0, 7.2 Hz, 1 H), 3.42 (dt, *J* = 9.2, 6.4 Hz, 1 H), 3.31 (dt, *J* = 9.2, 6.4 Hz, 1 H), 2.78 (dq, *J* = 8.5, 5.9 Hz, 1 H), 2.68 (q, *J* = 8.2 Hz, 1 H), 2.29 (m, 2 H), 1.83 (m, 1 H), 1.50 (m, 3 H), 1.44 (s, 9 H), 1.31 (m, 2 H), 1.07 (s, 9 H), 0.88 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 105.0, 87.1, 80.0, 69.8, 45.9, 41.6, 37.4, 36.6, 35.5, 32.1, 29.7, 29.0, 28.1, 19.3, 13.9; MS *m/z* (relative intensity) 325 ($M^+ + 1$, 1), 267 (2), 211 (4), 56 (19); HRMS calcd for $C_{16}H_{27}O_3$ ($M^+ - C_4H_9$) 267.1961 found 267.1954. **18f**: IR (CCl_4) 1740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.05 (s, 2 H), 3.61 (m, 1 H), 3.36 (dt, *J* = 9.0, 6.4 Hz, 1 H), 3.21 (dt, *J* = 9.0, 6.4 Hz, 1 H), 2.63 (ddd, *J* = 10.3, 7.5, 6.7 Hz, 1 H), 2.38 (ddd, *J* = 13.1, 6.3, 4.9 Hz, 1 H), 2.10 (m, 3 H), 1.93 (dt, *J* = 12.1, 7.0 Hz, 1 H), 1.44 (s, 9 H), 1.30 (m, 4 H), 1.06 (s, 9 H), 0.87 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 109.9, 80.8, 79.8, 71.7, 68.6, 46.5, 42.0, 36.5, 36.1, 35.6, 31.9, 29.1, 28.1, 19.4, 14.0; MS *m/z* (relative intensity) 324 (M^+, 1), 267 (2), 211 (5), 56 (15); HRMS calcd for $C_{16}H_{26}O_3$ ($M^+ - C_4H_{10}$) 266.1883, found 266.1873. **17f**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.93 (d, *J* = 1.3 Hz, 1 H), 4.81 (s, 1 H), 3.75 (ddd, *J* = 6.6, 5.4, 3.8 Hz, 1 H), 3.41 (dt, *J* = 9.2, 6.6 Hz, 1 H), 3.28 (dt, *J* = 9.2, 6.6 Hz, 1 H), 2.85 (m, 1 H), 2.60 (m, 1 H), 2.27 (dtd, *J* = 12.9, 7.8, 1.2 Hz, 1 H), 2.07 (ddd, *J* = 13.4, 9.3, 6.7 Hz, 1 H); 1.50 (m, 3 H), 1.44 (s, 9 H), 1.32 (m, 2 H), 1.07 (s, 9 H), 0.88 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 162.0, 105.8, 87.6, 80.0, 69.5, 47.8, 43.2, 39.6, 36.6, 35.2, 32.1, 28.9, 28.1, 19.3, 13.9; MS *m/z* (relative intensity) 267 ($M^+ - C_4H_9$, 2), 211 (4), 56 (20); HRMS calcd for $C_{16}H_{27}O_3$ (M^+-C_4H_9) 267.1961, found 267.1938. **20f**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.03 (d, *J* = 1 Hz, 1 H), 5.02 (d, *J* = 0.7 Hz, 1 H), 3.67 (t, *J* = 4.1 Hz, 1 H), 3.35 (dt, *J* = 9.2, 6.5 Hz, 1 H), 3.28 (dt, *J* = 9.2, 6.5 Hz, 1 H), 2.93 (m, 1 H), 2.58 (ddd, *J* = 12.1, 7.8, 4.0 Hz, 1 H), 2.08 (m, 2 H), 1.95 (m, 2 H), 1.45 (m, 2 H), 1.44 (s, 9 H), 1.33 (m, 2 H), 1.07 (s, 9 H), 0.88 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 176.6, 154.0, 109.4, 82.5, 79.8, 69.2, 44.9, 41.1, 36.6, 36.2, 32.0, 29.7, 29.0, 28.1, 19.4, 14.1; MS *m/z* (relative intensity) 267 ($M^+ - C_4H_9$, 3), 211 (4), 56 (21); HRMS calcd for $C_{16}H_{27}O_3$ ($M^+ - C_9H_{17}O_2$) 167.1437, found 167.0336.

Reaction of 1,1-Dimethylethyl 2-Ethenyl-2-methyl-1-cyclopropanecarboxylate (11d) with Butyl Vinyl Ether. Following general procedure B, a solution containing 1,1-dimethylethyl 2-ethenyl-2-methyl-1-cyclopropanecarboxylate (**11d**) (50 mg, 0.27 mmol), trimethylaluminum (16 mg, 0.22 mmol), butyl vinyl ether (412 mg, 4.12 mmol), phenyl disulfide (60 mg, 0.27 mmol), and AIBN (9 mg, 0.05 mmol) was irradiated for 75 h. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 54 mg (69%) of cyclopentane products (diastereomer ratio: 1.8 (**17g**):1.0 (**18g**)) as a clear oil. **17g**: IR (CCl_4) 1730 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.06 (dd, *J* = 17.5, 10.7 Hz, 1 H), 5.23 (dd, *J* = 17.5, 1.3 Hz, 1 H), 5.11 (dd, *J* = 10.7, 1.3 Hz, 1 H), 3.70 (t, *J* = 7.1 Hz, 1 H), 3.37 (m, 2 H), 3.03 (m, 1 H), 2.56 (ddd, *J* = 13.5, 7.2, 6.2 Hz, 1 H), 2.17 (dd, *J* = 13.1, 8.8 Hz, 1 H), 2.00 (ddd, *J* = 13.4, 10.7, 7.0 Hz, 1 H), 1.91 (dd, *J* = 13.1, 9.1 Hz, 1 H), 1.58 (m, 2 H), 1.53 (s, 9 H), 1.45 (m, 2 H), 1.23 (s, 3 H), 0.98 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.8, 146.4, 111.7, 85.9, 80.0, 70.0, 48.2, 40.2, 39.9, 32.8, 32.1, 28.1, 19.4, 17.8, 13.9; MS *m/z* (relative intensity) 226 ($M^+ - C_4H_8$, 4), 153 (23), 56 (20); HRMS calcd for $C_{13}H_{22}O_3$ ($M^+ - C_4H_8$) 226.1525, found 226.1558. **18g**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.48 (dd, *J* = 17.7, 10.9 Hz, 1 H), 5.25 (dd, *J* = 17.7, 1.5 Hz, 1 H), 5.23 (dd, *J* = 10.9, 1.5 Hz, 1 H), 3.50 (dt,

J = 9.0, 6.3 Hz, 1 H), 3.29 (dt, J = 9.0, 6.3 Hz, 1 H), 2.83 (m, 1 H), 2.57 (dd, J = 12.9, 8.3 Hz, 1 H), 2.38 (ddd, J = 13.7, 7.4, 5.1 Hz, 1 H), 2.13 (ddd, J = 13.7, 9.8, 5.5 Hz, 1 H), 1.78 (dd, J = 12.9, 9.2 Hz, 1 H), 1.60 (m, 2 H), 1.53 (s, 9 H), 1.50 (m, 2 H), 1.06 (s, 3 H), 1.00 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 174.8, 143.5, 112.2, 88.1, 79.4, 69.3, 48.7, 40.9, 39.4, 33.4, 32.4, 28.1, 23.8, 19.8, 14.1; MS m/z (relative intensity) 225 ($M^+ - C_4H_9$, 6), 152 ($M^+ - C_8H_{18}O$, 36), 56 ($(CH_3)_2C{=}CH_2^+$, 16); HRMS calc for $C_{13}H_{22}O_3$ ($M^+ - C_4H_8$) 226.1525, found 226.1579.

Reaction of 1,1-Dimethylethyl 2-Ethenyl-3-methyl-1-cyclopropanecarboxylate (21) with Butyl Vinyl Ether. Following general procedure B, a solution containing 1,1-dimethylethyl 2-ethenyl-3-methyl-1-cyclopropanecarboxylate (**21**) (50 mg, 0.27 mmol), butyl vinyl ether (412 mg, 4.12 mmol), trimethylaluminum (16 mg, 0.22 mmol), phenyl disulfide (60 mg, 0.27 mmol), and AIBN (9 mg, 0.05 mmol) was irradiated for 36 h. Purification of the residue by flash chromatography using 5% Et_2O in hexane as eluent yielded 57 mg (74%) of cyclopentane products (diastereomer ratio: 16.3 (**22a**):14.0 (**22b**):2.3 (**22c**):1 (**22d**)) as a clear oil. **22a**: IR (CCl_4) 1712 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, J = 17.2, 10.3, 8.4 Hz, 1 H), 5.09 (m, 2 H), 3.82 (ddd, J = 7.9, 6.1, 3.3 Hz, 1 H), 3.40 (m, 2 H), 3.01 (dt, J = 9.2, 7.3 Hz, 1 H), 2.61 (dd, J = 6.7, 4.4 Hz, 1 H), 2.51 (sextet, J = 7.2 Hz), 2.36 (ddd, J = 14.2, 9.4, 7.9 Hz, 1 H), 1.77 (ddd, J = 13.3, 9.9, 3.3 Hz, 1 H), 1.50 (m, 2 H), 1.45 (s, 9 H), 1.34 (m, 2 H), 0.91 (t, J = 6.9 Hz, 3 H), 0.79 (d, J = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 137.9, 116.3, 83.1, 80.2, 69.4, 55.1, 47.4, 39.7, 32.1, 29.7, 28.2, 19.4, 13.9, 11.6; MS m/z (relative intensity) 226 ($M^+ - C_4H_8$, 14), 182 (3), 152 (3), 56 (19); HRMS calc for $C_{13}H_{21}O_3$ ($M^+ - C_4H_8$) 226.1525, found 226.1573. **22b**: IR (CCl_4) 1705 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 5.78 (ddd, J = 17.1, 10.1, 8.5 Hz), 5.21 (ddd, J = 17.1, 2.1, 0.9 Hz, 1 H), 5.14 (ddd, J = 10.1, 1.8, 0.5 Hz, 1 H), 3.74 (m, 1 H), 3.39 (m, 2 H), 2.68 (dd, J = 18.8, 9.0 Hz, 1 H), 2.41 (ddd, J = 13.4, 8.8, 7.7 Hz, 1 H), 2.26 (m, 1 H), 2.09 (m, 2 H), 1.63 (m, 2 H), 1.53 (s, 9 H), 1.47 (m, 2 H), 1.23 (d, J = 6.5 Hz, 3 H), 0.99 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 139.5, 115.9, 84.0, 80.1, 69.4, 59.0, 49.9, 42.4, 34.8, 32.0, 28.1, 19.3, 17.3, 13.9; MS m/z (relative intensity) 226 ($M^+ - C_4H_8$, 14), 169 (3), 153 (13), 56 (15); HRMS calcd for $C_{13}H_{21}O_3$ ($M^+ - C_4H_8$) 226.1525, found 226.1583. +22c: IR (CCl_4) 1745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (ddd, J = 17.2, 10.2, 9.2 Hz, 1 H), 5.04 (m, 2 H), 3.74 (td, J = 5.2, 3.4 Hz, 1 H), 3.44 (dt, J = 9.1, 6.5 Hz, 1 H), 3.26 (dt, J = 9.1, 6.5 Hz, 1 H), 2.22 (td, J = 9.6, 7.3 Hz, 1 H), 2.15 (m, 1 H), 2.07 (m, 2 H), 1.95 (td, J = 9.9, 5.2 Hz, 1 H), 1.50 (m, 2 H), 1.45 (s, 9 H), 1.34 (m, 2 H), 1.00 (d, J = 6.5 Hz, 3 H), 0.89 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 137.6, 116.3, 82.0, 79.9, 68.7, 57.8, 50.9, 41.4, 34.4, 32.0, 28.1, 19.4, 17.6, 14.0; MS m/z (relative intensity) 226 ($M^+ - C_4H_8$, 9), 153 (15), 56 (15); HRMS calcd for $C_{13}H_{21}O_3$ ($M^+ - C_4H_8$) 226.1525, found 226.1555. **22d**: IR (CCl_4) 1735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (ddd, J = 17.1, 10.2, 8.3 Hz, 1 H), 5.11 (ddd, J = 17.1, 1.8, 1 Hz, 1 H), 5.05 (ddd, J = 10.2, 1.8, 0.5 Hz, 1 H), 3.58 (q, J = 8.3 Hz, 1 H), 3.44 (t, J = 6.6 Hz, 2 H), 2.75 (q, J = 8.3 Hz, 1 H), 2.25 (q, J = 8.5 Hz, 1 H), 2.18 (dt, J = 13.1, 7.8 Hz, 1 H), 1.95 (m, 2 H), 1.52 (m, 2 H), 1.46 (s, 9 H), 1.35 (m, 2 H), 0.98 (d, J = 7.0 Hz, 3 H), 0.89 (d, J = 7.4 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 173.9, 139.9, 115.9, 84.0, 80.4, 69.5, 56.3, 45.4, 39.1, 33.6, 32.1, 28.2, 19.3, 15.0, 13.9; MS m/z (relative intensity) 226 ($M^+ - C_4H_8$, 3), 153 (7), 56 (17); HRMS calcd for $C_{13}H_{21}O_3$ ($M^+ - C_8H_{16}$) 170.0943, found 170.0528.

Reaction of 1,1-Dimethoxy-2-ethenylcyclopropane (10g) with Methyl Acrylate. Following general procedure B, a solution of 1,1,dimethoxy-2-ethenylcyclopropane (**10g**) (100 mg, 0.781 mmol), methyl acrylate (1.01 g, 1.17 mmol), phenyl disulfide (170 mg, 0.781 mmol), and AIBN (26 mg, 0.16 mmol) in refluxing benzene was irradiated for 2.25 h. Purification of the residue by flash chromatography using 6% Et_2O in hexane as eluent yielded 72 mg (43%) of cyclopentane products (diastereomer ratio: 2.5 (**24a**):1.0 (**24b**)) as a yellow oil. **24a**: IR (CCl_4) 1750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (ddd, J = 17.1, 10.2, 8.4 Hz, 1 H), 5.04 (ddd, J = 17.1, 1.6, 1.0 Hz, 1 H), 4.99 (ddd, J = 10.1, 1.3, 0.4 Hz, 1 H), 3.63 (s, 3 H), 3.25 (s, 3 H), 3.18 (s, 3 H), 3.08 (q, J = 8.5 Hz, 1 H), 2.97 (m, 1 H), 2.25–2.07 (m, 3 H), 1.85 (dd, J = 13.5, 7.9 Hz, 1 H); ^{13}C NMR (75 MHz, C_6H_6) δ 174.0, 139.1, 116.1, 110.9, 51.4, 50.2, 48.7, 46.8, 44.6, 40.2, 37.1; MS m/z (relative intensity) 214 (M^+, 6), 183 (40); HRMS calcd for $C_{11}H_{18}O_4$ 214.1205, found 214.1209. **24b**: IR (CCl_4) 1750 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 6.05 (ddd, J = 17.2, 10.3, 8.9 Hz, 1 H), 5.14 (ddd, J = 17.2, 1.9, 0.9 Hz, 1 H), 5.03 (ddd, 10.4, 2.1, 0.7 Hz, 1 H), 3.33 (s, 3 H), 3.26 (m, 1 H), 3.08 (s, 3 H), 2.98 (s, 3 H), 2.27 (m, 1 H), 1.90 (m, 2 H), 1.68 (m, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.0, 137.1, 116.2, 110.0, 54.3, 51.8, 49.4, 49.3, 49.0, 33.8, 25.6; MS m/z (relative intensity) 214 (M^+, 7), 183 (50); HRMS calcd for $C_{11}H_{18}O_4$ 214.1205, found 214.1201.

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Registry No. **10a**, 128261-39-2; **10b**, 137144-75-3; **10c**, 137144-76-4; **10d**, 137144-77-5; **10e**, 137144-78-6; **10f**, 113975-50-1; **10g**, 137144-79-7; **11a**, 113975-48-7; **11b**, 113975-49-8; **11c**, 121352-20-3; **11d**, 137144-80-0; **12a**, 128261-52-9; **12b**, 137144-82-2; **12c**, 137144-83-3; **12d**, 137144-84-4; **12e**, 137144-85-5; **12f**, 137144-86-6; **12g**, 137144-87-7; **12i**, 137144-88-8; **12j**, 137144-89-9; **13a**, 128301-57-5; **13b**, 137252-51-8; **13c**, 137252-54-1; **13d**, 137252-57-4; **13e**, 137252-60-9; **13f**, 137252-63-2; **13g**, 137252-66-5; **13h**, 114030-38-5; **13i**, 137252-69-8; **13j**, 137252-72-3; **14a**, 128301-56-4; **14b**, 137252-52-9; **14c**, 137252-55-2; **14d**, 137252-58-5; **14e**, 137252-61-0; **14f**, 137252-64-3; **14g**, 137252-67-6; **14h**, 114030-39-6; **14i**, 137252-70-1; **14j**, 137252-73-4; **15a**, 128301-58-6; **15b**, 137252-53-0; **15c**, 137252-56-3; **15d**, 137252-59-6; **15e**, 137252-62-1; **15f**, 137252-65-4; **15g**, 137252-68-7; **15h**, 113975-54-5; **15i**, 137252-71-2; **15j**, 137252-74-5; **17a**, 137144-90-2; **17b**, 114127-30-9; **17c**, 113975-51-2; **17d**, 137144-91-3; **17e**, 113975-52-3; **17f**, 137144-92-4; **17g**, 137144-93-5; **18a**, 137252-75-6; **18b**, 113975-53-4; **18c**, 114030-32-9; **18d**, 137252-79-0; **18e**, 114030-35-2; **18f**, 137252-81-4; **18g**, 137252-84-7; **19a**, 137252-76-7; **19b**, 137252-78-9; **19c**, 114030-34-1; **19d**, 137252-80-3; **19e**, 114030-36-3; **19f**, 137252-82-5; **20a**, 137252-77-8; **20b**, 114030-37-4; **20c**, 114030-33-0; **20d**, 137328-40-6; **20**, 137252-83-6; **21**, 137144-81-1; **22a**, 137144-94-6; **22b**, 137252-85-8; **22c**, 137252-86-9; **22d**, 137252-87-0; **24a**, 137144-96-8; **24b**, 137144-97-9; **32b**, 137175-32-7; **32c**, 137144-95-7; **33**, 2348-55-2; **34**, 137175-33-8; **35**, 2887-44-7; $H_2C{=}CHOBu$, 111-34-2; Ph_2S_2, 882-33-7; PhS$^\bullet$, 4985-62-0; $H_3COCH_2^\bullet$, 16520-04-0; $OHCOCH_2^\bullet$, 3122-12-1; $OHCCH_2^\bullet$, 4400-01-5; $H_2C{=}CHCO_2CH_3$, 96-33-3; $H_2C{=}CHCO_2Bu$-t, 1663-39-4; $H_2C{=}CHOCOCH_3$, 108-05-4; $H_2C{=}CHOCOBu$-t, 3377-92-2; cyclic vinylene carbonate, 872-36-6.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra for all cyclopentanes described in this study; DNOE data for **12a–15a**, **12d–15d**, **12g–15g**, **13h–15h**, **12i–14i**, **17a–20a**, **17b**, **18b**, **20b**, **17c–20c**, **17d–20d**, **17e–19e**, **17f–20f**, **17g**, **18g**, **22a–d**, and **24a/b**, retention time correlation for cyclopentane methanols derived from **12b–15b** and **12a–15a** and cyclopentanols derived from **12c–15c** and **12b–15b**, and ^{1}H NMR correlation of **12e–15e** and **12f–15f** with **12a–15a**; complete ^{1}H NMR peak and mass spectra fragment ion assignments (130 pages). Ordering information is given on any current masthead page.