Intramolecular Anodic Olefin Coupling Reactions and the Use of Electron-Rich Aryl Rings[1]

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The utility of intramolecular anodic olefin coupling reactions involving electron-rich aromatic rings for constructing fused, bicyclic ring skeletons has been examined. Reactions involving alkoxy-substituted phenyl rings were found to benefit strongly from a 3-methoxy substituent on the phenyl ring. Although overoxidation of the bicyclic product was observed in these reactions, this problem could be minimized with the use of controlled potential electrolysis conditions when a monomethoxy phenyl ring was used and avoided entirely with the use of a vinyl sulfide moiety as the initiator when a more electron-rich phenyl ring was used. Reactions involving 4-alkoxy-substituted phenyl rings as substrates did not lead to good yields of fused products. Furan rings were found to be excellent coupling partners for the reactions and afforded products having fused, bicyclic furan ring skeletons. Cyclizations involving furans were shown to be compatible with the formation of both six- and seven-membered rings, the generation of a quaternary carbon, and the use of a variety of electron-rich olefins as the other coupling partner. It appears that the furan can serve as either the initiating group or the terminating group for the cyclizations. Finally, the reactions were shown to be compatible with the use of a pyrrole ring as one of the participants.

The intramolecular anodic olefin coupling reaction can provide a unique means for generating new carbon−carbon bonds.[2] The potential of this method is highlighted by the general way in which electrochemistry can be used to generate reactive radical cation intermediates from enol ether functional groups under neutral conditions. The net result is to reverse the polarity of the enol ether so that it will undergo coupling reactions with nucleophiles. To date, intramolecular anodic olefin coupling reactions have proven compatible with the formation of five-, six-, and seven-membered rings, the generation of quaternary carbons, and the synthesis of angularly fused tricyclic ring skeletons. Our interest in the use of intramolecular anodic olefin coupling reactions for constructing fused polycyclic ring skeletons led us to consider the use of aromatic rings as participants in these reactions (Figure 1). In accord with earlier observations, coupling reactions of this nature were expected to lead to an addition of the aromatic ring to the olefin with a regiochemistry opposite to what would be anticipated for the corresponding Friedel−Crafts type of alkylation.

Surprisingly, cyclization reactions of this type had not been studied previously, even though aromatic rings had played critical roles in earlier anodic coupling reactions. For example, intramolecular coupling reactions of aromatic rings have been used to synthesize a variety of biphenyl ring skeletons[3] and intramolecular coupling reactions of substituted phenols and olefins have been used to synthesize spirocyclic ring skeletons.[4] These later reactions are closely related to the cyclizations proposed. Two examples are outlined in Scheme 1. Although related, it is important to note that there is a significant difference between these cyclizations and the ones proposed in Figure 1. In the reactions outlined in Scheme 1, the initial oxidation involved the removal of an electron from the electron-rich aromatic ring. The resulting radical cation was then trapped by the olefin to form a spirocyclic ring. The formation of the spirocyclic ring was essential because it prevented reformation of the aromatic ring in the product and hence removed the electroactive species from the reaction. There was no chance for overoxidation of the product because the product did not contain a functional group with a low enough oxidation potential to compete with the initial oxidation of the electron-rich phenyl ring. This would not be the case for

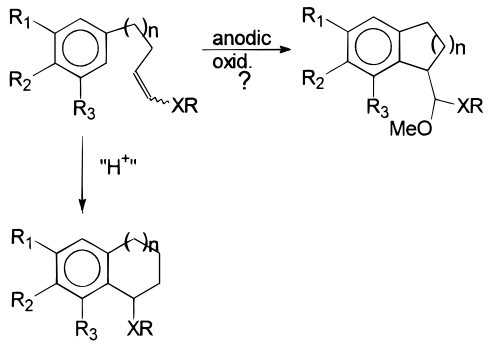

Figure 1.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Taken in part from the following: New, D. G. Ph.D. Thesis, Washington University, St. Louis, MO, 1994, and Tesfai, Z. Ph.D. Thesis, Washington University, St. Louis, MO, 1995. For preliminary accounts of this work, see refs 2a,b.

(2) (a) Moeller, K. D.; New, D. G. *Tetrahedron Lett.* **1994**, *35*, 2857. (b) Tesfai, Z.; Moeller, K. D. *J. Electrochem. Soc. Jpn. (Denki Kagaku)* **1994**, *62*, 1115. (c) Hudson, C. M.; Moeller, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 3347. (d) Tinao-Wooldridge, L. V.; Moeller, K. D.; Hudson, C. M. *J. Org. Chem.* **1994**, *59*, 2381. (e) Moeller, K. D.; Tinao, L. V. *J. Am. Chem. Soc.* **1992**, *114*, 1033. (f) Hudson, C. M.; Marzabadi, M. R.; Moeller, K. D.; New, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 7372.

(3) For a review, see: Yoshida, K. *Electrooxidation in Organic Chemistry: The Role of Cation Radicals as Synthetic Intermediates;* John Wiley and Sons: New York, 1984; pp 136−151.

(4) (a) Swenton, J. S.; Carpenter, K.; Chen, Y.; Kerns, M. L.; Morrow, G. W. *J. Org. Chem.* **1993**, *58*, 3308. (b) Maki, S.; Toyoda, K.; Kosemura, S.; Yamamura, S. *Chem. Lett.* **1992**, 1059. (c) Maki, S.; Kosemura, S.; Yamamura, S.; Kawano, S.; Ohba, S. *Chem Lett.* **1992**, 651. (d) Yamamura, S. In *Electroorganic Synthesis*; Little, R. D., Weinberg, N. L., Eds.; Marcel Dekker: New York, 1991; pp 309−315. (e) Yamamura, S.; Shizuri, Y.; Shigemori, H.; Okuno, Y.; Ohkubo, M. *Tetrahedron* **1991**, *47*, 635. (f) Morrow, G. W.; Chen, Y.; Swenton, J. S. *Tetrahedron* **1991**, *47*, 655. (g) Callinan, A.; Chen, Y.; Morrow, G. W.; Swenton, J. S. *Tetrahedron Lett.* **1990**, *31*, 4551. (h) Morrow, G. W.; Swenton, J. S. *Tetrahedron Lett.* **1987**, *28*, 5445.

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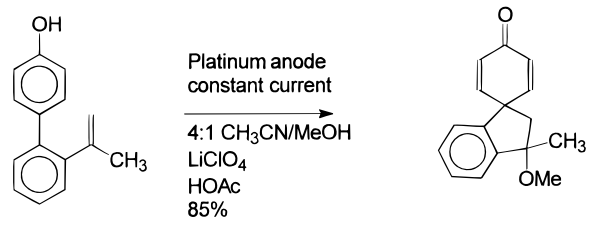
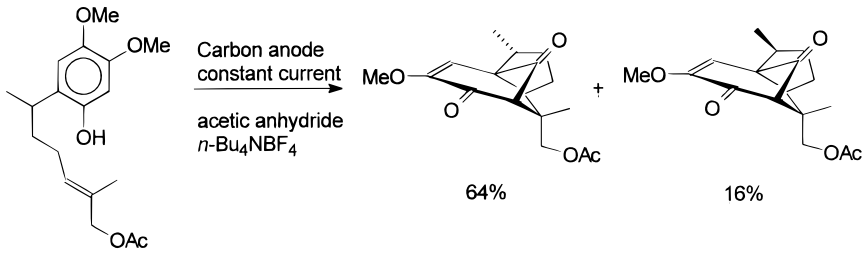
Scheme 1

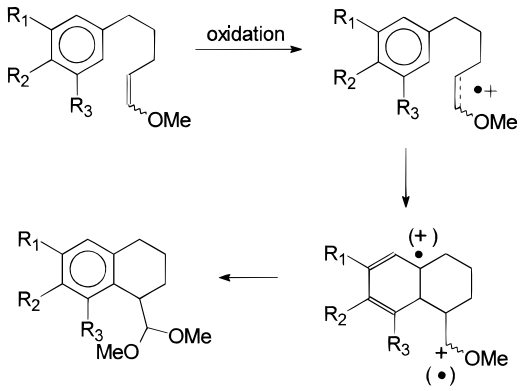
Swenton, J. S. *et. al. J. Org. Chem.* **1993**, *58*, 3308.



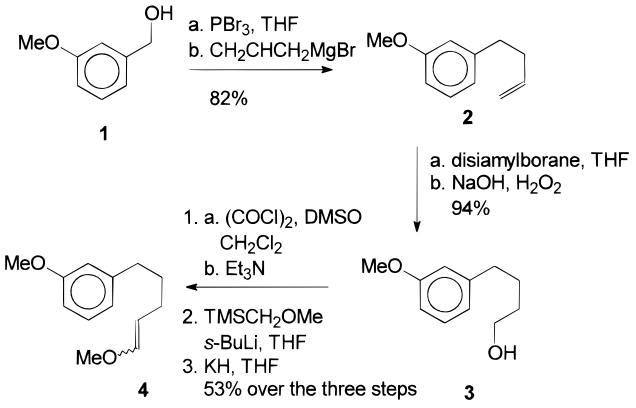
Yamamura, S. *et. al. Tetrahedron* **1991**, *47*, 635.



Scheme 2



Scheme 3



the cyclization reactions suggested in Figure 1. In these cases, the aromatic ring would be preserved in the product and still available for oxidation. In fact, the cyclization reaction itself would add an alkyl substituent to the aromatic ring and lower its oxidation potential. If the initial oxidation step involved the aryl ring, then it would be impossible to avoid overoxidation since the product would oxidize more readily than the starting material. Therefore, for the cyclizations proposed in Figure 1 to be successful the nature of the initiating and terminating groups in the cyclization reaction must be opposite to that of the cyclization reactions outlined in Scheme 1. The initial oxidation step must involve the removal of an electron from the olefin coupling partner (Scheme 2). Furthermore, if overoxidation is to be avoided, then the oxidation potential of the olefin in the substrate must be lower than the oxidation potential of the aromatic ring in the cyclized product. This difference in oxidation potential must be large enough to allow for selectivity. We report herein our recent efforts to probe the viability of these cyclization reactions.

Initially, substrate **4** was selected for study (Scheme 3). This substrate was chosen because enol ethers have a substantially lower oxidation potential ($E_{p/2} = +1.40$ V vs Ag/AgCl)[2e,5] than 3-methoxy-substituted phenyl rings ($E_{p/2}$ measured for methyl 3-methoxyphenylacetate $= +1.63$ V vs Ag/AgCl)[6] and because the phenyl ring was ideally substituted for "attacking" the radical cation of the enol ether once generated. Substrate **4** was constructed in a straightforward fashion from 3-methoxybenzyl alcohol. A Peterson olefination reaction[7] was used to put in the methoxy enol ether moiety instead of the corresponding Wittig reaction because of the difficulty encountered in trying to separate the triphenylphosphine oxide byproduct from the desired enol ether.

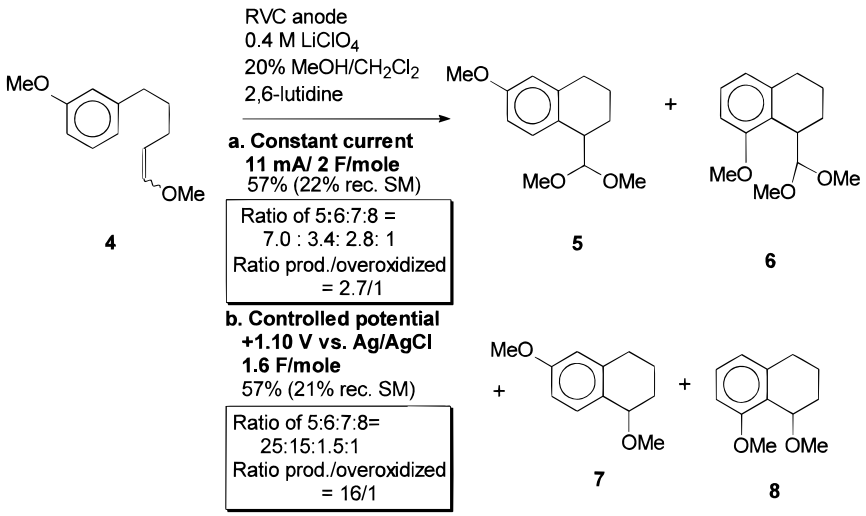
The first attempt at cyclizing substrate **4** utilized conditions that had been successful in a number of earlier anodic olefin coupling reactions (Scheme 4). These conditions utilized an undivided cell, a reticulated vitreous carbon (RVC) anode, a carbon rod cathode, a 0.4 M $LiClO_4$ in 20% MeOH/CH_2Cl_2 electrolyte solution, 2,6-lutidine as a proton scavanger, and a constant current of 11.1 mA. The reaction was continued until 2.0 faradays/mol of charge had been passed. This reaction led to the formation of four cyclized products in a combined yield of 57% and a ratio of 7.0:3.4:2.8:1. The

(5) All of the substrates reported here gave rise to irreversible waves when examined by cyclic voltammetry. For this reason, all of the $E_{p/2}$ values reported were obtained using identical conditions. The values were obtained using a BAS 100B electrochemical analyzer, a platinum anode, a Ag/AgCl reference electrode (purchased from BAS), a sweep rate of 25 mV/s, and a 0.1 N $LiClO_4$ electrolyte solution. The quality of the reference electrode was checked, and the potentials were calibrated with the use of a simple methoxy enol ether.[2e]

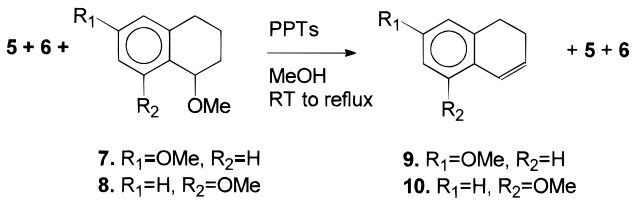
(6) Moeller, K. D.; Wang, P. W.; Tarazi, S.; Marzabadi, M. R.; Wong, P. L. *J. Org. Chem.* **1991**, *56*, 1058.

(7) For a review, see: Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43.

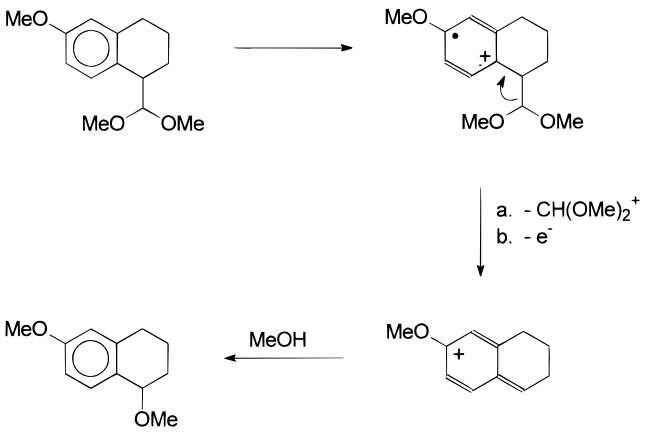
Scheme 4



Scheme 5



Scheme 6



ratio of products was obtained by integration of the ^{1}H NMR obtained for the crude reaction product. This analysis utilized the acetal protons of **5** and **6** and the benzylic methine protons of **7** and **8**. All four of these signals were in the δ 4−5 range, clearly visible, and cleanly resolved from each other. In addition to the cyclized products, a 22% yield of recovered starting material was obtained. The structures of products **7** and **8** were tentatively assigned on the basis of methine peaks at δ 4.26 for product **7** and δ 4.56 for product **8** and methoxy peaks at δ 3.39 for **7** and δ 3.44 for **8** in the ^{1}H NMR spectrum for a mixture of **6**, **7**, and **8**. Compounds **6**, **7**, and **8** were inseparable by chromatography. In order to gain further evidence for the structure of compounds **7** and **8**, the crude product was treated with pyridinium *p*-toluenesulfonate in methanol in order to eliminate the benzylic methoxy substituents in **7** and **8** and form the corresponding cyclic styrene derivatives **9** and **10** (Scheme 5). At this point, the products could be readily separated and characterized.

Minor products **7** and **8** were derived from overoxidation of the initially formed products **5** and **6**. When the electrolysis was allowed to run until 4 faradays/mol had been passed, compounds **7** and **8** were formed as the major products. Apparently, a one-electron oxidation of the cyclized product led to the radical cation of the aromatic ring (Scheme 6). Elimination of the dimethoxymethyl substituent followed by a second one-electron oxidation led to a methylated quinone methide[8] that in turn trapped methanol to form the final product. The fact that the overoxidized product was formed in a minor amount in the 2 faradays/mol experimtent suggested that the starting material did oxidize at a lower potential than the product and that a chance for selectivity existed. Along these lines, three potential solutions were apparent. First, the inherent selectivity of the reaction could be enhanced with the use of controlled potential electrolysis conditions.[9] Second, the gap in oxidation potential between the aromatic ring and the electron-rich olefin could be widened by finding an electron-rich olefin that had a much lower oxidation potential than an enol ether. Third, the gap in oxidation potential between the aromatic ring and the enol ether initiator could be widened by raising the oxidation potential of the aromatic ring. This alteration could be accomplished either by removing the 3-methoxy substituent on the phenyl ring or by replacing it with a less electron donating substituent.

Experimentally, the simplest solution was to utilize a controlled potential electrolysis. In order to maximize selectivity, the potential was set at the lowest value that would allow for a stable current flow. This value for the potential was obtained by starting the electrolysis with a potential of 0.0 V vs a Ag/AgCl reference electrode and then slowly raising the potential until the flow of current in the electrolysis was about the same as that used in the constant current electrolysis experiment described earlier. The potential derived in this fashion (+1.10 V vs Ag/AgCl) was maintained throughout the course of the

(8) For leading references, please see: Angle, S. R.; Arnaiz, D. O.; Boyce, J. P.; Frutos, R. P.; Louie, M. S.; Mattson-Arnaiz, H. L.; Rainier, J. D.; Turnbull, K. D.; Yang, W. *J. Org. Chem.* **1994**, *59*, 6322 and references therein.

(9) For a general description of electrochemical techniques and an excellent review of background material, please see: *Organic Electrochemistry: An Introduction and A Guide*, 2nd ed.; Baizer, M. M., Lund. H., M. Dekker, Eds.; New York, 1983.

cyclization reaction. Except for the use of the controlled potential, all of the reaction parameters were kept the same as in the constant current electrolysis (Scheme 3). In this experiment, a 57% isolated yield of cyclized products was again obtained along with a 21% yield of recovered starting material. However, the ratio of the products formed was dramatically different than in the previous constant current electrolysis. This time the ratio of desired cyclized product to overoxidized product was 16:1. Clearly, the controlled potential electrolysis was useful for dramatically increasing the selectivity of the reaction.

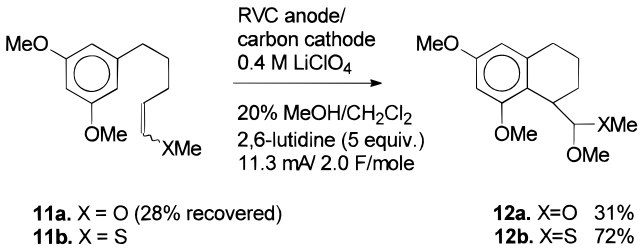
Although the use of a controlled potential electrolysis helped with selectivity in the case of substrate **4**, it was difficult to forward controlled potential electrolyses as a general solution for eliminating overoxidation in cyclization reactions involving electron-rich phenyl rings. In fact, even the oxidation of **4** had pushed the limits of a preparative scale controlled potential electrolysis. The reaction took approximately 24 h to proceed to 80% completion. Since the current drops off exponentially with reaction time in a controlled potential electrolysis, completion of the reaction would have required at least an additional 12 h. What would happen if a more electron-rich phenyl ring were to be used? To maintain the same level of selectivity the potential for the reaction would have to be lowered still further and the reaction rate slowed even more. Of course, once the potential of the aromatic ring became lower than that of the enol ether, any selectivity would be impossible and overoxidation would dominate. Clearly, an alternative way of inducing selectivity needed to be found.

Because we hoped to maintain the versatility of the reactions with respect to the aromatic ring participant, initial efforts were aimed at identifying a suitable alternative to the enol ether as the initiator for the reactions. To this end, substrates **11a** and **11b** were synthesized and electrolyzed. The substrates were made in a fashion identical to that outlined for substrate **4** above, and their syntheses are detailed in the Experimental Section. The vinyl sulfide substrate was selected as an alternative to the enol ether because of its increased hydrolytic stability and because of its lower oxidation potential ($E_{p/2}$ *ca.* +0.9 to +1.0 V vs Ag/AgCl reference electrode/Pt working and auxiliary electrodes/0.1 N $LiClO_4$ in CH_3CN electrolyte solution/25 mV/s sweep rate).

The anodic oxidation of substrate **11a** at a retriculated vitreous carbon anode in an undivided cell using a carbon auxiliary electrode, 2,6-lutidine as a proton scavanger, a 0.4 N $LiClO_4$ in 20% $MeOH/CH_2Cl_2$ electrolyte solution, and a constant current of 11.2 mA (2.0 faradays/mol) led to the formation of a 64% yield of cyclized product along with a 28% yield of recovered starting material (Scheme 7). In this example, the ratio of desired product to overoxidized material was 1:1. Clearly, this would be a more difficult oxidation to fix using controlled potential conditions than was the oxidation of substrate **4**.

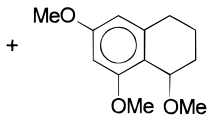
However, the anodic oxidation of substrate **11b** using a vinyl sulfide initiator provided a nice solution to this problem. In this example, *no overoxidized material was obtained*. This reaction worked so well that it was tempting to go back and try to fix the oxidation of substrate **4** with the use of a vinyl sulfide. For this reason, substrate **4b** was synthesized and oxidized. The cyclization of **4b** was not as successful as the earlier cyclization of **4a**. Although no overoxidized material was obtained, the mass balance of the reaction was very low.

Scheme 7



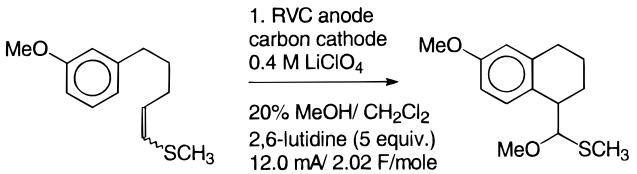
11a. X = O (28% recovered)
11b. X = S

12a. X=O 31%
12b. X=S 72%



13. 33%

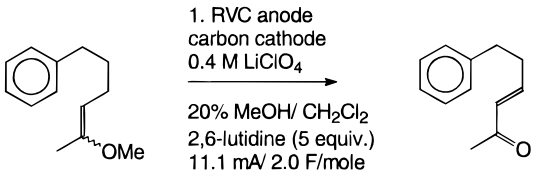
Scheme 8



4b

5b. 38%

Scheme 9



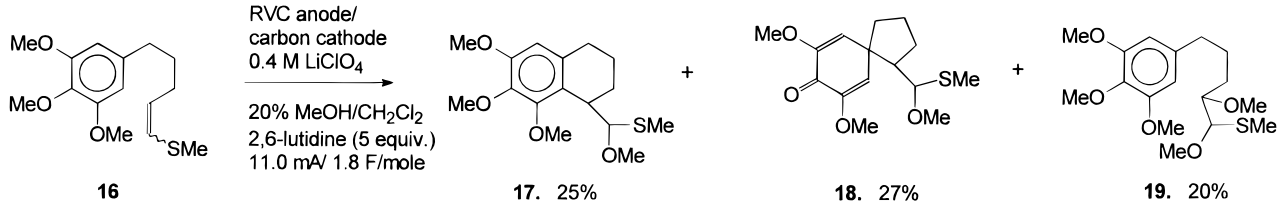
14

15. 51%

Surprisingly, none of the cyclized product arising from ortho substitution of the phenyl ring was obtained. With such a poor mass balance for the reaction, it was impossible to reach a definitive conclusion about this experiment, other than that the earlier cyclization reaction originating from oxidation of the vinyl sulfide group had benefited strongly from the use of the more nucleophillic dialkoxy phenyl ring (Scheme 8).

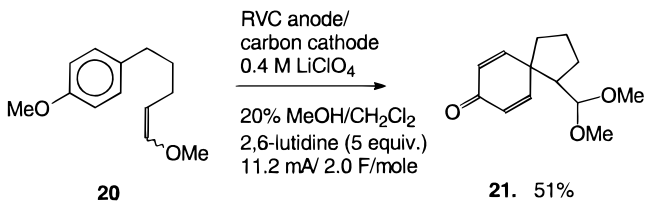
Having established that the cyclization reactions were possible and that the reactions could be initiated successfully in the presence of very electron-rich phenyl rings, attention was turned toward understanding how the nature of substituents on the phenyl ring would influence the coupling reaction. For starters, substrate **14** was studied in order to determine if activation of the phenyl ring was required for cyclization (Scheme 9). The synthesis of the substrate **14** is detailed in the Experimental Section. The extra methyl group was added to the enol ether in order to lower the oxidation potential of the substrate and stabilize the radical cation in an effort to aid the cyclization reaction. However, the anodic oxidation of **14** did not lead to the formation of any cyclized product. Instead, the oxidation gave rise to an unsaturated acetal. This acetal was most likely formed from the elimination of a proton from the carbon α to the radical cation of the enol ether before the cyclization could occur.[10] The formation of this product was confirmed by hydrolysis of the acetal to form the α,β-unsaturated ketone **15**. Clearly, the 3-methoxy substit-

Scheme 10



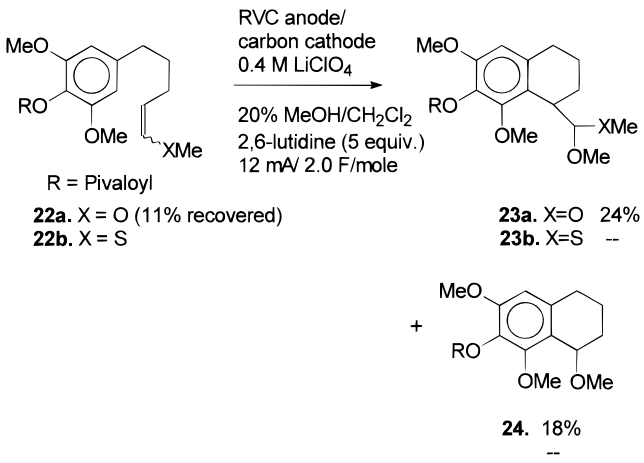
16 **17.** 25% **18.** 27% **19.** 20%

Scheme 11



20 **21.** 51%

Scheme 12



R = Pivaloyl

22a. X = O (11% recovered)
22b. X = S

23a. X=O 24%
23b. X=S --

24. 18%
--

uents utilized in the previous cyclizations were important for cyclization.

Having established that the phenyl ring needed to be activated for cyclization, we turned our attention toward exploring if the reactions would be compatible with even more electron-rich phenyl rings. For this reason, substrate **16** was synthesized and oxidized. Once again, the synthesis directly paralleled the synthesis of **4** and is detailed in the Experimental Section. The anodic oxidation of **16** (Scheme 10) was accomplished in an undivided cell using the conditions outlined previously and led to the formation of a 25% yield of the desired cyclized product **17**, a 27% yield of spirocyclic product **18**, and a 20% yield of a product that has tentatively been assigned as the uncyclized product **19** on the basis of its 300 MHz ^{1}H NMR spectrum. The presence of such a significant amount of uncyclized material indicated that the trimethoxy-substituted phenyl ring was not as effective of a coupling partner as either the 3-methoxy-substituted phenyl ring or the 3,5-dimethoxy-substituted phenyl ring studied earlier.[11]

The formation of the spirocyclic product indicated a "crossover" into the chemistry of Swenton and Yamamura (*vide infra*) and appeared to be a direct result of the electron-donating group on the 4-position of the phenyl ring. In order to confirm this conclusion, the coupling reaction utilizing a simple 4-methoxy-substituted phenyl ring was examined (Scheme 11). As expected, this cyclization led to the formation of a spirocyclic product. No evidence for a fused bicyclic product was obtained.

From these results, it became clear that if 4-alkoxy-substituted phenyl rings were to be used in the synthesis of fused ring skeletons, then the alkoxy group would have to be protected in a fashion that removed its electron-donating ability. In the past, it has been shown that a pivaloyloxy group can serve as an electronically neutral substituent in anodic oxidation reactions.[6] In order to test the effect of a 4-pivaloyloxy group on the current cyclizations, substrates **22a** and **22b** were synthesized in a fashion directly analogous to the earlier syntheses of **4a** and **4b**. The oxidation of **22a** led to a 42% yield of cyclized products along with an 11% yield of recovered starting material (Scheme 12). The cyclized material was isolated as an inseparable 1.3 to 1 mixture of compounds **23a** and **24**. No spirocyclic product was observed. Although the mass balance for the reaction was far lower than desired, it was clear that the use of the 4-pivaloyloxy substituent had a dramatic impact on the course of the reaction. No longer was a spirocyclic product competitive with the formation of the fused products.

Because the oxidation of **22a** led to a significant amount of overoxidized product, the vinyl sulfide substrate **22b** was studied. It was hoped that the use of the vinyl sulfide would both eliminate the formation of the overoxidation product **24** and increase the overall mass balance of the reaction. Unfortunately attempts to oxidize **22b** have met with failure. While it is clear that the vinyl sulfide group is cleanly oxidized (high yields of the methanol trapping of the resulting radical cation can be obtained), in all but one case the substrate did not cyclize. In one instance a small amount (*ca.* 20%) of the desired product was formed. In this example, none of the overoxidized product was apparent by analysis of the crude mixture by ^{1}H NMR. However, in spite of extensive efforts we have been unable to repeat this cyclization.

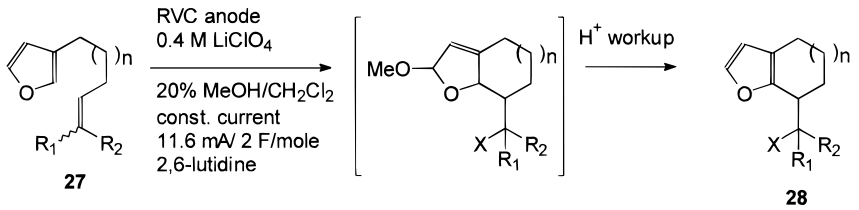
It is very clear that the 4-pivaloyloxy substituent badly damages the substrates ability to afford cyclized products, especially when compared to the 3,5-dimethoxy-substituted phenyl ring of substrate **11a** and **11b**. This result when combined with the earlier described studies using 4-methoxy-substituted phenyl rings has led us to the general conclusion that for the synthesis of fused bicyclic ring systems 4-alkoxy-substituted phenyl rings need to be avoided.

Having completed our study concerning the utility of electron-rich phenyl rings for the coupling reactions, we turned our attention to exploring the compatibility of heteroatomic aromatic rings with the anodic oxidation reactions. As a starting point for this work, furan rings were selected for study. It was hoped that the use of furan rings in the coupling reactions would lead to bicyclic ring skeletons that could be either directly

(10) For an analogous chemical oxidation of enol ethers to unsaturated carbonyls, see: Evans, P. A.; Longmire, J. M.; Modi, D. P. *Tetrahedron Lett.* **1995**, *36*, 3985.

(11) For examples of the effect of ortho sustituents on the ability of methoxy groups to donate electron density to the π-system of aromatic rings, see: Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399.

Table 1



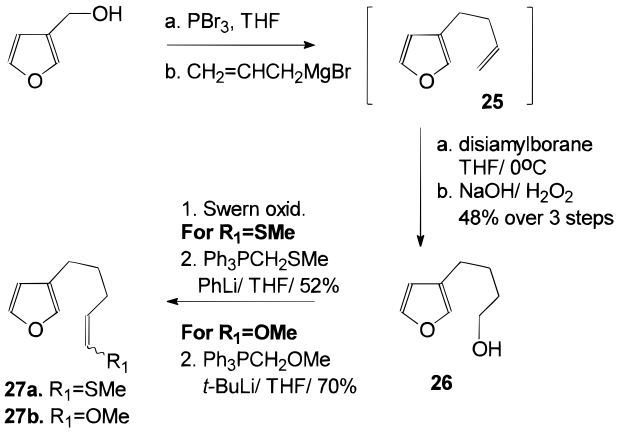
1	**27a**: R_1 = SMe, R_2 = H, n = 1		**28a**: 54% (R_1 = SMe, X = OMe) **28b**: 17% (R_1 = OMe, X = OMe)
2	**27a**: R_1 = SMe, R_2 = H, n = 1	MeOH solvent	**28a**: 67% (R_1 = SMe, X = OMe) **28b**: 10% (R_1 = OMe, X = OMe)
3	**27b**: R_1 = OMe, R_2 = H, n = 1		**28b**: 75% (X = OMe)
4	**27c**: R_1 = Ph, R_2 = H, n = 1		**28c**: 71% (X = OMe)
5	**27d**: R_1 = CH_2TMS, R_2 = H, n = 1		**28d**: 49% (no X, R_1 = CH_2)[a]
6	**27e**: R_1 = CH_2TMS, R_2 = CH_3, n = 1		**28e**: 51% (no X, R_1 = CH_2)
7	**27f**: R_1 = CH_3, R_2 = CH_3, n = 1		**28f**: 24% (X = OMe) **28e**: 51% (no X, R_1 = CH_2)
8	**27g**: R_1 = OMe, R_2 = H, n = 2		**28g**: 62% (X = OMe)
9	**27g**: R_1 = OMe, R_2 = H, n = 2	MeOH solvent	**28g**: 58% (X = OMe)
10	**27h**: R_1 = Ph, R_2 = H, n = 2		**28h**: 41% (X = OMe)[b]
11	**27h**: R_1 = Ph, R_2 = H, n = 2	MeOH solvent	**28h**: 48% (X = OMe)[b]
12	**27i**: R_1 = CH_3, R_2 = CH_3, n = 2		**28i**:[c] 26% (no X, R_1 = CH_2)[b] **28ii**: 6% (X = OMe)[b]
13	**27j**: R_1 = OMe, R_2 = H, n = 3		**28j**:[d] 32% (X = OMe)[b,e]

[a] The product formed cleanly but was volatile. [b] Unoptimized yield. [c] This reaction also led to an uncyclized product resulting from oxidation of the furan ring (see text). [d] This reaction also led to an uncyclized product resulting from oxidation of the enol ether (see text). [e] This reaction used n-Bu_4NBF_4 as the electrolyte. The yield using $LiClO_4$ was 24%.

transformed into a variety of bicyclic furan-containing natural products[12] or used in the synthesis of polycyclic natural products by taking advantage of the utility of furans as synthetic intermediates.[13]

Like the earlier electron-rich phenyl rings, furan rings had previously served as substrates for anodic oxidation reactions.[14] However, with one notable exception (the trapping of the resulting radical cation with cyanide) these reactions had not been used to synthesize either carbon−carbon bonds or bicyclic ring systems. In order to study the use of furans in anodic cyclization reactions, a series of substituted furan substrates were synthesized. A general route for the synthesis of the substrates is outlined in Scheme 13 for the construction of **27a** (R_1 = SMe) and **27b** (R_1 = OMe). In this synthesis, olefin **25** proved difficult to isolate. The overall yields of the process benefited strongly from carrying the material all the way through to alcohol **26** without purification. The syntheses of the remaining furan-based substrates (Table 1, **27c**−**j**) were essentially identical except for a change in the anion used to generate **25** (vary the number of methylene carbons in order to vary n), a change in the final Wittig step (vary R_1 and R_2), or both. The details of these syntheses are described in the Experimental Section.

Scheme 13



The first furan substrate studied was **27a** (Table 1, entry 1). The vinyl sulfide was chosen as the initiator to ensure that the furan ring in the desired product would not compete with oxidation of the substrate. In this manner, it was hoped that overoxidation of the product would be avoided. The conditions used for the electrolysis were identical to the constant current experiments described above. In this experiment, the initial product formed was not the desired bicyclic furan, but rather appeared to be a mixture of products from initial cyclization of the radical cation to form a bicyclic radical cation followed by trapping of this resulting radical cation with methanol, a second oxidation, and then trapping of the incipient cation with a second equivalent of methanol. This initial product mixture could be readily converted to the desired product **28a** by treatment with *p*-toluenesulfonic acid in methanol. More conveniently, it was found that the desired product **28a** could be generated directly by adding 5 equiv of *p*-toluenesulfonic acid to the electrolysis cell following the oxidation and then allowing the resulting mixture to stir at room temperature overnight. After workup and purification, these conditions

(12) (a) Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. *J. Am. Chem. Soc.* **1989**, *111*, 4407. (b) Carté, B.; Kernan, M. R.; Barrabee, E. B.; Faulkner, D. J. *J. Org. Chem.* **1986**, *51*, 3528. (c) Gopalan, A.; Magnus, P. *J. Org. Chem.* **1984**, *49*, 2317. (d) Tanis, S. P.; Dixon, L. A. *Tetrahedron Lett.* **1987**, *28*, 2495. (e) Hiroi, K.; Sato, H. *Synthesis* **1987**, 811. (f) Padwa, A.; Ishida, M. *Tetrahedron Lett.* **1991**, *32*, 5673.

(13) For reviews, see: (a) Dean, F. M. *Adv. Heterocycl. Chem.* **1982**, *30*, 161. (b) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795.

(14) (a) Clauson-Kaas, N.; Limborg, F.; Dietrich, P. *Acta Chem. Scand.* **1952**, *6*, 545. (b) Baggaley, A. J.; Brettle, R. *J. Chem. Soc. C* **1968**, 969. (c) Yoshida, K.; Fueno, T. *J. Org. Chem.* **1971**, *36*, 1523. (d) Panomarev, A. A.; Markushina, I. A. *J. Gen. Chem. USSR* **1963**, *33*, 3892. (e) Shono, T.; Matsumura, Y. *Tetrahedron Lett.* **1976**, *17*, 1363. (f) Shono, T.; Matsumura, Y.; Hamaguchi, H.; Nakamura, K. *Chem. Lett.* **1976**, 1249. (g) Shono, T.; Hamaguchi, H.; Aoki, K. *Chem. Lett.* **1977**, 1053. (h) Shono, T.; Matsumura, Y.; Tsubata, K.; Takata, J. *Chem. Lett.* **1981**, 1121.

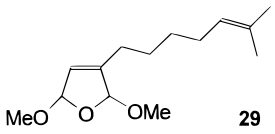
led to a 71% isolated yield of the bicyclic furan as a mixture of acetals.

It is important to note that this cyclization also proceeded nicely in pure methanol solvent (Table 1, entry 2). This observation has been characteristic of only the best anodic olefin coupling reactions to date. For example, intramolecular anodic olefin coupling reactions between enol ethers were shown to lead to both five- and six-membered ring formation in pure methanol,[2e] while analogous coupling reactions between either enol ethers and allylsilanes or enol ethers and styrenes required the use of a cosolvent.[2f] In pure methanol, these later cases led to methanol trapping of the radical cation before cyclization. In six-membered ring cases, no cyclized material was obtained. However, in the current oxidation no uncyclized material was observed.

Since the initial product from the oxidation and cyclization was not a furan, no possibility for overoxidation of the product existed. This observation led us to examine the anodic coupling reactions of furans with a variety of electron-rich olefins. With respect to the synthesis of six-membered rings, the furan ring could be coupled with an enol ether, a styrene, a pair of allylsilanes, and a simple trialkyl-substituted olefin (entries 3−7). All of the reactions proceeded smoothly and with the exception of the allylsilane afforded good yields of bicyclic furan products. In the case of the allylsilane substrate (entry 5), the low yield appeared to be due to the volatility of the product. Both TLC and NMR data on the crude reaction mixture indicated that the product had been formed cleanly.

The reactions also proved to be compatible with the synthesis of seven-membered rings (entries 8−12). For example, the cyclization of substrate **27g** involving the coupling of a furan ring and an enol ether led to a 62% yield of the seven-membered ring product. No evidence for an uncyclized product was obtained. This observation also held for the cyclization of **27g** in pure methanol solvent (entry 9). In this case, a 58% yield of the cyclized product was obtained. The formation of a seven-membered ring in pure methanol solvent was surprising, especially since the corresponding intramolecular coupling of bis enol ether substrates (our most efficient cyclizations to date) required the use of a cosolvent for the formation of a seven-membered ring.[2e] Even more surprising was the seven-membered ring cyclization resulting from the anodic coupling of a furan ring and a styrene (Table 1, entries 10 and 11). Once again, this cyclization did not require a cosolvent for formation of a seven-membered ring. For comparison, the corresponding anodic coupling reaction between an enol ether and a styrene required the use of a cosolvent even when forming a six-membered ring. Clearly, the furan ring represents one of the most reactive coupling partners that we have studied to date.

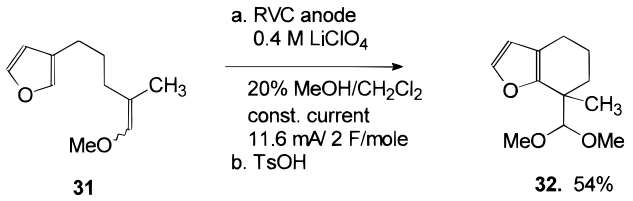
The anodic oxidation of substrate **27i** (entry 12) also proved to be interesting. In this case, the cyclization afforded only a 32% yield of cyclized product. In addition, a 25% yield of the uncyclized product **29** was obtained.



29

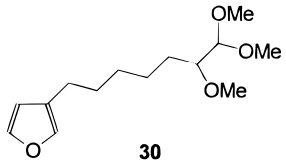
Apparently, this product was formed from methanol trapping of a radical cation derived from the furan. The trisubstituted olefin was untouched. No product having the initial monosubstituted furan intact was observed in the 300 MHz ^{1}H NMR of the crude reaction mixture. The yield of **29** could be raised to 54% with the use of a carbon rod anode in place of the retriculated vitreous carbon anode used above. The formation of **29**, the presence of the trisubstituted olefin, and the complete absence of products with the initial furan ring intact suggested that in this example the furan ring was being oxidized and serving as the initiator for the subsequent chemistry.

Scheme 14



31 **32.** 54%

In the coupling reactions between furans and enol ethers, the furan ring appeared to serve as the terminating group for the cyclization. For example, the anodic oxidation of substrate **27j** (entry 13) led to the formation of both the eight-membered ring product **28j** in a 32% yield and the uncyclized product **30** in a 16% yield. This



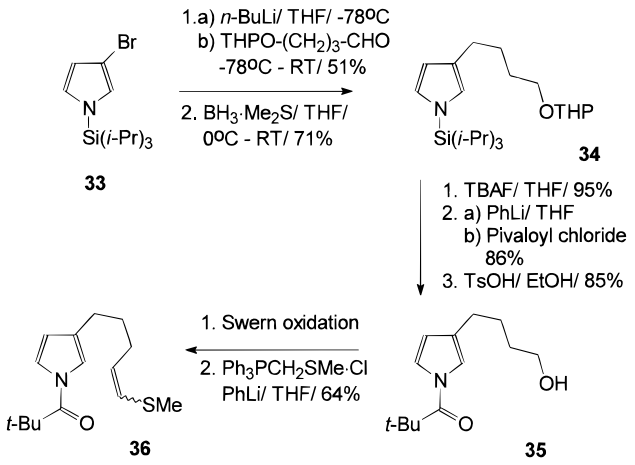
30

reaction was the first intramolecular anodic olefin coupling reaction to give rise to an eight-membered ring. Once again, the furan ring proved to be the most reactive coupling partner that we have studied. The uncyclized material in this example apparently arose from methanol trapping of the radical cation derived from the enol ether. The ^{1}H NMR of the crude reaction mixture gave no indication of a product having the initial enol ether intact. Apparently, the enol ether was oxidized in preference to the furan ring. The formation of uncyclized products **29** and **30** suggested that the furan ring can serve as either the terminator or the initiator for the reaction depending on the nature of the coupling partner.

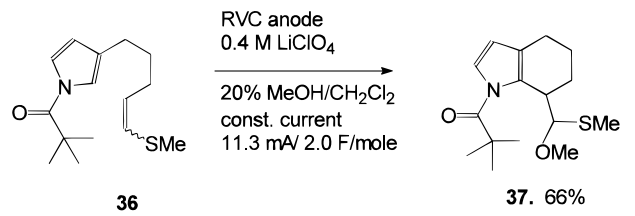
The coupling reaction of furans and enol ethers also proved to be compatible with the construction of a quaternary center (Scheme 14). The synthesis of substrate **31** is detailed in the Experimental Section. In this experiment, the trisubstituted enol ether **31** was oxidized and the crude product treated with *p*-toluenesulfonic acid in order to form product **32** in a 54% isolated yield. Once again, this result was consistent with the furan ring being an excellent coupling partner. For comparison, the coupling of bis enol ether substrates was shown to be compatible with the simultaneous formation of both a six-membered ring and a quaternary center. However, the coupling reaction of an enol ether and an allylsilane could not overcome the difficulties associated with synthesizing a six-membered ring and a quaternary center at the same time.[2d] The allylsilane moiety was simply not reactive enough as a trapping group for the enol ether radical cation.

Finally, we were curious as to whether the chemistry developed above for cyclization reactions involving furans could be extended to additional heteroatomic aryl rings.

Scheme 15



Scheme 16



For this reason, the pyrrole-based substrate **36** was synthesized (Scheme 15). The starting material for the synthesis was made using the published procedure.[15] A vinyl sulfide was used as the initiator and the pyrrole protected as the pivaloyl amide in order to ensure initial oxidation of the electron-rich olefin and to avoid potential overoxidation problems.

The oxidation of **36** was again conducted in a fashion that was directly analogous to the earlier constant current electrolyses (Scheme 16). A 66% isolated yield of cyclized product was obtained as a mixture of two diastereomers (**37**). Unlike the furan cases, the majority of the bicyclic product obtained directly from the electrolysis without acid treatment was the bicyclic aromatic compound. Only a tiny amount of methanol-trapped product could be observed. This product could be eliminated to the pyrrole product **37** in a fashion directly analogous to the furan cases.

In conclusion, we have found that intramolecular anodic olefin coupling reactions utilizing electron-rich olefins and aryl rings can provide an effective means for synthesizing fused, bicyclic ring skeletons. Reactions involving phenyl rings benefited strongly from a 3-methoxy substituent on the phenyl ring. Although overoxidation of the cyclized products in these cases was observed, this problem could be addressed with the use of controlled potential electrolysis conditions when a monomethoxy phenyl ring was used and with the use of a vinyl sulfide moiety as the initiator when a more electron-rich phenyl ring was used. When the phenyl rings contained a 4-methoxy substituent, spirocyclic product formation began to compete with the desired fused bicyclic products. Although it appeared that this side reaction could be controlled with the use of a less electron donating 4-pivaloyoxy substituent, yields for this process were not synthetically viable and it is currently best to avoid the use of a 4-alkoxy substituent on the phenyl ring. Furan rings were found to be excellent coupling partners for the reactions. Cyclizations involving furans were shown to be compatible with the formation of both six- and seven-membered rings, the generation of a quaternary carbon, and the use of a variety of electron-rich olefins ranging from enol ethers and vinyl sulfides to simple alkyl-substituted olefins. It appears that the furans will serve as either the initiating or the terminating group for the oxidative coupling reaction depending on the nature of the electron-rich olefin. Finally, the intramolecular anodic olefin coupling reaction was shown to be compatible with the use of a pyrrole ring as one of the participants. Work aimed at elucidating the overall utility of these reactions for organic synthesis is currently underway.

Experimental Section[16]

4-(3-Methoxyphenyl)-1-butene (2). To a round-bottom flask cooled in an ice bath were added 11.12 g (80.5 mmol) of 3-methoxybenzyl alcohol, 40 mL of THF, and 7.20 g (26.6 mmol) of phosphorus tribromide. After 30 min the reaction mixture was checked by TLC. The TLC still showed some of the starting alcohol so 0.54 g (2.0 mmol) more of the phosphorus tribromide was added. The reaction mixture was checked after another 30 min. This TLC showed that the reaction mixture still contained starting material, so an additional 2.31 g (8.5 mmol) of phosphorus tribromide was added. The reaction mixture was checked again after 30 min showing that all of the starting material had been consumed. To the reaction mixture was added 30.0 mL of THF followed by 161.0 mL (161.0 mmol) of a 1.0 M solution of allylmagnesium bromide in ether. After 1 h, the reaction mixture still showed the presence of some of the intermediate by TLC so an additional 20.0 mL (20.0 mmol) of the allylmagnesium bromide solution was added. The reaction mixture was stirred for an additional 2 h. The reaction was quenched with 10 N H_2SO_4, and the mixture was diluted with H_2O and then extracted three times with ether. The ether layers were washed once with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was chromatographed through 800 mL of silica gel using a gradient elution from straight hexane to 10% ether/hexane (1% steps every 750 mL of eluent) to afford 10.66 g (82%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17−7.23 (m, 1 H), 6.71−6.80 (m, 3 H), 5.86 (ddt, J = 17.0 Hz, J = 10.3 Hz, J = 6.6 Hz, 1 H), 5.05 (dq, J = 15.0 Hz, J = 1.7 Hz, 1 H), 4.98 (d of multiplets, J = 9.0 Hz, 1 H), 3.79 (s, 3 H), 2.69 (t, J = 7.9 Hz, 2 H), 2.37 (dt, J = 8.3 Hz, J = 7.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5,-138.0, 129.2, 120.8, 114.9, 114.2, 111.0, 55.1, 35.4; IR (neat, NaCl) 3076, 3001, 2977, 2938, 2856, 2835, 1611, 1601, 1594, 1585, 1492, 1465, 1455, 1436, 1416, 1335, 1312, 1290, 1259, 1190, 1165, 1152,1052, 996, 913, 862, 778, 741 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 121 (100), 163 (62), 149 (21), 122 (19), 161 (14), 164 (13), 162 (13), 191 (4), 203 (2); HRMS (EI) *m/e* calcd for $C_{11}H_{14}O$ 162.1041, found 162.1045.

4-(3-Methoxyphenyl)-1-butanol (3). To a round-bottom flask cooled in an ice bath were added 50.0 mL of THF and 6.25 mL (62.5 mmol) of borane−dimethyl sulfide complex. To this solution was added 8.529 g (121.7 mmol) of 2-methyl-2-butene. The reaction mixture was stirred for 1 h, and then 5.064 g (31.2 mmol) of **6** was added. The reaction mixture was stirred for 1 h, and then the reaction was quenched SLOWLY with a solution of 62.4 mL of 3 N NaOH and 28.8 mL of 30% H_2O_2 that had been cooled in an ice bath. The resulting mixture was stirred for 1 h, diluted with H_2O, and then extracted with ether until TLC analysis showed that no more product was being extracted. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting oil was chromatographed through 400 mL of silica gel with a gradient elution of hexane to 50% ether in hexane (5% steps

(15) Bray B. L.; Mathies, P. H.; Naef, R.; Solas, D. R.; Tidwell, T. T.; Artis, D. R.; Muchowski, J. M. *J. Org. Chem.* **1990**, *55*, 6317.

(16) For a description of general experimental details, please see: Wong, P. L.; Moeller, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 11434.

every 500 mL of eluent) to afford 5.307 g (94%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14−7.19 (m, 1 H), 6.69−6.77 (m, 3 H), 3.75 (s, 3 H), 3.58 (t, J = 6.4 Hz, 2 H), 2.59 (t, J = 7.5 Hz, 2 H), 2.46 (br s, 1 H), 1.51−1.71 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 144.1, 129.3, 120.9, 114.2, 111.0, 62.5, 55.1, 35.7, 32.3, 27.5; IR (neat, NaCl) 3300 br, 3000, 2936, 2885, 2861, 2837, 1610, 1601, 1594, 1585, 1488, 1465, 1454, 1436, 1380, 1369, 1333, 1314, 1261, 1190, 1164, 1151, 1043, 996, 984, 874, 778, 738, 696 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 163 (100), 121 (37), 164 (21), 181 (8), 122 (8); HRMS (EI) *m/e* calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1157.

(*E,Z*)-1-Methoxy-5-(3-methoxyphenyl)-1-pentene (4). To a round-bottom flask were added 3.501 g (19.4 mmol) of **3**, 1.820 g (23.3 mmol) of dimethyl sulfoxide, and 20 mL of dichloromethane. The solution was cooled to −78 °C. After 15 min, 2.716 g (21.4 mmol) of oxalyl chloride was added and the reaction mixture was allowed to warm to between −50 and −60 °C. After 15 min, 9.837 (97.2 mmol) of triethylamine was added and the reaction mixture allowed to warm to room temperature. Water was added and most of the dichloromethane evaporated *in vacuo*. The remaining solution was extracted three times with ether. The ether layers were then washed once with brine and dried over $MgSO_4$. The resulting aldehyde was taken up in 40 mL of THF and then used in the Peterson olefination below.

A round-bottom flask was charged with 6.885 g (58.2 mmol) of (methoxymethyl)trimethylsilane and 40 mL of THF. The mixture was cooled to −78 °C and then 44.8 mL (58.2 mmol) of *sec*-butyllithium was added. The reaction mixture was allowed to warm to between −25 and −35 °C for 30 min. The reaction mixture was then recooled to -78 °C and the aldehyde generated above added to the flask. This mixture was allowed to warm slowly to room temperature and stirred for 16 h. At that time, the reaction was quenched with H_2O, and the mixture was extracted with ether. The ether layers were washed with brine, dried over $MgSO_4$, and filtered, and the solvent was removed *in vacuo*. To the Peterson adduct was then added 20 mL of THF. In a separate flask 8 g of potassium hydride (35 wt % in mineral oil) was washed 2× with hexane. THF (5 mL) was added to the potassium hydride, and then the Peterson adduct was added to the flask. The reaction was stirred for 1 h and then checked by TLC to see if all of the Peterson adduct was gone. Upon completion, the reaction mixture was cooled to 0 °C and slowly quenched with methanol. After quenching, the reaction mixture was diluted with H_2O and extracted three times with ether. The ether layer was dried over $MgSO_4$ and filtered and then the solvent removed *in vacuo*. The crude product was then chromatographed through 300 mL of silica gel using a gradient elution of hexane to 15% ether in hexane (1.5% steps every 500 mL of eluent) to afford a 2.133 g (53%) yield of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14−7.20 (m, 1 H), 6.69−6.77 (m, 3 H), 6.28 (d, J = 12.6 Hz, 0.47 H), 5.88 (dt, J = 6.2 Hz, J = 1.5 Hz, 0.53 H), 4.72 (dt, J = 12.6 Hz, J = 7.3 Hz, 0.47 H), 4.34 (dt, J = 6.2 Hz, J = 7.3 Hz, 0.53 H), 3.76 (s, 3 H), 3.55 (s, 1.59 H), 3.48 (s, 1.41 H), 2.55−2.61 (m, 2 H), 2.11 (dt, J = 7.1 Hz, J = 7.7 Hz, 1.14 H), 1.95 (dt, J = 7.14 Hz, J = 7.4 Hz, 0.86 H), 1.60−1.70 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 147.4, 146.4, 144.4, 144.2, 129.2, 129.1, 120.9, 114.2, 110.9, 106.4, 102.5, 59.4, 55.8, 55.0, 35.6, 35.3, 32.4, 31.6, 27.3, 23.6; IR (neat, NaCl) 3032, 3000, 2936, 2932, 2856, 2835, 1601, 1594, 1584, 1487, 1465, 1456, 1437, 1390, 1314, 1261, 1209, 1190, 1180, 1164, 1152, 1132, 1109, 1044, 935, 873, 778, 738, 696 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 175 (100), 121 (35), 147 (23), 71 (19), 122 (13), 203 (10), 174 (8), 149 (7), 171 6); HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1313. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.93.

Anodic Oxidation of (*E,Z*)-1-Methoxy-5-(3-methoxyphenyl)-1-pentene (4). Constant Current Electrolysis. To a 100 mL round-bottom flask were added 0.500 g (2.4 mmol) of **4**, 1.299 g (12.1 mmol) of 2,6-lutidine, 4.120 g (38.7 mmol) of lithium perchlorate, 19.4 mL of methanol, and 77.4 mL of dichloromethane. This mixture was degassed by sonication for 45 min and then oxidized at a constant current of 11.1 mA until 449.0 C had been passed. The current was then reduced to 10.3 mA current until a total of 467.1 C had passed (2.0 faradays/mol). Upon completion, the reaction mixture was diluted with H_2O and extracted with ether. The ether layer was washed once with brine, dried over $MgSO_4$, and filtered, and the solvent was removed *in vacuo*. The crude product was then chromatographed using 100 mL of silica gel that had been slurry packed with a solution of 1% triethylamine in hexane. A gradient elution from hexane to 20% ether in hexane (2% steps every 100 mL of eluent) afforded 0.111 g (22%) of the recovered starting material and 0.328 g (57%) of a mixture of the desired products. From the 300 MHz ^{1}H NMR a 2.8:1 ratio of product (**5** and **6**) to overoxidized material (**7** and **8**) and a 2.2:1 ratio of major products (where cyclization occurred at the position para to the methoxy group) **5** and **7** to minor products (where cyclization occurred at the position ortho to the methoxy group) **6** and **8** was obtained.

Controlled Potential Electrolysis. To a 100 mL round-bottom flask were added 0.321 g (1.6 mmol) of **4**, 0.836 g (7.8 mmol) of 2,6-lutidine, 2.656 g (25.0 mmol) of lithium perchlorate, 12.4 mL of methanol, and 49.8 mL of dichloromethane. This mixture was degassed by sonication for 45 min and then oxidized at a voltage of +1.10 V (vs Ag/AgCl) until a total of 250.5 C had passed (1.66 faradays/mol). Upon completion, the reaction mixture was diluted with H_2O and extracted with ether. The ether layer was washed once with brine, dried over $MgSO_4$, and filtered, and the solvent was removed *in vacuo*. The crude product was then chromatographed on a column of 45 mL of silica gel that had been slurry packed with a solution of 1% triethylamine in hexane. A gradient elution from hexane to 20% ether in hexane (2% steps every 75 mL of eluent) led to the isolation of 0.0685 g (21%) of the recovered starting material and 0.213 g (57%) of a mixture of the desired products. From the 300 MHz ^{1}H NMR a 16:1 ratio of product to overoxidized product and 1.6:1 ratio of major products (where cyclization occurred at the position para to the methoxy group) **5** and **7** to minor products (where cyclization occurred at the position ortho to the methoxy group) **6** and **8** was obtained.

6-Methoxy-1,2,3,4-tetrahydronaphthalenecarboxaldehyde dimethyl acetal (5): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.6 Hz, 1 H), 6.69 (dd, J = 8.6 Hz, J = 2.8 Hz, 1 H), 6.61 (d, J = 2.8 Hz, 1 H), 4.36 (d, J = 6.5 Hz, 1 H), 3.76 (s, 3 H), 3.34 (s, 6 H), 2.98 (dt, J = 5.5 Hz, J = 5.7 Hz, 1 H), 2.71−2.79 (m, 2 H), 1.65−2.03 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 139.2, 131.4, 128.2, 113.4, 111.6, 108.2, 55.8, 55.7, 55.1, 55.0, 53.7, 53.6, 39.9, 30.0, 24.1, 20.1; IR (neat, NaCl) 2933, 2914, 2833, 1608, 1584, 1576, 1501, 1465, 1254, 1233, 1190, 1154, 1115, 1075, 971, 938, 913, 871, 835, 813, 732 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 205 (100), 173 (68), 237 (54), 204 (45), 206 (42), 233 (19), 203 (19) 171 (18), 201 (15); HRMS (EI) *m/e* calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1418. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.31; H, 8.52.

8-Methoxy-1,2,3,4-tetrahydronaphthalenecarboxaldehyde dimethyl acetal (6): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (t, J = 7.9 Hz, 1 H), 6.71 (d, J = 7.8 Hz, 1 H), 6.67 (d, J = 7.8 Hz, 1 H), 4.64 (d, J = 3.1 Hz, 1 H), 3.82 (s, 3 H), 3.38−3.43 (m, 4 H includes s 3.43), 3.14 (s, 3 H), 2.60−2.81 (m, 2 H), 2.03−2.26 (m, 2 H), 1.53−1.68 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 140.8, 126.5, 124.9, 121.6, 108.4, 107.4, 57.0, 55.6, 55.2, 35.4, 29.7, 21.8, 20.5; IR (neat, NaCl) 2934, 2833, 1599, 1584, 1467, 1439, 1373, 1337, 1322, 1293, 1265, 1251, 1212, 1189, 1148, 1123, 1096, 1068, 1002, 962, 893, 833, 804, 784, 774, 751, 734, 701 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 173 (100), 205 (95), 204 (47), 75 (29), 174 (24), 203 (24), 206 (22), 175 (12), 201 (11), 172 (10), 237 (1); HRMS (EI) *m/e* calcd for $C_{14}H_{20}O_3$, 236.1412, found 236.1414. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.48; H, 8.40.

2-Methoxy-5,6-dihydronaphthalene (9) and 1-Methoxy-7,8-dihydronaphthalene (10). In order to help identify the overoxidized material, a mixture of the four compounds was treated with PPTS in methanol to eliminate the overoxidized material. To a round-bottom flask were added 2.403 g of a mixture of **5**, **6**, **7**, and **8** (the ratio of the mixture was 7.3:3.5:3:1, respectively), 5.125 g (20.4 mmol) of PPTS, and 50

mL of methanol. The reaction mixture was refluxed for 4 h and then gently heated for 16 h. Upon completion, the reaction mixture was diluted with H_2O and extracted with ether. The ether layer was washed once with brine, dried over $MgSO_4$, and filtered, and the solvent was removed *in vacuo*. The crude product was then chromatographed on a column of 500 mL of silica gel using a gradient elution from hexane to 20% ether in hexane (3% steps every 300 mL of eluent) in order to afford 42.8 mg (0.26 mmol) of **10**, 271.6 mg (1.70 mmol) of **9**, 232.9 mg (1.23 mmol) of the aldehyde derived from the hydrolysis of **6** (which could be returned to acetal **6** with 0.5 g Montmorillonite Clay K-10 and 0.8 mL of trimethyl orthoformate followed by filtration through Celite), and 1.185 g (5.02 mmol) of a mixture of **5** and **6**. Compound **9** was contaminated with a small amount of an unidentified product.

Spectral data for 2-methoxy-5,6-dihydronaphthalene (9): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92−6.94 (m, 1 H), 6.65−6.67 (m, 2 H), 6.40 (d, J = 9.6 Hz, 1H), 5.88 (dt, J = 9.6 Hz, J = 4.4 Hz, 1 H), 3.77 (s, 3 H), 2.76 (t, J = 8.2 Hz, 2 H), 2.23−2.31 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 137.2, 127.3, 127.1, 126.8, 125.9, 113.8, 111.0, 55.2, 28.0, 23.0; GCMS (PCI) *m/e* (rel intensity) 161 (100), 160 (53), 57 (46), 103 (30), 189 (29), 88 (25), 83 (20), 115 (20), 66 (19), 85 (18), 94 (13), 55 (13), 146 (8), 201 (5); HRMS (EI) *m/e* calcd for $C_{11}H_{12}O$ 160.0888, found 160.0880.

Spectral data for 1-methoxy-7,8-dihydronaphthalene (10): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (t, J = 7.8 Hz, 1 H), 6.84 (d of multiplets, J = 9.9 Hz, 1 H), 6.72 (d, J = 7.6 Hz, 1 H), 6.71 (d, J = 8.4 Hz, 1 H), 6.03 (dt, J = 9.8 Hz, J = 4.4 Hz, 1 H), 3.81 (s, 3H), 2.75 (t, J = 8.3 Hz, 2 H), 2.23−2.31 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 137.0, 127.6, 127.3, 122.8, 121.5, 120.7, 108.7, 55.5, 27.7, 22.8.

4-(3,5-Dimethoxyphenyl)-1-butene. To a round-bottom flask was added 4.201 g (24.9 mmol) of 3,5-dimethoxybenzyl alcohol in 15 mL of THF. The mixture was warmed in order to melt the alcohol, and then 2.281 g (12.5 mmol) of phosphorus tribromide was added. After 30 min, the reaction mixture was diluted with H_2O and then extracted with ether. The ether layers were dried over $MgSO_4$ and filtered and the solvent removed *in vacuo*. The crude mixture was then diluted with 24 mL of THF and 35.4 mL (35.4 mmol) of allylmagnesium bromide (1.0 M solution in ether) added. The reaction mixture was stirred for 12 h, then the reaction was quenched with 25 mL of 10 N H_2SO_4, and the mixture was diluted with H_2O and extracted with ether. The resulting ether layer was washed once with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude reaction mixture was chromatographed through 250 mL of silica gel using a gradient elution of hexane to 21% ether in hexane (3% steps every 500 mL of eluent) to afford 3.551 g (74%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (d, J = 2.2 Hz, 2 H), 6.31 (t, J = 2.2 Hz, 1 H), 5.86 (ddt, J = 17.0 Hz, J = 10.3 Hz, J = 6.5 Hz, 1 H), 5.05 (dq, J = 17.1 Hz, J = 1.7 Hz, 1 H), 4.98 (d of multiplets, J = 10.2 Hz, 1 H), 3.78 (s, 6 H), 2.65 (t, J = 7.8 Hz, 2 H), 2.36 (dt, J = 8.3 Hz, J = 6.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 144.3 138.0, 114.9 106.5 97.8, 55.2, 35.7, 35.3; IR (neat, NaCl) 3079, 2999, 2937, 2855, 2838, 1641, 1607, 1596, 1462, 1429, 1350, 1319, 1295, 1206, 1194, 1158, 1150, 1066, 1061, 993, 920, 830, 695 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 193 (100), 194 (22), 151 (18), 221 (14), 192 (14), 191 (7), 179 (5), 233 (5); HRMS (EI) *m/e* calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1153.

4-(3,5-Dimethoxyphenyl)-1-butanol. The hydroboration was carried out in a similar fashion to that described above for the synthesis of **3**. In this example, 2.502 g (13.0 mmol) of 4-(3,5-dimethoxyphenyl)-1-butene, 3.558 g (50.8 mmol) of 2-methyl-2-butene, 2.6 mL (26.0 mmol) of the borane−dimethyl sulfide complex, and 100 mL of THF were used. The reaction mixture was worked up with 15 mL of 3 N NaOH and 7.5 mL of H_2O_2. The crude reaction mixture was washed once with a saturated solution of sodium sulfite, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was then chromatographed through 400 mL of silica gel using a gradient elution from hexane to 30% ether in hexane (5% steps every 300 mL of eluent) to afford 2.640 g (97%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.34 (d, J = 2.2 Hz, 2 H), 6.29 (t, J = 2.2 Hz, 1 H), 3.75 (s, 6 H), 3.60 (t, J = 6.3 Hz, 2 H), 2.56 (t, J = 7.3 Hz, 2 H), 2.53 (br s, 1 H), 1.52−1.71 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 144.8, 106.5, 97.6, 62.5, 55.2, 36.0, 32.3, 27.4; IR (neat, NaCl) 3300 br, 2998, 2938, 2863, 2839, 1604, 1596, 1593, 1462, 1428, 1348, 1324, 1314, 1293, 1204, 1157, 1152, 1147, 1058, 939, 921, 833, 696 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 211 (100), 193 (67), 212 (22), 151 (17), 194 (15), 210 (11) 152 (8), 239 (7), 209 (7), 179 (3), 191 (3), 251, (3); HRMS (EI) *m/e* calcd for $C_{12}H_{18}O_3$ 210.1255, found 210.1253.

***(E,Z)*-5-(3,5-Dimethoxyphenyl)-1-methoxy-1-pentene (11a).** The reaction sequence was carried out in a similar fashion to that described above for the synthesis of **4**. In this example, 1.421 g (6.8 mmol) of the alcohol, 1.029 g (8.1 mmol) of oxalyl chloride, 0.680 g (8.7 mmol) of dimethyl sulfoxide, 3.390 g (33.5 mmol) of triethylamine, and 13 mL of dichloromethane were used. After workup the aldehyde was diluted with 10 mL of THF and added to the ylide synthesized below. The ylide was formed from 6.952 g (20.3 mmol) of (methoxymethyl)triphenylphosphonium chloride, 11.9 mL (20.3 mmol) of *tert*-butyllithium, and 50 mL of THF. Workup and chromatography afforded 0.815 g (51%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27−6.36 (m, 3.67 H), 5.89 (d, J = 6.2 Hz, 0.33 H), 4.73 (dt, J = 12.6 Hz, J = 7.3 Hz, 0.67 H), 4.35 (dt, J = 6.3 Hz, J = 7.3 Hz, 0.33 H), 3.76 (s, 6 H), 3.57 (s, 1 H), 3.50 (s, 2 H), 2.55 (t, J = 7.7 Hz, 2 H), 2.11 (dt, J = 7.5 Hz, J = 7.3 Hz, 0.66 H), 1.97 (dt, J = 7.6 Hz, J = 7.2 Hz, 1.34 H), 1.60−1.70 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 160.6, 147.3, 146.4, 145.2, 144.9, 106.4, 106.3, 102.5, 97.6, 59.4, 55.8, 55.2, 35.8, 35.5, 32.2, 31.4, 27.2, 23.6; IR (neat, NaCl) 3055, 3032, 2999, 2940, 2929, 2855, 2838, 1656, 1605, 1596, 1461, 1454, 1429, 1346, 1324, 1310, 1292, 1265, 1205, 1149, 1134, 1109, 1067, 1061, 933, 836, 747, 689 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 205 (100), 237 (44), 152 (33), 71 (28), 57 (25), 223 (22), 177 (21), 206 (16), 204 (14), 61 (13), 55 (13), 251 (13), 265 (5); HRMS (EI) *m/e* calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1433. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.18; H, 8.55.

Anodic Oxidation of 11a: Formation of 6,8-Dimethoxy-1,2,3,4-tetrahydronaphthalenecarboxaldehyde Dimethyl Acetal (12a) and 1,6,8-Trimethoxy-1,2,3,4-tetrahydronaphthalene (13). The oxidation of **11a** was done in a fashion similar to the constant current electrolysis of substrate **4**. In this case 0.243 g (1.0 mmol) of **11a**, 0.548 g (5.2 mmol) of 2,6-lutidine, 1.767 g (16.5 mmol) of lithium perchlorate, 8.2 mL of methanol, and 33.0 mL of dichloromethane were oxidized at a constant current of 11.4 mA until 198.8 C (2.00 faradays/mol) of charge had been passed. Workup and chromatography afforded 0.0608 g (25%) of the recovered starting material, 0.0856 g (31%) of the desired product (**12a**), and 0.0752 g (33%) of the overoxidized material (**13**). The spectral data for **12a** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (d, J = 2.2 Hz, 1 H), 6.26 (s, 1 H), 4.60 (d, J = 3.1 Hz, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.43 (s, 3 H), 3.16 (s, 3 H), 3.28−3.31 (m, 1 H), 2.57−2.78 (m, 2 H), 2.00−2.24 (m, 2 H), 1.53−1.66 (m, 2 H); $_{13}$C NMR (75 MHz, $CDCl_3$) δ 158.5, 141.3, 117.4, 108.6, 104.7, 96.2, 96.1, 57.1, 57.0, 55.7, 55.6, 55.4, 55.3, 55.2, 55.1, 35.1, 30.2, 29.8, 21.8, 20.6, 20.5; IR (neat, NaCl) 2937, 2935, 2857, 1652, 1635, 1606, 1593, 1559, 1540, 1506, 1488, 1464, 1457, 1436, 1424, 1355, 1339, 1297, 1276, 1214, 1201, 1144, 1123, 1103, 1084, 1053, 964, 826 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 203 (100), 235 (92), 234 (86), 233 (34), 220 (33), 75 (18), 236 (15), 221 (9), 202 (9), 217 (8), 189 (8), 263 (6); HRMS (EI) *m/e* calcd for $C_{15}H_{22}O_4$ 266.15180, found 266.15141. The spectral data for **13** (mixed with *ca.* 25% of **12a**) are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (s, 1 H), 6.22 (s, 1 H), 4.47 (bd s, 1 H), 3.82 (s, 3 H), 3.77 (s, 3 H), 3.42 (s, 3 H), 2.68 (m, 2 H), 2.21 (bd d, J = *ca.* 14 Hz, 1 H), 1.94 (m, 1 H), 1.69 (m, 1 H), 1.47 (tt, J_t = 14 Hz, J_t = 3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 159.5, 139.9, 118.2, 104.3, 96.4, 70.0, 56.7, 55.6, 55.3, 29.7, 26.7, 17.3; IR (neat, NaCl) 2935, 2836, 1600, 1463, 1347, 1304, 1280, 1217, 1206, 1192, 1156, 1142, 1125, 1103, 1083, 1048 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1245.

***(E,Z)*-5-(3,5-Dimethoxyphenyl)-1-(methylthio)-1-pentene (11b).** A solution of 5.273 g (25.1 mmol) of the alcohol

and 2.548 g (32.6 mmol) of dimethyl sulfoxide in 50 mL of dichloromethane was cooled to −78 °C. After 15 min, 3.822 g (30.1 mmol) of oxalyl chloride was added and the reaction mixture allowed to warm to between −50 and −60 °C. After another 15 min, 12.701 g (125.5 mmol) of triethylamine was added and the reaction allowed to warm to room temperature. Water was added to the mixture and then the dichloromethane evaporated *in vacuo*. The remaining solution was extracted with ether, and then the combined ether layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. As this was happening, a solution of 17.4 g (48.5 mmol) of [(methylthio)methyl]triphenylphosphonium chloride in 150 mL of THF was cooled to 0 °C and treated with 26.9 mL (48.5 mmol) of a phenyllithium in a 70:30 cyclohexane:ether solution. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The aldehyde from above was then diluted with THF and transferred into the flask containing the ylide. After 16 h, the reaction was quenched with water and ether. The layers were separated, and then the aqueous layer was extracted with ether. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was chromatographed through silica gel using a gradient elution from hexane to 18% ether in hexane by adding an additional 3% of ether for every 250 mL of eluent used in order to afford 3.798 g (60%) of the desired vinyl sulfide: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29−6.35 (m, 3 H), 5.98 (dt, J = 15.1 Hz, J = 1.5 Hz, 0.4 H), 5.90 (d, J = 9.4 Hz, 0.6 H), 5.54 (dt, J = 9.4 Hz, J = 7.1 Hz, 0.4 H), 5.44 (dt, J = 14.9 Hz, J = 7.0 Hz, 0.6 H), 3.77 (s, 6 H), 2.53−2.60 (m 2 H), 2.26 (s, 1.2 H), 2.21 (s, 1.8 H), 2.09−2.20 (m, 2 H), 1.65−1.75 (m 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 144.8, 144.7, 128.3, 127.2, 126.9, 124.2, 106.50, 106.45, 97.75, 97.70, 55.2, 35.8, 35.6, 32.6, 30.9, 30.6, 28.8, 17.1, 15.1; IR (neat, NaCl) 2999, 2936, 2923, 2920, 2857, 2837, 1608, 1604, 1594, 1461, 1428, 1351, 1323, 1310, 1292, 1205, 1193, 1154, 1068, 1059, 940, 831, 696 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 253 (100), 205 (90), 206 (58), 281 (57), 152 (49), 267 (41), 191 (37), 177 (34), 219 (34), 204 (33), 254 (31), 87 (23), 233 (21), 63 (16), 151 (14), 255 (14), 282 (10), 295 (10), 293 (8); HRMS (EI) *m/e* calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1186. Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99. Found: C, 66.54; H, 8.05.

Anodic Oxidation of 11b: Formation of 6,8-Dimethoxy-1,2,3,4-tetrahydronaphthalenecarboxaldehyde Dimethyl Thioacetal (12b). Again the anodic oxidation was done in a fashion similar to the constant current electrolysis of substrate **4**. In this example, 0.418 g (1.7 mmol) of **11b**, 0.890 g (8.3 mmol) of 2,6-lutidine, 2.826 g (26.6 mmol) of lithium perchlorate, 13.3 mL of methanol, and 53.1 mL of dichloromethane were oxidized at a constant current of 11.3 mA until 320.9 C (2.0 faradays/mol) of charge had been passed. Workup and chromatography afforded 0.338 g (72%) of the desired product (**12b**) as a mixture of two diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24−6.28 (m, 2 H), 4.89 (d, J = 4.8 Hz, 0.5 H), 4.79 (d, J = 4.3 Hz, 0.5 H), 3.785 (s, 1.5 H), 3.780 (s, 1.5 H), 3.76 (s, 3 H), 3.61−3.69 (m, 0.5H), 3.40−3.47 (m, 2 H includes 1.5H s), 3.22 (s, 1.5 H), 2.56−2.82 (m, 2 H), 1.47−2.26 (m, includes 2.17 (s), 1.89 (s), 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 158.6, 158.5, 158.4, 141.4, 140.7, 118.5, 117.5, 104.7, 104.5, 96.2, 96.0, 94.6, 93.2, 57.3, 57.0, 55.25, 55.20, 55.1, 37.0, 30.5, 29.8, 24.1, 23.8, 21.1, 20.1, 15.1, 14.1; IR (neat, NaCl) 2933, 2836, 1605, 1595, 1488, 1463, 1424, 1353, 1302, 1277, 1216, 1200, 1148, 1100, 1079, 1052, 947, 910, 848, 827, 732 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 251 (100), 250 (66), 203 (59), 252 (34), 204 (25), 236 (17), 249 (14), 253 (8), 279 (8), 205 (7), 237 (6), 231 (5); HRMS (EI) *m/e* calcd for $C_{15}H_{22}O_3S$ 282.1290, found 282.1277.

(*E,Z*)-5-(3-Methoxyphenyl)-1-(methylthio)-1-pentene (4b). Compound **4b** was made in a fashion directly analogous to **11b** above. In this case, 1.217 g (6.8 mmol) of **3**, 0.686 g (8.8 mmol) of dimethyl sulfoxide, 13.0 mL of dichloromethane, 1.028 g (8.1 mmol) of oxalyl chloride, and 3.416 g (33.8 mmol) of triethylamine were used in the Swern oxidation. The resulting aldehyde was added to the ylide derived from 4.845 g (13.5 mmol) of [(methylthio)methyl]triphenylphosphonium chloride in 10 mL of THF and 7.5 mL (13.5 mmol) of a 1.8 M solution of phenyllithium in 70:30 cyclohexane:ether. After workup and chromatography, the reaction mixture afforded 0.885 g (59%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14−7.19 (m, 1 H), 6.69−6.77 (m, 3 H), 5.96 (dt, J = 14.9 Hz, J = 1.6 Hz, 0.57 H), 5.88 (dt, J = 9.3 Hz, J = 1.3 Hz 0.43 H), 5.52 (dt, J = 9.4 Hz, J = 7.1 Hz, 0.43 H), 5.42 (dt, J = 14.9 Hz, J = 7.0 Hz, 0.57 H), 3.75 (s, 3 H), 2.55−2.62 (m, 2 H), 2.22 (s, 1.29 H), 2.19 (s, 1.71 H), 2.07−2.16 (m, 2 H), 1.64−1.75 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 144.0, 143.9, 129.2, 128.3, 127.3, 126.8, 124.2, 120.9, 114.2, 114.1, 111.05, 111.00, 55.1, 54.9, 35.7, 35.3,32.7, 31.1, 30.7, 28.8, 17.0, 15.0; IR (neat, NaCl) 3023, 3000, 2935, 2921, 2857, 2834, 1610, 1594, 1584, 1487, 1465, 1456, 1436, 1313, 1291, 1260, 1165, 1152, 1043, 938, 873, 778, 735, 696 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 223 (100), 175 (98), 251 (83), 224 (55), 121 (46), 147 (44), 203 (40), 176 (34), 174 (26), 225 (24), 222 (23), 161 (21); HRMS (EI) *m/e* calcd for $C_{13}H_{18}OS$ 222.1078, found 222.1091. Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 70.35; H, 8.23.

6-Methoxy-1,2,3,4-tetrahydronaphthalenecarboxaldehyde Dimethyl Thioacetal (5b). Compound **4b** was oxidized in a manner similar to the constant current oxidation of compound **4a**. In this experiment, 0.364 g (1.64 mmol) of **4b**, 0.879 g (8.2 mmol) of 2,6-lutidine, 2.792 g (26.2 mmol) of lithium perchlorate, 13.1 mL of methanol, and 52.4 mL of dichloromethane were electrolyzed at a constant current of 12.0 mA until 319.2 C (2.02 faradays/mol) of charge had been passed. Workup and chromatography afforded 0.159 g (38%) of the desired product as a mixture of two diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 0.67 H), 7.19 (J = 8.6 Hz, 0.33 H), 6.59−6.70 (m, 2 H), 4.52 (d, J = 4.9 Hz, 0.67 H), 4.39 (d, J = 7.4 Hz, 0.33 H), 3.755, 3.750 (2 s, 3 H), 3.37 (s, 2 H), 3.34 (s, 1 H), 3.08−3.22 (m, 1 H), 2.64−2.84 (m, 2 H), 1.62−2.14 (m, including 2.09 (s), 2.02 (s), 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 157.7, 139.3, 138.8, 131.3, 130.4, 129.1, 128.9, 113.5, 113.4, 111.4, 94.5, 93.4, 56.8, 56.5, 55.1, 55.0, 47.6, 41.1, 29.9, 25.8, 25.3, 20.5, 20.1, 14.1, 11.7; IR (neat, NaCl) 2989, 2983, 2977, 2930, 2883, 2866, 2833, 1464, 1457, 1447, 1436, 1428, 1419, 1326, 1318, 1298, 1273, 1255, 1238, 1187, 1154, 1123, 1099, 1080, 1041, 946, 871, 835, 816, 787, 774 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 147 (100), 173 (78), 221 (74), 113 (69), 63 (68), 148 (59), 61 (27), 175 (23), 121 (21), 249 (20), 174 (19), 95 (19); HRMS (EI) *m/e* calcd for $C_{16}H_{20}O_2S$ 252.1184, found 252.1175.

(*E,Z*)-2-Methoxy-6-phenyl-2-hexene (14). The oxidation of 4-phenyl-1-butanol (1.931 g, 12.9 mmol) was done under the same Swern oxidation conditions described above for the syntheses of **4** and **4b**. In this case, 1.794 g (14.1 mmol) of oxalyl chloride, 1.209 g (15.6 mmol) of dimethyl sulfoxide, 6.527 g (64.5 mmol) of triethylamine, and 20 mL of dichloromethane were used. After the usual workup, the reaction mixture was added to the reaction mixture described below.

Lithium diisopropylamide (LDA) was synthesized by adding 15.5 mL (38.7 mmol) of *n*-butyllithium to 3.916 g (38.7 mmol) of diisopropylamine in 10.0 mL of THF at −78 °C. After 1 h at −78 °C, the LDA was added to a −78 °C solution of 10.066 g (38.7 mmol) of (methoxyethyl)diphenylphosphine oxide in 20 mL of THF. To the resulting mixture was added the aldehyde made above. The reaction was held at −78 °C for 1 h and then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched with H_2O. Triethylamine (10 mL) was added to the mixture before completing the workup in order to minimize hydrolysis of the enol ether. The resulting solution was extracted three times with ether, and then the organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. It is important to note that the crude reaction mixture was concentrated without warming the bath since the product proved to be sensitive to heat. The crude product was chromatographed through 300 mL of activity III basic alumina with a gradient elution of hexane to 15% ether in hexane (3% steps every 200 mL of eluent) to afford 1.383 g (61%) of the slightly impure (<5% impurity by NMR) desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13−7.31 (m, 5 H), 4.44 (t, J = 7.3 Hz, 0.35 H), 4.38 (t, J = 7.3 Hz, 0.65 H), 3.49 (s, 1.05 H), 3.53 (s, 1.95 H), 2.58−2.68 (m, 2 H), 1.98−2.13 (m, 2 H), 1.83 (s, 1.05 H), 1.76 (s, 1.95 H), 1.58−1.73 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 151.7, 143.5,

143.3, 129.0, 128.85, 128.80, 126.2, 126.1, 111.8, 108.6, 96.6, 55.9, 54.3, 46.5, 35.9, 35.6, 32.8, 32.0, 26.7, 24.6, 17.6, 16.3; IR (neat, NaCl) 3062, 3027, 2998, 2931, 2856, 1669, 1603, 1496, 1463, 1453, 1439, 1391, 1274, 1261, 1224, 1181, 1140, 1083, 1030, 806, 745, 699 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 117 (100), 159 (56), 191 (53), 85 (22), 91 (21), 145 (20), 192 (12), 118 (12), 189 (10), 81 (10), 160 (9); HRMS (EI) *m/e* calcd for $C_{13}H_{18}O$ 190.1358, found 190.1345.

(*E*)-6-Phenyl-3-hexen-2-one (15). In a fashion similar to the oxidation of compound **4**, 0.256 g (1.3 mmol) of **14**, 0.780 g (7.3 mmol) of 2,6-lutidine, 2.468 g (23.2 mmol) of lithium perchlorate, 11.6 mL of methanol, and 46.4 mL of dichloromethane were oxidized at a constant current of 11.3 mA until 285.0 C (2.03 faradays/mol) of charge had been passed. After workup, the products were taken up in 15 mL of acetone and 1.011 g (4.0 mmol) of PPTS was added. The reaction mixture was allowed to stir for 72 h and then worked up by being diluted with H_2O and then extracting the resulting mixture three times with ether. The ether layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude oil was then chromatographed through 45 mL of silica gel using a gradient elution from hexane to 30% ether/hexane (3% steps every 75 mL of eluent) to afford 0.120 g (51%) of the desired product. NMR analysis showed that the product contained a few percent of an unidentified impurity. **15:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12−7.28 (m, 5 H), 6.78 (dt, J = 16.0 Hz, J = 6.8 Hz, 1 H), 6.05 (d, J = 16.0 Hz, 1 H), 2.75 (t, J = 7.6 Hz, 2 H), 2.50 (dt, J = 7.1 Hz, J = 7.4 Hz, 2 H), 2.18 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 147.1, 140.6, 131.7, 128.5, 128.3, 126.2, 34.4, 34.1, 26.9; IR (neat, NaCl) 3085, 3062, 3028, 3003, 2927, 2857, 1697, 1675, 1626, 1602, 1496, 1454, 1429, 1360, 1317, 1292, 1254, 1187, 1161, 1088, 1078, 1029, 1021, 976, 748, 700 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 175 (100), 71 (94), 91 (35), 117 (28), 119 (18), 176 (17), 203 (17), 105 (16), 157 (12), 116 (11), 131 (10), 174 (6); HRMS (EI) *m/e* calcd for $C_{12}H_{14}O$ 174.1045, found 174.1051.

4-(3,4,5-Trimethoxyphenyl)-1-butene. The desired olefin product was synthesized in a fashion directly analogous to the previously described synthesis of olefin **2**. In this example, 5.006 g (25.3 mmol) of 3,4,5-trimethoxybenzyl alcohol, 3.420 g (12.6 mmol) of phosphorus tribromide, and 100 mL of THF were used. Upon completion, 50.5 mL (50.5 mmol) of a 1.0 M solution of allylmagnesium bromide in ether was added. Workup and chromatography afforded 2.777 g (49%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 2 H), 5.86 (ddt, J = 17.0 Hz, J = 10.3 Hz, J = 6.6 Hz, 1 H), 5.06 (dq, J = 17.2 Hz, J = 1.7 Hz, 1 H), 4.99 (d of multiplets, J = 11.9 Hz, 1 H), 3.84 (s, 6 H), 3.82 (s, 3 H), 2.65 (t, J = 7.9 Hz, 2 H), 2.37 (dt, J = 7.0 Hz, J = 7.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 138.1, 137.8, 136.1, 115.1, 105.3, 60.9, 56.1, 56.0, 35.9, 35.7; IR (neat, NaCl) 3074, 2997, 2939, 2838, 1640, 1589, 1509, 1457, 1420, 1345, 1325, 1237, 1183, 1151, 1133, 1128, 1042, 1011, 966, 913, 842, 822, 781 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 223 (100), 181 (91), 222 (24), 208 (18), 209 (17), 221 (15), 224 (15), 182 (10); HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1262.

4-(3,4,5-Trimethoxyphenyl)-1-butanol. The hydroboration was carried out in a similar fashion to that described above for the synthesis of **3**. In this example, 20.960 g (94.3 mmol) of the olefin, 25.789 g (367.9 mmol) of 2-methyl-2-butene, 18.9 mL (188.7 mmol) of the borane−dimethylsulfide complex, and 300 mL of THF were used. The reaction was worked up with 120 mL of 3 N NaOH and 60 mL of H_2O_2. Workup and chromatography afforded 9.659 g (43%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (s, 2 H), 3.85 (s, 6 H), 3.82 (s, 3 H), 3.66 (t, J = 6.2 Hz, 2 H), 2.59 (t, J = 7.4 Hz, 2 H), 1.87 (br peak, 1 H), 1.59−1.74 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 138.2, 135.9, 105.2, 62.7, 60.8, 56.0, 36.1, 32.3, 27.7; IR (neat, NaCl) 3354 br, 2993, 2935, 2861, 2840, 1589, 1509, 1460, 1420, 1382, 1368, 1343, 1333, 1323, 1237, 1183, 1150, 1129, 1124, 1065, 1031, 1009, 973, 832, 828, 780, 735 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 241 (100), 223 (75), 181 (31), 79 (25), 239 (24), 240 (24), 221 (16), 242 (14), 193 (13), 224 (12), 151 (11), 61 (11); HRMS (EI) *m/e* calcd for $C_{13}H_{20}O_4$ 240.1361, found 240.1360.

(*E,Z*)-1-(Methylthio)-5-(3,4,5-trimethoxyphenyl)-1-pentene (16). The reaction sequence was carried out in a similar fashion to that described above for the synthesis of **4b**. In this example, 2.603 g (10.8 mmol) of the alcohol, 1.645 g (13.0 mmol) of oxalyl chloride, 1.097 g (14.0 mmol) of dimethyl sulfoxide, 5.465 g (54.0 mmol) of triethylamine, and 22 mL of dichloromethane were used. After workup the aldehyde was diluted with 75 mL of THF and added to a solution of the ylide formed from 7.752 g (21.6 mmol) of [(methylthio)methyl]-triphenylphosphine chloride, 12.0 mL (21.6 mmol) of phenyllithium, and 12 mL of THF. Workup and chromatography afforded 2.131 g (70%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 0.9 H), 6.39 (s, 1.1 H), 6.01 (d, J = 15.1 Hz, 0.55 H), 5.92 (d, J = 9.3 Hz, 0.45 H), 5.55 (dt, J = 9.4 Hz, J = 7.2 Hz, 0.45 H), 5.46 (dt, J = 14.9 Hz, J = 7.0 Hz, 0.55 H), 3.85 (s, 6 H), 3.82 (s, 3 H), 2.54−2.61 (m, 2 H), 2.27 (s, 1.35 H), 2.23 (s, 1.65 H), 2.12−2.21 (m, 2 H), 1.66−1.77 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 138.2, 138.1 128.2, 127.2, 126.8, 124.2, 105.2, 60.8, 56.0, 35.9, 35.7, 32.7, 31.2, 30.8, 28.8, 17.0, 15.1; IR (neat, NaCl) 2994, 2935, 2925, 2856, 2837, 1589, 1559, 1508, 1457, 1420, 1349, 1332, 1319, 1238, 1183, 1131, 1126, 1039, 1011, 958, 939, 824, 780, 668 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 282 (100), 235 (83), 284 (26), 61 (26), 181 (25), 79 (24), 63 (22), 87 (22), 282 (20), 207 (15), 236 (14), 115 (12); HRMS (EI) *m/e* calcd for $C_{15}H_{22}O_3S$ 282.1290, found 282.1294. Anal. Calcd for $C_{15}H_{22}O_3S$: C, 63.80; H, 7.85. Found: C, 63.84; H, 7.63.

Anodic Oxidation of Substrate 16: 6,7,8-Trimethoxy-1,2,3,4-tetrahydronaphthalenecarboxaldehyde Dimethyl Thioacetal (17) and 7,9-Dimethoxy-8-oxospiro[4.5]deca-6,9-dienecarboxaldehyde Dimethyl Thioacetal (18). Compound **16** was oxidized in a manner similar to the constant current oxidation of compound **4**. In this experiment, 0.210 g (0.74 mmol) of **16**, 0.399 g (3.72 mmol) of 2,6-lutidine, 1.260 g (11.8 mmol) of lithium perchlorate, 5.9 mL of methanol, and 23.7 mL of dichloromethane were used. The oxidation was conducted with a constant current of 11.0 mA until 130.4 C (1.8 faradays/mol) of charge had been passed. Workup and chromatography afforded 58.7 mg (25%) of the desired product (**17**) as a mixture of diastereomers and 59.7 mg (27%) of the spirocyclic compound (**18**) as a mixture of diastereomers. In addition, a 21% yield of material that was tentatively assigned by ^{1}H NMR as the uncyclized product **19** was obtained. The spectral data for compound **17** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (s, 1 H), 4.87 (d, J = 3.8 Hz, 0.33 H), 4.79 (d, J = 5.7 Hz, 0.67 H), 3.90 (s, 2H), 3.85 (s, 1 H), 3.83 (s, 6 H) 3.55−3.61 (m, 0.67 H), 3.33−3.38 (m, 0.33 H), 3.43 (s, 2 H), 3.23 (s, 1 H), 2.57−2.78 (m, 2 H), 2.21 (s, 1 H), 1.52−2.08 (m, including 1.97 s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 139.8, 134.6 123.1, 122.4, 107.4, 94.3, 94.2, 60.8, 60.7, 57.8, 57.1, 55.7, 38.2, 37.2, 29.7, 29.6, 24.1, 23.7, 20.5, 20.4, 14.5, 14.2; IR (neat, NaCl) 2977, 2934, 2879, 2834, 1599, 1581, 1493, 1463, 1457, 1432, 1407, 1349, 1271, 1193, 1141, 1122, 1094, 1082, 1034, 1022, 1009, 946, 910, 823, 796 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 265 (100), 233 (84), 264 (80), 263 (29), 266 (24), 234 (21), 218 (16), 249 (13), 237 (9), 219 (9), 191 (8), 293 (7); HRMS (EI) *m/e* calcd for $C_{16}H_{24}O_4S$ 312.1395, found 312.1365. The spectral data for compound **18** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (d, J = 1.8 Hz, 0.25 H), 5.91 (d, J = 0.9 Hz, 0.75 H), 5.81 (d, J = 1.8 Hz, 0.75 H), 5.69 (d, J = 0.9 Hz, 0.25 H), 3.89 (d, J = 5.7 Hz, 0.5 H), 3.80−3.85 (m, 0.5 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.46 (s, 0.25 H), 3.22 (s, 0.75 H), 3.06 (s, 2 H), 2.54−2.61 (m, 1 H), 1.67−2.32 (m, includes 1.97(s), 1.96 (s), 1.94 (s), 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.7, 176.9, 176.8, 151.0, 150.8, 149.6, 149.6, 125.0, 122.6, 122.5, 1220.5, 117.4, 115.3, 89.2, 86.4, 84.7, 58.1, 57.4, 55.3, 55.3, 55.1, 54.9, 54.7, 49.5, 48.9, 40.5, 39.9, 29.5, 28.4, 5.6, 25.5, 22.3, 21.7, 18.2, 14.7, 11.6, 9.2; IR (neat, NaCl) 2953, 2936, 2926, 2883, 2878, 2854, 2831, 1663, 1659, 1616, 1591, 1463, 1457, 1265, 1229, 1192, 1114, 1080, 1008, 938, 913, 900, 876, 866, 730 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 219 (100), 251 (67), 63 (58), 95 (55), 221 (49), 97 (46), 267 (41), 250 (25), 253 (22), 167 (22), 91 (21), 57 (19), 299 (2); HRMS (EI) *m/e* calcd for $C_{15}H_{22}O_4S$ 298.12387, found 298.12251. The proton NMR data for tentatively assigned **19** (contaminated with the corresponding aldehyde product and another small impurity)

are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (s, 2 H), 4.30 (d, J = 6 Hz, 1 H), 3.86 (s, 6 H), 3.81 (s, 3 H), 3.45 (s with shoulder, 6 H for **19** (the signal integrates low because of the presence of the aldehyde)), 3.39 (m, 1 H) 2.59 (m, 2 H), 2.13 and 2.12 (two singlets, 3 H (the signal integrates low because of the presence of the aldehyde)), 1.80 (m, 2 H), 1.67 (m, 2 H).

(*E,Z*)-1-Methoxy-5-(4-methoxyphenyl)-1-pentene (20). Substrate **20** was synthesized in a fashion identical to that described above for the synthesis of substrate **4**. In this example, 1.524 g (8.5 mmol) of 4-(4′-methoxyphenyl)-1-butanol, 1.287 g (10.1 mmol) of oxalyl chloride, 0.859 g (11.0 mmol) of dimethyl sulfoxide, 4.276 g (42.3 mmol) of triethylamine, and 16 mL of dichloromethane were used. After workup the aldehyde was diluted with 75 mL of THF and added to the ylide. The ylide was formed from 8.690 g (25.4 mmol) of (methoxymethyl)triphenylphosphonium chloride, 14.9 mL (25.4 mmol) of a 1.7 M solution of *tert*-butyllithium in pentane, and 75 mL of THF. Workup and chromatography afforded 1.302 g (75%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, J = 8.6 Hz, J = 2.2 Hz, 2 H), 6.79 (dd, J = 8.6 Hz, J = 2.2 Hz, 2 H), 6.27 (d, J = 12.7 Hz, 0.55 H), 5.86 (d with fine, J = 6.3 Hz, J = 1.5, 0.45 H), 4.71 (dt, J = 12.6 Hz, J = 7.4 Hz, 0.55 H), 4.34 (dt, J = 6.5 Hz, J = 7.2 Hz, 0.45 H), 3.73 (s, 3 H), 3.53 (s, 0.45 H), 3.48 (s, 0.55 H), 2.50−2.57 (m, 2 H), 2.09 (dtd, J = 7.3 Hz, J = 7.5 Hz, J = 1.4 Hz, 0.9 H), 1.93 (dt, J = 7.1 Hz, J = 7.4 Hz, 1.1 H), 1.57−1.67 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.65, 157.60, 147.3, 146.3, 134.7, 134.5, 129.3, 113.65, 113.60, 106.4, 102.5, 59.4, 55.7, 55.1, 34.6, 34.3, 32.7, 31.9, 27.2, 23.6; IR (neat, NaCl) 3029, 2999, 2932, 2854, 2834, 1663, 1653, 1635, 1612, 1584, 1513, 1464, 1457, 1441, 1390, 1300, 1245, 1209, 1177, 1151, 1132, 1108, 1037, 934, 831, 810, 749, 739, 700 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 175 (100) 193 (77), 176 (56), 121 (56), 203 (38), 177 (34), 142 (24), 174 (23), 122 (19), 207 (16), 192 (16), 206 (15), 120 (11); HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1316. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.14; H, 7.98.

Anodic Oxidation of 20: 8-Oxospiro[4.5]deca-6,9-dienecarboxaldehyde Dimethyl Acetal (21). Compound **20** was oxidized in a manner similar to the constant current oxidation of compound **4**. In this experiment, 0.124 g (0.6 mmol) of **20**, 0.323 g (3.0 mmol) of 2,6-lutidine, 1.027 g (9.7 mmol) of lithium perchlorate, 4.8 mL of methanol, and 19.3 mL of dichloromethane were used. The oxidation was conducted with a constant current of 11.2 mA until 116.6 C (2.0 faradays/mol) of charge had been passed. Workup and chromatography afforded 68.2 mg (51%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (dd, J = 10.0 Hz, J = 2.9 Hz, 1 H), 6.83 (dd, J = 9.8 Hz, J = 2.9 Hz, 1 H), 6.30 (dd, J = *ca.* 10.2 Hz, J = 1.9 Hz, 1 H), 6.26 (dd, J = 9.8 Hz, J = 1.9 Hz, 1 H), 4.05 (d, J = 7.4 Hz, 1 H), 3.28 (s, 3 H), 3.18 (s, 3 H), 2.43−2.51 (m, 1 H), 1.69−2.09 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.8, 156.5, 150.1, 128.3, 127.8, 105.5, 54.9, 53.6, 52.8, 50.5, 38.8, 26.1, 22.6; IR (neat, NaCl) 2952, 2881, 2832, 1623, 1598, 1456, 1448, 1408, 1394, 1387, 1368, 1361, 1263, 1246, 1189, 1145, 1132, 1094, 1062, 1035, 1023, 985, 953, 932, 908, 861, 772 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 191 (100), 159 (90), 187 (20), 190 (18), 160 (14), 192 (13), 161 (13), 219 (11), 189 (8); HRMS (EI) *m/e* calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1241. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.14; H, 7.98.

4-(3,5-Dimethoxy-4-hydroxyphenyl)-1-butene. The alkylation was accomplished in the same way as the synthesis of **2**. In this example, 7.2 g (39.1 mmol) of the 3,5-dimethoxy-4-hydroxybenzyl alcohol, 5.3 g (19.6 mmol) of phosphorus tribromide, and 100 mL of THF were used. Upon completion of the bromination, 156 mL (156 mmol) of a 1.0 M solution of allylmagnesium bromide in ether was added. Workup and chromatography afforded 4.68 g (58%) of a slightly impure (5% impurity by NMR) product that was carried on without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 2 H), 5.85 (ddt, J = 17.0 Hz, J = 10.3 Hz, J = 6.6 Hz, 1 H), 5.05 (d of d, J = 17.9 Hz, J = 1.8 Hz, 1 H), 4.98 (d of multiplets, J = 10.3 Hz, 1 H), 4.55 (br peak, 1 H), 3.85 (s, 6 H), 2.63 (t, J = 7.8 Hz, 2 H), 2.34 (dt, J = 8.2 Hz, J = 6.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 138.1, 133.0, 132.8, 115.0, 105.0, 56.2, 35.9, 35.6; IR (neat, NaCl) 3463 br, 3074, 2999, 2975, 2937, 2840, 1459, 1455, 1428, 1364, 1342, 1320, 1289, 1269, 1239, 1214, 1207, 1151, 1123, 1118, 1110, 1106, 1042, 1017, 998, 911, 824, 803, 793 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 209 (100), 210 (45), 237 (32), 207 (26), 205 (18), 195 (12), 249 (11), 208 (6); HRMS (EI) *m/e* calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1099.

4-(3,5-Dimethoxy-4-(pivaloyloxy)phenyl)-1-butanol. Protection of the phenol derivative synthesized above was accomplished at 0 °C using 3.705 g (17.8 mmol) of the phenol, 9.660 g (80.1 mmol) of trimethylacetyl chloride, 8.106 g (80.1 mmol) of triethylamine, and 75 mL of dichloromethane. The reaction mixture was stirred for 1 h, then the reaction was quenched with water, and the mixture was diluted with ether, extracted once with 3 N NaOH, and then washed three times with H_2O. The ether layers were washed once with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*, and then the resulting oil was filtered through 150 mL of silica gel. This material was then used directly in a hydroboration reaction that was done in a fashion directly analogous to the procedure described for the synthesis of **3**. In this example, the 4-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)-1-butene synthesized in the first step, 7.362 g (105.2 mmol) of 2-methyl-2-butene, 5.34 mL (53.4 mmol) of the borane−dimethyl sulfide complex, and 150 mL of THF were used. The reaction was quenched with 25 mL of 3 N NaOH and 12.5 mL of H_2O_2. Workup and chromatography afforded 4.212 g (76%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 2 H), 3.77 (s, 6 H), 3.62 (t, J = 6.3 Hz, 2 H), 2.59 (t, J = 7.4 Hz, 2 H), 1.86 (s, 1 H), 1.53−1.73 (m, 4 H), 1.37 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 151.9, 140.5, 127.0, 105.0, 62.6, 56.1, 39.1, 32.3, 27.6, 27.2; IR (neat, NaCl) 3316 br, 2971, 2939, 2870, 2842, 1753, 1603, 1510, 1479, 1463, 1423, 1397, 1368, 1345, 1325, 1281, 1242, 1204, 1190, 1130, 1050, 1029 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 227 (100), 209 (98), 85 (94), 207 (65), 210 (54), 103 (50), 177 (38), 226 (32), 167 (31), 208 (28), 293 (24), 87 (23), 311 (22), 79 (21), 310 (10); HRMS (EI) *m/e* calcd for $C_{17}H_{26}O_5$ 310.1780, found 310.1792.

(*E,Z*)-5-(3,5-Dimethoxy-4-(pivaloyloxy)phenyl)-1-methoxy-1-pentene (22a). The reaction sequence was carried out in a similar fashion to the procedure described above for the synthesis of **4**. In this example, 1.640 g (5.3 mmol) of the alcohol synthesized in the previous experiment, 0.804 g (6.3 mmol) of oxalyl chloride, 0.536 g (6.9 mmol) of dimethyl sulfoxide, 2.672 g (26.4 mmol) of triethylamine, and 11 mL of dichloromethane were used. After workup, the aldehyde was diluted with 75 mL of THF and added to the ylide. The ylide was formed from 5.430 g (15.8 mmol) of (methoxymethyl)-triphenylphosphonium chloride, 9.3 mL (15.8 mmol) of *tert*-butyllithium, and 75 mL of THF. Workup and chromatography afforded 1.360 g (76%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (s, 0.42 H), 6.40 (s, 0.58 H), 6.29 (d, J = 12.6 Hz, 0.58 H), 5.90 (d, J = 6.3 Hz, 0.42 H), 4.74 (dt J = 12.6 Hz, J = 7.3 Hz, 0.58 H), 4.36 (dt, J = 6.3 Hz, J = 7.5 Hz, 0.42 H), 3.77 (s, 6 H), 3.58 (s, 1.26 H), 3.51 (s, 1.76 H), 2.57 (t, J = 7.7 Hz, 2H), 2.12 (dt, J = 6.7 Hz, J = 7.8 Hz, 0.84 H), 1.97 (dt, J = 7.2 Hz, J = 7.2 Hz, 1.16 H), 1.58−1.71 (m, 2 H), 1.37 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 152.05, 152.00, 147.4, 146.5, 141.0, 140.7, 106.4, 105.2, 102.6, 59.6, 56.2, 56.1, 39.1, 36.1, 35.9, 32.5, 31.7, 27.3, 23.6; IR (neat, NaCl) 2962, 2936, 2870, 2857, 2841, 1754, 1654, 1602, 1510, 1479, 1462, 1422, 1338, 1279, 1242, 1207, 1125, 1029, 936, 822, 757, 737 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 221 (100), 253 (80), 71 (70), 85 (62), 337 (62), 239 (49), 103 (40), 222 (24), 87 (23), 167 (22), 252 (21), 305 (19), 365 (16), 86 (16); HRMS (EI) *m/e* calcd for $C_{19}H_{28}O_5$ 336.1937, found 336.1917.

Anodic Oxidation of 22a: 6,8-Dimethoxy-7-(pivaloyloxy)-1,2,3,4-tetrahydronaphthalenecarboxaldehyde Dimethyl Acetal (23a) and 1,6,8-Trimethoxy-7-(pivaloyloxy)-1,2,3,4-tetrahydronaphthalene (24). Compound **22a** was oxidized in a manner similar to the constant current oxidation of compound **4**. In this experiment, 0.155 g (0.5 mmol) of **22a**, 0.246 g (2.3 mmol) of 2,6-lutidine, 0.781 g (7.3 mmol) of lithium perchlorate, 3.6 mL of methanol, and 14.7 mL of dichloromethane were used. The reaction was oxidized with a constant current of 12.1 mA until 90.3 C (2.04 faradays/

mol) of charge had been passed. Workup and chromatography afforded an inseparable mixture of 71.0 mg (42%) of product **23a** and the overoxidized material **24**. The ratio of product to overoxidized material was determined to be approximately 1.3:1 by integration of the acetal proton in **23a** and the benzylic methine proton of **24** in the ^{1}H NMR of the crude product. The products were identified by ^{1}H NMR in direct analogy to products **5** and **7**. In addition to the oxidation products, 17.5 mg (11%) of the starting material was recovered. The following spectral data are for a 60:40 mixture of the two products. Integrals are reported as 0.6 H for one proton in the major product and 0.4 H for one proton in the minor product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (s, 0.6 H), 6.44 (s, 0.4 H), 4.58 (d, J = 3.8 Hz, 0.6 H), 4.48 (t, J = 2.7 Hz, 0.4 H), 3.85 (s, 1.2 H), 3.78 (s, 1.8 H), 3.75 (s, 3 H), 3.43 (s, 1 H) 3.40 (s, 1.5 H), 3.23−3.27 (m, 0.6 H), 3.17 (s, 1.5 H), 2.58−2.82 (m, 2 H), 1.56−2.27 (m, 4 H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 151.9, 151.7, 151.1, 150.2, 137.3, 136.0, 131.1, 123.2, 121.9, 108.6, 107.7, 107.6, 107.5, 70.6, 69.0, 63.8, 61.8, 61.0, 56.75, 56.70, 56.65, 56.60, 56.1, 56.0, 55.95, 55.90, 53.4, 39.1, 39.0, 35.7, 29.7, 29.4, 27.3, 27.2, 26.2, 25.7, 21.7, 20.3, 17.2, 15.8; IR (neat, NaCl) 2973, 2966, 2957, 2938, 2875, 2838, 1747, 1609, 1396, 1362, 1349, 1329, 1303, 1282, 1222, 1210, 1190, 1152, 1115, 1081, 973, 736 cm^{-1}; GCMS for the desired prodcut (PCI) *m*/*e* (rel intensity) 75 (100), 57(82), 335 (36), 251 (14), 303 (13), 334 (10), 85 (9), 336 (7), 219 (7), 333 (5); HRMS for the desired product (EI) *m*/*e* calcd for $C_{20}H_{30}O_6$ 366.2043, found 366.2025.

(*E*,*Z*)-5-(3,5-Dimethoxy-4-(pivaloyloxy)phenyl)-1-methoxy-1-pentene (22b). The reaction sequence was carried out in a similar fashion to the procedure described above for the synthesis of **4b**. In this example, 1.640 g (5.3 mmol) of 4-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)-1-butanol, 0.804 g (6.3 mmol) of oxalyl chloride, 0.536 g (6.9 mmol) of dimethyl sulfoxide, 2.672 g (26.4 mmol) of triethylamine, and 11 mL of dichloromethane were used. After workup, the aldehyde was diluted with 75 mL of THF and added to the ylide. The ylide was formed from 5.430 g (15.8 mmol) of (methoxymethyl)triphenylphosphonium chloride, 9.3 mL (15.8 mmol) of *tert*-butyllithium, and 75 mL of THF. Workup and chromatography afforded 1.360 g (76%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (s, 0.42 H), 6.40 (s, 0.58 H), 6.29 (d, J = 12.6 Hz, 0.58 H), 5.90 (d, J = 6.3 Hz, 0.42 H), 4.74 (dt J = 12.6 Hz, J = 7.3 Hz, 0.58 H), 4.36 (dt, J = 6.3 Hz, J = 7.5 Hz, 0.42 H), 3.77 (s, 6 H), 3.58 (s, 1.26 H), 3.51 (s, 1.76 H), 2.57 (t, J = 7.7 Hz, 2H), 2.12 (dt, J = 6.7 Hz, J = 7.8 Hz, 0.84 H), 1.97 (dt, J = 7.2 Hz, J = 7.2 Hz, 1.16 H), 1.58−1.71 (m, 2 H), 1.37 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 152.05, 152.00, 147.4, 146.5, 141.0, 140.7, 106.4, 105.2, 102.6, 59.6, 56.2, 56.1, 39.1, 36.1, 35.9, 32.5, 31.7, 27.3, 23.6; IR (neat, NaCl) 2962, 2936, 2870, 2857, 2841, 1754, 1654, 1602, 1510, 1479, 1462, 1422, 1338, 1279, 1242, 1207, 1125, 1029, 936, 822, 757, 737 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 221 (100), 253 (80), 71 (70), 85 (62), 337 (62), 239 (49), 103 (40), 222 (24), 87 (23), 167 (22), 252 (21), 305 (19), 365 (16), 86 (16); HRMS (EI) *m*/*e* calcd for $C_{19}H_{28}O_5$ 336.19366, found 336.19171.

Anodic Oxidation of 22b: 6,8-Dimethoxy-7-(pivaloyloxy)-1,2,3,4-tetrahydronaphthalenecarboxaldehyde Dimethyl Thioacetal (23b). Compound **22b** was oxidized in a manner similar to the constant current oxidation of compound **4b** and under a variety of conditions. In the experiment that led to cyclization, 0.351 g (1.0 mmol) of **22b**, 0.533 g (5.0 mmol) of 2,6-lutidine, 1.685 g (15.8 mmol) of lithium perchlorate, 7.9 mL of methanol, and 31.7 mL of dichloromethane were used. The oxidation was conducted with a constant current of 10.9 mA until 191.5 C (2.0 faradays/mol) of charge had been passed. Workup and chromatography afforded 76.4 mg (20%) of the desired product as a mixture of diastereomers. As mentioned in the text, efforts to repeat this experiment have not been successful and for the most part the cyclizations led to methoxylation of the vinyl sulfide without cyclization in analogy to the formation of product **19**. **23b:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45, (s, 1 H), 4.88 (d, J = 3.0 Hz, 0.5 H), 4.72 (d, J = 5.6 Hz, 0.5 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.55−3.61 (m, 0.5 H), 3.41 (s, 1.5 H), 3.30−3.35 (m, 0.5 H), 3.19 (s, 1.5 H), 2.59−2.79 (m, 3 H), 1.37−2.09 (m, 15 H); IR (neat, NaCl) 2957, 2933, 2871, 1756, 1734, 1604, 1506, 1491, 1480, 1458, 1415, 1395, 1352, 1304, 1280, 1243, 1231, 1215, 1191, 1116, 1083, 1029, 952, 736 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 57 (100), 63 (35), 95 (22), 335 (21), 97 (20), 303 (19), 334 (17), 251 (12), 85 (11), 219 (10), 91 (9), 51 (7); HRMS (EI) *m*/*e* calcd for $C_{20}H_{30}O_5S$ 382.18138, found 382.18037.

4-(3′-Furyl)-1-butanol (26). To a solution of 5.001 g (51.0 mmol) of 3-furanmethanol in 49.0 mL of THF at 0 °C was added 4.832 g (17.8 mmol) of phosphorus tribromide. The reaction was stirred until the starting alcohol disappeared as monitored by thin layer chromatography. The reaction was quenched with water, and the mixture was extracted with ether. The ether layers were washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was then taken up in 150 mL of THF and cooled to 0 °C. To this solution was added 102 mL (102 mmol) of a 1.0 M allylmagnesium bromide in ether solution. The reaction mixture was allowed to warm to room temperature and was stirred for 18 h. The reaction was then quenched with 50 mL of 10.0 M sulfuric acid at 0 °C. The crude reaction mixture was diluted with water and extracted with ether. The combined organic extracts were washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, and filtered, and the solvent was removed at atmospheric pressure. The crude olefin obtained in this fashion was added to a solution of disiamylborane prepared as follows: To a stirred solution of 10.2 mL (102 mmol) of borane−dimethyl sulfide complex in 60 mL of THF at 0 °C was added 14.300 g (204 mmol) of 2-methyl-2-butene. The reaction mixture was stirred for 1 h and then the crude product from above added. The resulting mixture was allowed to stir for an additional 1 h, and then the reaction was quenched carefully and slowly with 73 mL of 3 N sodium hydroxide followed by 27 mL of 30% hydrogen peroxide that had been cooled in an ice bath. The reaction was stirred for an additional 1 h, diluted with water, and extracted with ether. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was loaded on a silica gel column that was slurry-packed using a 20% ethyl acetate in hexane solution that contained 1% triethylamine. Elution with 35% ethyl acetate in hexane afforded 3.499 g (49%) of the desired alcohol **26** over three steps starting from 3-furanmethanol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 1H), 7.21 (s, 1H), 6.26 (s, 1H), 3.63 (t, J = 6.2 Hz, 2H), 2.44 (t, J = 6.8 Hz, 2H), 2.38 (s, 1H), 1.57−1.65 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 142.7, 138.8, 125.0, 110.0, 62.5, 32.3, 26.2, 24.6; IR (neat, NaCl) 3346 br, 3084, 2936, 2863, 1501, 1472, 1458, 1446, 1419, 1382, 1344, 1163, 1105, 1063, 992, 873, 779, 730 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 13 (100), 81 (49), 124 (27), 141 (19), 95 (14), 109 (13), 151 (10), 82 (9), 122 (9), 121 (8), 121 (6), 125 (6), 163 (3); HRMS (EI) *m*/*e* calcd for $C_8H_{12}O_2$ 140.0837, found 140.0838.

(*E*,*Z*)-5-(3-Furyl)-1-(methylthio)-1-pentene (27a). The reaction sequence was carried out in a similar fashion to that described above for the synthesis of **11b**. In this example, 1.106 g (7.3 mmol) of **26**, 1.104 (8.2 mmol) of oxalyl chloride, 0.736 g (9.4 mmol) of dimethyl sulfoxide, 3.669 g (36.3 mmol) of triethylamine, and 21 mL of dichloromethane was used. After workup the aldehyde was diluted with 100 mL of THF and added to the ylide. The ylide was formed from 7.806 g (21.8 mmol) of [(methylthio)methyl]triphenylphosphine chloride, 12.1 mL (21.8 mmol) of phenyllithium, and 20 mL of THF. Workup and chromatography afforded 0.931 g (70%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34, 7.33 (2 s, 1 H), 7.22 (s, 0.45 H), 7.20 (s, 0.55 H), 6.27 (d, J = 1.1 Hz, 0.45 H), 6.25 (d, J = 1.1 Hz, 0.55 H), 5.98 (d of multiplets, J = 15.0, Hz, 0.55 H), 5.90 (dt, J = 9.4 Hz, J = 1.5 Hz, 0.45 H), 5.53 (dt, J = 9.4 Hz, J = 7.2 Hz, 0.45 H), 5.43 (dt, J = 14.9 Hz, J = 7.0 Hz, 0.55 H), 2.39−2.46 (m, 2 H), 2.26 (s, 1.35 H), 2.22 (s, 1.65 H), 2.09−2.19 (m, 2 H), 1.59−1.70 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 142.6, 138.8, 128.2, 127.2, 126.7, 124.8, 124.7, 124.1, 111.2, 110.9, 32.6, 29.7, 29.3, 28.7, 24.3, 24.0, 17.0, 15.0; IR (neat, NaCl) 3132, 3005, 2986, 2980, 2921, 2857, 1609, 1560, 1501, 1455, 1437, 1382, 1351, 1310, 1244, 1163, 1065, 1027, 960, 938, 873, 779, 725, 703, 690 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 135 (100), 61 (58), 183 (54), 136 (51), 81 (48), 107 (39), 211 (20), 163 (18), 134 (18), 100

(16), 87 (15), 82 (12), 184 (11); HRMS (EI) *m/e* calcd for $C_{10}H_{14}OS$ 182.07653, found 182.07434. Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.89; H, 7.72.

Anodic Oxidation of (*E,Z*)-5-(3-Furyl)-1-(methylthio)-1-pentene (27a): Synthesis of 4,5,6,7-Tetrahydrobenzo[*b*]furan-7-carboxaldehyde Dimethyl Thioacetal (28a) and 4,5,6,7-Tetrahydrobenzo[*b*]furan-7-carboxaldehyde Dimethyl Acetal (28b). Solvent System A: 20% Methanol: 80% Dichloromethane. Compound **27a** was oxidized in a manner similar to the constant current electrolysis of compound **4**. In this experiment, 0.212 g (1.2 mmol) of **27a**, 0.623 g (5.82 mmol) of 2,6-lutidine, 1.975 g (18.6 mmol) of lithium perchlorate, 9.3 mL of methanol, and 37.1 mL of dichloromethane were used. The oxidation was conducted with a constant current of 11.3 mA until 224.0 C (2.0 faradays/mol) of charge had been passed. For the optimal set of conditions, 1.107 g (5.8 mmol) of TsOH was added to the solution after completion of the electrolysis. The mixture was stirred overnight. Workup and chromatography as described above afforded 0.132 g (54%) of the mixed acetal product **28a** as a 1.2:1 mixture of diastereomers and 0.0391 g (17%) of the dimethoxy acetal product **28b**.

Solvent System B: 100% Methanol. In a similar fashion, compound **27a** was oxidized in methanol solvent. In this experiment, 0.203 g (1.1 mmol) of **27a**, 0.597 g (5.57 mmol) of 2,6-lutidine, 1.890 g (17.8 mmol) of lithium perchlorate, and 44.4 mL of methanol were used. The oxidation was conducted with a constant current of 11.3 mA until 220.7 C (2.06 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.059 g (5.6 mmol) of TsOH was added and the mixture stirred overnight. Workup and chromatography afforded 0.159 g (67%) of the mixed acetal product **28a** as an approximately 1:1 mixture of diastereomers and 0.022 g (10%) of the dimethoxy acetal product **28b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 2.1 Hz, 1 H), 6.19−6.21 (m, 1 H), 4.61 (d, J = 4.7 Hz, 0.37 H), 4.55 (d, J = 6.7 Hz, 0.63 H), 3.46 (s, 1.89 H), 3.40 (s, 1.11 H), 3.15−3.25 (m, 1 H), 2.36−2.48 (m, 2 H), 1.60−2.20 (m, 7 H, includes 2.13 (s) and 2.07 (s)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 149.7, 141.0, 140.8, 119.0, 118.7, 110.4, 110.3, 91.5, 90.4, 56.8, 56.3, 40.3, 39.1, 25.9, 25.0, 22.25, 22.20, 21.5, 13.0, 12.2; IR (neat, NaCl) 2984, 2925, 2855, 2822, 1684, 1575, 1569, 1559, 1503, 1444, 1304, 1288, 1237, 1217, 1191, 1182, 1152, 1136, 1099, 1074, 1037, 1028, 961, 938, 730 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 165 (100), 164 (94), 91 (62), 133 (45), 163 (31), 150 (28), 166 (27), 181 (24), 105 (12), 193 (11), 161 (8), 149 (8); HRMS (EI) *m/e* calcd for $C_{11}H_{16}O_2S$ 212.08709, found 212.08757. Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.24; H, 7.60. Found: C, 62.13; H, 7.59.

(*E,Z*)-5-(3-Furyl)-1-methoxy-1-pentene (27b). The reaction sequence was carried out in a similar fashion to that described above for the synthesis of **4**. In this example, 1.010 g (7.2 mmol) of **26**, 1.098 g (8.7 mmol) of oxalyl chloride, 0.732 g (9.4 mmol) of dimethyl sulfoxide, 3.198 g (31.6 mmol) of triethylamine, and 21 mL of dichloromethane were used. After workup the aldehyde was diluted with 75 mL of THF and added to the ylide. The ylide used was generated from 7.415 g (21.6 mmol) of (methoxymethyl)triphenylphosphonium chloride, 12.7 mL (21.6 mmol) of a 1.7 M solution of *tert*-butyllithium in pentane, and 20 mL of THF. Workup and chromatography afforded 0.618 g (52%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 1 H), 7.20 (s, 1 H), 6.26−6.31 (m, 1.78 H), 5.89 (d, J = 6.2 Hz, 0.22 H), 4.72 (dt, J = 12.6 Hz, J = 7.4 Hz, 0.78 H), 4.34 (dt, J = 6.3 Hz, J = 7.4 Hz, 0.22 H), 3.57 (s, 0.66 H), 3.50 (s, 2.34 H), 2.41 (t, J = 7.6 Hz, 2 H), 2.11 (dt, J = 7.3 H, J = 7.5 Hz, 0.44 H), 1.96 (dt, J = 7.6 Hz, 7.2 Hz, 1.56 H), 1.54−1.64 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 146.4, 142.7, 142.6, 138.8, 125.2, 125.0, 111.4, 111.15, 111.10, 106.3, 102.55, 102.50, 59.5, 55.9, 31.0, 30.2, 27.3, 24.3, 24.0, 23.6; IR (neat, NaCl) 3056, 3033, 3001, 2931, 2926, 2857, 2832, 1733, 1725, 1717, 1700, 1696, 1684, 1675, 1671, 1652, 1636, 1628, 1575, 1569, 1559, 1540, 1521, 1516, 1501, 1457, 1443, 1390, 1382, 1265, 1239, 1209, 1182, 1161, 1131, 1109, 1065, 1024, 934, 873, 782, 725 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 135 (100), 107 (76), 81 (45), 167 (26), 163 (24), 136 (20), 71 (19), 79 (13), 84 (13), 117 (12), 82 12), 83 (12); HRMS (EI) *m/e* calcd for $C_{10}H_{14}O_2$ 166.09937, found 166.09949. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.95; H, 8.37.

Anodic Oxidation of Substrate 27b: 4,5,6,7-Tetrahydrobenzo[*b*]furan-7-carboxaldehyde Dimethyl Acetal (28b). Compound **27b** was oxidized in a manner similar to the constant current electrolysis of compound **4** described above. In this experiment, 0.203 g (1.2 mmol) of **27b**, 0.655 g (6.1 mmol) of 2,6-lutidine, 2.077 g (19.5 mmol) of lithium perchlorate, 9.8 mL of methanol, and 39.0 mL of dichloromethane were used. The oxidation was conducted with a constant current of 11.3 mA until 235.4 C (2.0 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.160 g (6.1 mmol) of TsOH was added and the resulting mixture stirred overnight. Workup and chromatography afforded 0.179 g (75%) of the desired product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 1.9 Hz, 1 H), 6.19 (d, J = 1.8 Hz, 1 H), 4.46 (d, J = 6.2 Hz, 1 H), 3.43 (s, 3 H), 3.36 (s, 3 H), 3.01−3.07 (m, 1 H), 2.35−2.48 (m, 2 H), 1.77−1.92 (m, 3 H), 1.60−1.72 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 141.1, 118.9, 110.3, 106.0, 54.6, 54.3, 37.3, 24.2, 22.2, 21.2; IR (neat, NaCl) 2933, 2854, 2832, 1505, 1457, 1447, 1374, 1303, 1236, 1217, 1189, 1159, 1122, 1106, 1077, 1059, 991, 976, 966, 954, 892, 730, 691 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 75 (100), 165 (95), 166 (12), 164 (11), 74 (9), 133 (7), 135 (6), 76 (5), 61 (5) 163 (5), 195 (4); HRMS (EI) *m/e* calcd for $C_{11}H_{16}O_3$ 196.10994, found 196.10805. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.31; H, 8.22. Found: C, 67.14; H, 8.20.

(*E,Z*)-5-(3′-Furyl)-1-phenyl-1-pentene (27c). This styrene-based substrate was prepared in a fashion directly analogous to the synthesis of substrate **4a**. In this experiment, a solution of 1.982 g (14.2 mmol) of the alcohol (**26**), 1.220 g (15.6 mmol) of dimethyl sulfoxide, 35.0 mL of dichloromethane, 2.163 g (17.0 mmol) of oxalyl chloride, and 4.311 g (42.6 mmol) of triethylamine were used in the Swern oxidation. The resulting aldehyde was added to an ylide derived from 18.445 g (42.6 mmol) of benzyltriphenylphosphonium bromide in 84.0 mL of THF and 32.8 mL (42.6 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. After workup and chromatography, the reaction mixture afforded 1.600 g (53%) of the desired product (**27c**) as a mixture of cis and trans olefins. The spectral data for this mixture were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16−7.35 (m, 7H), 6.17−6.46 (m, 2.6 H), 5.64−5.69 (dt, J = 7.3 Hz, J = 11.7 Hz, 0.4 H), 2.33−2.49 (m, 3 H), 2.21−2.28 (m, 1 H), 1.6−1.78 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 142.6, 138.8, 132.4, 130.4, 130.2, 129.2, 128.7, 128.5, 128.1, 126.8, 126.5, 125.9, 110.9, 32.5, 30.2, 29.5, 28.0, 24.3, 24.2; IR (neat, NaCl) 3059, 3027, 2925, 2859, 1621, 1500, 1446, 1168, 1070, 1030, 974, 890, 780, 760, cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 131 (100), 213 (50), 132 (21), 121 (17), 82 (16), 214 (14), 159 (14), 169 (14), 107 (12), 83 (7); HRMS (EI) *m/e* calcd for $C_{15}H_{16}O$ 212.1201, found 212.1206.

Electrolysis of Compound 27c: Synthesis of 7-(1′-Methoxy-1′-phenylmethyl)-4,5,6,7-tetrahydrobenzo[*b*]furan (28c). A 100 mL round bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.181 g (0.85 mmol) of **27c**, 0.455 g (4.2 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. The mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 164.4 C (2.0 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.522 g (8.0 mmol) of *p*-toluenesulfonic acid was added, and the solution was stirred for 30 min. The reaction was diluted with ether and washed with water, saturated sodium bicarbonate, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was chromatographed through a silica gel column that was slurry-packed using a 1% triethylamine/hexane solution. The column was eluted with hexane to afford 0.146 g (71%) of the desired product (**28c**) as a 1:1 mixture of diastereomers. The spectral data for the mixture of diastereomers are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18−7.34 (m, 6 H), 6.17 (d, J = 1.8 Hz, 1 H), 4.64 (d, J = 4.5 Hz, 0.5 H), 4.43 (d, J = 6.8 Hz, 0.5 H), 3.27 (s, 1.5 H), 3.18−3.22 (m, 2 H), 3.05 (m, 0.5 H), 2.36−2.46 (m, 1 H), 2.24−2.34 (m, 1 H), 1.67−1.87 (m, 1 H), 1.38−1.64 (m, 3 H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 140.8, 140.4, 128.0, 127.4, 127.2, 127.0, 110.3, 110.2, 85.5, 83.6, 57.3, 57.0, 41.6, 40.4, 24.9, 23.5, 22.2, 22.1, 21.8, 21.1; IR (neat, NaCl) 2920, 3051, 3020, 2925, 2857, 1496, 1443, 1165, 1153, 1104, 1064, 1024, 874, 780, 750 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 121 (100), 122 (32), 211 (26), 165 (10), 212 (7), 107 (5), 91 (5), 123 (4), 149 (2), 75 (2); HRMS (EI) *m/e* calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1355.

(*E,Z*)-6-(3′-Furyl)-1-(trimethylsilyl)-2-hexene (27d). A stirred solution of 1.254 g (8.9 mmol) of the alcohol (**26**), 0.765 g (9.8 mmol) of dimethyl sulfoxide, and 23.0 mL of dichloromethane was treated with 1.356 g (10.7 mmol) of oxalyl chloride at −78 °C. The reaction mixture was stirred for 15 min and the temperature then raised to between −50 and −60 °C. After an additional 15 min, 2.702 g (26.7 mmol) of triethylamine was added and the reaction mixture was allowed to warm to room temperature. The reaction was diluted with ether and washed with water, saturated sodium bicarbonate, and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting aldehyde was added to the following silyl-containing ylide without further purification. To a suspension of 9.538 g (26.7 mmol) of methyltriphenylphosphonium bromide in 54 mL of terahydrofuran at 0 °C was added 10.7 mL (26.7 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The mixture was allowed to warm to room temperature, allowed to stir for 1 h, and then cooled to 0 °C. To this mixture was added dropwise 5.717 g (26.7 mmol) of (iodomethyl)trimethylsilane. The mixture was again allowed to warm to room temperature. After 1 h, the reaction mixture was cooled to −78 °C and treated with an additional 10.7 mL (26.7 mmol) of the 2.5 M solution of *n*-butyllithium in hexane. The dark red solution was allowed to warm to room temperature and stirred for 1.5 h. The reaction was recooled to −78 °C, and then a solution of the crude aldehyde prepared above in 25 mL of THF added with the use of a cannula. The reaction mixture was allowed to slowly warm to room temperature and then stirred for 17 h. The reaction was quenched with saturated aqueous ammonium chloride and the aqueous layer extracted with ether. The combined organic layers were washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude reaction product was taken up in 50 mL of hexane to precipitate most of the triphenylphosphine oxide. The hexane was removed *in vacuo*. The crude product was eluted with hexane through a silica gel column that was slurry-packed using a 1% triethylamine in hexane solution to afford 0.790 g (40%) of the desired product **27d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 1 H), 7.20 (s, 1 H), 6.26 (s, 1 H), 5.38−5.44 (m, 1 H), 5.27−5.32 (m, 1 H), 2.43 (t, J = 7.6 Hz, 2 H), 2.02−2.06 (m, 2 H), 1.58−1.66 (m, 2 H), 1.44−1.57 (m, 2 H), 0.00−0.04 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.8, 128.3, 126.9, 126.6, 125.9, 125.1, 110.9, 32.3, 30.3, 30.1, 26.6, 24.4, 24.1, 22.6, 18.5, −1.8, −1.9; IR (neat, NaCl) 3008, 2954, 2873, 2858, 1642, 1503, 1457, 1247, 1152, 1027, 852, 841, 773 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 73 (100), 207 (28), 133 (20), 74 (9), 208 (5), 223 (4), 131 (4), 134 (2), 91 (2); HRMS (EI) *m/e* calcd for $C_{13}H_{22}OSi$ 222.1440, found 222.1441.

Electrolysis of Compound 27d. Synthesis of 7-Ethylidene-4,5,6,7-tetrahydrobenzo[*b*]furan (28d). The constant current electrolysis of **27d** was performed in a similar manner to that described above for the oxidation of **27c.** In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.242 g (1.1 mmol) of **27d**, 0.589 g (5.5 mmol) of 2,6-lutidine, 1.491 g (14.0 mmol) of lithium perchlorate, 7.0 mL of methanol, and 28.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 477.7 C (4.5 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.674 g (8.8 mmol) of *p*-toluenesulfonic acid was added and the mixture stirred for 30 min. The reaction was diluted with ether and washed with water, saturated sodium bicarbonate, and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was chromatographed through a silica gel column that was slurry-packed using a 1% triethylamine in hexane solution. Elution of the column with hexane afforded 0.079 g (49%) of the desired product **28d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (bs, 1 H), 6.19 (bs, 1 H), 5.79−5.91 (m, 1 H), 5.06−5.11 (m, 2 H), 3.34−3.43 (m, 1 H), 2.38−2.43 (m, 2 H), 1.64−1.98 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 140.8, 139.5, 117.4, 115.4, 110.3, 38.9, 30.1, 22.2, 21.1; IR (neat, NaCl) 2927, 2922, 2852, 1646, 1503, 1465, 1446, 1437, 1150, 1105, 890, 726 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 149 (100), 121 (19), 147 (15), 148 (14), 81 (4), 119 (4), 131 (3), 107 (3); HRMS (EI) *m/e* calcd for $C_{10}H_{12}O$ 148.0888, found 148.0876.

(*E,Z*)-6-(3′-Furyl)-2-methyl-1-(trimethylsilyl)-2-hexene (27e). This allylsilane was prepared in a fashion directly analogous to the synthesis described above for **27d**. In this experiment, the desired aldehyde was made using 2.623 g (18.7 mmol) of the alcohol **26**, 1.611 g (20.6 mmol) of dimethyl sulfoxide, 47.0 mL of dichloromethane, 2.855 g (22.5 mmol) of oxalyl chloride, and 5.689 g (56.2 mmol) of triethylamine. The resulting aldehyde was added to the following silyl-containing ylide without further purification. To a 0 °C suspension of 20.872 g (56.2 mmol) of ethyltriphenylphosphonium bromide in 112 mL of terahydrofuran was added 22.5 mL (56.2 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The mixture was raised to room temperature, allowed to stir for 1 h, and then cooled to 0 °C. To this mixture was added dropwise 12.033 g (56.2 mmol) of (iodomethyl)trimethylsilane. The mixture was again allowed to warm to room temperature. After 1 h, the reaction mixture was cooled to −78 °C and treated with additional 10.7 mL (26.7 mmol) of a 2.5 M *n*-butyllithium in hexane solution. The dark red solution was allowed to warm to room temperature and stirred for 1.5 h. The solution was then recooled to −78 °C and a solution of the crude aldehyde prepared above in 50 mL of THF added by cannulation. The resulting mixture was allowed to slowly warm to room temperature and stirred for 17 h. Workup and chromatography as described above for previous Wittig reactions afforded 2.255 g (51%) of the desired product **27e** which showed a small amount (5% by NMR) of an unidentified impurity: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (s, 1 H), 7.18 (s, 1 H), 6.25 (s, 1 H), 4.93−5.01 (m, 1 H), 2.40 (t, J = 7.6 Hz, 2 H), 1.98−2.05 (m, 2.5 H), 1.48−1.67 (m, 6.5 H), 0.02−0.09 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 138.8, 138.7 133.3, 133.0, 125.2, 122.1, 121.7, 110.9, 30.5, 30.3, 29.8, 29.7, 28.1, 27.7, 26.2, 24.5, 24.3, 23.2, 18.6, −0.73, −1.25; IR (neat, NaCl) 3008, 2954, 2873, 2858, 1642, 1503, 1457, 1247, 1152, 1027, 852, 841, 773 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 73 (100) 74 (18), 161 (9), 75 (8), 235 (7), 236 (2), 251 (2); HRMS (EI) *m/e* calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1596.

Electrolysis of Compound 27e. Synthesis of 7-(1′-Methylethylidene)-4,5,6,7-tetrahydrobenzo[*b*]furan (28e). The anodic oxidation of **27e** was performed in a similar fashion to that described for the oxidation of **27c**. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.234 g (1.0 mmol) of **27e**, 0.536 g (5.0 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 429.9 C (4.5 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.536 g (8.0 mmol) of *p*-toluenesulfonic acid was added to the mixture and the reaction mixture stirred for 30 min. Workup and chromatography afforded 0.082 g (51%) of slightly impure (<5% impurity by NMR) **28e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 1 H), 6.18 (s, 1 H), 4.88 (s, 1 H), 4.65 (s, 1 H), 3.40−3.45 (m, 1 H), 2.43−2.46 (m, 2 H), 1.61−1.92 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 146.3, 140.7, 118.2, 112.4, 110.1, 42.3, 28.9, 22.2, 21.3, 20.0; IR (neat, NaCl) 2923, 2921, 2853, 1647, 1504, 1464, 1457, 1447, 1436, 1374, 1149, 1105, 892, 725 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 163 (100), 164 (26), 121 (25), 162 (21), 161 (20), 135 (9), 191 (7), 133 (7), 107 (6), 147 (5), 122 (5); HRMS (EI) *m/e* calcd for $C_{11}H_{14}O$, 162.1044, found 162.1048.

(*E,Z*)-6-(3′-Furyl)-2-methyl-2-hexene (27f). The trisubstituted olefin substrate was prepared in an analogous fashion to the synthesis of substate **4** described above. In this

experiment, 1.989 g (14.2 mmol) of the alcohol (**26**), 1.220 g (15.6 mmol) of dimethyl sulfoxide, 36 mL of dichloromethane, 2.163 g (20.0 mmol) of oxalyl chloride, and 4.311 g (42.6 mmol) of triethylamine were used in the Swern oxidation. The resulting aldehyde was added without further purification to the ylide generated from 18.416 g (42.6 mmol) of isopropyltriphenylphosphonium iodide in 84 mL of THF and 32.8 mL (42.6 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. Workup and purification (chromatography followed by Kugelrohr distillation) afforded 1.118 g (48%) of the desired product **27f** without any triphenylphosphine oxide: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 1 H), 7.19 (s, 1 H), 6.26 (s, 1 H), 5.14 (m, 1 H), 2.38−2.43 (t, J = 7.7 Hz, 2 H), 2.00−2.05 (m, 2 H), 1.98 (s, 3 H), 1.56−1.70 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.8, 131.6, 125.1, 124.2, 110.9, 30.1, 27.6, 25.7, 24.3, 17.7; IR (neat, NaCl) 2965, 2929, 2858, 1605, 1502, 1447, 1377, 1163, 1065, 1025, 873, 776 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 199 (100), 81 (100), 165 (55), 82 (45), 147 (35), 109 (33), 83 (27), 107 (23), 95 (23); HRMS (EI) *m/e* calcd for $C_{11}H_{16}O$ 164.11201, found 164.1210.

Electrolysis of Compound 27f. Synthesis of 7-(1′-Methylethylidene)-4,5,6,7-tetrahydrobenzo[*b*]furan (28e) and 7-(1′-Methoxy-1′-methylethyl)-4,5,6,7-tetrahydrobenzo[*b*]furan (28f). The anodic oxidation of **27f** was performed in a similar manner to that of described for the electrolysis of substrate **27c**. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.191 g (1.2 mmol) of **22**, 0.624 g (5.8 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 223.9 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.765 g (9.3 mmol) of *p*-toluenesulfonic acid was added and the mixture stirred for 30 min. Workup and chromatography then afforded 0.0961 g (51%) of **28e** and 0.0541 g (24%) of **28f**. The spectral data for compound **28e** were the same as those reported above. The spectral data for compound **28f** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 1.6 Hz, 1 H), 6.18 (d, J = 1.7 Hz, 1 H), 3.26 (s, 3 H), 2.98−3.00 (m, 1 H), 2.38−2.43 (m, 2 H), 1.91−1.94 (m, 2 H), 1.51−1.68 (m, 2 H), 1.34 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 140.4, 119.3, 110.2, 49.0, 42.3, 25.6, 24.3, 22.8, 22.6, 22.4; IR (neat, NaCl) 2973, 2942, 2937, 2933, 2928, 2853, 1506, 1457, 1380, 1366, 1216, 1140, 1131, 1104, 1080, 1068, 893, 720 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 73 (100), 163 (91), 164 (19), 74 (14), 161 (4), 179 (4), 121 (4), 193 (3), 122 (2), 165 (2), 123 (2); HRMS (EI) *m/e* calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1372.

5-(3′-Furyl)-1-pentanol. Into a flame-dried 500 mL three-necked flask equipped with a condenser, an addition funnel, and a nitrogen inlet was added 2.552 g (105.0 mmol) of magnesium powder, 100 mL of THF, and half of the total required amount of 13.501 g (100.0 mmol) of 4-bromo-1-butene. The reaction was stirred vigorously until the Grignard formation was initiated. The other half of the bromo compound was diluted with 150 mL of THF and added slowly to the reaction mixture over a period of 4 h. In a separate flask, 3-furylmethyl bromide was prepared by treating 4.905 g (50.0 mmol) of 3-furanmethanol with 4.737 g (17.5 mmol) of phosphorus tribromide in 50.0 mL of THF at 0 °C. The reaction was stopped when no more of the alcohol was present as evidenced by thin layer chromatography. The reaction was quenched with water and the mixture extracted with ether. The ether layer was washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was diluted with 100 mL of THF and was placed in the addition funnel used above during the generation of the Grignard reagent. The Grignard reagent solution prepared above was cooled to a range of −30 to −50 °C and then treated with 1.904 g (10.0 mmol) of anhydrous copper iodide. The cold temperature was maintained and the bromide added from the addition funnel over a 2 h period. The reaction was allowed to warm to room temperature and stirred for 18 h. The reaction was quenched with 10 M sulfuric acid at 0 °C, diluted with water, and extracted with ether. The combined organic extracts were washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, and filtered. The solvent was removed by distillation at atmospheric pressure. The crude olefin obtained was added to disiamylborane without further purification.

To a stirred solution of 10.0 mL (100 mmol) of borane−dimethyl sulfide complex in 50.0 mL of THF at 0 °C was added 14.028 g (200 mmol) of 2-methyl-2-butene. The reaction mixture was stirred for 1 h and then the olefin prepared above added. The reaction mixture was stirred for an additional 1 h and then the reaction quenched *carefully* with 71.4 mL of 3 N NaOH followed by 26.0 mL of 30% hydrogen peroxide. The mixture was stirred for an additional 1 h, diluted with water, and extracted with ether. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Chromatography through a silica gel column that was slurry-packed using a 20% ethyl acetate in hexane solution containing 1% triethylamine using 30% ethyl acetate in hexane as eluent afforded 4.850 g (63%) of the desired alcohol over the three steps from 3-furanmethanol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1 H), 7.19 (s, 1 H), 6.24 (s, 1 H), 3.57 (t, J = 6.7 Hz, 2 H), 3.12 (s, 1 H), 2.40 (t, J = 7.5 Hz, 2 H), 1.51−1.61 (m, 4 H), 1.34−1.42 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 138.5, 121.9, 110.8, 52.2, 32.2, 29.6, 25.2, 24.5; IR (neat, NaCl) 3352 br, 2932, 2858, 1501, 1464, 1350, 1323, 1160, 1060, 1027, 870, 777 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 81 (100), 137 (86), 155 (29), 109 (21), 82 (15), 119 (14), 95 (9), 138 (8), 93 (6), 71 (5), 55 (4); HRMS (EI) *m/e* calcd for $C_9H_{14}O_2$ 154.0994, found 154.0979.

(*E*,*Z*)-6-(3′-Furyl)-1-methoxy-1-hexene (27g). This enol ether was prepared in an analogous fashion to substrate **4a**. In this experiment, 3.251 g (21.1 mmol) of 5-(3′-furyl)-1-pentanol, 0.842 g (10.8 mmol) of dimethyl sulfoxide, 53.0 mL of dichloromethane, 1.492 g (11.8 mmol) of oxalyl chloride, and 6.405 g (63.3 mmol) of triethylamine were used in the Swern oxidation. The resulting aldehyde was added to the ylide generated from 21.699 g (63.3 mmol) of (methoxymethyl)-triphenylphosphonium chloride in 126 mL of THF and 48.7 mL (63.3 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. Workup and chromatography afforded 2.051 g (54%) of the desired product **27g** as a mixture of cis and trans olefin isomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 1 H), 7.19 (s, 1 H), 6.24−6.29 (m, 1.7 H), 5.84 (d, J = 4.4 Hz, 0.3 H), 4.69 (dt, J_d = 9.6 Hz, J_t = 12.3 Hz, 0.7 H), 4.31 (dt, J_t = 6.5 Hz, J_d = 7.3 Hz, 0.3 H), 3.53 (s, 0.8 H), 3.46 (s, 2.2 H), 2.39 (t, J = 7.5 Hz, 2 H), 2.07−2.09 (m, 0.5 H), 1.89−1.91 (m, 1.5 H), 1.53−1.58 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 146.1, 142.5, 138.6, 125.1, 125.0, 110.9, 106.5, 102.6, 59.2, 55.6, 30.3, 29.4, 29.3, 27.4, 24.5, 23.5; IR (neat, NaCl) 2929, 2856, 1655, 1501, 1462, 1209, 1162, 1130, 1109, 1025, 873, 778 cm^{-1}; GCMS (PCI) *m/e* (rel intensity) 149 (100), 81 (54), 121 (40), 150 (26), 181 (20), 109 (10), 82 (10), 107 (9), 148 (9), 147 (81), 122 (7); HRMS (EI) *m/e* calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1163.

Electrolysis of compound 27g. Synthesis of 8-(1′,1′-Dimethoxymethyl)cyclohepta[*b*]furan (28g). Solvent System A: 20% Methanol:80% Dichloromethane. The constant current electrolysis of **27g** was performed in a fashion that was directly analogous to the electrolysis of **27c** described above. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.110 g (0.61 mmol) of **27g**, 0.328 g (3.1 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 177.7 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 0.928 g (4.9 mmol) of *p*-toluenesulfonic acid was added to the mixture and the reaction mixture was stirred for 30 min. Following workup and chromatography, 0.0794 g (62%) of the desired product **28g** was obtained.

Solvent System B: 100% Methanol. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.110 g (0.61 mmol) of **27g**, 0.328 g (5

mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, and 25.0 mL of methanol. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 177.7 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 0.928 g (8 mmol) of *p*-toluenesulfonic acid was added to the mixture and the reaction mixture stirred for 30 min. Following workup and chromatography, the reaction mixture afforded 0.074 g (58%) of the desired product **28g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 1.8 Hz, 1 H), 6.11 (d, J = 1.8 Hz, 1 H), 4.56 (d, J = 7.6 Hz, 1 H), 3.35 (s, 3 H), 3.28 (s, 3 H), 3.25 (m, 1 H), 2.46−2.49 (m, 2 H), 1.41−2.1.82 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 139.2, 121.5, 113.0, 104.4, 54.3, 53.2, 41.3, 28.4, 26.8, 25.6; IR (neat, NaCl) 2933, 2854, 1505, 1457, 1447, 1374, 1303, 1233, 1218, 1156, 1108, 1068, 986, 953, 890, 730 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 179 (100), 75 (87), 147 (45), 180 (40), 76 (38), 177 (19), 74 (14), 121 (13), 209 (8), 178 (7), 77 (5); HRMS (EI) *m*/*e* calcd for $C_{11}H_{15}O_2$ ($M^+ - OCH_3$) 179.1072, found 179.1064.

(*E*,*Z*)-6-(3′-Furyl)-1-phenyl-1-hexene (27h). This styrene-based substrate was prepared in a fashion analogous to the synthesis of substrate **4a**. In this experiment, the Swern oxidation was performed with 1.234 g (8.0 mmol) of 5-(3′-furyl)-1-pentanol, 0.688 g (8.8 mmol) of dimethyl sulfoxide, 20.0 mL of dichloromethane, 1.218 g (9.6 mmol) of oxalyl chloride, and 2.429 g (24.0 mmol) of triethylamine. The resulting aldehyde was added to a ylide generated from 10.392 g (24.0 mmol) of benzyltriphenylphosphonium bromide in 48.0 mL of THF and 18.5 mL (24.0 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. After the reaction was complete, workup and chromatography as before afforded 1.010 g (56%) of the desired product **27h** as a mixture of cis and trans olefin isomers. The spectral data for the mixture of isomers are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10−7.49 (m, 7 H), 6.41 (d, J = 11.7 Hz, 1 H), 6.23 (s, 1 H), 5.64 (dt, J = 7.3 Hz, J = 11.7, 1 H), 2.30−2.41 (m, 4 H), 1.45−1.62 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.7, 132.8, 128.9, 128.7, 128.6, 128.4, 128.1, 127.6, 126.4, 124.9, 110.9, 29.5, 29.4, 28.3, 24.5; IR (neat, NaCl) 3092, 3015, 2940, 2856, 1615, 1503, 1491, 1443, 1162, 1062, 1025, 962, 872, 778, 745 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 91 (100), 227 (87); HRMS (EI) *m*/*e* calcd for $C_{16}H_{18}O$ 226.1358, found 226.1352.

Electrolysis of Compound 27h. Synthesis of 8-(1′-Methoxy-1′-phenylmethyl)cyclohepta[*b*]furan (28h). Solvent System A: 20% Methanol:80% Dichloromethane. The anodic oxidation of **27h** was performed in a manner that was directly analogous to the electrolysis of **27c** described above. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.217 g (0.96 mmol) of **27h**, 0.514 g (4.8 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 185.3 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.461 g (7.7 mmol) of *p*-toluenesulfonic acid was added to the reaction and the mixture then stirred for 30 min. Workup and chromatography as described earlier afforded 0.143 g (58%) of the desired product (**28h**) as a 1:1 mixture of diastereomers.

Solvent System B: 100% Methanol. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.238 g (0.098 mmol) of **27h**, 0.523 g (4.9 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, and 25.0 mL of methanol. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 189.1 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.491 g (7.8 mmol) of *p*-toluenesulfonic acid was added to the reaction and the mixture then stirred for 30 min. Workup and chromatography afforded 0.108 g (43%) of the desired product **28h** as a 1:1 mixture of diastereomers. The spectral data for compound **28h** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22−7.33 (m, 5 H), 7.09 (m, 1 H), 6.84 (s, 0.5 H), 6.15 (s, 0.5 H), 4.45 (d, J = 8.4 Hz, 0.5 H), 4.41 (d, J = 8.8 Hz, 0.5 H), 3.23 (1.5 H), 3.11 (br s, 2.5 H), 2.47−2.53 (m, 2.35 H), 2.15−2.83 (m, 0.65 H), 1.73−1.84 (m, 2 H), 1.41−1.70 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 140.2, 139.1, 138.7, 128.2, 127.9, 127.6, 127.5, 127.3, 127.1, 126.7, 121.5, 120.7, 113.0, 112.8, 84.9, 82.7, 56.9, 56.8, 46.4, 45.2, 28.3, 28.3, 27.2, 26.8, 26.1, 25.7, 25.5; IR (neat, NaCl) 3052, 2934, 2850, 1490, 1446, 1102, 1056, 1026, 873, 776, 693 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 121 (100), 135 (39), 122 (27), 225 (25), 179 (4), 136 (2); HRMS (EI) *m*/*e* calcd for $C_{16}H_{18}O$ ($M^+ - CH_2O$) 226.1357, found 226.1358.

(*E*,*Z*)-7-(3′-Furyl)-2-methyl-2-heptene (27i). Substrate **27i** was prepared using chemistry that was directly analogous to the synthesis of substrate **4a**. In this experiment, 1.989 g (8.2 mmol) of 5-(3′-furyl)-1-pentanol, 0.705 g (9.0 mmol) of dimethyl sulfoxide, 21.0 mL of dichloromethane, 1.249 g (9.8 mmol) of oxalyl chloride, and 2.489 g (24.6 mmol) of triethylamine were used for the Swern oxidation. The resulting aldehyde was added to an ylide generated from 10.634 g (24.6 mmol) of isopropyltriphenylphosphonium iodide in 49.0 mL of THF and 18.9 mL (24.6 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. When the reaction was complete, workup and purification (chromatography and Kulgerohr distillation) afforded 0.844 g (58%) of the desired product **27i**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1 H), 7.19 (s, 1 H), 6.25 (s, 1 H), 5.08−5.14 (m, 1 H), 2.4 (t, J = 7.41 Hz, 2 H), 1.96−2.03 (m, 2 H), 1.68 (s, 3 H), 1.50−1.59 (m, 5 H), 1.34−1.41 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.7, 131.4, 125.2, 124.6, 110.0, 29.7, 29.5, 25.7, 24.7, 17.6; IR (neat, NaCl) 2962, 2930, 2920, 2857, 1631, 1502, 1448, 1378, 1162, 1064, 1027, 873, 775 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 179 (100), 81 (16), 123 (12), 161 (11), 82 (8), 109 (5), 178 (0.5); HRMS (EI) *m*/*e* calcd for $C_{12}H_{18}O$ 178.1358, found 178.1360.

Electrolysis of Compound 27i. Synthesis of 8-(1′-Methylethylidene)cyclohepta[*b*]furan (28i), 7-(2′-Methoxy-2′-propyl)cyclohepta[*b*]furan (28ii), and 7-[3′-(2′,5′-Dimethoxy-2′,5′-dihydrofurnyl)]-2-methyl-2-heptene (29). The anodic oxidation of **27i** was performed in a fashion that was directly analogous to the electrolysis of **27c** described above. In this experiment, a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.192 g (1.1 mmol) of **27i**, 0.589 g (5.5 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 212.3 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.674 g (98.8 mmol) of *p*-toluenesulfonic acid was added to the mixture and the reaction mixture stirred for 30 min. Workup and purification then afforded 0.050 g (26%) of **28i**, 0.0014 g (6%) of **28ii**, and 0.062 g (25%) of **29**. Another reaction was carried out under the same set of electrolysis conditions except that a carbon rod was employed as an anode in place of the RVC anode used above. This experiment led to the formation of 0.142 g (54%) of **29**. The spectral data for compound **28i** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 1.7 Hz), 6.14 (d, J = 1.7 Hz, 1 H), 4.87 (s, 1 H), 4.42 (s, 1 H), 3.55−3.57 (m, 1 H), 2.44−2.49 (m, 2 H), 1.96−1.99 (m, 1 H), 1.55−1.86 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 139.2, 121.4, 112.4, 112.9, 112.4, 46.6, 30.2, 28.5, 25.6, 21.2; IR (neat, NaCl) 2927, 2920, 2852, 1647, 1503, 1465, 1447, 1435, 1374, 1150, 1106, 893, 724 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 177 (100), 135 (30), 178 (23), 121 (22), 175 (21), 175 (20), 81 (14), 95 (11), 109 (10), 149 (9), 57 (8); HRMS (EI) *m*/*e* calcd for $C_{12}H_{16}O$ 176.1201, found 176.1206. The spectral data for compound **28ii** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, J = 1.7 Hz, 1 H), 6.13 (d, J = 1.7 Hz), 3.21 (s, 3 H), 3.02−3.04 (m, 1 H), 2.53−2.65 (m, 1.44 H), 2.38−2.45 (m, 1.36 H), 1.70−2.01 (m, 5.20 H), 1.27 (s, 3 H), 1.17 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 138.7, 121.6, 112.9, 48.9, 47.0, 27.7, 26.5, 26.0, 24.6, 24.3, 23.6; IR (neat, NaCl) 2973, 2972, 2941, 2930, 2854, 1507, 1380, 1367, 1216, 1164, 1153, 1130, 1080, 1064, 1025, 893, 721 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 73 (100), 177 (32), 74 (14), 178 (8), 135 (3), 121 (2), 193 (1); HRMS (EI) *m*/*e* calcd $C_{12}H_{16}O$ [$M - CH_3OH$], 176.1200, found 176.1205. The spectral data for compound **29** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ

5.82 (d, J = 1.1 Hz, 0.5 H), 5.80 (d, J = 2.6 Hz, 0.5 H), 5.69 (s, 1 H), 5.53 (s, 0.5 H), 5.42 (s, 0.5 H), 5.09−5.10 (m, 1 H), 3.36−3.41 (m, 6 H), 2.09−2.14 (m, 2 H), 1.95−2.00 (m, 2 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.49−1.57 (m, 2 H), 1.35−1.42 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 145.6, 131.5, 124.2, 123.8, 123.8, 123.5, 108.9, 107.6, 106.8, 54.1, 54.0, 53.5, 53.5, 29.5, 29.4, 27.6, 26.7, 26.4, 26.3, 25.6, 17.6; IR (neat, NaCl) 2956, 2880, 2830, 1615, 1480, 1386, 1180, 1230, 1125, 1110, 1010, 1003,980, 875 cm^{-1}; LRFAB 209.2 [M + H − CH_3OH]; HRFAB Calcd for $C_{13}H_{21}O_2$ [M + H − CH_3OH] 209.1546, found 209.1555.

6-(3′-Furyl)-1-hexanol. The desired alcohol was synthesized in a manner similar to the preparation of compound **26** described above. In this experiment, the Grignard reagent was prepared from 2.551 g (105.0 mmol) of magnesium powder, 110 mL of THF, and 14.904 g (100 mmol) of 5-bromo-1-pentene. As described above, 3-furylmethyl bromide was prepared using 4.905 g (50 mmol) of 3-furanmethanol, 4.738 g (17.5 mmol) of phosphorus tribromide, and 53.0 mL of THF. The crude 3-furylmethyl bromide was diluted with 150 mL of THF and then added to a −30 to −50 °C solution of the Grignard reagent and 1.904 g (10.0 mmol) of anhydrous copper iodide over a period of 3 h. The reaction mixture was then allowed to warm to room temperature and stirred for 18 h. Workup as described earlier afforded the desired olefin which was then used crude in the hydroboration reaction described below.

To a stirred solution of 10.0 mL (100 mmol) of borane−dimethyl sulfide complex in 50 mL of THF at 0 °C was added 14.027 g (200 mmol) of 2-methyl-2-butene. The reaction mixture was stirred for 1 h and the olefin prepared above added. The reaction mixture was stirred for an additional 1 h. At that time, the reaction was quenched *carefully* with 71.4 mL of a 3 N solution of sodium hydroxide followed by 26.5 mL of a 30% aqueous hydrogen peroxide solution. Column chromatography through a silica gel column that was slurry-packed using a 25% ethyl acetate in hexane solution containing 1% triethylamine using 25% ethyl acetate in hexane as the eluant afforded 4.032 g (48%) of the desired alcohol over three steps from 3-furanmethanol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 1.8 Hz, 1 H), 7.19 (s, 1 H), 3.59 (t, J = 6.6 Hz, 2 H), 2.51 (s, 1 H), 2.40 (t, J = 7.6 Hz, 2 H), 1.50−1.58 (m, 4 H), 1.34−1.37 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 138.5, 125.0, 110.9, 62.5, 32.5, 29.8, 28.9, 25.4, 24.5; IR (neat, NaCl) 3300 br, 2940, 2860, 1510, 1492, 1370, 1280, 1200, 1080, 1050, 890, 810 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 82 (100), 95 (24), 168 (20), 67 (8); HRMS (EI) *m*/*e* calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1153.

(*E*,*Z*)-7-(3′-Furyl)-1-methoxy-1-heptene (27j). This enol ether substrate was prepared in a fashion directly analogous to the preparation of substrate **4a**. In this experiment, 2.245 g (13.4 mmol) of 6-(3′-furyl)-1-hexanol, 1.152 g (14.7 mmol) of dimethyl sulfoxide, 34.0 mL of dichloromethane, 2.041 g (16.1 mmol) of oxalyl chloride, and 4.068 g (63.3 mmol) of triethylamine were used in the Swern oxidation. The resulting aldehyde was added to a ylide generated from 13.781 g (40.2 mmol) of (methoxymethyl)triphenylphosphonium chloride in 80.4 mL of THF and 31.0 mL (40.2 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. When the reaction was complete, workup and chromatography afforded 1.326 g (51%) of the desired product **27j** as a mixture of cis and trans isomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 1.6 Hz, 1 H), 7.19 (s, 1 H), 6.25−6.29 (m, 1.6 H), 5.85 (d, J = 6.3 Hz, 0.4 H), 4.71 (dt, J_t = 7.3 Hz, J_d = 12.6 Hz, 0.6 H), 4.32 (dt, J_d = 6.4 Hz, J_t = 7.3 Hz, 0.4 H), 3.55 (s, 1.2 H), 3.48 (s, 1.8 H), 2.39 (t, J = 7.6 Hz, 2 H), 2.04−2.07 (m, 0.6 H), 1.90−1.92 (m, 1.4 H), 1.52−1.56 (m, 2 H), 1.33−1.36 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 145.9, 142.5, 142.4, 138.6, 125.2, 125.1, 110.9, 106.8, 102.8, 59.3, 55.7, 30.5, 29.7, 29.5, 28.8, 28.5, 27.5, 24.6, 23.7; IR (neat, NaCl) 2940, 2865, 1655, 1506, 1480, 1350, 1210, 1158, 1120, 1030, 880, 770 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 163 (100), 81 (91), 71 (50), 121 (29), 195 (38), 135 (28), 95 (26), 109 (23), 164 (21), 82 (18), 145 (13); HRMS (EI) *m*/*e* calcd for $C_{12}H_{18}O_2$ 194.1306, found 194.1323.

Electrolysis of Compound 27j. Synthesis of 9-(1′,1′-Dimethoxymethyl)cycloocta[*b*]furan (28j) and 7-(3′-Furyl)-1,1,2-trimethoxyheptane (30). A 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet was charged with 0.092 g (0.47 mmol) of **27j**, 0.252 g (2.35 mmol) of 2,6-lutidine, 3.293 g (10.0 mmol) of tetrabutylammonium tetrafluoroborate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. The mixture was degassed by sonication for 30 min and then oxidized at a constant current of 11.6 mA until 117.6 C (2.6 faradays/mol) of charge had been passed. Upon completion of the oxidation, 0.723 g (3.8 mmol) of *p*-toluenesulfonic acid was added to the mixture and the reaction stirred for 30 min. Workup and chromatography as described above afforded 0.152 g (32%) of **28j**. Compound **28j** was contamintated with an inseparable side product. In addition, 0.018 g (16%) of **30** was obtained**.** The spectral data for compound **28j** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 1.7 Hz, 1 H), 6.42 (d, J = 1.7 Hz, 1 H), 4.80 (d, J = 7.4 Hz, 1 H), 3.40 (s, 3 H), 3.37 (s, 3 H), 3.29 (m, 1 H), 2.43−2.48 (m, 2 H), 1.72−1.82 (m, 4 H), 1.49−1.61 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 140.0, 138.6, 113.2, 112.0, 105.5, 54.1, 53.9, 39.6, 30.5, 29.5, 26.3, 25.3, 24.7; IR (neat, NaCl) 2951, 2863, 2840, 1507, 1462, 1443, 1320, 1234, 1160, 1102, 1060, 970, 940, 880 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 75 (100), 193 (40), 76 (13), 194 (9), 74 (3), 223 (2), 195 (1); HRMS (EI) *m*/*e* calcd for $C_{13}H_{20}O_3$ [M^+ − CH_3OH], 192.1150, found 192.1148. The spectral data for compound **30** are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 1 H), 7.20 (s, 1 H), 6.26 (s, 1 H), 4.20 (d, J = 5.5 Hz, 1 H), 3.46 (s, 6 H), 3.42 (s, 3 H), 3.12−3.18 (m, 1 H), 2.41 (t, J = 7.4 Hz, 2 H), 1.34−1.59 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 138.4, 124.5, 105.4, 103.2, 81.2, 58.6, 55.2, 54.6, 29.5, 29.2, 28.6, 25.4, 24.8; IR (neat, NaCl) 2940, 2852, 1508, 1425, 1275, 1233, 1187, 1131, 1080, 1050, 1025, 1020, 1015, 1008, 97, 843 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 193 (100), 75 (23), 194 (22), 161 (15), 121 (6), 191 (6), 133 (6), 221 (4), 162 (4), 195 (3); HRMS (EI) *m*/*e* calcd for $C_{14}H_{24}O_4$ [M^+ − CH_3OH] 224.1412, found 224.1409.

5-(3-Furyl)-2-pentanol. A stirred solution of 0.906 g (11.6 mmol) of **26**, 0.997 g (12.8 mmol) of dimethyl sulfoxide, and 30.0 mL of dichloromethane was cooled to −78 °C. After 15 min, 1.767 g (13.9 mmol) of oxalyl chloride was added and the reaction mixture was allowed to warm to a temperature range of −50 to −60 °C. After 20 min, the reaction was quenched with 3.521 g (34.8 mmol) of triethylamine and mixture brought to room temperature. After being diluted with ether, the crude aldehyde was washed with water, saturated sodium bicarbonate, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The concentrated crude aldehyde was placed in a round-bottom flask with 50 mL of THF and cooled to −78 °C. To this mixture was slowly added 11.6 mL (34.8 mmol) of a 3.0 M solution of methylmagnesium bromide in ether. The reaction mixture was stirred for 15 h and then the reaction quenched with 26.0 mL of 10 M sulfuric acid at 0 °C. This mixture was diluted with water and extracted with ether. The combined ether layers were washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The crude material was chromatographed through a silica gel column that was slurry-packed using a 1% triethylamine in hexane solution. The column was eluted with a 15% ethyl acetate in hexane solution to afford 0.625 g (35%) of the desired product and 0.372 g (23%) of the recovered starting alcohol. The spectral data for the desired alcohol are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 1 H), 7.21 (s, 1 H), 6.27 (s, 1 H), 3.78−3.84 (m, 1 H), 2.41−2.46 (t, J = 7.6 Hz, 2 H), 1.41−1.72 (m, 5 H), 1.18−1.2 (d, J = 9.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 138.8, 124.9, 110.9, 67.9, 38.8, 26.1, 24.7, 23.5; IR (neat, NaCl) 3430 br, 2984, 2956, 2881, 1508, 1450, 1390, 1180, 1150, 1108, 1105, 960, 800 cm^{-1}; LRMS (EI) *m*/*e* (rel intensity) 94 (100), 95 (27), 154 (23), 107 (9), 121 (8), 136 (6); HRMS (EI) *m*/*e* calcd for $C_9H_{14}O_2$ 154.0994, found 154.0996.

(*E*,*Z*)-5-(3′-Furyl)-1-methoxy-2-methyl-1-pentene (31). This enol ether substrate was prepared in a fashion that was directly analogous to the synthesis used for preparing substrate **4**. In this experiment, the Swern oxidation utilized 1.272 g (7.1 mmol) of 5-(3-furyl)-2-pentanol, 0.609 g (7.8 mmol) of dimethyl sulfoxide, 18.0 mL of dichloromethane, 1.081 g (8.5

mmol) of oxalyl chloride, and 2.155 g (21.3 mmol) of triethylamine. The resulting aldehyde was added to the ylide prepared from 7.302 g (21.3 mmol) of (methoxymethyl)-triphenylphosphonium chloride in 43.0 mL of THF and 16.4 mL (21.3 mmol) of a 1.3 M solution of *sec*-butyllithium in cyclohexane. After the reaction was complete, workup and chromatography afforded 0.741 g (58%) of **31** as a mixture of cis and trans olefin isomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 1 H), 7.21 (s, 1 H), 6.27 (s, 1 H), 5.77 (s, 1 H), 3.54 (s, 1.3 H), 3.52 (s, 1.7 H), 2.35−2.42 (m, 2 H), 2.11 (t, 1.3 H), 1.89 (t, 0.7 H), 1.89−1.58 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 142.5, 142.5, 142.0, 141.9, 138.7, 125.2, 113.8, 111.0, 110.9, 59.1, 33.4, 28.5, 28.1, 27.8, 245.4, 17.1, 12.6; IR (neat, NaCl) 2957, 2874, 1648, 1505, 1483, 1348, 1215, 1161, 1130, 1035, 1020, 984, 886, 770 cm^{-1}; HRMS (EI) *m*/*e* calcd for $C_{11}H_{16}O_2$ 180.1150, found, 180.1150.

Electrolysis of Compound 31. Synthesis of 7-(1′,1′-Dimethoxymethyl)-7-methyl-4,5,6,7-tetrahydrobenzo[*b*]-furan (32). To a 100 mL round-bottom flask equipped with a reticulated vitreous carbon anode, a carbon rod cathode, and a nitrogen inlet were added 0.193 g (0.92 mmol) of **31**, 0.494 g (2.4 mmol) of 2,6-lutidine, 1.064 g (10.0 mmol) of lithium perchlorate, 5.0 mL of methanol, and 20.0 mL of dichloromethane. This mixture was degassed by sonication for 30 min and then oxidized at a constant curent of 11.6 mA until 177.5 C (2 faradays/mol) of charge had been passed. Upon completion of the oxidation, 1.401 g (7.4 mmol) of *p*-toluenesulfonic acid was added. The mixture was stirred for 30 min. Workup and chromatography as described earlier afforded 0.100 g (52%) of the desired product **32**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 1 H), 6.17 (s, 1 H), 4.32 (s, 1 H), 3.45 (s, 3 H), 3.34 (s, 3 H), 2.38−2.43 (m, 2 H), 1.97−2.07 (m, 1 H), 1.78−1.94 (m, 1 H), 1.63−1.74 (m, 1 H), 1.45−1.54 (m, 1 H), 1.24 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 140.5, 117.7, 111.2, 110.2, 57.9, 57.7, 40.9, 31.2, 22.4, 21.5, 20.1; IR (neat, NaCl) 2943, 2852, 2835, 1506, 1454, 1446, 1374, 1301, 1240, 1231, 1185, 1121, 1105, 1074, 1054, 992, 954, 889, 730, 689 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 179 (100), 75 (55), 147 (8), 61 (7), 74 (6), 145 (4), 203(3); HRMS (EI) *m*/*e* calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1255.

4-(*N*-(Triisopropylsilyl)-3-pyrrolyl)-1-(2′-tetrahydropyranoxy)butanol (34). To a round-bottom flask was added 0.771 g (2.6 mmol) of 3-bromo-1-triisopropylpyrrole[14] in 2 mL of THF. The solution was cooled to −78 °C and after 15 min 1.6 mL (2.6 mmol) of a 1.6 M *n*-butyllithium in hexane solution added. The mixture was then stirred for 30 min and then the THP ether of 4-hydroxybutanal added. The aldehyde was synthesized from the monoprotected 1,4-butanediol by a Swern oxidation in a fashion directly analogous to the synthesis of compound **4** described above. This experiment was done using 0.871 g (5.1 mmol) of the alcohol, 0.777 g (6.1 mmol) of oxalyl chloride, 0.518 g (6.1 mmol) of dimethyl sulfoxide, 2.581 g (25.5 mmol) of triethylamine, and 10 mL of dichloromethane. After addition of the aldehyde to the anion generated from the bromide, the reaction mixture was slowly warmed to room temperature and stirred for 16 h. The reaction was then quenched with H_2O and the mixture extracted with ether. The combined ether layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was chromatographed through 100 mL of silica gel using a gradient elution from hexane to 25% ether in hexane by adding an additional 2% of ether for every 100 mL of eluent to afford 0.510 g (51%) of the pure, alkylated product. For convenience, the alcohol on the carbon next to the pyrrole ring was immediately removed by diluting the purified product with 10 mL of THF, cooling the mixture to 0 °C, and then adding 1 mL (10 mmol) of borane−dimethyl sulfide. The reaction mixture was allowed to warm to room temperature and monitored by TLC. After 3 h, the reaction mixture still showed starting material so the reaction mixture was placed in warm tap water. After an additional 30 min, the reaction was complete. The reaction was then quenched with H_2O, ether was added, and the layers were seperated. The aqueous layer was extracted with ether, and the combined ether layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting oil was chromatographed through 50 mL of silica gel using a gradient elution from hexane to 25% ether in hexane by adding an additional 2% of ether for every 100 mL of eluent to afford 0.380 g (71%) of the desired product **34**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.68 (t, J = 2.4 Hz, 1 H), 6.52 (s, 1 H), 6.15 (s, 1 H), 4.57−4.59 (m, 1 H), 3.72−3.91 (m, 2 H), 3.37−3.53 (m, 2 H), 1.21−1.88 (m, 13 H), 1.10 (s, 9 H), 1.07 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.1, 124.0, 121.1, 110.7, 98.8, 67.6, 62.3, 30.9, 29.6, 27.8, 26.9, 25.6, 19.7, 18.0, 17.9, 17.8, 11.8; IR (neat, NaCl) 2943, 2928, 2894, 2867, 1479, 1464, 1384, 1367, 1352, 1270, 1200, 1185, 1157, 1136, 1119, 1101, 1076, 1033, 1021, 994, 972, 920, 906, 691, 658 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 296 (100), 122 (51), 85 (40), 252 (37), 297 (33), 295 (29), 278 (27), 294 (23), 236 (15), 324 (13), 253 (12), 279 (10); HRMS (EI) *m*/*e* calcd for $C_{22}H_{41}NO_2Si$ 379.2906, found 379.2907.

4-(*N*-Pivaloyl-3-pyrrolyl)-1-butanol (35). A round-bottom flask was charged with 1.838 g (4.8 mmol) of **34**, 40 mL of THF, and 9.7 mL (9.7 mmol) of tetrabutylammonium fluoride (1.0 M in THF). After 30 min, the reaction was checked by TLC at which time the reaction was complete. The reaction was quenched with H_2O, the mixture was diluted with ether, and the layers were separated. The combined organic layers were then dried over $MgSO_4$ and concentrated *in vacuo*. The resulting oil was chromatographed through 75 mL of silica gel with 10 g of activity 3 neutral alumina on top. A gradient elution from hexane to 30% ether in hexane was performed by adding an additional 3% of ether for every 100 mL of eluent in order to afford 1.127 g (>100%) of the desired product. This product was utilized directly for the next step without further purification. In a sample procedure, 1.080 g (4.8 mmol) of the product was diluted with 20 mL of THF, the mixture cooled to 0 °C, and 8.1 mL (14.5 mmol) of phenyllithium added. The reaction mixture was stirred for 15 min, and then 1.605 g (13.3 mmol) of trimethylacetyl chloride was added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h, and then the reaction was quenched with H_2O. The crude mixture was stirred for an additional 10 min and then extracted with ether. The combined ether layers were washed with brine, dried over $MgSO_4$, and then concentrated *in vacuo*. The resulting oil was chromatographed through 75 mL of silica gel using a gradient elution from hexane to 30% ether in hexane by adding an additional 3% of ether for every 100 mL of eluent used in order to afford 1.281 g (86% over two steps) of the desired product. This product was then carried directly on to the next step, where in a 25 mL 14/20 round-bottom flask the 1.281 g (4.2 mmol) of diprotected pyrrole was diluted with 50 mL of ethanol, cooled to 0 °C, and treated with 0.198 g (1.0 mmol) of *p*-toluenesulfonic acid. The reaction mixture was stirred overnight and then diluted with ether and water. The layers were separated, and the aqueous layer was extracted with ether. The combined ether layers were then dried over $MgSO_4$ and concentrated *in vacuo*. The resulting oil was chromatographed through 75 mL of silica gel with a gradient elution from hexane to 30% ether/hexane by adding an additional 3% of ether for every 100 mL of eluent used to afford 0.791 g (85%) of the desired product **35**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (t, J = *ca.* 3 Hz, 1 H), 7.19 (s, 1 H), 6.12 (dd, J = *ca.* 3 Hz, J = 1.6 Hz, 1 H), 3.66 (t, J = 6.2 Hz, 2 H), 2.44−2.48 (m, 2 H), 1.92 (s, 1 H), 1.57−1.68 (m, 4 H), 1.44 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 127.6, 120.7, 117.7, 113.0, 62.7, 40.4, 32.4, 28.6, 26.6, 26.3; IR (neat, NaCl) 3310 br, 2975, 2936, 2875, 2863, 1701, 1478, 1461, 1406, 1371, 1341, 1310, 1165, 1070, 1038, 908, 811, 784, 756 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 224 (100), 57 (89), 122 (48), 206 (24), 140 (23), 85 (19), 225 (17), 58 (15), 223 (11), 120 (9), 252 (8); HRMS (EI) *m*/*e* calcd for $C_{13}H_{21}NO_2$ 223.1572, found 223.1574.

(*E*,*Z*)-5-(*N*-Pivaloyl-3-pyrrolyl)-1-(methylthio)-1-pentene (36). The reaction sequence was carried out in a similar fashion to that described above for the synthesis of **11b**. In this example, 0.505 g (2.3 mmol) of **35**, 0.345 g (2.7 mmol) of oxalyl chloride, 0.230 g (2.9 mmol) of dimethyl sulfoxide, 1.144 g (11.3 mmol) of triethylamine, and 5 mL of dichloromethane were used. After workup the aldehyde was diluted with 10 mL of THF and added to the ylide. The ylide was formed from 2.0278 g (5.7 mmol) of [(methylthio)methyl]triphenylphosphonium chloride, 3.14 mL (5.65 mmol) of a 1.8 M phenyllithium in 70/30 cyclohexane/ether solution, and 20 mL of THF.

Workup and chromatography afforded 0.382 g (64%) of the desired product: ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.41 (br s, 1 H), 7.28 (br s, 1 H), 6.15 (br s, 1 H), 6.03 (d, J = 14.9 Hz, 0.6 H), 5.96 (dt, J = 9.4 Hz, J = 1.3 Hz, 0.4 H), 5.54 (dt, J = 9.3 Hz, J = 7.2 Hz, 0.4 H), 5.44 (dt, J = 14.9 Hz, J = 7.0 Hz, 0.6 H), 2.41−2.47 (m, 2 H), 2.23 (s, 1.2 H), 2.19 (s, 1.8 H), 2.14−2.19 (m, 2 H), 1.60−1.71 (m, 2 H), 1.41 (s, 9 H); ^{13}C NMR (75 MHz, CD_3 $COCD_3$) δ 175.7, 128.4, 128.2, 128.0, 127.0, 125.1, 121.4, 121.3, 118.05, 118.00, 113.4, 40.9, 33.3, 30.7, 29.3, 28.6, 26.9, 26.7, 16.7, 14.7; IR (neat, NaCl) 2977, 2931, 2922, 2877, 2856, 1700, 1661, 1477, 1466, 1438, 1405, 1370, 1354, 1309, 1165, 1073, 1038, 938, 811, 793, 755, 703 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 57 (100), 218 (86), 134 (69), 266 (39), 165 (19), 294 (18), 219 (14), 182 (12), 58 (10), 87 (10), 135 (8); HRMS (EI) *m*/*e* calcd for $C_{15}H_{23}NOS$ 265.1500, found 265.1442. Anal. Calcd for $C_{15}H_{23}NOS$: C, 67.89; H, 8.74; N, 5.28. Found: C, 67.65; H, 8.74; N, 5.09.

1-*N*-Pivaloyl-4,5,6,7-tetrahydroindole-7-carboxaldehyde Dimethyl Thioacetal (37). Compound **36** was oxidized in a manner similar to the constant current oxidation of compound **4**. In this experiment, 0.196 g (0.7 mmol) of **36**, 0.375 g (3.5 mmol) of 2,6-lutidine, 1.277 g (12.0 mmol) of lithium perchlorate, 5.6 mL of methanol, and 22.4 mL of dichloromethane were used. A constant current of 11.7 mA until 143.0 C (2.0 faradays/mol) of charge had been passed. Workup and chromatography afforded 0.145 g (66%) of the desired product as a mixture of diastereomers: ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.35 (d, J = 3.4 Hz, 0.31 H), 7.24 (d, J = 3.4 Hz, 0.69 H), 5.98 (d, J = 3.5 Hz, 0.31 H), 5.93 (d, J = 3.4 H, 0.69 H), 4.44 (d, J = 5.5 Hz, 0.31 H), 4.20 (d, J = 8.9 Hz, 0.69 H), 3.95−3.97 (m, 0.69 H), 3.81−3.85 (m, 0.31 H), 3.26 (s, 0.93 H), 3.25 (s, 2.07 H), 2.42−2.46 (m, 2 H), 2.14−2.18 (m, 1 H), 2.03 (s, 0.93 H), 1.96 (s, 2.07 H), 1.65−1.76 (m, 3 H), 1.43 (s, 2.79 H), 1.40 (s, 6.21 H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 180, 130.8, 122.7, 121.5, 121.1, 111.4, 110.2, 93.3, 91.8, 56.9, 56.6, 41.9, 38.8, 36.5, 29.0, 28.9, 28.6, 26.1, 25.4, 23.6, 20.1, 19.7, 13.3, 9.8; IR (neat, NaCl) 3100, 2975, 2930, 2869, 2843, 2822, 1708, 1487, 1479, 1461, 1444, 1428, 1398, 1368, 1356, 1294, 1275, 1244, 1217, 1191, 1175, 1141, 1095, 1074, 940, 915, 865, 789, 755, 716, 696 cm^{-1}; GCMS (PCI) *m*/*e* (rel intensity) 248 (100), 247 (71), 164 (56), 216 (38), 264 (26), 246 (24), 249 (21), 85 (20), 95 (18), 276 (17), 56 (17), 97 (16), 103 (14); HRMS (EI) *m*/*e* calcd for $C_{16}H_{25}NO_2S$ 295.1606, found 295.1620.

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Supporting Information Available: Proton and carbon NMR data for all new compounds (127 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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