# Catalytic Isomerization of 1-Alkynyl-2,3-epoxy Alcohols to Substituted Furans: Succinct Routes to Furanoid Fatty Acids and Difurylmethanes

Charles M. Marson*,† and Steven Harper‡

*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.*

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A versatile procedure for the preparation of synthetically valuable 2,5-disubstituted and 2,3,5-trisubstituted furans via mercury(II)-mediated isomerization of 1-alkynyl-2,3-epoxy alcohols is described. Mercury(II)-catalyzed isomerization of alkynyl epoxides **3a**−**k** derived from *cyclic* α-alkynyl allylic alcohols furnishes 2,3,5-substituted furans bearing an aldehyde or keto group on the C-2 side chain. The reaction is used in a succinct and efficient synthesis of the furanoid fatty acid $F_5$. In contrast, the mercury(II)-catalyzed reaction of a series of alkynyl epoxides **3m**−**p** lacking ring fusion affords difurylmethanes **5**, presumably by the dimerization of intermediate 2-(α-hydroxyalkyl)furans **4**.

The furan ring[1] is a ubiquitous structural element of a variety of natural products, notably marine natural products such as the pseudopteranolide kallolide B[2] (Figure 1), calicogorin B,[3] and the furanoid fatty acids.[4] In addition, furans serve as diverse intermediates in organic synthesis,[5] and the variety of pharmaceuticals and compounds of notable flavor and fragrance[1] that contain the furan ring underlies their importance. Consequently, the construction of the furan ring enjoys continued development of new methods. In view of the difficulty that can be associated with the regioselective introduction of carbon substituents to a furan ring, many synthetic approaches rely on intramolecular cyclization of an acyclic substrate, usually by formation of a C−O bond. Several classes of acyclic acetylenic compounds, including 2-alken-4-yn-1-ols,[6−10] 4-alken-1-yn-3-ols,[10] 2-alkylidene-3-yn-1-ols,[8] β,γ-alkynyl ketones,[11,12] and 3,4-epoxyalkynes,[13−17] undergo cyclization to furans, and such reactions have proved valuable in the synthesis of natural products.[18] However, although 4-alkynyl-1,2-epoxides furnish furans under both acidic[13] and basic[14,16] conditions, and esters of 1-alkynyl-2,3-epoxy alcohols undergo reductive elimination to 2-alken-4-yn-1-ols that cyclize to the corresponding furan,[19] the utility of the related 1-alkynyl-2,3-epoxy alcohols in furan-forming reactions has only recently been disclosed in two preliminary accounts.[20,21]

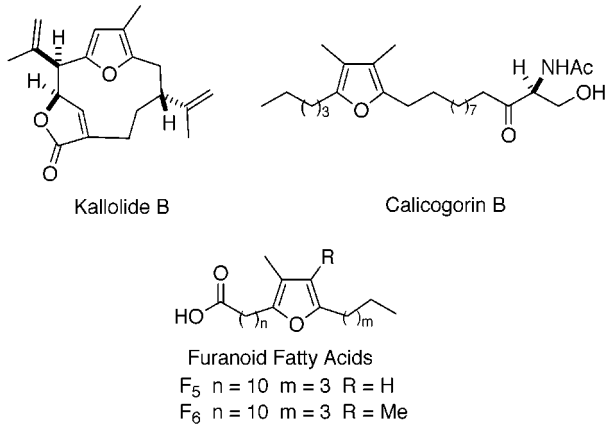


**Figure 1.**

† Current address: Department of Chemistry, Queen Mary and Westfield College, University of London, London E1 4NS, U.K.

‡ Present address: IRBM, Via Pontina km 30,600, 00040 Pomezia, Rome.

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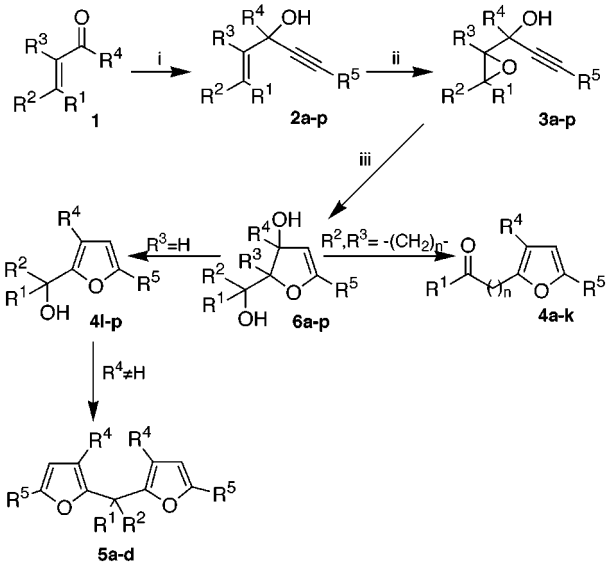
Herein are described mild and efficient isomerizations of secondary and tertiary 1-alkynyl-2,3-epoxy alcohols mediated by catalytic aqueous mercury(II) in dilute sulfuric acid (Scheme 1). Advantages of such isomerizations include (a) ease of assembly of the starting materials, (b) catalytic processes that proceed at 25 °C, and (c) generality, allowing access to a wide variety of substituted furans, including those bearing sensitive functionality and of the three different types of furan substitution in groups **4a**−**k**, **4l**, and **5a**−**d**. The isomerization of 1-alkynyl-2,3-epoxy alcohols derived from tertiary alicyclic allylic alcohols **2a**−**k** and certain secondary acyclic allylic alcohols such as **2l** affords, respectively, 2,3,5-trisubstituted and 2,5-disubstituted furans. A notable feature of these reactions is the presence in the product of additional oxygenated functionality on the C-2 substituent of the furan. In contrast to the above, 1-alkynyl-2,3-epoxy alcohols derived from tertiary acyclic allylic alcohols **2m**−**p** undergo an isomerization−dimerization sequence to afford the substituted difurylmethanes **5a**−**d**. Such furan-forming reactions have potential use in the synthesis of biologically active natural products, as demonstrated herein by a synthesis of the furanoid fatty acid $F_5$.

**Scheme 1**[a]




[a] Key: (i) $R^5$-≡, *n*-BuLi; (ii) *t*-BuOOH, $VO(acac)_2$; (iii) HgO in 2.5% v/v $H_2SO_4$.

1-Alkynyl-2-alken-1-ols **2a**−**p** (Tables 1 and 2) were prepared in good yield by reaction of a cycloalkenyl ketone **1**, either readily available via methodology previously described[22] or prepared by reacting a commercially available α,*β*-unsaturated carbonyl compound with the alkynyllithium generated by addition of excess *n*-butyllithium to a terminal alkyne at 20 °C. In none of the cases investigated was 1,4-addition realized to an inconvenient extent. The alcohols **2** were epoxidized[22−24] at 20 °C using *tert*-butyl hydroperoxide in the presence of a catalytic amount of vanadyl acetylacetonate to give a mixture of *syn*- and *anti*-epoxy alcohols **3**.[25] In accord with the findings of our previous studies,[22,26] epoxidation of the tertiary cycloalkenyl alcohols **2a**−**k** proceeded with marked preference for the syn isomer. Even in the least favorable cases, a syn diastereoselection in excess of 2:1 was observed. As expected,[23] epoxidation of the acyclic alcohols **2l**−**p** proved somewhat less selective, the corresponding epoxides **3l**−**p** typically being obtained in the region of a 7:3 ratio in favor of the syn isomer.

The tertiary cyclic alkynyl epoxides **3a**−**k** (Table 1) underwent efficient isomerization to the corresponding furans **4a**−**k** upon treatment with a dilute solution of aqueous mercury(II), obtained by dissolving yellow mercury(II) oxide in 2.5% v/v sulfuric acid; the catalytic amount of mercury(II) used was in the range 1.5−4 mol %. In general, syn/anti mixtures of the substrate epoxy alcohols were used. The reaction products were not found to be affected by the stereochemical configuration of the substrate. Thus, isomerization of both *syn*-**3c** and *anti*-**3c** gave, in each case, a comparable yield of the same furanoid product **4c** (Table 1). Each of the furans **4a**−**k** contains a carbonyl group at a position determined by the size of the alicyclic ring in the corresponding epoxy alcohol **3**. The examples illustrated show the reaction to be general for 5- to 12-membered alicyclic epoxy alcohols. For entries 3 and 4, the stereoelectronic nature of the alkynyl moiety, which has been found to influence the cyclization of certain alkynes to furans,[27] did not have a significant effect on the reaction. The isomerization of epoxy alcohol **3b** without loss of the acid-sensitive tetrahydropyranyl group is noteworthy and exemplifies the scope of the reaction and the mild conditions involved. Furanoid products were also obtained from the isomerization of acyclic alkynyl epoxy alcohols **3l**−**p** (Table 2). In the case of the secondary epoxy alcohol **3l**, the sole isolated product was the 2-(α-hydroxyalkyl)furan **4l**, while the tertiary epoxy alcohols **3m**−**p** furnished the symmetrical difurylmethanes **5a**−**d**.

The formation of the furans **4** and **5** can be rationalized by invoking an intermediate of the form **6**. Isomerization of the acyclic alkynyl epoxy alcohols **3l**−**p** presumably results in formation of the intermediates **6l**−**p** ($R^3$ = H), which can undergo direct dehydration, presumably via the corresponding oxonium ion, to afford the 2-(α-hydroxyalkyl)furans **4l**−**p**. In accordance with the acid-catalyzed self-condensation of two molecules of a 2-(α-hydroxyalkyl)furan bearing substituents at both the C-3 and C-5 positions,[28] epoxy alcohols **3m**−**p** furnish the corresponding bisfurans **5a**−**d**, while **4l**, which lacks an activating substituent in the C-3 position, did not undergo further reaction. For the alicyclic examples, direct dehydration of the intermediates **6a**−**k** is blocked, and the alternative fragmentation with aromatization occurs, giving the furans **4a**−**k**. The formation of **5a**−**d** arises by presumed protonation of the furan ring of **4l**−**p**,

(20) For a preliminary account of some of these mercury(II)-catalyzed isomerizations, see: Marson, C. M.; Harper, S.; Wrigglesworth, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1879.

(21) For a preliminary account of the synthesis of furanoid fatty acid $\mathbf{F_5}$ see: Marson; C. M.; Harper, S. *Tetrahedron Lett.* **1998**, *39*, 333.

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(25) For a full explanation and definition of the terms syn and anti as used herein see: Marson, C. M.; Benzies, D. W. M.; Hobson, A. D. *Tetrahedron* **1991**, *47*, 5491.

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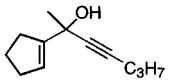
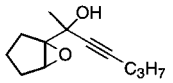
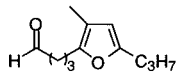
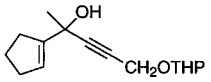
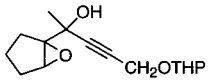
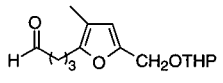
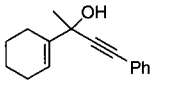
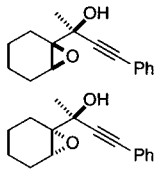
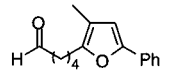
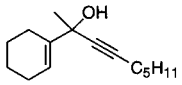
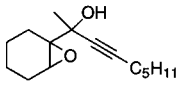
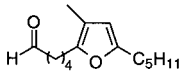
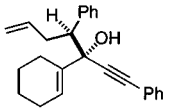
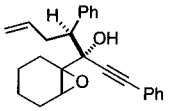
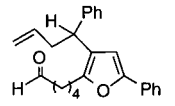
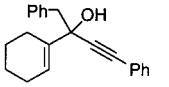
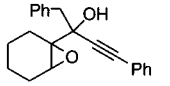
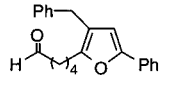
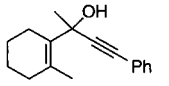
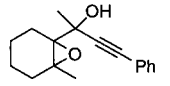
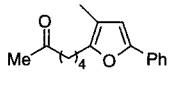
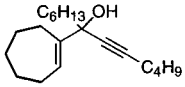
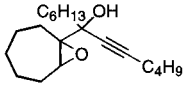
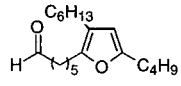
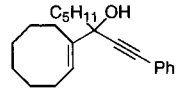
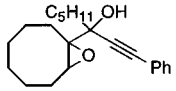
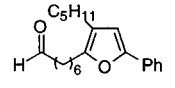
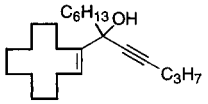
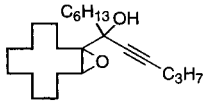
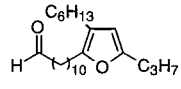
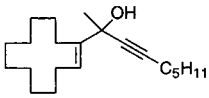
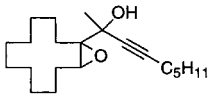
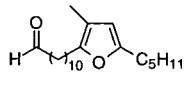
**Table 1. Preparation of Tertiary Alicyclic Alkynyl Epoxy Alcohols and Their Mercury(II)-Catalyzed Isomerization to 2,3,5-Trisubstituted Furans**

| Entry | Alcohol[a,b] | | Epoxide[a,c] | | Diastereo-isomer ratio | Yield[d] (%) | Furan[e] | | Yield[d] (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 |  | **2a** |  | **3a** | 5:1 | 48 |  | **4a** | 85 |
| 2 |  | **2b** |  | **3b** | 2:1 | 59 |  | **4b** | 55 |
| 3 |  | **2c** |  *syn*-**3c**[f] *anti*-**3c**[f] | | 4:1 | 83 |  | **4c** | 76 81 |
| 4 |  | **2d** |  | **3d** | 17:3 | 63 |  | **4d** | 85 |
| 5 |  | **2e**[g] |  | **3e**[g] | 30:1 | 81 |  | **4e** | 78 |
| 6 |  | **2f** |  | **3f** | 3:1 | 52 |  | **4f** | 48 |
| 7 |  | **2g** |  | **3g** | 7:1 | 66 |  | **4g** | 86 |
| 8 |  | **2h** |  | **3h** | 5:3 | 58 |  | **4h** | 82 |
| 9 |  | **2i** |  | **3i** | 8:3 | 72 |  | **4i** | 83 |
| 10 |  | **2j** |  | **3j** | 17:3 | 77 |  | **4j** | 60 |
| 11 |  | **2k** |  | **3k** | 4:1 | 69 |  | **4k** | 88 |

[a] All configurations depicted refer to racemic modifications. [b] The cycloalkenyl ketone[22] in THF was added to the alkynyllithium (generated by addition of excess *n*-BuLi to the alkyne at 20 °C) and stirred for 30 min. [c] The allylic alcohol in benzene was treated with VO (acac)$_2$ (20 mg) and *t*-BuOOH (2 equiv) at 20 °C and monitored to completion by TLC. [d] Isolated yield. [e] The epoxide in acetone was treated with a 0.1 M solution of $Hg^{II}$ (from HgO dissolved in 2.5% v/v sulfuric acid) and monitored to completion by TLC. [f] Reference 28. [g] Reference 24.

followed by cleavage of the 2-substituent (as the carbonyl compound); the resulting furan then attacks the carbocation derived from **4l**−**p** by protonation on the hydroxy group. Alternatively, acid-catalyzed fragmentation of **6a**−**p** could be the route by which the 2-substituent is cleaved.

The utility of these reactions with regard to the synthesis of biologically active natural products was demonstrated by synthesis of the furanoid fatty acid $F_5$. The furanoid fatty acids (F acids)[29] were originally isolated from *Exocarpus* seed oil;[30] they are abundant in fish lipids[31] and other natural sources,[32,33] can selectively esterify cholesterol, and have been linked with reproduction in fish.[31a,c] Addition of 1-heptynyllithium to 1-acetyl-1-cyclododecene afforded **2k**, which on epoxidation gave **3k** as an 4:1 mixture of diastereoisomers. This mixture of **3k** was treated with 0.32 mol % of mecury(II) in

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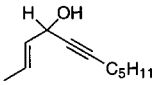
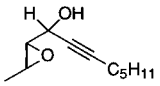
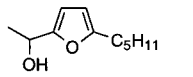
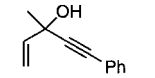
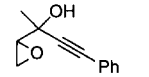
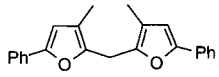
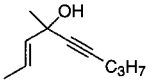
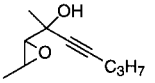
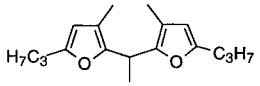
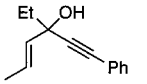
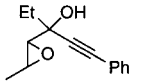
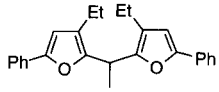
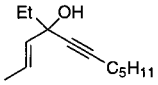
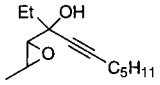
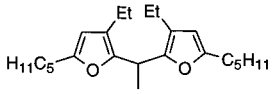
(31) (a) Glass, R. L.; Krick, T. P.; Eckhardt, A. E. *Lipids* **1974**, *9*, 1004. (b) Glass, R. L.; Krick, T. P.; Sand, D. M.; Rahn, C. H.; Schlenk, H. *Lipids* **1975**, *10*, 695. (c) Glass, R. L.; Krick, T. P.; Olson, D. L.; Thorson, R. L. *Lipids* **1977**, *12*, 828. (d) Gunstone, F. D.; Wijesundra, R. C.; Love, R. M.; Ross, D. *J. Chem. Soc., Chem. Commun.* **1976**, 630.

(32) Ciminiello, P.; Fattorusso, E.; Magno, S.; Mangoni, A.; Ialenti, A.; Dirosa, M. *Experientia* **1991**, *47*, 739.

(33) Hasma, H.; Subramanian, A. *Lipids* **1978**, *13*, 905.

**Table 2. Preparation of Acyclic Alkynyl Epoxy Alcohols and Their Mercury(II) Catalyzed Conversion into Substituted Furans**

| Entry | Alcohol[a] | | Epoxide[b] | | Diastereo isomer ratio | Yield[c] (%) | Furan[d] | | Yield[c] (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 |  | **2l** |  | **3l** | 7:3 | 68 |  | **4l** | 73 |
| 2 |  | **2m** |  | **3m** | 1:1 | 66 |  | **5a** | 84 |
| 3 |  | **2n** |  | **3n** | 6:4 | 67 |  | **5b** | 67 |
| 4 |  | **2o** |  | **3o** | 7:3 | 66 |  | **5c** | 74 |
| 5 |  | **2p** |  | **3p** | 7:3 | 71 |  | **5d** | 83 |

[a] The α,β-unsaturated carbonyl compound in THF was added to the alkynyllithium (generated by addition of *n*-BuLi to the alkyne at 20 °C) and stirred for 30 min. [b] The allylic alcohol in benzene was treated with VO (acac)$_2$ (20 mg) and *t*-BuOOH (2 equiv) at 20 °C and monitored to completion by TLC. [c] Isolated yield. [d] The epoxide in acetone was treated with a 0.1 M solution of $Hg^{II}$ (from HgO dissolved in 2.5% v/v sulfuric acid) and monitored to completion by TLC.

aqueous 1.5 mM sulfuric acid, giving **4k** (88%) which with 4 equiv of PDC[34] in DMF at room temperature resulted in a smooth oxidation of the aldehyde group, the furanoid fatty acid $F_5$ being isolated in 65% yield. This synthesis and other reactions herein described illustrate the suitability of the mercury(II)-catalyzed isomerizations for the synthesis of a variety of furanoid natural products under extremely mild conditions.

## Experimental Section

$^1$H and $^{13}$C NMR spectra were obtained at 250 and 68.8 MHz and were recorded in $CDCl_3$. Mass spectra were obtained in the chemical-ionization (CI) or electron-impact (EI) mode, as specified. Thin-layer chromatography was performed on precoated 0.2 mm aluminum-backed silica plates, and products were visualized under ultraviolet light or developed using cerium(IV) sulfate spray. Column chromatography was performed on 70−230 mesh silica gel under gravity. Petroleum ether (40−60 fraction) and ethyl acetate were distilled prior to use. THF was freshly distilled from sodium benzophenone ketyl prior to use. Evaporation refers to the removal of solvent under reduced pressure.

Diastereoisomeric ratios of 2,3-epoxy alcohols were determined from $^1$H NMR spectra of the products prior to chromatography. Compounds **2c** and **3c** were prepared according to literature procedures.[26]

**Preparation of α-Alkynyl Allylic Alcohols 2: General Procedure A. 2-(1-Cyclopentenyl)-3-heptyn-2-ol (2a).** A stirred solution of 1-pentyne (2.97 g, 43.6 mmol) in THF (100 mL) was treated dropwise at 20 °C with a solution of *n*-butyllithium (18.9 mL, 47.2 mmol, 2.5 M in hexanes). The mixture was stirred for 30 min and then treated with a solution of 1-acetyl-1-cyclopentene (4.00 g, 36.3 mmol) in THF (100 mL). After a further 3 h, the mixture was poured into saturated aqueous ammonium chloride (100 mL). The aqueous layer was separated and extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2a** as a pale yellow oil (3.92 g, 61%): IR (neat) 3390, 2240 cm$^{-1}$; $^1$H NMR δ 5.20 (1H, m) 2.58−2.20 (5H, m), 2.01 (2H, t, $J$ = 6.0 Hz), 1.73 (2H, m), 1.36 (3H, s), 1.30 (2H, m), 0.55 (3H, t, $J$ = 6 Hz); $^{13}$C NMR δ 148.2 (s), 124.9 (d), 83.6 (s), 83.5 (s), 67.3 (s), 32.3 (t), 31.1 (t), 29.2 (q), 23.7 (t), 22.1 (t), 20.3 (t), 13.4 (q); LRMS (EI) *m*/*z* 177 (M-1, 21), 163 (100), 149 (72); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1364.

**2-(1-Cyclopentenyl)-5-(tetrahydropyran-2-yloxy)-3-pentyn-1-ol (2b).** Following general procedure A above, 1-acetyl-1-cyclopentene (3.60 g, 32.7 mmol) when treated with a solution of [3-(tetrahydropyran-2-yloxy)-1-propynyl]lithium [prepared from 3-(tetrahydropyran-2-yloxy)-1-propyne (5.52 g, 39.0 mmol) and *n*-butyllithium (17.0 mL, 42.5 mmol, 2.5 M) at −10 °C] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2b** as a pale yellow oil (5.83 g, 71%): IR (neat) 3425, 1705 cm$^{-1}$; $^1$H NMR δ 5.79 (1H, m), 4.82 (1H, t, $J$ = 3 Hz), 4.28 (2H, $q_{AB}$), 3.82 (1H, m), 2.53 (1H, m), 2.48−2.21 (4H, m), 1.92−1.42 (9H, m), 1.57 (3H, s); $^{13}$C NMR δ 147.3 (s), 125.2 (d), 96.3 (d), 89.0 (s), 78.8 (s), 66.8 (s), 61.6 (t), 54.0 (t), 32.0 (t), 30.9 (t), 30.0 (t), 28.7 (t), 25.1 (t), 23.5 (t), 18.7 (q); LRMS (EI) *m*/*z* 232 (M − 18, 35), 148 (32), 130, (27), 105 (48), 85, (100); HRMS calcd for $C_{15}H_{20}O_2$ (M − $H_2O$) 232.1463, found 232.1469.

**2-(1-Cyclohexenyl)-3-nonyn-2-ol (2d).** Following general procedure A above, 1-(1-oxoethyl)-1-cyclohexene (2.00 g, 16.1 mmol) when treated with a solution of 1-heptynyllithium [prepared from 1-heptyne (1.86 g, 19.3 mmol) and *n*-butyllithium (8.41 mL, 21.0 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2d** as a pale yellow oil (3.30 g, 93%): IR (neat) 3390, 2240 cm$^{-1}$; $^1$H NMR δ 6.02 (1H, m), 2.18 (2H, t, $J$ = 7 Hz), 2.17−2.02 (4H, m), 1.90 (1H, bs), 1.58−1.41 (6H, m), 1.51 (3H, s), 1.40−1.22 (4H, m), 0.88 (3H, t, $J$ = 7 Hz); $^{13}$C NMR δ 140.7 (d), 118.1 (s), 83.5 (s), 82.9 (s), 70.6 (s), 31.0 (t), 29.1 (q), 28.4 (t), 25.0 (t), 23.9 (t), 22.9 (t), 22.2 (t), 22.1 (t), 18.6 (t), 13.9 (q); LRMS (EI) *m*/*z* 219 (M-1, 52), 205 (86), 163 (78), 149 (24), 91 (39), 43 (100); HRMS calcd for $C_{14}H_{21}O$ (M − $CH_3$) 205.1592, found 205.1591.

**2-(1-Cyclohexenyl)-1,4-diphenyl-3-butyn-2-ol (2f).** Following general procedure A above, 1-(1-oxo-2-phenylethyl)-1-

(34) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

cyclohexene (3.00 g, 20.3 mmol) when treated with a solution of (1-phenylethynyl)lithium [prepared from phenylacetylene (1.84 g, 18.0 mmol) and *n*-butyllithium (7.80 mL, 19.50 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2f** as a yellow oil (2.91 g, 64%): IR (neat) 3400, 2240 $cm^{-1}$; $^1H$ NMR $\delta$ 7.32 (10H, m), 6.06 (1H, m), 3.10 (2H, $q_{AB}$), 2.48 (2H, m), 2.20 (1H, s), 2.06 (2H, m), 1.75−1.55 (4H, m); $^{13}C$ NMR $\delta$ 138.7 (s), 136.3 (s), 131.5 (d), 130.9 (d), 128.2 (d), 128.2 (d), 127.8 (d), 126.8 (d), 123.4 (d), 122.8 (s), 91.1 (s), 86.7 (s), 74.2 (s), 47.3 (t), 25.1 (t), 24.5 (t), 22.9 (t), 22.2 (t); HRMS calcd for $C_{22}H_{22}O$ 302.1671, found 302.1676.

**2-(2-Methyl-1-cyclohexenyl)-4-phenyl-3-butyn-2-ol (2g).** Following general procedure A above, 1-(1-oxoethyl)-2-methyl-1-cyclohexene (0.50 g, 3.60 mmol) when treated with a solution of (1-phenylethynyl)lithium [prepared from phenylacetylene (0.55 g, 5.40 mmol) and *n*-butyllithium (2.30 mL, 5.75 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2g** as a pale yellow oil (0.37 g, 43%): IR (neat) 3540, 2220 $cm^{-1}$; $^1H$ NMR $\delta$ 7.48 (2H, m), 7.38 (3H, m), 2.29−1.92 (4H, m), 1.96 (3H, s), 1.68 (3H, s), 1.56 (5H, m); $^{13}C$ NMR $\delta$ 132.9 (s), 131.5 (d), 130.4 (s), 128.2 (d), 128.1 (d), 123.1 (s), 93.9 (s), 83.5 (s), 70.5 (s), 33.7 (t), 29.6 (q), 26.7 (t), 23.4 (t), 22.7 (t), 21.3 (q); HRMS calcd for $C_{17}H_{20}O$ 240.1514, found 240.1508.

**7-(1-Cycloheptenyl)-5-tridecyn-7-ol (2h).** Following general procedure A above, 1-(1-oxoheptyl)-1-cycloheptene (1.50 g, 7.20 mmol) when treated with a solution of 1-hexynyllithium [prepared from 1-hexyne (0.71 g, 8.65 mmol) and *n*-butyllithium (4.0 mL, 10.0 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2h** as a pale yellow oil (1.38 g, 66%): $^1H$ NMR $\delta$ 6.19 (1H, t, $J$ = 6.5 Hz), 2.28−2.12 (4H, m), 2.22 (2H, t, $J$ = 7 Hz), 1.81−1.21 (21H, m), 0.86 (3H, t, $J$ = 7 Hz), 0.73 (3H, t, $J$ = 6.5 Hz); $^{13}C$ NMR $\delta$ 146.2 (s), 126.8 (d), 85.8 (s), 82.5 (s), 75.0 (s), 40.4 (t), 32.9 (t), 31.8 (t), 30.9 (t), 29.3 (t), 28.5 (t), 28.1 (t), 27.2 (t), 26.8 (t), 24.6 (t), 22.6 (t), 22.0 (t), 18.4 (t), 14.1 (q), 13.6 (q); LRMS (EI) *m*/*z* 290 (M, 21), 209 (71), 181 (91), 112 (100); HRMS calcd for $C_{20}H_{34}O$ 290.2610, found 290.2608.

**3-(1-Cyclooctenyl)-1-phenyl-1-octyn-3-ol (2i).** Following general procedure A above, 1-(1-oxohexyl)-1-cyclooctene (2.51 g, 12.0 mmol) when treated with a solution of (1-phenylethynyl)lithium [prepared from phenylacetylene (2.65 g, 26.0 mmol) and *n*-butyllithium (11.3 mL, 28.3 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **2i** as a pale yellow oil (5.80 g, 87%): IR (neat) 3465 $cm^{-1}$; $^1H$ NMR $\delta$ 7.50−7.20 (5H, m), 6.07 (1H, t, $J$ = 7.5 Hz), 2.50 (2H, t, $J$ = 7 Hz), 2.21 (2H, m), 2.01 (1H, bs), 1.86−1.40 (4H, m), 1.38−1.15 (12H, m), 0.89 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 142.4 (s), 131.8 (d), 128.5 (d), 128.4 (d), 125.6 (d), 123.3 (s), 92.4 (s), 85.3 (s), 75.3 (s), 41.3 (t), 32.1 (t), 31.0 (t), 29.1 (t), 26.7 (t), 26.5 (t), 26.2 (t), 26.1 (t), 24.5 (t), 22.8 (t), 14.3 (q); LRMS (EI) *m*/*z* 310 (M, 6), 292 (19), 84 (100); HRMS calcd for $C_{22}H_{30}O$ 310.2297, found 310.2289.

**6-(1-Cyclododecenyl)-4-dodecyn-5-ol (2j).** Following general procedure A above, 1-(1-oxoheptyl)-1-cyclododecene (1.50 g, 5.39 mmol) when treated with a solution of 1-pentynyllithium [prepared from 1-pentyne (0.45 g, 6.61 mmol) and *n*-butyllithium (2.80 mL, 7.00 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2j** as a pale yellow oil (0.93 g, 50%): $^1H$ NMR $\delta$ 5.88 (1H, t, $J$ = 8 Hz), 2.20 (2H, t, $J$ = 7 Hz), 2.00 (4H, m), 1.83 (1H, bs), 1.77−1.16 (28H, m), 0.98 (3H, t, $J$ = 7 Hz), 0.86 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 141.7 (s), 127.7 (d), 85.7 (s), 83.4 (s), 75.1 (s), 42.2 (t), 31.8 (t), 29.3 (t), 28.4 (t), 26.9 (t), 26.2 (t), 26.0 (t), 25.8 (t), 24.8 (t), 24.7 (t), 24.6 (t), 24.5 (t), 23.4 (t), 22.6 (t), 22.4 (t), 22.1 (t), 20.7 (t), 14.0 (q), 13.5 (q); LRMS (EI) *m*/*z* 346 (M, 7), 328 (28), 285 (28), 261 (100), 181 (36); HRMS calcd for $C_{24}H_{42}O$ 346.3236, found 346.3231.

**2-(1-Cyclododecenyl)-3-nonyn-2-ol (2k).** Following general procedure A above, 1-acetyl-1-cyclododecene[21,22] (0.80 g, 3.84 mmol) when treated with a solution of 1-heptynyllithium [prepared from 1-heptyne (0.45 g, 4.67 mmol) and *n*-butyllithium (2.0 mL, 5.00 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2k** as a pale yellow oil (0.79 g, 68%): IR (neat) 3450, 2240 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.88 (1H, t, $J$ = 8 Hz), 2.37−1.98 (4H, m), 2.23 (2H, t, $J$ = 7 Hz), 1.91 (1H, s), 1.73−1.20 (22H, m), 1.56 (3H, s), 0.91 (3H, s); $^{13}C$ NMR $\delta$ 142.8 (s), 126.1 (d), 84.2 (s), 71.1 (s), 71.1 (s), 30.9 (t), 30.9 (t), 28.1 (t), 26.7 (t), 25.9 (t), 25.7 (t), 25.5 (t), 25.2 (t), 24.9 (t), 24.6 (t), 24.4 (t), 23.2 (t), 22.3 (t), 22.0 (t), 18.5 (q), 13.7 (q); LRMS (EI) *m*/*z* 304 (M, 16), 289 (25), 247 (32), 208 (100), 183 (47), 137 (55); HRMS calcd for $C_{21}H_{36}O$ 304.2766, found 304.2758.

**2-Undecen-5-yn-2-ol (2l).** Following general procedure A (above), 2-butenal (3.5 g, 0.05 mol) when treated with a solution of 1-heptynyllithium [prepared from 1-heptyne (5.75 g, 0.06 mol) and *n*-butyllithium (26.0 mL, 65.0 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2l** as a pale yellow oil (6.37 g, 77%): IR (neat) 3350, 2220 $cm^{-1}$; $^1H$ NMR $\delta$ 5.87 (1H, ddq, $J$ = 15, 6, 1.5 Hz), 5.60 (1H, ddq, $J$ = 15, 6, 1 Hz), 4.77 (1H, d, $J$ = 6 Hz), 2.22 (2H, dt, $J$ = 7, 1.5 Hz), 1.87 (1H, bs), 1.57 (3H, dd, $J$ = 6, 1.5 Hz), 1.52 (2H, m), 1.27 (4H, m), 0.89 (3H, t, $J$ = 6.5 Hz); $^{13}C$ NMR $\delta$ 130.9 (d), 128.1 (d), 86.7 (s), 79.6 (s), 63.0 (d), 31.0 (t), 28.3 (t), 22.1 (t), 18.7 (t), 17.4 (q), 13.9 (q); HRMS calcd for $C_{11}H_{18}O$ 166.1358, found 166.1364.

**3-Methyl-5-phenyl-1-penten-4-yn-3-ol (2m).** Following general procedure A above, 3-buten-2-one (1.00 g, 14.3 mmol) when treated with a solution of (1-phenylethynyl)lithium [prepared from phenylacetylene (1.74 g, 17.0 mmol) and *n*-butyllithium (7.42 mL, 18.6 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **2m** as a pale yellow oil (1.86 g, 76%): IR (liquid film) 3370, 2190 $cm^{-1}$; $^1H$ NMR $\delta$ 7.45 (2H, m), 7.32 (3H, m), 6.06 (1H, dd, $J$ = 17, 10 Hz), 5.58 (1H, dd, $J$ = 17, 1 Hz), 5.17 (1H, dd, $J$ = 10, 1 Hz), 2.23 (1H, bs), 1.51 (3H, s); $^{13}C$ NMR $\delta$ 142.1 (d), 131.7 (d), 128.7 (d), 128.4 (d), 122.6 (s), 113.7 (t), 91.0 (s), 84.8 (s), 68.7 (s), 30.1 (q); HRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0880.

**4-Methyl-2-nonen-5-yn-4-ol (2n)**. Following general procedure A above, 3-penten-2-one (1.0 g, 11.9 mmol) when treated with a solution of 1-pentynyllithium [prepared from 1-pentyne (0.97 g, 14.3 mmol) and *n*-butyllithium (6.20 mL, 15.5 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **2n** as a yellow oil (1.43 g, 79%): IR (neat) 3370, 2230 $cm^{-1}$; $^1H$ NMR $\delta$ 5.92 (1H, dq, $J$ = 16, 7 Hz), 5.56 (1H, dq, $J$ = 16, 1 Hz), 2.11 (2H, t, $J$ = 7 Hz), 1.69 (3H, dd, $J$ = 7, 1 Hz), 1.42−1.56 (3H, m), 1.51 (3H, s), 0.95 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 135.8 (d), 124.7 (d), 84.8 (s), 83.0 (s), 72.0 (s), 30.6 (q), 22.1 (t), 20.6 (t), 17.2 (q), 13.4 (q); LRMS (EI) *m*/*z* 137 (M-15, 100), 123 (90); HRMS calcd for $C_{10}H_{16}O$ 152.1201, found 152.1209.

**1-Phenyl-3-ethyl-4-hexen-1-yn-3-ol (2o).** Following general procedure A above, 4-hexen-3-one (2.02 g, 20.4 mmol) when treated with a solution of (1-phenylethynyl)lithium [prepared from phenylacetylene (2.50 g, 24.5 mmol) and *n*-butyllithium (14.7 mL, 36.8 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2o** as a pale yellow oil (2.74 g, 67%): IR (neat) 3365 $cm^{-1}$; $^1H$ NMR $\delta$ 7.45 (2H, m), 7.33 (3H, m), 6.05 (1H, dd, $J$ = 15, 6.5 Hz), 5.57 (1H, dd, $J$ = 15, 1.5 Hz), 2.53 (1H, bs), 1.82−1.72 (2H, m), 1.73 (3H. dd, $J$ = 6.5, 1.5 Hz), 1.25 (3H, t, $J$ = 7.5 Hz); $^{13}C$ NMR $\delta$ 134.2 (d), 131.6 (d), 128.2 (d), 128.2 (d), 126.4 (d), 122.8 (s), 90.5 (s), 85.6 (s), 72.2 (s), 35.7 (t), 17.3 (q), 8.8 (q); LRMS (EI) *m*/*z* 200 (M, 10), 185 (11), 171 (100); HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1197.

**4-Ethyl-2-undecen-5-yn-4-ol (2p).** Following general procedure A above, 4-hexen-3-one (1.01 g, 10.2 mmol) when treated with a solution of 1-heptynyllithium [prepared from 1-heptyne (1.18 g, 12.27 mmol) and *n*-butyllithium (4.90 mL, 12.25 mmol, 2.5 M)] gave a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **2p** as a light yellow oil (1.33 g, 67%): IR (neat)

3385, 2235 $cm^{-1}$; $^1H$ NMR $\delta$ 5.98 (1H, dq, $J$ = 15, 6.5 Hz), 5.51 (1H, dq, $J$ = 15, 1.5 Hz), 2.24 (2H, t, $J$ = 7 Hz), 2.12 (1H, bs), 1.73 (3H, dd, $J$ = 6.5, 1.5 Hz), 1.80−1.30 (8H, m), 0.97 (3H, t, $J$ = 7.5 Hz), 0.91 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 134.7 (d), 126.0 (d), 86.3 (s), 81.4 (s), 72.0 (s), 35.8 (t), 31.0 (t), 28.5 (t), 22.1 (t), 18.6 (t), 17.3 (q), 13.9 (q), 8.9 (q); LRMS (EI) *m/z* 176 (M-18, 13), 165 (100); HRMS calcd for $C_{13}H_{20}$ (M − $H_2O$) 176.1565, found 176.1561.

**Preparation of 2,3-Epoxy Alcohols. General Procedure B. 2-(1,2-Epoxycyclopentyl)-3-heptyn-2-ol (3a).** A solution of **2a** (3.00 g, 16.9 mmol) and vanadyl acetylacetonate (20 mg) in benzene (100 mL) was treated dropwise at room temperature with a 70% aqueous solution of *tert*-butyl hydroperoxide (4.34 g, 33.7 mmol). The mixture was stirred at 20 °C and judged to be complete (TLC) after 4 h. The mixture was washed with saturated sodium sulfite solution (50 mL), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give *syn*-**3a** as a colorless oil (1.56 g, 48%) [IR (neat) 3470, 2245 $cm^{-1}$; $^1H$ NMR $\delta$ 3.48 (1H, s), 2.77 (1H, bs), 2.13 (2H, t, $J$ = 7 Hz), 2.04−1.91 (2H, m), 1.65−1.50 (6H, m), 1.49 (3H, s), 0.92 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 84.3 (s), 82.0 (s), 73.1 (s), 65.9 (s), 61.3 (d), 27.3 (t), 26.2 (t), 26.1 (t), 21.9 (t), 20.5 (t), 19.4 (q), 13.3 (q); LRMS (EI) *m/z* 194 (M, 34), 111 (100); HRMS calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1299] and a mixture of *syn*- and *anti*-**3a** as a colorless oil (0.57 g, 17%).

**2-(1,2-Epoxycyclopentyl)-5-(tetrahydropyran-2-yloxy)-3-pentyn-2-ol (3b).** Following general procedure B above, **2b** (1.80 g, 14.4 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3b** as a light yellow oil (1.13 g, 59%): IR (neat) 3430, 2225 $cm^{-1}$; $^1H$ NMR $\delta$ 4.80 (1H, t, $J$ = 3.5, Hz), 4.34 (1H, d, $J$ = 15 Hz), 4.24 (1H, d, $J$ = 15 Hz), 3.82 (1H, m), 3.51 (2H, m), 2.11−1.42 (13H, m), 1.54 (3H, s); LRMS (EI) *m/z* 265 (M − 1, 1), 164 (4), 85 (100); HRMS calcd for $C_{10}H_{12}O_2$ (M − $C_5H_{10}O_2$) 164.0837, found 164.0841.

**2-(1,2-Epoxycyclohexyl)-3-nonyn-2-ol (3d).** Following general procedure B above, **2d** (1.50 g, 6.81 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3d** as a colorless oil (1.01 g, 63%): IR (neat) 3440, 2940, 2860, 2125 $cm^{-1}$; $^1H$ NMR $\delta$ 3.32 (1H, m), 2.60 (1H, m), 2.16 (2H, t, $J$ = 7 Hz), 1.95 (2H, m), 1.55−1.15 (12H, m), 1.42 (3H, s), 0.86 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 84.4 (s), 81.5 (s), 67.8 (s), 64.3 (s), 55.2 (d), 31.0 (t), 28.2 (t), 25.6 (q), 25.0 (t), 24.5 (t), 22.4 (t), 20.7 (t), 20.5 (t), 18.5 (t), 13.9 (q); LRMS (EI) *m/z* 236 (M, 12), 218 (13), 98 (100); HRMS calcd for $C_{13}H_{19}O_2$ (M − $C_2H_5$) 207.1385, found 207.1378.

**2-(1,2-Epoxycyclohexyl)-1,4-diphenyl-3-butyn-2-ol (3f).** Following general procedure B above, **2f** (1.50 g, 4.96 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3f** as a colorless oil (0.83 g, 52%): $^1H$ NMR $\delta$ 7.50−7.22 (10H, m), 3.20 (2H, $q_{AB}$, $J$ = 14 Hz), 3.02 (1H, m), 2.88 (1H, bs), 2.14 (2H, m), 1.89 (1H, m), 1.70−1.20 (5H, m); $^{13}C$ NMR $\delta$ 135.7 (s), 131.7 (d), 130.9 (d), 128.4 (d), 128.2 (d), 127.9 (d), 126.9 (d), 122.6 (s), 89.8 (s), 85.5 (s), 71.5 (s), 62.9 (s), 55.9 (d), 44.3 (t), 25.2 (t), 24.3 (t), 20.4 (t), 19.0 (t); LRMS (EI) *m/z* 318 (M, 4), 227 (18), 129 (100); HRMS calcd for $C_{15}H_{15}O_2$ (M − $CH_2$-Ph) 227.1072, found 227.1067.

**2-(1,2-Epoxy-2-methylcyclohexyl)-4-phenyl-3-butyn-2-ol (3g).** Following general procedure B above, **2g** (0.3 g, 1.17 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3g** as a colorless oil (0.21 g, 66%): $^1H$ NMR $\delta$ 7.40 (2H, m), 7.25 (3H, m), 3.01 (1H, bs), 2.03 (2H, m), 1.75−1.08 (6H, m), 1.55 (3H, s), 1.52 (3H, s); $^{13}C$ NMR $\delta$ 131.6 (d), 128.1 (d), 128.1 (d), 122.8 (s), 91.7 (s), 83.6 (s), 69.6 (s), 68.6 (s), 63.8 (s), 33.9 (t), 27.6 (t), 24.9 (q), 21.9 (t), 20.3 (q), 19.6 (t); LRMS (EI) *m/z* 256 (M, 1), 145 (83), 112 (100); HRMS calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1457.

**7-(1,2-Epoxycycloheptyl)-5-tridecyn-7-ol (3h).** Following general procedure B above, **2h** (1.20 g, 4.13 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3h** as a colorless oil (0.73 g, 58%): IR (neat) 3445, 2235 $cm^{-1}$; $^1H$ NMR $\delta$ 3.33 (1H, dd, $J$ = 6, 1 Hz), 2.45 (1H, bs), 2.30 (1H, dd, $J$ = 14, 6 Hz), 2.16 (2H, t, $J$ = 7 Hz), 2.12 (1H, m), 1.83−1.13 (22H, m), 0.87 (3H, t, $J$ = 6 Hz), 0.84 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 85.0 (s), 81.4 (s), 72.2 (s), 66.7 (s), 57.6 (d), 38.1 (t), 31.7 (t), 31.0 (t), 30.7 (t), 29.4 (t), 28.8 (t), 27.8 (t), 24.2 (t), 23.6 (t), 23.4 (t), 22.5 (t), 21.8 (t), 18.3 (t), 14.0 (q), 13.5 (q); LRMS (EI) *m/z* 306 (M, 12), 112 (100); HRMS calcd for $C_{20}H_{34}O_2$ 306.2559, found 306.2554.

**3-(1,2-Epoxycyclooctyl)-1-phenyl-1-octyn-3-ol (3i).** Following general procedure B above, **2h** (1.50 g, 4.84 mmol) afforded a residue that was purified by column chromatography on silica (24:1 petroleum ether/ethyl acetate) to give *syn*-**3i** as a colorless oil (0.65 g, 41%) [IR (neat) 3450, 2225 $cm^{-1}$; $^1H$ NMR $\delta$ 7.45 (2H, m), 7.28 (3H, m), 3.22 (1H, m), 2.90 (1H, bs), 2.17 (1H, m), 2.25 (1H, m), 1.96−1.25 (18H, m), 0.95 (3H, t, $J$ = 6 Hz); $^{13}C$ NMR $\delta$ 131.7 (d), 128.3 (d), 128.2 (d), 122.8 (s), 90.2 (s), 85.5 (s), 73.1 (s), 65.5 (s), 58.8 (d), 39.3 (t), 32.2 (t), 28.8 (t), 27.2 (t), 26.4 (t), 26.0 (t), 24.6 (t), 24.6 (t), 24.1 (t), 22.7 (t), 14.1 (q); LRMS (EI) *m/z* 326 (M, 41), 201 (100); HRMS calcd for $C_{22}H_{30}O_2$ 326.2246, found 326.2241] *anti*-**3i** as a pale yellow oil (0.32 g, 20%) by $^1H$ NMR ($CDCl_3$), and a mixture of *syn*- and *anti*-**3i** as a pale yellow oil (0.17 g, 11%).

**6-(1,2-Epoxycyclododecyl)-4-dodecyn-5-ol (3j).** Following general procedure B above, **2j** (0.35 g, 1.01 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3j** as a colorless oil (0.28 g 77%): IR (neat) 3450, 2240 $cm^{-1}$; $^1H$ NMR $\delta$ 3.09 (m, 1 H), 2.74 (1H, bs), 2.18 (2H, t, $J$ = 6 Hz), 1.75−1.25 (32H, m), 0.94 (3H, t, $J$ = 7 Hz), 0.82 (3H, t, $J$ = 6 Hz); $^{13}C$ NMR $\delta$ 85.2 (s), 81.2 (s), 71.1 (s), 67.6 (s), 59.7 (d), 39.2 (t), 31.7 (t), 29.5 (t), 27.0 (t), 26.8 (t), 26.4 (t), 26.4 (t), 25.4 (t), 25.1 (t), 23.9 (t), 23.9 (t), 23.2 (t), 22.8 (t), 22.5 (t), 22.0 (t), 21.9 (t), 20.6 (t), 14.0 (q), 13.4 (q); LRMS (EI) *m/z* 362 (M, 15), 182 (100); HRMS calcd for $C_{24}H_{42}O_2$ 362.3175, found 362.3175.

**2-(1,2-Epoxycyclododecyl)-3-nonyn-2-ol (3k).** Following general procedure B above, **2k** (0.40 g, 1.31 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3k** as a colorless oil (0.29 g, 69%): IR (neat) 3480, 2240 $cm^{-1}$; $^1H$ NMR $\delta$ 3.05 (1H, m), 2.82 (1H, bs), 2.15 (2H, t, $J$ = 7 Hz), 1.72−1.15 (26H, m), 1.45 (3H, s), 0.83 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 84.8 (s), 81.8 (s), 68.1 (s), 67.7 (s), 59.8 (d), 31.0 (t), 28.3 (t), 27.2 (q), 27.1 (t), 26.9 (t), 26.7 (t), 26.5 (t), 25.7 (t), 25.1 (t), 24.0 (t), 23.5 (t), 22.9 (t), 22.2 (t), 21.9 (t), 18.6 (t), 14.0 (q); LRMS (EI) *m/z* 320 (M, 28), 165 (100); HRMS calcd for $C_{21}H_{36}O_2$ 320.2715, found 320.2709.

**2,3-Epoxy-5-undecyn-4-ol (3l).** Following general procedure B above, **2l** (2.00 g, 12.0 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3l** as a colorless oil (1.31 g, 69%): IR (neat) 3410, 2240 $cm^{-1}$; $^1H$ NMR $\delta$ 4.57 and 4.29 (1H, m), 3.18 and 3.06 (1H, m), 2.97 and 2.75 (1H, m), 2.29 (1H, m), 2.21 (2H, dt, $J$ = 6.5, 1.5 Hz), 1.52 (2H, m), 1.41−1.20 (7H, m), 0.91 (3H, t, $J$ = 7 Hz); $^{13}C$ NMR $\delta$ 87.3 (s), 86.9 (s), 77.3 (s), 76.7 (s), 62.4 (d), 61.8 (d), 61.1 (d), 61.0 (d), 52.6 (d), 52.2 (d), 31.0 (t), 28.1 (t), 22.1 (t), 18.6 (t), 16.9 (q), 14.1 (q), 13.9 (q); LRMS (EI) *m/z* 181 (M-1, 38), 81 (100); HRMS calcd for $C_{11}H_{17}O_2$ (M − H) 181.1229, found 181.1232.

**1,2-Epoxy-3-methyl-5-phenyl-4-pentyn-3-ol (3m).** Following general procedure B above, **2m** (4.00 g, 23.3 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **3m** as a colorless oil (2.87 g, 66%): IR (neat) 3425, 2240 $cm^{-1}$; $^1H$ NMR $\delta$ 7.45 (2H, m), 7.27 (3H, m), 3.29 and 3.21 (1H, dd, $J$ = 3, 4 Hz), 3.01 and 2.92 (1H, dd, $J$ = 5, 3 Hz), 2.86 and 2.78 (1H, dd, $J$ = 5, 4 Hz), 2.51 (1H, bs), 1.67 and 1.60 (3H, s); $^{13}C$ NMR $\delta$ 131.8 (d), 128.6 (d), 128.6 (d), 128.3 (d), 123.3 (s), 123.2 (s), 90.2 (s), 88.4 (s), 84.9 (s), 84.0 (s), 67.2 (s), 65.8 (s), 57.8 (d), 57.7 (d), 45.2 (t), 44.2 (t), 27.3 (q), 25.7 (q); LRMS (EI) *m/z* 188 (M, 12), 145 (100); HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0833.

**2,3-Epoxy-4-methyl-5-nonyn-4-ol (3n).** Following general procedure B above, **2n** (2.01 g, 13.2 mmol) afforded a residue that was purified by column chromatography on silica

(9:1 petroleum ether/ethyl acetate) to give **3n** as a colorless oil (1.48 g, 67%): $^1$H NMR $\delta$ 3.16 and 3.09 (1H, dq, $J$ = 5, 2 Hz), 2.83 and 2.79 (1H, d, $J$ = 2 Hz), 2.54 (1H, bs), 2.12 (2H, t, $J$ = 7 Hz), 1.48 and 1.44 (3H, s), 1.32 and 1.30 (3H, d, $J$ = 5 Hz), 1.20−1.00 (2H, m), 0.92 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 85.0 (s), 84.3 (s), 81.6 (s), 80.2 (s), 66.3 (s), 65.5 (s), 64.9 (d), 64.8 (d), 52.7 (d), 52.2 (d), 27.3 (q), 26.0 (q), 21.8 (t), 20.4 (t), 16.8 (q), 13.3 (q); LRMS (EI) *m*/*z* 167 (M − 1, 85), 125 (87), 58 (100); HRMS calcd for $C_{10}H_{16}O_2$ 168.1147, found 168.1150.

**1-Phenyl-4,5-epoxy-3-ethyl-1-hexyn-3-ol (3o).** Following general procedure B above, **2n** (1.20 g, 6.00 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give *syn*-**3o** as a colorless oil (0.18 g, 14%) [IR (neat) 3420, 2240 cm$^{-1}$; $^1$H NMR $\delta$ 7.42 (2H, m), 7.28 (3H, m), 3.19 (1H, dq, $J$ = 5, 2 Hz), 2.96 (1H, d, $J$ = 2 Hz), 2.63 (1H, m), 1.83 (2H, dq, $J$ = 7, 2.5 Hz), 1.33 (3H, d, $J$ = 5 Hz), 1.12 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 131.7 (d), 128.4 (d), 128.1 (d), 122.4 (s), 89.4 (s), 84.7 (s), 69.1 (s), 64.1 (d), 51.5 (d), 32.0 (t), 16.8 (q), 8.1 (q); LRMS (EI) *m*/*z* 216 (M, 6), 159 (100)], *anti*-**3o** as a pale yellow oil (0.14 g, 11%) [IR (neat) 3405, 2218 cm$^{-1}$; $^1$H NMR $\delta$ 7.44 (2H, m), 7.28 (3H, m), 3.28 (1H, dq, $J$ = 5.5, 2 Hz), 2.90 (1H, d, $J$ = 2 Hz), 2.68 (1H, m), 1.85 (2H, m), 1.35 (3H, d, $J$ = 5.5 Hz), 1.10 (3H, t, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 131.8 (d), 128.5 (d), 128.4 (d), 122.2 (s), 87.5 (s), 85.7 (s), 70.7 (s), 63.8 (d), 52.9 (d), 33.2 (t), 16.9 (q), 8.4 (q); LRMS (EI) *m*/*z* 216 (30), 187 (32), 159 (100), 129 (60), 115 (11), 57 (34); HRMS calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1157], and a mixture of *syn*- and *anti*-**3o** as a pale yellow oil (0.53 g, 41%).

**2,3-Epoxy-4-ethylundec-5-yn-4-ol (3p).** Following general procedure B above, **2o** (1.50 g, 7.73 mmol) afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give *syn*-**3p** as a colorless oil (0.58 g, 36%) [IR (neat) 3450, 2240 cm$^{-1}$; $^1$H NMR $\delta$ 3.12 (1H, dq, $J$ = 5, 2 Hz), 2.82 (1H, d, $J$ = 2 Hz), 2.50 (1H, bs), 2.06 (2H, t, $J$ = 7 Hz), 1.69 (2H, dq, $J$ = 7 Hz), 1.59−1.15. (6H, m), 1.31 (3H, d, $J$ = 5 Hz), 1.03 (3H, t, $J$ = 7 Hz), 0.86 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 85.5 (s), 80.5 (s), 68.8 (s), 64.3 (d), 51.5 (d), 32.2 (t), 31.0 (t), 28.3 (t), 22.1 (t), 18.5 (t), 16.8 (q), 13.9 (q), 8.1 (q); LRMS (EI) *m*/*z* 181 (M-29, 11), 153 (100); HRMS calcd for $C_{11}H_{17}O_2$ (M−$C_2H_5$) 181.1229, found 181.1225], *anti*-**3p** as a colorless oil (0.37 g, 23%) [$^1$H NMR $\delta$ 3.13 (1H, dq, $J$ = 5, 1 Hz), 2.74 (1H, d, $J$ = 1 Hz), 2.53 (1H, bs), 2.13 (2H, t, $J$ = 6 Hz), 1.80−1.60 (2H, m), 1.54−1.20 (6H, m), 1.28 (3H, d, $J$ = 5 Hz), 1.00 (3H, t, $J$ = 7 Hz), 0.83 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 86.4 (t), 78.6 (t), 70.1 (t), 63.9 (t), 52.5 (t), 33.2 (t), 30.8 (t), 28.1 (t), 22.0 (t), 18.4 (t), 16.8 (t), 13.8 (t), 8.3 (t)], and a mixture of *syn*- and *anti*-**3p** as a colorless oil (0.19 g, 12%).

**Mercury(II)-Catalyzed Isomerization of 2,3-Epoxy Alcohols. General Procedure C. 4-[(3-Methyl-5-propyl)-2-furyl]butanal (4a).** A solution of **3a** (300 mg, 1.54 mmol) in acetone (30 mL) was treated at 20 °C with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.25 mL). The mixture was stirred for 10 min and neutralized by the addition of solid sodium hydrogen carbonate. The resulting mixture was filtered and evaporated to give a residue that was taken up in water (5 mL) and ether (10 mL). The layers were separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Purification of the residue by column chromatography on silica (19:1 petroleum ether/ethyl acetate) gave **4a** as an oil (254 mg, 85%): IR (neat) 1730 cm$^{-1}$; $^1$H NMR $\delta$ 9.65 (1H, t, $J$ = 1 Hz), 5.71 (1H, s), 2.56 (2H, t, $J$ = 6 Hz), 2.47 (2H, t, $J$ = 6 Hz), 2.40 (2H, dt, $J$ = 7, 1 Hz), 1.92 (3H, s), 1.70−1.50 (4H, m), 0.92 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 202.2 (d), 153.8 (s), 147.6 (s), 114.9 (s), 107.8 (d), 42.9 (t), 29.9 (t), 24.9 (t), 21.4 (t), 21.2 (t), 13.7 (q), 9.7 (q); LRMS (EI) *m*/*z* 194 (M, 19), 137 (100); HRMS calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1300.

**4-[[3-Methyl-5-(tetrahydropyran-2-yloxy)methyl]-2-furyl]butanal (4b).** Following general procedure C above, *syn*-/*anti*-**3b** (200 mg, 0.55 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.5 mL) for 35 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **4b** as a pale yellow oil (109 mg, 55%): IR (neat) 1730 cm$^{-1}$; $^1$H NMR $\delta$ 9.67 (1H, t, $J$ = 1.5 Hz), 6.08 (1H, s), 4.67 (1H, t, $J$ = 3.5 Hz), 4.50 (2H, $q_{AB}$, $J$ = 18 Hz), 3.87 (1H, m), 3.51 (1H, m), 2.58 (2H, t, $J$ = 6 Hz), 2.40 (2H, dt, $J$ = 7, 1.5 Hz), 1.89 (3H, s), 1.80−1.40 (8H, m); $^{13}$C NMR $\delta$ 202.0 (d), 150.1 (s), 149.1 (s), 115.3 (s), 112.6 (d), 97.0 (d), 61.9 (t), 60.6 (t), 42.9 (t), 30.3 (t), 25.3 (t), 24.9 (t), 21.0 (t), 19.1 (t), 9.6 (q); LRMS (EI) *m*/*z* 266 (M, 17), 121 (100); HRMS calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1523.

**5-[(3-Methyl-5-phenyl)-2-furyl]pentanal (4c). Method A.** Following general procedure C above, *syn*-**3c** (300 mg, 1.24 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.5 mL) for 15 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (98:2 petroleum ether/ethyl acetate) to give **4c** as a pale yellow oil (242 mg, 81%): IR (neat) 1730 cm$^{-1}$; $^1$H NMR $\delta$ 9.31 (1H, t, $J$ = 1 Hz), 7.18 (2H, m), 6.91 (2H, m), 6.77 (1H, tt, $J$ = 7, 1 Hz), 6.03 (1H, s), 2.23 (2H, m), 2.03 (2H, m), 1.57 (3H, s), 1.35 (4H, m); $^{13}$C NMR $\delta$ 202.4 (d), 151.1 (s), 150.6 (s), 131.2 (s), 128.6 (d), 126.7 (d), 123.2 (d), 116.3 (s), 108.4 (d), 43.6 (t), 28.1 (t), 25.8 (t), 21.6 (t), 10.0 (q); LRMS (EI) *m*/*z* 242 (M, 12), 105 (100); HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1300.

**Method B.** Following typical procedure C (above), *anti*-**3c** (105 mg, 0.43 mmol), when treated with a 0.1 M solution of yellow HgO in 2.5% (v/v) $H_2SO_4$ (0.5 mL) for 3 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **4c** as a pale yellow oil (80 mg 76%).

**5-[(3-Methyl-5-pentyl)-2-furyl]pentanal (4d).** Following general procedure C (above), *syn*-/*anti*-**3d** (300 mg, 1.55 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.25 mL) for 10 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **4d** as a pale yellow oil (254 mg, 85%): IR (neat) 1730 cm$^{-1}$; $^1$H NMR $\delta$ 9.73 (1H, t, $J$ = 2 Hz), 5.65 (1H, m), 2.50−2.30 (6H, m), 1.85 (3H, s), 1.55 (6H, m), 1.25 (4H, m), 0.84 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 202.6 (d), 154.2 (s), 148.4 (s), 114.3 (s), 107.7 (d), 43.6 (t), 31.4 (t), 28.2 (t), 28.0 (t), 27.8 (t), 25.5 (t), 22.4 (t), 21.6 (t), 14.0 (q), 9.8 (q); LRMS (EI) *m*/*z* 236 (M, 23), 165 (100); HRMS calcd for $C_{15}H_{24}O_2$ 236.1776, found 236.1771.

**6-[(3-(1-Phenyl-3-butenyl)-5-phenyl)-2-furyl]hexanal (4e).** Following general procedure C (above), *syn*-**3e** (200 mg, 0.56 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.1 mL) for 10 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (98:2 petroleum ether/ethyl acetate) to give **4e** as a pale yellow oil (155 mg, 78%): IR (neat) 1730, 1640 cm$^{-1}$; $^1$H NMR $\delta$ 9.58 (1H, t, $J$ = 1.5 Hz), 7.53 (2H, m), 7.30−7.10 (8H, m), 6.06 (1H, s), 5.65 (1H, m), 4.97 (1H, dm, $J$ = 17 Hz), 4.90 (1H, dm, $J$ = 10 Hz), 3.76 (1H, t, $J$ = 8 Hz), 2.70−2.50 (4H, m), 2.28 (2H, m), 1.48 (12H, m); $^{13}$C NMR $\delta$ 202.3 (d), 151.5 (s), 150.7 (s), 144.6 (s), 136.7 (d), 131.1 (s), 128.6 (d), 128.4 (d), 127.5 (d), 126.8 (d), 126.2 (d), 124.1 (s), 123.3 (d), 116.4 (t), 105.5 (d), 43.5 (t), 41.8 (d), 40.6 (t), 27.9 (t), 25.9 (t), 21.6 (t); LRMS (EI) *m*/*z* 358 (M, 20), 91 (100); HRMS calcd for $C_{25}H_{34}O_2$ 358.1933, found 358.1925.

**5-[(5-Phenyl-3-benzyl)-2-furyl]pentanal (4f).** Following general procedure C (above), *syn*-/*anti*-**3f** (0.40 g, 1.26 mmol), when treated with a solution (0.2 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 5% v/v $H_2SO_4$ (0.4 mL) for 1 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **4f** as a pale yellow oil (0.19 g, 48%): IR (neat) 1730 cm$^{-1}$; $^1$H NMR $\delta$ 9.75 (1H, t, $J$ = 2 Hz), 7.60 (4H, m), 7.45−7.15 (6H, m), 6.45 (1H, s), 3.75 (2H, s), 2.70 (2H, t, $J$ = 7 Hz), 2.45 (2H, dt, $J$ = 7, 2 Hz), 1.75 (4H, m); $^{13}$C NMR $\delta$ 202.2 (d), 151.5 (s), 150.9 (s), 140.6 (s), 131.0 (s), 128.5

(d), 128.5 (d), 128.4 (d), 128.3 (d), 126.0 (d), 123.2 (d), 123.2 (d), 107.5 (d), 43.5 (t), 31.0 (t), 28.0 (t), 25.8 (t), 21.5 (t); HRMS calcd for $C_{22}H_{22}O_2$ 318.1620, found 318.1612.

**6-[(3-Methyl-5-phenyl)-2-furyl]-2-hexanone (4g).** Following general procedure C (above), *syn*-/*anti*-**3g** (73 mg, 0.28 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.1 mL) for 1 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **4g** as a pale yellow oil (62 mg, 86%): $^1$H NMR $\delta$ 7.53 (2H, dd, $J$ = 8, 1 Hz), 7.32−7.20 (3H, m), 6.38 (1H, s), 2.57 (2H, t, $J$ = 7 Hz), 2.38 (2H, t, $J$ = 7 Hz), 2.07 (3H, s), 1.91 (3H, s), 1.71−1.50 (4H, m); $^{13}$C NMR $\delta$ 208.9 (s), 151.0 (s), 150.8 (s), 131.3 (s), 128.6 (d), 126.6 (d), 123.2 (d), 116.2 (s) 108.4 (d), 43.4 (t), 29.8 (q), 28.0 (t), 25.8 (t), 23.3 (t), 9.9 (q); HRMS calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1470.

**6-[(5-Butyl-3-hexyl)-2-furyl]hexanal (4h).** Following general procedure C (above), *syn*-**3h** (200 mg, 0.65 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.25 mL) for 2 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (98:2 petroleum ether/ethyl acetate) to give **4h** as a clear oil (163 mg, 82%): $^1$H NMR $\delta$ 9.74 (1H, t, $J$ = 2 Hz), 5.75 (1H, s), 2.50 (4H, m), 2.41 (2H, dt, $J$ = 7, 2 Hz), 2.22 (2H, t, $J$ = 7.5 Hz), 1.64−1.15 (18H, m), 0.91 (3H, t, $J$ = 7 Hz), 0.87 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 202.7 (d), 153.7 (s), 148.5 (s), 119.5 (s), 106.3 (d), 43.8 (t), 31.7 (t), 30.6 (t), 30.2 (t), 29.1 (t), 28.7 (t), 28.6 (t), 27.8 (t), 25.7 (t), 24.8 (t), 22.6 (t), 22.3 (t), 21.9 (t), 14.1 (q), 13.8 (q); LRMS (EI) *m*/*z* 306 (M, 8), 259 (100); HRMS calcd for $C_{20}H_{34}O_2$ 306.2559, found 306.2566.

**7-[(3-Pentyl-5-phenyl)-2-furyl]heptanal (4i).** Following general procedure C (above), *syn*-**3i** (200 mg, 0.61 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.25 mL) for 40 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (98:2 petroleum ether/ethyl acetate) to give **4i** as a pale yellow oil (165 mg, 83%): $^1$H NMR $\delta$ 9.73 (1H, t, $J$ = 1.5 Hz), 7.58 (2H, dd, $J$ = 6, 1 Hz), 7.38−7.12 (3H, m), 6.49 (1H, s), 2.58 (2H, t, $J$ = 6 Hz), 2.40 (2H, dt, $J$ = 6, 1.5 Hz), 2.32 (2H, t, $J$ = 6 Hz), 1.55−1.48 (6H, m), 1.45−1.25 (8H, m), 0.88 (3H, t, $J$ = 6 Hz); $^{13}$C NMR $\delta$ 202.8 (d), 151.0 (s), 150.9 (s), 131.3 (s), 128.5 (d), 126.5 (d), 123.2 (d), 121.4 (s) 107.1 (d), 43.8 (t), 31.5 (t), 30.2 (t), 28.9 (t), 28.9 (t), 28.5 (t), 26.0 (t), 24.7 (t), 22.5 (t), 22.0 (t), 14.1 (q); LRMS (EI) *m*/*z* 326 (M, 81), 227 (100); HRMS calcd for $C_{22}H_{30}O_2$ 326.2246, found 326.2242.

**11-[(3-Hexyl-5-propyl)-2-furyl]undecanal (4j).** Following general procedure C (above), *syn*-/*anti*-**3j** (300 mg, 1.54 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.5 mL) for 10 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (19:1 petroleum ether/ethyl acetate) to give **4j** as a pale yellow oil (180 mg, 60%): $^1$H NMR $\delta$ 9.75 (1H, t, $J$ = 1.5 hz), 5.73 (1H, s), 2.53−2.45 (4H, m), 2.41 (2H, dt, $J$ = 5, 1.5 Hz), 2.23 (2H, t, $J$ = 7 Hz), 1.70−1.15 (26H, m), 0.93 (3H, t, $J$ = 7 Hz), 0.86 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 202.7 (d), 153.3 (s), 149.0 (s), 119.2 (s), 106.4 (d), 43.9 (t), 31.7 (t), 30.6 (t), 30.1 (t), 29.7 (t), 29.5 (t), 29.3 (t), 29.3 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.9 (t), 25.9 (t), 24.8 (t), 22.6 (t), 22.1 (t), 21.4 (t), 14.0 (q), 13.7 (q); LRMS (EI) *m*/*z* 362 (M, 72), 207 (100); HRMS calcd for $C_{24}H_{42}O_2$ 362.3185, found 362.3179.

**11-[(3-Methyl-5-pentyl)-2-furyl]undecanal (4k).** Following general procedure C (above), *syn*-/*anti*-**3k** (100 mg, 3.13 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.1 mL) for 10 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (9:1 petroleum ether/ethyl acetate) to give **4k** as a pale yellow oil (88 mg, 88%): IR (neat) 1730 cm$^{-1}$; $^1$H NMR $\delta$ 9.75 (1H, t, $J$ = 2 Hz), 5.72 (1H, s), 2.49 (4H, m), 2.40 (2H, dt, $J$ = 7, 2 Hz), 1.90 (3H, s), 1.79−1.48 (6H, m), 1.40−1.15 (16H, m), 0.88 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 202.8 (d), 153.5 (s), 149.3 (s), 113.8 (s), 107.6 (d), 43.9 (t), 31.4 (t), 29.5 (t), 29.3 (t), 29.3 (t), 29.1 (t), 29.1 (t), 29.0 (t), 28.7 (t), 28.0 (t), 27.8 (t), 25.9 (t), 22.4 (t), 22.1 (t), 14.6 (q), 9.8 (q); LRMS (EI) *m*/*z* 320 (M, 5), 139 (100); HRMS calcd for $C_{21}H_{36}O_2$ 320.2715, found 320.2723.

**1-(5-Pentyl-2-furyl)ethan-1-ol (4l).** Following typical procedure C (above), *syn*-/*anti*-**3l** (300 mg, 1.64 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.5 mL) for 2 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (98:2 petroleum ether/ethyl acetate) to give **4l** as a colorless oil (220 mg, 73%): IR (neat) 3460 cm$^{-1}$; $^1$H NMR $\delta$ 6.06 (1H, dd, $J$ = 3, 0.5 Hz), 5.92 (1H, dt, $J$ = 3, 0.5 Hz), 4.72 (1H, m), 4.14 (1H, d, $J$ = 5 Hz), 2.56 (2H, dt, $J$ = 7.5, 0.5 Hz), 1.56 (2H, m), 1.41 (3H, d, $J$ = 7 Hz), 1.30 (4H, m), 0.90 (3H, t, $J$ = 7 Hz); $^{13}$C NMR $\delta$ 158.1 (s), 155.8 (s), 105.8 (d), 105.7 (d), 63.6 (d), 32.1 (t), 28.5 (t), 28.4 (t), 23.0 (t), 22.2 (q), 14.3 (q); LRMS (EI) *m*/*z* 182 (M, 25), 167 (100); HRMS calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1313.

**1,1-Bis[(3-methyl-5-phenyl)-2-furyl]methane (5a).** Following general procedure C (above), *syn*-/*anti*-**3m** (150 mg, 0.80 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.3 mL) for 2.5 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (39:1 petroleum ether/ethyl acetate) to give **5a** as a pale oil (110 mg, 84%): IR (neat) 1605, 1555 cm$^{-1}$; $^1$H NMR $\delta$ 7.52 (4H, m), 7.25 (4H, m), 7.10 (2H, m), 6.36 (2H, s), 3.90 (2H, s), 1.94 (6H, s); $^{13}$C NMR $\delta$ 151.4 (s), 146.7 (s), 131.1 (s), 128.6 (d), 126.8 (d), 123.4 (d), 117.3 (s), 108.7 (d), 24.1 (t), 9.9 (q); LRMS (EI) *m*/*z* 328 (M, 100), 313 (39); HRMS calcd for $C_{23}H_{20}O_2$ 328.1463, found 328.1456.

**1,1-Bis-[(3-methyl-5-*n*-propyl)-2-furyl]ethane (5b).** Following general procedure C (above), *syn*-/*anti*-**3n** (200 mg, 1.19 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.2 mL) for 15 min and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (39:1 petroleum ether/ethyl acetate) to give **5b** as a pale yellow oil (117 mg, 72%): IR (neat) 1630, 1570 cm$^{-1}$; $^1$H NMR $\delta$ 5.76 (2H, s), 4.17 (1H, q, $J$ = 7 Hz), 2.55 (4H, dt, $J$ = 8, 1 Hz), 1.82 (6H, s), 1.64 (4H, m), 1.59 (3H, d, $J$ = 7 Hz), 0.98 (6H, t, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 153.3 (s), 149.1 (s), 113.7 (s), 108.3 (d), 30.0 (d), 30.0 (t), 21.5 (t), 17.8 (q), 13.7 (q), 9.6 (q); LRMS (EI) *m*/*z* 274 (M, 18), 259 (100); HRMS calcd for $C_{18}H_{26}O_2$ 274.1933, found 274.1924.

**1,1-Bis[(3-ethyl-5-phenyl)-2-furyl]ethane (5c).** Following general procedure C (above), *syn*-/*anti*-**3o** (220 mg, 1.02 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.5 mL) for 2 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (petroleum ether) to give **5c** as a pale yellow oil (140 mg, 74%): IR (neat) 2960, 2865, 1600 cm$^{-1}$; $^1$H NMR $\delta$ 7.54 (4H, dd, $J$ = 7, 1 Hz), 7.29 (4H, m), 7.09 (2H, m), 6.41 (2H, m), 4.25 (1H, q, $J$ = 7 Hz), 2.24 (4H, q, $J$ = 7.5 Hz), 1.64 (3H, d, $J$ = 7 Hz), 1.01 (6H, t, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 151.3 (s), 150.1 (s), 131.3 (s), 128.6 (d), 126.8 (d), 123.4 (d), 122.9 (s), 107.1 (d), 30.5 (d), 18.4 (q), 17.9 (t), 15.1 (q); LRMS (EI) *m*/*z* 370 (M, 25), 199 (100); HRMS calcd for $C_{26}H_{26}O_2$ 370.1933, found 370.1925.

**1,1-Bis[(3-ethyl-5-*n*-pentyl)-2-furyl]ethane (5d).** Following general procedure C (above), *syn*-/*anti*-**3p** (325 mg, 1.55 mmol), when treated with a solution (0.1 M in $Hg^{II}$) obtained by dissolving yellow mercury(II) oxide in 2.5% v/v $H_2SO_4$ (0.5 mL) for 2 h and worked up as for **4a**, afforded a residue that was purified by column chromatography on silica (98:2 petroleum ether/ethyl acetate) to give **5d** as a pale yellow oil (231 mg, 83%): $^1$H NMR $\delta$ 5.72 (2H, s), 4.08 (1H, q, $J$ = 7 Hz), 2.46 (4H, t, $J$ = 7.5 Hz), 2.13 (4H, q, $J$ = 6 Hz), 1.51−1.44 (4H, m), 1.46 (3H, d, $J$ = 6 Hz), 1.33−1.17 (8H, m), 0.96 (6H, t, $J$ = 7.5 Hz), 0.82 (6H, t, $J$ = 6 Hz); $^{13}$C NMR $\delta$ 153.8 (s), 148.5 (s), 120.5 (s), 106.3 (d), 31.4 (t), 30.0 (d), 28.0 (t), 27.8 (t), 22.4 (t), 18.2 (q), 17.7 (t), 15.0 (q), 14.0 (q); LRMS (EI) *m*/*z* 358 (M, 18), 343 (100); HRMS calcd for $C_{24}H_{38}O_2$ 358.2872, found 358.2864.

**11-[(3-Methyl-5-pentyl)-2-furyl]undecanoic Acid ($F_5$).** A solution of **4k** (21.2 mg, 0.066 mmol) in dichloromethane (1

mL) was treated with pyridinium dichromate (124 mg, 0.331 mmol) at room temperature. The mixture was stirred for 6 h and then diluted with water (10 mL). The mixture was extracted with ether (4 × 5 mL) and with ether/*n*-pentane (50:50) (3 × 5 mL). The combined extracts were washed with brine (5 mL) and concentrated to afford an oil that was purified by column chromatography on silica (183:15:2 petroleum ether/ethyl acetate/acetic acid) to afford **F$_5$** as a colorless oil (14.6 mg, 65%): $^1$H NMR $\delta$ 5.73 (1H, s), 2.50 (4H, m), 2.34 (2H, t, $J$ = 8 Hz), 1.89 (3H, s), 1.58 (6H, m), 1.29 (16H, m), 0.89 (3H, m); $^{13}$C NMR $\delta$ 179.3 (s), 153.5 (s), 149.4 (s), 113.8 (s), 107.6, (d), 33.9 (t), 31.4 (t), 29.7 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 29.1 (t), 28.7 (t), 28.0 (t), 27.8 (t), 25.9 (t), 24.7 (t), 22.4 (t), 14.0 (q), 9.9 (q); HRMS calcd for $C_{21}H_{26}O_3$ 336.2664, found 336.2657.

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**Supporting Information Available:** Copies of the $^1$H NMR spectra of selected compounds (39 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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