deaerated benzene (3 mL) was added to the flask under Ar. To the green suspension thus prepared was added ethyl nitrite (1.4 mL of 15% solution, 0.87 × 2.5 mmol). The mixture became a brown homogeneous solution. Subsequently, the substrate (0.87 mmol) was added by syringe, and the solution was stirred for 25 h at room temperature. After the addition of water (10 mL) to the reaction mixture, the product was extracted with ether (2 × 10 mL). The ethyl layer was dried with Na_2SO_4 and concentrated. Acetophenone oxime was isolated in a 94% yield (110 mg) after purification by column chromatography (Wakogel C-200, and eluted with 20% ethyl acetate/hexane, R_f 0.29). By a similar procedure, various oximes were prepared as listed in Table I and II. Spectral data are presented below: *o*-(allyloxy)acetophenone oxime, ^{1}H NMR δ 2.26 (s, 3 H), 4.52–4.60 (m, 2 H), 5.18–5.47 (m, 2 H), 5.86–6.23 (m, 1 H), 6.84–7.40 (m, 4 H), 9.2 (br s, 1 H); ^{13}C NMR δ 15.39 (q), 69.33 (t), 112.73 (d), 117.42 (t), 120.93 (d), 127.48 (s), 129.58 (d), 130.11 (d), 133.21 (d), 156.61 (s), 157.08 (s); 3-oxo-3-phenyl-1-propanol oxime, ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 3.07 (t, J = 6.8 Hz, 2 H), 3.82 (br t, J = 6.8 Hz, 2 H), 7.22–7.74 (m, 5 H), 10.75 (s, 1 H); mass (M^+) 165; 3-methoxypropiophenone oxime, ^{1}H NMR δ 3.13 (t, J = 6.0 Hz, 2 H), 3.34 (s, 3 H), 3.65 (t, J = 6.0 Hz, 2 H), 7.30–7.75 (m, 5 H).

In the reaction of phenylacetylene (phenylacetylene, 1.27 mmol; $ClCo^{III}(DH)_2py$, 0.25 mmol; Et_4NBH_4, 1.30 mmol; EtONO (15% solution), 1.4 mL; benzene 3 mL for 47 h at room temperature), acetophenone oxime was formed in a 4.7% yield by GC analysis. An orange complex crystallized out during the workup. The complex was washed successively with ether, water, and ether (the complex was slightly soluble in ether), dried in vacuo, and identified as bis(dimethylglyoximato)(1-phenyl-1-ethenyl)-pyridinecobalt(III),[17] (**1b**) (34 mg, 29% yield on the basis of the amount of cobalt complex used).

The deuterium incorporation study was carried out by using 1,2-dihydronaphthalene as the substrate (0.845 mmol) and $NaBD_4$ as the reductant (2 × 0.845 mmol) for 36 h at room temperature. After the usual workup, 37 mg of the substrate was recovered (34% yield) and 89 mg (65% yield on a used substrate basis) of oxime was isolated. The deuterium content of the recovered dihydronaphthalene was estimated by the integral ratio of NMR spectra, and the ratio of the products having d_0, d_1, and d_2 atom(s) was determined by mass spectroscopy.

The reaction of **1a** (95 mg, 0.20 mmol) with EtONO (0.5 mL, ca. 0.8 mmol) was examined by stirring the mixture for 5 h in benzene (3 mL) under Ar at room temperature. The reaction products were identified by gas chromatography in the presence of diphenyl ether as the internal standard to be acetophenone oxime (45.9% yield) and styrene (45.5% yield). In the presence of an amount of Et_4NBH_4 equivalent to the complex, acetophenone oxime was the sole product in a yield of 75.0%. No ethylbenzene was formed.

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A 5C + 5C Bicycloaromatization Reaction via an Aldol Condensation Cascade: A Regioselective Synthesis of Functionalized Naphthalenes from Acyclic Precursors

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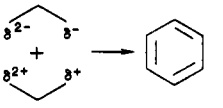
Received January 20, 1988

A regioselective synthesis of naphthalene derivatives **51** was developed by the reaction of 1,3,5-tris(trimethylsiloxy)-1-methoxyhexa-1,3,5-triene (**2**) with the 1,3,5-tris-electrophiles **50** and trimethylsilyl triflate. Three carbon–carbon bonds are formed in this aldol condensation cascade, where the regiochemistry is controlled by the different reactivities at the sites of the acyclic precursors.

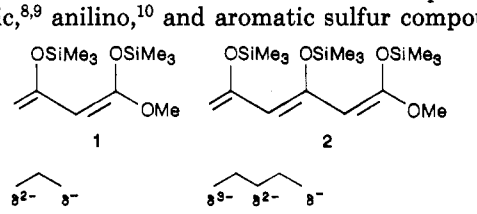
Introduction. A major challenge in organic synthesis today is to devise reactions that can form several carbon–carbon bonds in one operation leading to the construction of polycyclic structures with proper regio- and stereochemical control.

It is recognized that one of the important pathways in nature to assemble polycyclic compounds is the aldol-type reaction of β-polyketide precursors.[1-5] In the laboratory, the controlled aldol condensation of these precursors inspired by biogenetic considerations has been extensively studied by Harris. This has been applied in an elegant fashion to a biomimetic synthesis of 6-methylpretetramide.[6] However, the success of this approach is still somewhat limited due to the difficulty in controlling the direction of the condensation.

Recently, a cycloaromatization reaction was developed in our laboratories for the synthesis of methyl salicylates (eq 1).[7,8] It involves the condensation of 1,3-bis(trimethylsiloxy)-1-methoxybuta-1,3-diene (**1**), the dianion equivalent of methyl acetoacetate, with various 1,3-dielectrophiles under $TiCl_4$ promotion. The regiochemistry of the reaction is controlled by the differing reactivities at the sites of the nucleophilic and electrophilic components. The reaction has been further developed to give phenolic,[8,9] anilino,[10] and aromatic sulfur compounds.[11]



(1)



(1) Collie, J. N.; Myers, W. S. *J. Chem. Soc.* **1893**, 122.
(2) (a) Collie, J. N. *J. Chem. Soc.* **1893**, 329. (b) Collie, J. N. *J. Chem. Soc.* **1907**, 1806.
(3) Collie, J. N. *Proc. Chem. Soc., London* **1907**, *23*, 230.
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(6) Harris, T. M.; Harris, C. M. *Tetrahedron* **1977**, *33*, 2159. Mahalingam, S.; Kuzma, P. C.; Lee, J. Y. C.; Harris, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 7760.
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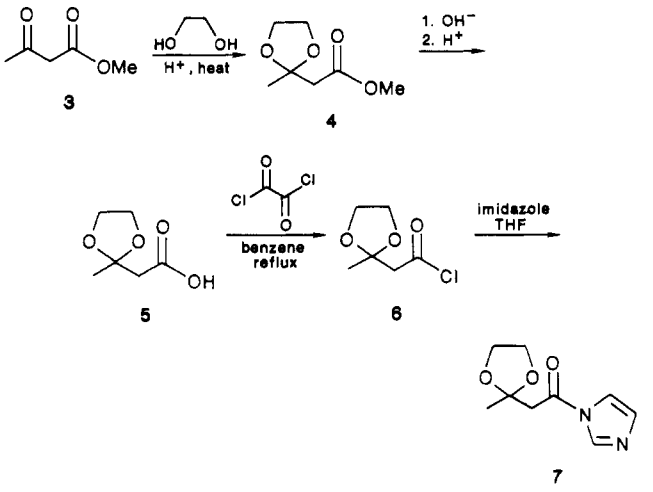
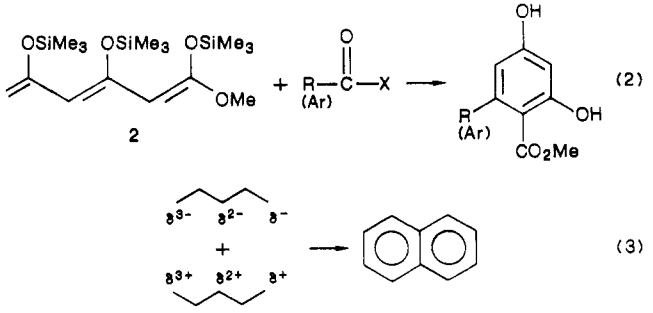
(8) Brownbridge, P.; Chan, T. H.; Brook, M. A.; Kang, G. J. *Can. J. Chem.* **1983**, *61*, 688.
(9) Chan, T. H.; Chaly, T. *Tetrahedron Lett.* **1982**, *23*, 2935.
(10) Chan, T. H.; Kang, G. J. *Tetrahedron Lett.* **1983**, *24*, 3051, 3187; *J. Org. Chem.* **1985**, *50*, 452.

0022-3263/88/1953-4901$01.50/0

Scheme I



In trying to extend the reaction to the synthesis of functionalized naphthalene systems, we have prepared 1,3,5-tris(trimethylsiloxy)-1-methoxyhexa-1,3,5-triene (**2**) as a β-tricarbonyl trianion equivalent. We have demonstrated that **2** reacts with carbon electrophiles initially at its ϵ-position. We further developed a 5C + 1C condensation based on the reaction of **2** (5C) with an acid chloride or equivalent (1C) to furnish 6-alkyl(aryl)-2,4-dihydroxybenzoates (eq 2).[12,13] In this paper we report on the 5C + 5C bicycloaromatization reaction of **2** with unsymmetrical 1,3,5-tris-electrophiles, which provides access to naphthalene derivatives in a regioselective manner according to eq 3.

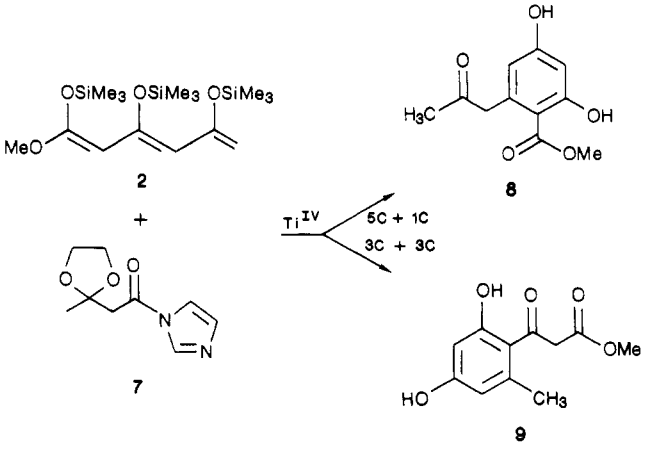


Reactions of Silyl Enol Ether 2 with 1,3-Bis-Electrophiles. The synthesis of the appropriate tris-electrophiles with the desired reactivity proved to be a nontrivial task. As a preliminary study, the reactions of **2** with some 1,3-bis-electrophiles were examined first. These electrophiles are already known[8,9] so that their preparation was straightforward.

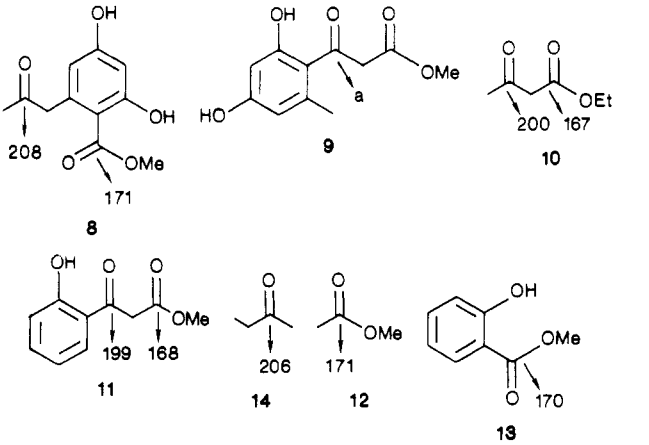
The first case studied was the reaction of **2** with **7**, which was easily prepared from methyl acetoacetate **3** (Scheme I). Compound **7** has two different electrophilic sites, the imidazolide being the more reactive and the ethylene ketal the less reactive.[8,9] It was particularly important to determine if the imidazolide **7** would react as previously reported,[12] leading to the 5C + 1C condensation, or if the ketal position of **7** would participate and react in a 3C + 3C fashion (Scheme II).

Experimentally, with the use of $TiCl_4$ as the Lewis acid, the first of these situations was realized. The only product, **8**, resulting from the reaction at the imidazolide in a 5C + 1C manner was obtained in 55% yield. The other possible product, **9**, was not detected (Scheme II).

Scheme II



To distinguish between the two structures **8** and **9**, the ^{13}C NMR spectrum of the product **8** was recorded and compared to that of ethyl acetoacetate (**10**), phenol derivative **11**, methyl acetate (**12**), and methyl salicylate (**13**).



The critical consideration was the chemical shifts of the two carbonyl carbons. In the product **8** these appear at 171 and 208 ppm. In ethyl acetoacetate as well as in phenol **11**, the ketone carbonyls resonate at 200 and 199 ppm respectively. In 2-butanone (**14**), the ketone carbonyl resonates at 206 ppm. It appears reasonable to assume that if **9** were formed, carbon a would resonate in the 199–200 ppm range; however, in **8** the value of 208 ppm appears closer to the "free" carbonyl of 2-butanone (206 ppm) than to the carbonyls of **10** or **11**. The mass spectrum was also supportive of structure **8**. It shows a strong signal (*m/e* 182, 41%) for the loss of ketene from the molecular ion (*m/e* 224, 33%), which is more in accordance with structure **8** possessing a methyl ketone moiety rather than with **9**.

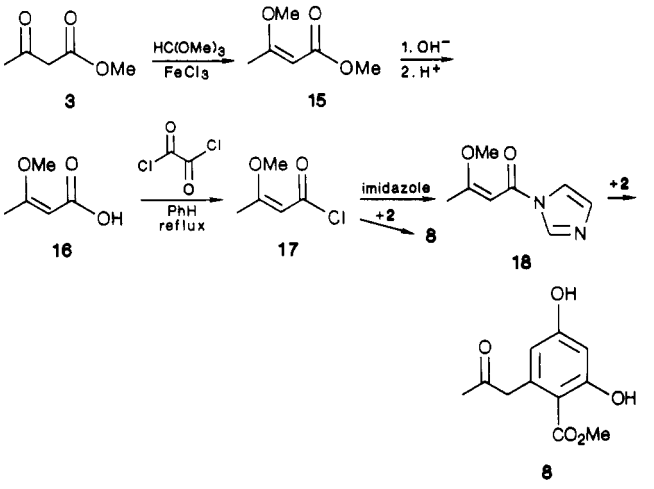
Other 1,3-dielectrophiles with an acid equivalent function behaved similarly; for example, **17** or **18** reacted with **2** to give the 5C + 1C condensation product **8** (Scheme III). The reaction was tried with $TiCl_4$, $SnCl_4$, and $ZnCl_2$ as the Lewis acids, and in all cases, **8** was obtained.

Other electrophiles such as **22**, **23**, and **24** (Scheme IV) were also tried but again resulted in the formation of the product resulting from a 5C + 1C condensation. The reactions of **22** and **24** with **2** were tried with $TiCl_4$ and $TiCl_2(i\text{-}OPr)_2$ as Lewis acids, and for **23**, in addition, $SbCl_5$ was used.

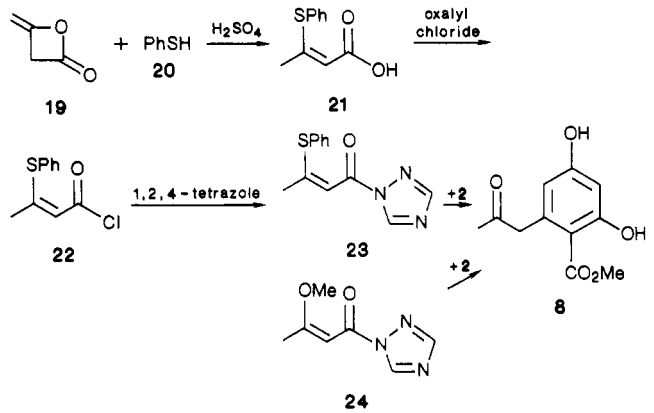
The conclusion so far is that when one of the electrophilic sites is an imidazolide or a similar acylating agent, the 5C + 1C condensation results. For the 3C + 3C con-

(11) Chan, T. H.; Prasad, C. V. C. *J. Org. Chem.* **1986**, *51*, 3012; **1987**, *52*, 110, 120.
(12) Chan, T. H.; Stossel, D. *J. Org. Chem.* **1986**, *51*, 2423.
(13) Stossel, D.; Chan, T. H. *J. Org. Chem.* **1987**, *52*, 2105.

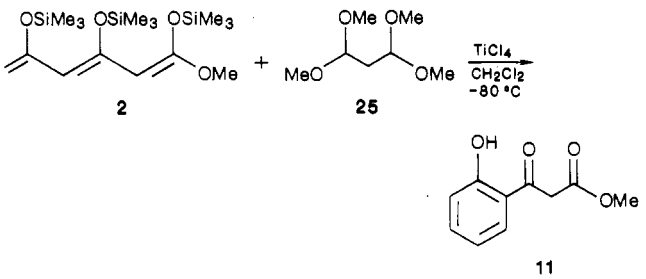
Scheme III



Scheme IV



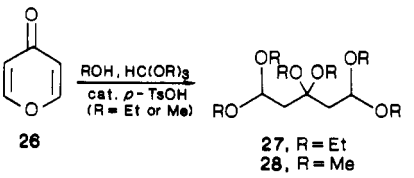
Scheme V



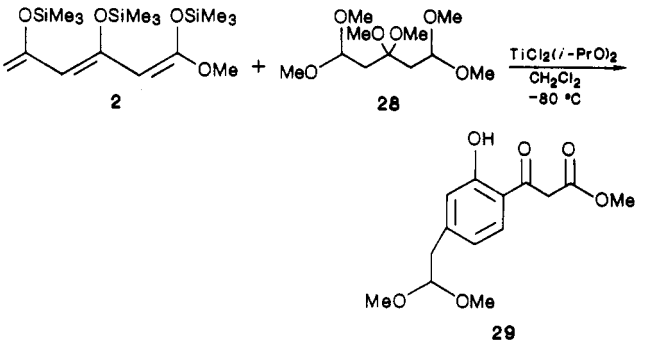
densation (and hence also for the 5C + 5C condensation) to take place, it appears that an electrophilic site with the oxidation level of a carboxylic acid or its equivalent, such as imidazolide or acid chloride, should not be present in the electrophilic component. In accord with this expectation, the condensation of silyl ether **2** with malonaldehyde bis(dimethyl acetal) (**25**) in the presence of $TiCl_4$ resulted in the formation of an aromatic product **11** in a 3C + 3C fashion (Scheme V). The successful reaction with 1,1,3,3-tetramethoxypropane is encouraging. It demonstrates that, with electrophiles that have the oxidation level equivalent of a ketone or aldehyde, the 3C + 3C condensation is indeed possible. Therefore, the structural requisite of 1,3,5-tris-electrophiles necessary for a successful 5C + 5C condensation to furnish naphthalene derivatives is to have solely acetal, ketal, or their equivalent at the electrophilic sites.

Reactions of 2 with 1,3,5-Tris-Electrophiles. A 5C + 5C Condensation. The first 1,3,5-tris-electrophile studied was 1,1,3,3,5,5-hexamethoxypentane (**28**), which is derived from γ-pyrone (**26**), using a modification of a literature procedure (Scheme VI).[14-17]

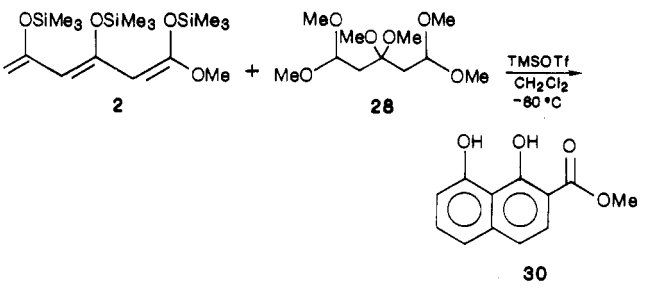
Scheme VI



Scheme VII



Scheme VIII

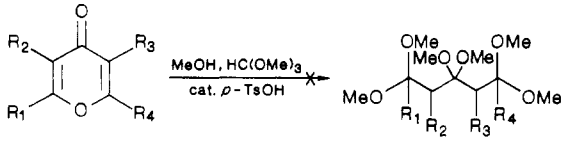


Upon reaction of **28** with silyl ether **2** with $TiCl_4$, however, no naphthalenoid derivative could be detected. When $TiCl_2(i\text{-}OPr)_2$ was used instead, a small amount (2% yield after purification) of **29** could be found (Scheme VII). The isolation of this product proves that two C–C bond formations have taken place in a 3C + 3C condensation. Compound **29** would arise from the initial reaction of **2** with the ketal functionality of **28**. The crude ^1H NMR spectrum of this reaction showed a series of broad signals, which suggested that polymerization could be the predominant reaction. In addition, it was always possible to recover from the reaction mixture varying amounts of the hydrolysis product of silyl ether **2**: triacetic acid methyl ester, according to ^1H NMR. Variation of the reaction conditions or the use of other Lewis acids did not lead to any improvement of the yield of **29** or to the observation of any product formed by a 5C + 5C condensation.

Noyori reported recently[18] on the trimethylsilyl trifluoromethanesulfonate (trimethylsilyl triflate) catalyzed reaction of silyl enol ethers with acetals, ketals, or orthoformates. Ketones or aldehydes were reported *not* to react under these conditions. The reaction of tris silyl enol ether **2** and 1,1,3,3,5,5-hexamethoxypentane **28** in CH_2Cl_2 with trimethylsilyl triflate at −80 °C was attempted and found to give 2-carbomethoxy-1,8-dihydroxynaphthalene (**30**) in

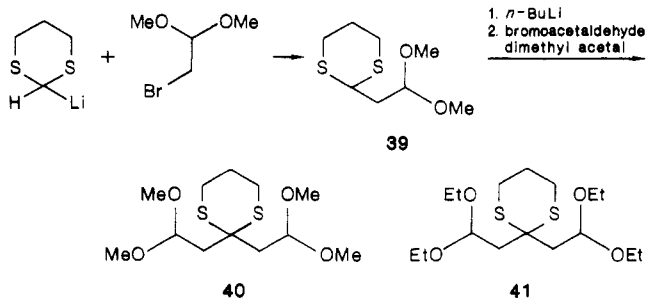
(14) Willstatter, R.; Pummerer, R. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 3733, 3740.
(15) Claisen, L. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 111.
(16) Willstatter, R.; Pummerer, R. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1461.
(17) Ichimoto, I.; Tatsumi, C. *Bull. Univ. Osaka Prefect., Ser. B* **1965**, *16*, 105; *Chem. Abstr.* **1966**, *65*, 3822g.
(18) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

Scheme IX



31	$R_1 = R_4 = H$, $R_2 = R_3 = CH_3$	**35**
32	$R_1 = R_4 = H$, $R_2 = R_3 = Ph$	**36**
33	$R_1 = R_2 = R_3 = H$, $R_4 = CH_3$	**37**
34	$R_2 = R_3 = H$, $R_1 = R_4 = CH_3$	**38**

Scheme X



39

40 **41**

12% yield (Scheme VIII). The product shows a characteristic blue fluorescence under exposure to UV radiation, and its other spectral characteristics confirm the structure.

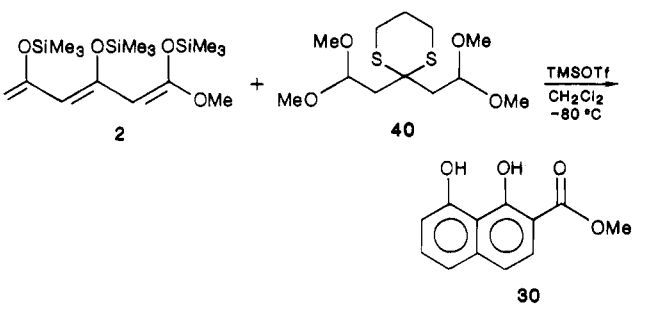
Our efforts to improve the yield of **30** included the following: (i) variation of the reaction time between 8 h and 3 days; (ii) the use of 100%, 200%, and 400% of excess electrophile; (iii) variation in the order of addition of electrophile, nucleophile, and catalyst; (iv) use of a range of other catalysts—trimethylsilyl triflate proved to be the most effective, and Ph_3CSnCl_5[19] also formed **30** but in only 5% yield, while $TiCl_4$, $TiCl_2(i\text{-PrO})_2$, $SnCl_4$, and $F_3B{\cdot}OEt_2$ were not effective; (v) variation of the concentration indicated that about 0.05 M was the optimum; (vi) changes in the amount of catalyst showed that for 1 mmol each of nucleophile and electrophile, 1.7, 2.5, or 5.0 mmol of catalyst did not vary significantly the yield from 12%; however, with 0.2 mmol or less of catalyst the reaction proceeded hardly at all. This contrasts significantly with the conditions used by Noyori[18] (1–5 mmol % of catalyst with monofunctional silyl enol ethers and electrophiles). The optimum yield for the formation of **30** remained at 12% at this stage.

In order to extend the generality of the 5C + 5C condensation it was necessary to synthesize other 1,3,5-tris-electrophiles. In this connection, 2,6-dimethyl-γ-pyrone (**34**) was available commercially while 3,5-dimethyl-γ-pyrone (**31**),[20] 3,5-diphenyl-γ-pyrone (**32**),[21] and 2-methyl-γ-pyrone (**33**)[22] were synthesized by available methods from the literature.

Unfortunately, it was not possible to obtain the corresponding hexamethoxy derivatives **35–38** from the pyrones **31–34** by any of the following methods using trimethyl orthoformate and methanol with: (i) *p*-toluenesulfonic acid, at room temperature or at reflux; (ii) $BF_3{\cdot}OEt_2$, reflux, 2 days; (iii) $FeCl_3$, reflux, 3 days; (iv) HCl, reflux, 1 day (Scheme IX). These results were surprising as it was possible to obtain 1,1,3,3,5,5-hexamethoxypentane from γ-pyrone at room temperature with stirring for 2–3 days.

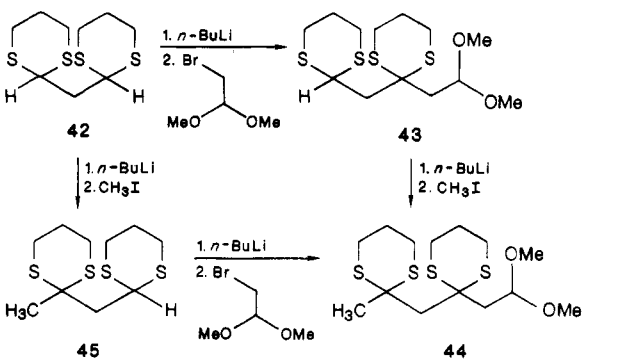
A different approach for the synthesis of the tris-electrophiles was therefore necessary. When the anion derived from 1,3-dithiane[23] was used, it was possible to obtain

Scheme XI



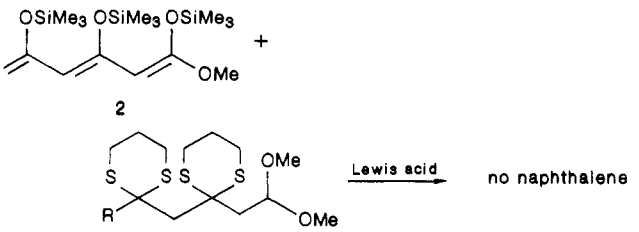
2 **40** **30**

Scheme XII



42 **43** **45** **44**

Scheme XIII



2

43, R = H
44, R = CH_3
44a, R = C_2H_5

compounds **39** and **40** by using bromoacetaldehyde dimethyl acetal as the alkyl halide (Scheme X).

Compound **40** is very similar to 1,1,3,3,5,5-hexamethoxypentane except that the central electrophilic site is occupied by the 1,3-dithiane moiety. By a similar route, but using bromoacetaldehyde diethyl acetal, it was possible to obtain **41**. Compound **40** reacted with silyl enol ether **2** and trimethylsilyl triflate to give naphthalene **30**. On the other hand, **41** did not react at all to give **30** (Scheme XI).

Again, only trimethylsilyl triflate was effective; $TiCl_4$, $SnCl_4$, and $BF_3{\cdot}OEt_2$ were not useful at all. The yield was also 12%. Another report by Seebach and Corey[24] studied some of the reactions of the bis(1,3-propylene dithioacetal) of malonaldehyde (**42**). As **42** has two active protons, by a protocol similar to the one used previously, it was possible to synthesize compounds **43**, **44**, and **45** (Scheme XII).

The reaction of **2** with **43** (or **44**) was not successful for the formation of naphthalene derivatives (Scheme XIII). A variety of Lewis acids, such as $TiCl_4$, trimethylsilyl triflate, zinc(II) triflate,[25] and mercury(II) triflate,[26] were tried.

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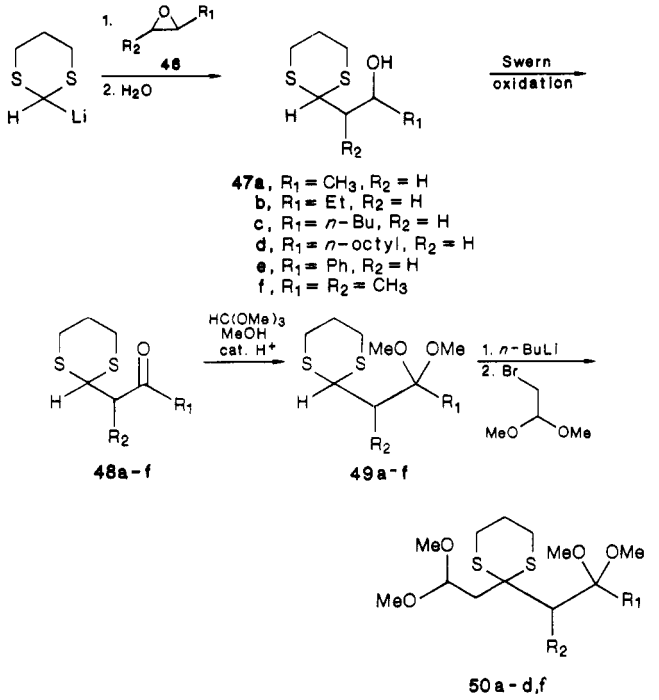
(20) Beak, G.; Carls, G. A. *J. Org. Chem.* **1964**, *29*, 2678.
(21) Benary, E.; Bitter, G. A. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 1057.
(22) Dorman, L. C. *J. Org. Chem.* **1967**, *32*, 4105.
(23) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231.
(24) Seebach, D.; Jones, N. R.; Corey, E. J. *J. Org. Chem.* **1968**, *33*, 300.
(25) Corey, E. J.; Shimoji, K. *Tetrahedron Lett.* **1983**, *24*, 169.
(26) Nishizawa, M.; Takenaka, H.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 1806.

Scheme XIV



It was clear that having a 1,3-dithiane moiety in the central site of the tris-electrophile with acetal functions at both ends provided an appropriate reagent for the 5C + 5C bicycloaromatization, but that placing a 1,3-dithiane unit at one of the terminal positions changed the reactivity to such an extent that reaction with silyl enol ether **2** to produce a naphthalene derivative was not possible. Apart from the loss of reactivity of a 1,3-dithiane vs a dimethoxy acetal (or ketal) in the terminal position, steric hindrance may also be a factor in the lack of reactivity of compounds **43** and **44**. We thus explored the next question: can this be a general reaction with unsymmetrical tris-electrophiles with different acetals (ketals) at the two ends, and would the reaction be regioselective?

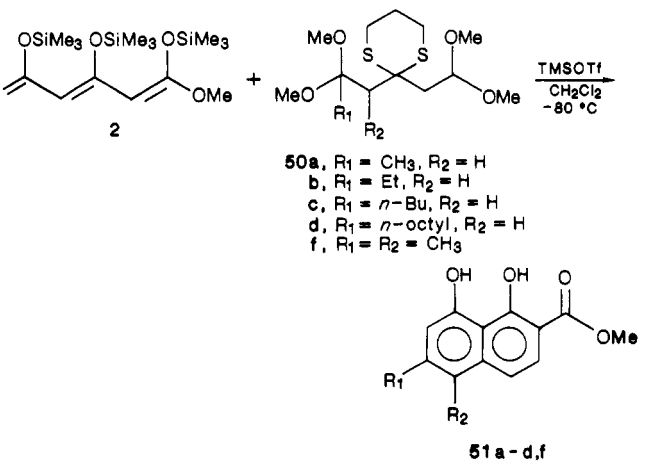
Synthesis of the unsymmetrical tris-electrophiles was achieved as follows. Treatment of 2-lithio-1,3-dithiane with epoxide **46** where R is hydrogen or an alkyl group gave alcohol **47**, which was oxidized by the method developed by Swern[27] to ketone **48**. The latter was in turn ketalized to compound **49**, which, upon sequential treatment with *n*-butyllithium and bromoacetaldehyde dimethyl acetal, furnished tris-electrophile **50** (Scheme XIV).

Some epoxides such as the ones derived from cyclooctene, cyclodecene, or cyclododecene did not react with 2-lithio-1,3-dithiane. Styrene did react to give the alcohol **47e**, R_1 = Ph, R_2 = H, and was oxidized to the corresponding ketone, which was ketalized; however, the second alkylation with bromoacetaldehyde dimethyl acetal did not seem to proceed as expected.

Reaction of these unsymmetrical tris-electrophiles **50a–f** with silyl enol ether **2** and trimethylsilyl triflate led to the formation of naphthalene derivatives **51a–f** in a regioselective manner (Scheme XV).

Although, in the ^{1}H NMR spectra of 2-carbomethoxy-1,8-dihydroxy-6-alkylnaphthalenes, the aromatic region appeared to show the presence of only one regioisomer, a second blue fluorescent spot, close in R_f to the major one, appeared in thin-layer chromatography. This may indicate

Scheme XV



the presence of a small amount of the other regioisomer (i.e., the alkyl group R_1 in the 3-position); however, from the ^{1}H NMR spectrum it follows that the regioisomeic purity must be at least 95%.

The isolated yield of the purified naphthalenes **51a–f** from the 5C + 5C condensation was 20–25%. It was observed that when the size of the column used for purification was reduced from 2.3-cm to 0.9-cm diameter, the recovery of material was optimized. It has not been possible to improve the yield so far beyond 25%. Polymeric material which accounted for the mass balance could be isolated.

The regiochemistry is evidently governed by the relative reactivity of the two electrophilic ends, with the ketal moiety being more reactive than the acetal group.

Conclusion. The present study demonstrates that a 5C + 5C condensation can be successfully achieved from acyclic precursors to give functionalized naphthalene derivatives. In spite of the modest yield, the reaction is of potential synthetic utility because it provides a regiocontrolled synthesis of these types of compounds in a convergent fashion. In terms of the development of a controlled β-polyketide condensation, the present reaction shows that (a) two different β-tricarbonyl fragments, one nucleophilic, the other electrophilic, can be assembled; and (b) the direction of the condensation is controlled by the different reactivities within each of the two fragments. It will be interesting to see if this type of aldol condensation cascade can be extended even further to embrace tricyclic or polycyclic structures.

Experimental Section

All the chemicals used were reagent grade. Solvents were dried prior to use: methylene chloride over phosporus pentoxide, THF over sodium metal/benzophenone, and hexanes over sodium metal/benzophenone. Melting points were taken with a Gallenkamp apparatus and are uncorrected. Nuclear magnetic resonance spectra were taken with a Varian T-60 or XL-200 spectrometer using tetramethylsilane as internal standard. NMR spectra are reported in parts per million with respect to TMS, and in parentheses are the multiplicity and the number of hydrogens. IR spectra were taken with a Perkin-Elmer Model 297 instrument and are reported in cm^{-1}. Mass spectra were taken at 60 eV with a Dupont 21-492B instrument and are reported as m/z (intensity in percent). Reactions were usually run in a nitrogen atmosphere, and all equipment was dried in an oven. Purifications involving column chromatography were performed with Merck silica gel 60 (230–400 mesh) by using flash chromatography.[28] TLC analyses were performed with aluminum-coated

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silica gel Merck 60 F_{254} plates 0.2 mm thick. Microanalyses were performed by Guelph Chemical Laboratories Ltd.

1,3,5-Tris(trimethylsiloxy)-1-methoxyhexa-1,3,5-triene (2) was prepared according to our previously published procedure.[12,13]

Methyl 3-oxobutanoate ethylene ketal (4) was prepared according to published procedure[29] except that trimethylchlorosilane, used as the acid catalyst, was added at 0 °C to a mixture of dry methanol, ethylene glycol, and methyl acetoacetate.

3-Oxobutanoic acid ethylene ketal (5) was prepared according to the literature procedure.[31]

3-Oxobutanoyl Chloride Ethylene Ketal (6). To 7.6 g (52 mmol) of the crude acid **5** in 60 mL of dry benzene was added oxalyl chloride (52 mmol, 4.6 mL). The mixture was heated to reflux for 2 h and the solvent evaporated on the rotavap to give crude **6** in 90% yield: ^{1}H NMR ($CDCl_3$) δ 1.5 (s, 3 H), 3.3 (s, 2 H), 4.1 (s, 4 H).

3-Oxobutanoimidazolide Ethylene Ketal (7). To the crude acid chloride **6** (8.08 g, 49 mmol) dissolved in 120 mL of dry THF was added imidazole (6.6 g, 98 mmol). The mixture was stirred overnight at room temperature and filtered, and the filtrate was concentrated to give a dark oil, which solidified upon standing. The solid, obtained in 86% yield, was used without further purification: mp 52–55 °C; IR (KBr) 3140, 3000, 2900, 1730, 1470, 1380, 1050, 840, 770, 650; ^{1}H NMR ($CDCl_3$) δ 1.5 (s, 3 H), 3.2 (s, 2 H), 4.0 (s, 4 H), 7.1 (m, 1 H), 7.5 (m, 1 H), 8.2 (m, 1 H); MS, 196 ($M^{\bullet+}$, 12), 181 (10), 168 (3), 131 (27), 87 (100); exact mass found for $C_9H_{12}O_3N_2$ 196.089, calcd 196.085.

(2-Carbomethoxy-3,5-dihydroxyphenyl)acetone (8). The imidazolide **7** (0.4 g, 2 mmol) was dissolved in 25 mL of dry CH_2Cl_2. After cooling to −78 °C, tris silyl ether **2** (4 mmol) and a mixture of $TiCl_4$ (6 mmol, 0.66 mL) and Ti(*i*-OPr)$_4$ (6 mmol, 1.8 mL) in 5 mL of CH_2Cl_2 were added. After reaction for 3 h at −78 °C and overnight at room temperature, the mixture was quenched with water and $NaHCO_3$(s) and stirred for 0.5 h. The mixture was extracted with ether, and the organic layer was dried, filtered, and concentrated in vacuo. After purification by column chromatography, compound **8** was obtained (280 mg, 60% yield): mp 129–130 °C; IR (KBr) 3000–3600, 1710, 1660, 1620, 1440, 1320, 1160, 950, 800; ^{1}H NMR ($CDCl_3$) δ 2.2 (s, 3 H), 3.8 (s, 3 H), 4.0 (s, 2 H), 6.2 (d, J = 2 Hz, 1 H), 6.3 (d, J = 2 Hz, 1 H), 11.5 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.8, 52.0, 52.3, 103.0, 105.3, 113.5, 139.6, 161.9, 165.7, 171.2, 207.9; MS, 224 ($M^{\bullet+}$, 33), 192 (61), 182 (41), 150 (98), 43 (100); exact mass found for $C_{11}H_{12}O_5$ 224.071, calcd 224.069.

3-Methoxy-2-butenoic acid (16) was prepared according to literature procedure.[31]

3-Methoxy-2-butenoyl Chloride (17). 3-Methoxy-2-butenoic acid (2.3 g, 20 mmol) was dissolved in 100 mL of dry benzene, and oxalyl chloride (25 mmol, 2.2 mL) was added. The mixture was refluxed for 1 h, and the volatiles were evaporated on the rotavap to give the crude acid chloride in 90% yield: ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3 H), 3.8 (s, 3 H), 5.4 (s, 1 H).

3-Methoxy-2-butenoimidazolide (18). Dry THF (100 mL), 3-methoxy-2-butenoyl chloride (2.0 g, 15 mmol), and imidazole (2.0 g, 30 mmol) were stirred overnight at room temperature. The mixture was filtered and the filtrate concentrated to give a solid in 89% yield: mp 83–85 °C; IR (KBr) 3120, 1705, 1600, 1220, 820; ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H), 3.9 (s, 3 H), 5.7 (s, 1 H), 7.2 (br, 1 H), 7.6 (br, 1 H), 8.4 (br, 1 H); MS, 166 ($M^{\bullet+}$, 9), 116 (2), 99 (100), 68 (21).

3-(Phenylthio)-2-butenoic acid (21) was prepared according to a literature procedure.[32]

3-(Phenylthio)-2-buteno-1,2,4-triazolide (23). 3-(Phenylthio)-2-butenoic acid (2.60 g, 13.4 mmol), oxalyl chloride (15 mmol, 1.31 mL), and 35 mL of dry benzene were refluxed for 1 h. The solvent was concentrated in vacuo to obtain the acid chloride in 90% yield, used in the next step without purification: ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H), 5.5 (s, 1 H), 7.5 (s, 1 H). The acid chloride was dissolved in 60 mL of dry THF, 1,2,4-triazole (1.36 g, 20 mmol) was added, and the mixture was stirred overnight at room temperature. The mixture was filtered and the filtrate concentrated to give a dark oil in 92% yield: ^{1}H NMR ($CDCl_3$) δ 2.6 (s, 3 H), 6.6 (s, 1 H), 7.5 (s, 5 H), 7.8 (s, 1 H), 9.7 (s, 1 H).

Methyl 3-(2-Hydroxyphenyl)-3-oxopropionate (11). To a mixture of malonaldehyde bis(dimethyl acetal) (5 mmol, 0.85 mL) and $TiCl_4$ (5 mmol, 0.55 mL) in 20 mL of dry CH_2Cl_2 was added tris silyl enol ether **2** (5 mmol) at −78 °C. The mixture was stirred at this temperature for 2 h, then gradually allowed to warm up to room temperature, and stirred overnight. The reaction mixture was quenched with aqueous $NaHCO_3$ and stirred for 3 h. It was extracted with ether, dried, and concentrated. Purification using column chromatography with 25/75 v/v ethyl acetate/hexanes as eluent gave **11** in 30% yield: IR (neat) 2960, 1740, 1650, 1440, 760; ^{1}H NMR ($CDCl_3$) δ 3.4 (s, 2 H), 4.0 (s, 3 H), 7.0 (m, 2 H), 7.5 (m, 2 H), 12.4 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 46.3, 53.2, 119.2, 119.8, 120.1, 131.3, 137.9, 163.4, 168.1; MS, 194 ($M^{\bullet+}$, 36), 162 (83), 120 (100), 92 (30); exact mass found for $C_{10}H_{10}O_4$ 194.055, calcd 194.058.

γ-Pyrone (26) was prepared according to a literature procedure.[14-17]

1,1,3,3,5,5-Hexamethoxypentane (28). γ-Pyrone (20 mmol, 1.9 g) was dissolved in 100 mL of dry methanol, and 20 mL of trimethyl orthoformate and a small amount of *p*-toluenesulfonic acid were added. After 1–2 h, the color of the reaction mixture began to darken, eventually turning dark violet. The mixture was stirred for 3 days at room temperature. The volatiles were evaporated in vacuo, and the crude dark oil was purified by column chromatography using 95/5 v/v (9/1 v/v hexanes/ethyl acetate)/methanol to give **28** in 60–65% yield: IR (neat) 2900–3000, 2820, 1610, 1440, 1380, 1360, 1300, 1260, 1240, 1180, 950, 810, 800; ^{1}H NMR ($CDCl_3$) δ 1.8 (d, J = 5 Hz, 4 H), 3.0 (s, 6 H), 3.2 (s, 12 H), 4.3 (t, J = 5 Hz, 2 H); MS, 221 ($M^{\bullet+}$ − CH_3O, 1), 205 (3), 163 (4), 157 (16), 115 (12), 85 (28), 75 (100).

2-(2,2-Dimethoxyethyl)-1,3-dithiane (39) was prepared from the reaction of 2-lithio-1,3-dithiane with 1 equiv of bromoacetaldehyde dimethyl acetal after 2 days of stirring at −20 °C. It was purified by column chromatography with 25/75 v/v ethyl acetate/hexanes as eluent and obtained in 82% yield as an oil: IR (neat) 2960, 2940, 2800, 1415, 1115; ^{1}H NMR ($CDCl_3$) δ 2.0–2.4 (m, 4 H), 2.8–3.2 (m, 4 H), 3.5 (s, 6 H), 4.2 (t, J = 7 Hz, 1 H), 4.8 (t, J = 5 Hz, 1 H); MS, 208 ($M^{\bullet+}$, 8), 176 (62), 161 (23), 145 (32), 133 (10), 119 (65), 102 (31), 75 (100); exact mass found for $C_{12}H_{16}O_2S_2$ 208.059, calcd 208.059.

2,2-Bis(2,2-dimethoxyethyl)-1,3-dithiane (40). To a solution of 1,3-dithiane (6.0 g, 50 mmol) in dry THF (100 mL) at −20 °C was added *n*-butyllithium (5.5 mL of a 10.5 M solution in hexanes). After 2 h, bromoacetaldehyde dimethyl acetal (50 mmol) was added. The mixture was stirred for 2 days at −20 °C. *n*-Butyllithium was added (55 mmol), and after 10 h, 50 mmol of bromoacetaldehyde dimethyl acetal was added. After 7 days at −20 °C, 200 mL of water was added and the mixture extracted with ether and washed twice each with water, 10% aqueous KOH, and water. The organic layer was dried, filtered, and concentrated in vacuo to give an oil. After purification by column chromatography (2/8 v/v ethyl acetate/hexanes), a 60% yield of **40** was obtained and 25% of the monoalkylated dithiane was recovered. Compound **40**: IR (neat) 2880–2940, 2820, 1430, 1410, 1380, 1350, 1180, 1100–1120, 1030–1080; ^{1}H NMR ($CDCl_3$) δ 1.7–2.0 (m, 2 H), 2.2 (d, J = 4 Hz, 4 H), 2.6–2.9 (m, 4 H), 3.3 (s, 12 H), 4.6 (t, J = 4 Hz, 2 H); MS, 296 ($M^{\bullet+}$, 11), 221 (2), 190 (2), 175 (4), 119 (5), 75 (100); exact mass found for $C_{12}H_{24}O_4S_2$ 296.108, calcd 296.111.

2,2-Bis(2,2-diethoxyethyl)-1,3-dithiane (41) was prepared in a similar way as **40** but by using bromoacetaldehyde diethyl acetal instead of the dimethyl acetal. Compound **41**: ^{1}H NMR ($CDCl_3$) δ 1.2 (t, J = 6 Hz, 12 H), 1.6–2.0 (m, 2 H), 2.2 (d, J = 4 Hz, 4 H), 2.6–2.9 (m, 4 H), 3.1–3.6 (m, 8 H), 4.6 (t, J = 4 Hz, 2 H).

Methyl 3-[4-(2,2-Dimethoxyethyl)-2-hydroxyphenyl]-3-oxopropionate (29). In a 100-mL flask at −78 °C was prepared a solution of dry methylene chloride (50 mL), 1,1,3,3,5,5-hexamethoxypentane (1 mmol), and **2** (2 mmol). A mixture of $TiCl_4$ (3 mmol) and Ti(^{i}OPr)$_4$ (3 mmol) in CH_2Cl_2 (5 mL) was added. After reaction for 3 h at −78 °C and overnight at room temperature, the mixture was quenched with aqueous $NaHCO_3$. After extraction with diethyl ether, the organic layer was dried, filtered,

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and concentrated in vacuo. The residue was purified by preparative TLC using 3/7 v/v ethyl acetate/hexanes as the eluent. Compound **29** (5 mg, 2% yield) was obtained: ^{1}H NMR ($CDCl_3$) δ 2.90 (d, J = 6 Hz, 2 H), 3.34 (s, 6 H), 3.76 (s, 3 H), 3.99 (s, 2 H), 4.60 (t, J = 6 Hz, 1 H), 6.81 (dd, J = 8 Hz, J = 1.5 Hz, 1 H), 6.93 (d, J = 1.5 Hz, 1 H), 7.62 (d, J = 8 Hz, 1 H), 11.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 39.7, 45.4, 52.5, 53.4, 104.2, 117.3, 119.1, 120.8, 130.0, 147.5, 162.6, 167.3, 197.5; MS, 282 ($M^{\bullet+}$, 0.4), 251 (4), 219 (11), 177 (12), 163 (7), 134 (9), 106 (9), 75 (100). From the crude reaction mixture, using column chromatography with ethyl acetate and methanol as eluents, we could also isolate a colored viscous material, presumably polymeric, which showed broad bands in the ^{1}H NMR.

Malonaldehyde bis(propylene dithioacetal) (42) was prepared according to a published procedure[24] except that BF_3·OEt_2 was used rather than a stream of dry HCl. It had mp 110–112 °C (lit. mp[24] 113–114.5 °C).

5,5-Dimethoxy-3-oxopentanal Bis(propylene dithioacetal) (43). In a 100-mL flask, compound **42** (2.5 g, 10 mmol) was dissolved in 50 mL of dry THF. After cooling to −20 °C, *n*-butyllithium (11 mmol) in hexane was added. After 3.5 h, bromoacetaldehyde dimethyl acetal (10 mmol, 1.2 mL) was added and the mixture stirred at −20 °C for 6 days. Then 150 mL of water was added, followed by extraction with ether. The ether layer was washed with water (2×), 10% aqueous KOH, and water, then dried, filtered, and concentrated in vacuo. The crude product was purified by column chromatography using 2/8 v/v ethyl acetate/hexanes to furnish **43** (70%): ^{1}H NMR ($CDCl_3$) δ 1.8–2.2 (m, 4 H), 2.4 (t, J = 4 Hz, 4 H), 2.7–3.2 (m, 8 H), 3.4 (s, 6 H), 4.4 (t, J = 4 Hz, 1 H), 4.8 (t, J = 4 Hz, 1 H).

6,6-Dimethoxy-2,4-hexanedione Bis(propylene dithioketal) (44) and 3-Oxobutanal Bis(propylene dithioacetal) (45). In a 100-mL flask, compound **42** (2.5 g, 10 mmol) was dissolved in 50 mL of dry THF, and *n*-butyllithium (11 mmol in hexanes) was added at −20 °C. After 4 h, methyl iodide (10 mmol) was added and the mixture stirred at −20 °C overnight. Then *n*-butyllithium (11 mmol in hexanes) was added. The mixture was stirred at −20 °C for 7 h, and bromoacetaldehyde dimethyl acetal (10 mmol) was added. The mixture was left at −20 °C for 7 days. After the mixture was quenched with 150 mL of water and extracted with ether, the organic phase was washed with water, 10% aqueous KOH, and then water. The organic solution was dried, filtered, and concentrated in vacuo and the residue purified by column chromatography using 2/8 v/v ethyl acetate/hexanes as the eluent to give **44** (50% yield) as an oil, along with **45** (30%).

Compound **44**: IR (neat) 2880–2940, 2900, 1730, 1430, 1410, 1360, 1270, 1180, 900; ^{1}H NMR ($CDCl_3$) δ 1.7–2.1 (m, 4 H), 2.0 (s, 3 H), 2.5 (d, J = 4 Hz, 2 H), 2.6–3.0 (m, 10 H), 3.3 (s, 6 H), 4.6 (t, J = 4 Hz, 1 H); MS, 354 ($M^{\bullet+}$, 1), 308 (1), 274 (2), 149 (14), 133 (35), 126 (16), 119 (21), 32 (100).

Compound **45**: IR (neat) 2890–2940, 1410, 1260, 990; ^{1}H NMR ($CDCl_3$) δ 1.6 (s, 3 H), 1.8–2.2 (m, 4 H), 2.3 (d, J = 4 Hz, 2 H), 2.6–3.1 (m, 8 H), 4.2 (t, J = 4 Hz, 1 H); MS, 266 ($M^{\bullet+}$, 6), 204 (34), 159 (28), 133 (90), 119 (55), 107 (33), 28 (100); exact mass found for $C_{10}H_{18}S_4$ 266.027, calcd 266.029.

7,7-Dimethoxy-3,5-heptanedione bis(propylene dithioketal) (44a) and 3-oxopentanal bis(propylene dithioacetal) (45a) were prepared in a similar way and with a similar yield as **44** and **45**.

Tris-electrophile **44a**: IR (neat) 2840–2960, 2810, 1730, 1430, 1410, 1370, 900; ^{1}H NMR ($CDCl_3$) δ 1.2 (t, J = 8 Hz, 3 H), 1.6–2.2 (m, 6 H), 2.1–2.4 (q, J = 8 Hz, 2 H), 2.5 (d, J = 4 Hz, 2 H), 2.6–3.0 (m, 8 H), 3.3 (s, 6 H), 4.6 (t, J = 4 Hz, 1 H); MS, 368 ($M^{\bullet+}$, 1), 296 (2), 280 (6), 173 (37), 147 (41), 119 (51), 106 (23), 75 (72), 31 (100).

Bis-electrophile **45a**: IR (neat) 2880–3940, 1420, 1370, 1270, 1230, 1160, 1110, 900; ^{1}H NMR ($CDCl_3$) δ 1.0 (t, J = 4 Hz, 3 H), 1.6–2.2 (m, 6 H), 2.2 (d, J = 4 Hz, 2 H), 2.6–3.0 (m, 8 H), 4.2 (t, J = 4 Hz, 1 H); MS, 280 ($M^{\bullet+}$, 31), 236 (5), 218 (4), 205 (38), 173 (66), 161 (30), 147 (73), 133 (33), 28 (100); exact mass found for $C_{11}H_{20}S_4$ 280.045, calcd 280.045.

Attempted Reaction of 43, 44, or 44a with 2. To a 100-mL flask at −78 °C were added 30 mL of dry CH_2Cl_2, the silyl ether **2** (1 mmol), and the electrophile (1 mmol), followed by the Lewis acid (3 mmol; trimethylsilyl triflate, BF_3·OEt_2, $SnCl_4$, Zn triflate,[25] and Hg(II) triflate[26] were tried). The reaction was followed by TLC but only starting material observed. Upon warming to room temperature, the reaction did not produce any naphthalene derivative.

General Procedure for the Preparation of Electrophiles 50a–f. To a solution of 1,3-dithiane (6.0 g, 50 mmol) in dry THF (150 mL) was added *n*-butyllithium (5.5 mL of a 10 M solution in hexanes) at −20 °C. After 2 h, the epoxide **46** was added (50 mmol) and the mixture stored at −15 °C for a week. Water was added, and the mixture was extracted with ether. The organic layer was washed with water, aqueous 10% KOH, and then water. It was dried, filtered, and concentrated in vacuo to give alcohol **47** in 80% yield, used without purification.

A solution of alcohol **47** (35 mmol) in methylene chloride (35 mL) was added to a mixture of oxalyl chloride (37 mmol, 3.5 mL) and dimethyl sulfoxide (66 mmol, 6.0 mL) in CH_2Cl_2 (200 mL) at −78 °C. After 1 h, dry triethylamine was added (20 mL), and after 10 min at −78 °C, the mixture was allowed to warm up to room temperature. Water was added (30 mL), and the aqueous layer was extracted once with methylene chloride. The organic phase was washed with water, saturated NaCl, water, 5% Na_2CO_3, and then water, dried, filtered, and concentrated to give ketone **48** in 80% yield, which was used without purification.

Ketone **48** (30 mmol) was treated with dry methanol (100 mL) and trimethyl orthoformate (10 mL) in the presence of a catalytic amount of *p*-toluenesulfonic acid for 3 days at room temperature. The volatiles were evaporated in vacuo, and the dark oil was purified by using column chromatography with 10/90 v/v ethyl acetate/hexanes as the eluent to give the ketal **49** in 80% yield. Compound **49** (4 mmol) was dissolved in dry THF (50 mL), and at −20 °C, *n*-butyllithium (4.2 mmol in hexanes) was added. The mixture was stirred at −20 °C for 5 h. Bromoacetaldehyde dimethyl acetal (4 mmol, 0.50 mL) was added and the mixture stored at −15 °C for 10 days. Water was added, the mixture was extracted with ether, and the organic phase was washed with water, aqueous 10% KOH, and water, then dried, filtered, and concentrated on the rotavap to furnish the tris-electrophile **50** after purification by column chromatography with 20/80 v/v ethyl acetate/hexanes. The overall yield of **50** was 15–25% starting from 1,3-dithiane.

2-(2-Hydroxy-*n*-propyl)-1,3-dithiane (47a, R_1 = CH_3, R_2 = H) was prepared according to a literature procedure.[24]

2-(2-Oxo-*n*-propyl)-1,3-dithiane (48a, R_1 = CH_3, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 1.8–2.1 (m, 2 H), 2.2 (s, 3 H), 2.6–3.0 (m, 6 H), 4.2 (t, J = 7 Hz, 1 H).

2-(2,2-Dimethoxy-*n*-propyl)-1,3-dithiane (49a, R_1 = CH_3, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 3 H), 1.8–2.1 (m, 4 H), 2.7–3.0 (m, 4 H), 3.2 (s, 6 H), 4.1 (t, J = 6 Hz, 1 H).

2-(2,2-Dimethoxyethyl)-2-(2,2-dimethoxy-*n*-propyl)-1,3-dithiane (50a, R_1 = CH_3, R_2 = H): IR (neat) 2900, 2870, 2800, 1100, 1030, 715; ^{1}H NMR ($CDCl_3$) δ 1.5 (s, 3 H), 1.7–2.1 (m, 2 H), 2.3 (s, 2 H), 2.4 (d, J = 5 Hz, 2 H), 2.7–3.0 (m, 4 H), 3.1 (s, 6 H), 3.3 (s, 6 H), 4.6 (t, J = 5 Hz, 1 H); MS, 310 ($M^{\bullet+}$, 1), 278 (2), 264 (5), 221 (3), 205 (3), 190 (19), 175 (19), 119 (42), 89 (49), 75 (100); exact mass found for $M^{\bullet+}$ − CH_3OH, $C_{12}H_{22}O_3S_2$, 278.100, calcd 278.101.

2-(2-Hydroxy-*n*-butyl)-1,3-dithiane (47b, R_1 = Et, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 6 Hz, 3 H), 1.2–2.4 (m, 6 H), 2.7–3.0 (m, 4 H), 3.6–4.0 (m, 2 H), 4.2 (t, J = 6 Hz, 1 H).

2-(2-Oxo-*n*-butyl)-1,3-dithiane (48b, R_1 = Et, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 6 Hz, 3 H), 1.7–2.0 (m, 2 H), 2.3 (q, J = 6 Hz, 2 H), 2.5–2.9 (m, 6 H), 4.4 (t, J = 6 Hz, 1 H).

2-(2,2-Dimethoxy-*n*-butyl)-1,3-dithiane (49b, R_1 = Et, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.9 (t, J = 6 Hz, 3 H), 1.6–2.1 (m, 6 H), 2.8–3.0 (m, 4 H), 3.2 (s, 6 H), 4.0 (t, J = 5 Hz, 1 H).

2-(2,2-Dimethoxy-*n*-butyl)-2-(2,2-dimethoxyethyl)-1,3-dithiane (50b, R_1 = Et, R_2 = H): IR (neat) 2880–2950, 2800, 1450, 1430, 1410, 1130, 1110, 1030–1050, 900; ^{1}H NMR ($CDCl_3$) δ 1.8 (t, J = 6 Hz, 3 H), 1.7–2.0 (m, 4 H), 2.1 (s, 2 H), 2.4 (d, J = 4 Hz, 2 H), 2.6–2.9 (m, 4 H), 3.0 (s, 6 H), 3.2 (s, 6 H), 4.6 (t, J = 6 Hz, 1 H); MS, 324 ($M^{\bullet+}$, 1), 292 (2), 278 (3), 207 (15), 103 (23), 75 (100).

2-(2-Hydroxy-*n*-hexyl)-1,3-dithiane (47c, R_1 = *n*-butyl, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.8–1.1 (m, 3 H), 1.2–1.6 (m, 6 H), 1.7–2.2 (m, 4 H), 2.7–3.0 (m, 4 H), 3.6–4.0 (m, 2 H), 4.2 (t, J = 7 Hz, 1 H).

2-(2-Oxo-*n*-hexyl)-1,3-dithiane (48c, R_1 = *n*-butyl, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.6–1.0 (m, 3 H), 1.0–1.5 (m, 4 H), 1.8–2.1 (m,

2 H), 2.2–2.5 (m, 2 H), 2.6–3.0 (m, 6 H), 4.2 (t, J = 6 Hz, 1 H).

2-(2,2-Dimethoxy-*n*-hexyl)-1,3-dithiane (49c, R_1 = *n*-butyl, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.7–1.0 (m, 3 H), 1.0–1.6 (m, 4 H), 1.6–2.1 (m, 4 H), 2.6–3.0 (m, 4 H), 3.1 (s, 6 H), 3.9 (t, J = 6 Hz, 1 H).

2-(2,2-Dimethoxyethyl)-2-(2,2-dimethoxy-*n*-hexyl)-1,3-dithiane (50c, R_1 = *n*-butyl, R_2 = H): IR (neat) 2880–2960, 2820, 1440, 1420, 1120, 1060, 940, 900; ^{1}H NMR ($CDCl_3$) δ 0.6–1.0 (m, 3 H), 1.0–1.6 (m, 6 H), 1.6–2.1 (m, 2 H), 2.1 (s, 2 H), 2.4 (d, J = 5 Hz, 2 H), 2.6–2.9 (m, 4 H), 3.0 (s, 6 H), 3.2 (s, 6 H), 4.6 (t, J = 5 Hz, 1 H); MS, 352 ($M^{\bullet+}$, 1), 320 (1), 289 (1), 258 (2), 213 (4), 207 (14), 201 (5), 175 (6), 131 (16), 119 (20), 75 (100).

2-(2-Hydroxy-*n*-decyl)-1,3-dithiane (47d, R_1 = *n*-octyl, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.6–1.0 (m, 3 H), 1.0–1.6 (m, 14 H), 1.6–2.2 (m, 4 H), 2.7–3.0 (m, 4 H), 3.6–4.0 (m, 2 H), 4.2 (t, J = 6 Hz, 1 H).

2-(2-Oxo-*n*-decyl)-1,3-dithiane (48d, R_1 = *n*-octyl, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.7–1.0 (m, 3 H), 1.0–2.5 (m, 12 H), 1.8–2.1 (m, 2 H), 2.2–2.4 (m, 2 H), 2.5–2.9 (m, 6 H), 4.4 (t, J = 6 Hz, 1 H).

2-(2,2-Dimethoxy-*n*-decyl)-1,3-dithiane (49d, R_1 = *n*-octyl, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 0.7–1.0 (m, 3 H), 1.0–1.6 (m, 14 H), 1.7–2.2 (m, 4 H), 2.7–3.0 (m, 4 H), 3.1 (s, 6 H), 4.0 (t, J = 6 Hz, 1 H).

2-(2,2-Dimethoxy-*n*-decyl)-2-(2,2-dimethoxyethyl)-1,3-dithiane (50d, R_1 = *n*-octyl, R_2 = H): IR (neat) 2880–2960, 2840, 1450, 1370, 1180, 1110, 1140, 950, 900; ^{1}H NMR ($CDCl_3$) δ 0.7–1.0 (m, 3 H), 1.0–1.5 (m, 14 H), 1.7–2.0 (m, 2 H), 2.1 (s, 2 H), 2.4 (d, J = 4 Hz, 2 H), 2.5–2.8 (m, 4 H), 3.1 (s, 6 H), 3.3 (s, 6 H), 4.0 (t, J = 4 Hz, 1 H); MS, 408 ($M^{\bullet+}$, 0.1), 376 (0.4), 362 (1), 288 (2), 252 (8), 220 (2), 187 (11), 163 (21), 119 (29), 75 (100).

2-(2-Hydroxy-2-phenylethyl)-1,3-dithiane (47e, R_1 = Ph, R_2 = H) was prepared according to a literature procedure.[23]

2-(2-Oxo-2-phenylethyl)-1,3-dithiane (48e, R_1 = Ph, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 1.8–2.2 (m, 4 H), 2.7–3.0 (m, 4 H), 3.3 (d, J = 7 Hz, 2 H), 4.6 (t, J = 7 Hz, 1 H), 7.2–7.5 (m, 3 H), 7.7–7.9 (m, 2 H).

2-(2,2-Dimethoxy-2-phenylethyl)-1,3-dithiane (49e, R_1 = Ph, R_2 = H): ^{1}H NMR ($CDCl_3$) δ 1.7–2.0 (m, 2 H), 2.2 (d, J = 6 Hz, 2 H), 2.5–2.7 (m, 4 H), 3.1 (s, 6 H), 3.6 (t, J = 6 Hz, 1 H), 7.1–7.5 (m, 5 H).

2-(3-Hydroxy-2-butyl)-1,3-dithiane (47f, R_1 = R_2 = CH_3): ^{1}H NMR ($CDCl_3$) δ 1.0 (d, J = 5 Hz, 3 H), 1.1 (d, J = 5 Hz, 3 H), 1.6–2.2 (m, 3 H), 2.6–3.0 (m, 4 H), 3.5–3.9 (m, 2 H), 4.4 (d, J = 4 Hz, 1 H).

2-(3-Oxo-2-butyl)-1,3-dithiane (48f, R_1 = R_2 = CH_3): ^{1}H NMR ($CDCl_3$) δ 1.2 (d, J = 7 Hz, 3 H), 1.7–2.2 (m, 3 H), 2.2 (s, 3 H), 2.6–2.9 (m, 4 H), 4.2 (d, J = 8 Hz, 1 H).

2-(3,3-Dimethoxy-2-butyl)-1,3-dithiane (49f, R_1 = R_2 = CH_3): ^{1}H NMR ($CDCl_3$) δ 0.9 (d, J = 8 Hz, 3 H), 1.1 (s, 3 H), 1.6–2.4 (m, 3 H), 2.7–3.0 (m, 4 H), 3.2 (d, J = 5 Hz, 6 H), 4.5 (d, J = 2 Hz, 1 H).

2-(2,2-Dimethoxyethyl)-2-(3,3-dimethoxy-2-butyl)-1,3-dithiane (50f, R_1 = R_2 = CH_3): IR (neat) 2800–2900, 2820, 1450, 1380, 1110, 1040, 900; ^{1}H NMR ($CDCl_3$) δ 1.0–1.4 (m, 6 H), 1.8–2.3 (m, 3 H), 2.3–3.0 (m, 6 H), 3.1 (d, J = 5 Hz, 6 H), 3.4 (s, 6 H), 4.6 (m, 1 H); MS, 324 ($M^{\bullet+}$, 1), 292 (0.6), 252 (1), 236 (4), 228 (2), 220 (3), 204 (37), 189 (23), 119 (69), 99 (55), 89 (70), 75 (100).

General Procedure for the Synthesis of Naphthalene Derivatives 51. The electrophile **50** (1 mmol) and the silyl ether **2** (1 mmol) were added to 20 mL of dry methylene chloride at −78 °C. Trimethylsilyl triflate (2 mmol, 0.4 mL) was added and the reaction mixture stirred at −78 °C overnight. Water (1 mL) was added and the mixture allowed to reach room temperature (0.5 h). The mixture was dried, filtered, and concentrated to give a dark red oil. The naphthalenes were purified by column chromatography using a 1.0-cm-diameter column with 5/95 v/v ethyl acetate/hexanes as eluent. The yields were 10–20%.

2-Carbomethoxy-1,8-dihydroxynaphthalene (30): mp 124–125 °C; IR (KBr) 3410, 3340, 1660, 1340, 1260, 800, 740; ^{1}H NMR ($CDCl_3$) δ 4.0 (s, 3 H), 6.93 (dd, J = 8 Hz, J = 1 Hz, 1 H), 7.26 (m, 2 H), 7.50 (t, J = 8 Hz, 1 H), 7.70 (d, J = 9 Hz, 1 H), 9.6 (s, 1 H), 13.4 (s, 1 H); MS, 218 ($M^{\bullet+}$, 34), 186 (100), 176 (14), 161 (25), 155 (29), 130 (40), 102 (77); exact mass found for $C_{12}H_{10}O_4$ 218.060, calcd 218.058. Anal. Found for $C_{12}H_{10}O_4$: C, 65.70; H, 4.72. Calcd: C, 66.10; H, 4.62.

2-Carbomethoxy-1,8-dihydroxy-6-methylnaphthalene (51a, R_1 = CH_3, R_2 = H): mp 130–132 °C; IR (KBr) 3410, 2970–3010, 1670, 1350, 1320, 870, 790; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 4.01 (s, 3 H), 6.78 (d, J = 1 Hz, 1 H), 7.06 (d, J = 1 Hz, 1 H), 7.16 (d, J = 9 Hz, 1 H), 7.64 (d, J = 9 Hz, 1 H), 9.49 (s, 1 H), 13.32 (s, 1 H); MS, 232 ($M^{\bullet+}$, 38), 200 (100), 144 (21), 115 (65), 89 (32); exact mass found for $C_{13}H_{12}O_4$ 232.077, calcd 232.074. Anal. Found for $C_{13}H_{12}O_4$: C, 66.94; H, 5.28. Calcd: C, 67.28; H, 5.21.

2-Carbomethoxy-1,8-dihydroxy-6-ethylnaphthalene (51b, R_1 = Et, R_2 = H): mp 90–93 °C; IR (KBr) 2940, 2900, 1670, 1340, 1200; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 8 Hz, 3 H), 2.74 (q, J = 8 Hz, 2 H), 4.00 (s, 3 H), 6.81 (d, J = 1 Hz, 1 H), 7.07 (d, J = 1 Hz, 1 H), 7.18 (d, J = 9 Hz, 1 H), 7.63 (d, J = 9 Hz, 1 H), 9.48 (s, 1 H), 13.28 (s, 1 H); MS, 246 ($M^{\bullet+}$, 27), 214 (100), 190 (11), 171 (35), 133 (55), 115 (33), 106 (46), 73 (67); exact mass found for $C_{14}H_{14}O_4$ 246.090, calcd 246.089.

2-Carbomethoxy-1,8-dihydroxy-6-*n*-butylnaphthalene (51c, R_1 = *n*-butyl, R_2 = H) was obtained as an oil: IR (neat) 3420, 2950, 2920, 1660, 1440, 1290; ^{1}H NMR ($CDCl_3$) δ 0.90–0.98 (t, J = 8 Hz, 3 H), 1.20–1.60 (m, 2 H), 1.80–2.20 (m, 2 H), 2.84 (t, J = 5 Hz, 2 H), 4.00 (s, 3 H), 6.79 (d, J = 2 Hz, 1 H), 7.05 (d, J = 2 Hz, 1 H), 7.17 (d, J = 9 Hz, 1 H), 7.63 (d, J = 9 Hz, 1 H), 6.9 (br, 1 H), 9.5 (br, 1 H); 274 ($M^{\bullet+}$, 3), 242 (8), 218 (34), 159 (32), 133 (52), 121 (35), 119 (100); exact mass found for $C_{16}H_{18}O_4$ 274.123, calcd 274.120; exact mass found for $M^{\bullet+} - C_4H_8$, $C_{12}H_{10}O_4$, 218.059, calcd 218.058.

2-Carbomethoxy-1,8-dihydroxy-6-*n*-octylnaphthalene (51d, R_1 = *n*-octyl, R_2 = H) was obtained as an oil: IR (neat) 3420, 2920, 2860, 1660, 1290, 1250; ^{1}H NMR ($CDCl_3$) δ 0.9–1.0 (m, 3 H), 1.2–1.5 (m, 10 H), 1.5–1.8 (m, 2 H), 2.7 (t, J = 5 Hz, 2 H), 4.0 (s, 3 H), 6.81 (d, J = 2 Hz, 1 H), 7.07 (d, J = 2 Hz, 1 H), 7.19 (d, J = 9 Hz, 1 H), 7.65 (d, J = 9 Hz, 1 H), 6.9 (br, 1 H), 9.5 (br, 1 H); MS, 274 (2), 266 (2), 246 (3), 236 (1), 220 (4), 205 (13), 141 (14), 133 (43), 119 (100), 101 (46).

2-Carbomethoxy-1,8-dihydroxy-5,6-dimethylnaphthalene (51f, R_1 = R_2 = CH_3): mp 128–132 °C; IR (KBr) 3320, 2880–2920, 1660, 1600, 1400, 1300, 1130; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 6 H), 4.00 (s, 3 H), 6.80 (s, 1 H), 7.40 (d, J = 9 Hz, 1 H), 7.67 (d, J = 9 Hz, 1 H), 9.5 (s, 1 H), 13.4 (s, 1 H); MS, 246 ($M^{\bullet+}$, 2), 236 (20), 214 (7), 190 (30), 162 (20), 147 (33), 133 (42), 119 (100); exact mass found for $C_{14}H_{14}O_4$ 246.086, calcd 246.089.

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