(Differential Scaning Calorimeter DSC4 Perkin-Elmer). ^{1}H NMR ($CDCl_3$): 2.3 (s, 12 H), 2.4 (s, 6 H). ^{13}C NMR (CD_2Cl_2): 16.6 (SCH_3), 18.0 (ring SCH_3), 110.95, 144.5 (tetrathioethylene carbons), 120.9, 141.3 (ring carbons). Anal. Calcd for $C_{16}H_{18}S_{10}$: C, 36.2; H, 3.4; S, 60.4. Found: C, 36.17; H, 3.3; S, 60.51. MS *m/z*: 531 (MH^+).

2-(Bis(methylthio)methylene)-4-nitro-1,3-benzodithiole (4): from 0.33 g (1.68×10^{-3} mol) of **1** and 0.17 g (0.86×10^{-3}) of 2-chloro-1,3-dinitrobenzene (**3**) in 2.5 mL of DMF; eluant, toluene/cyclohexane, 30/70 (v/v); 31 mg (11%) of a red solid was isolated. ^{1}H NMR ($CDCl_3$): 2.35 (s, 6 H), 7.21-7.24 and 7.27 (t, 1 H), 7.38-7.41 (d, 1 H), 8.04-8.08 (d, 1 H). Anal. Calcd for $C_{10}H_9NO_2S_4$: C, 39.6; H, 2.9; N, 4.6; S, 42.2. Found: C, 39.36; H, 2.71; N, 4.50; S, 42.01.

2-(Bis(methylthio)methylene)-4-chloro-1,3-benzodithiole (6): from 2.5 g (12.7×10^{-3} mol) of **1** and 1.62 g (8.4×10^{-3}) of 2,3-dichloro-1-nitrobenzene (**5**) in 10 mL of DMF; eluant, toluene/cyclohexane, 30/70 (v/v); 0.13 g (5 %) of **4** and 1.58 g (65 %) of **6** as a white solid recrystallized from ethanol and melting at 58.5 °C are obtained. ^{1}H NMR: 2.35 (s, 6 H), 7.0-7.2 (m, 3 H). Anal. Calcd for $C_{10}H_9ClS_4$: C, 41.0; H, 3.2; Cl, 12.1; S, 43.7. Found: C, 40.98; H, 3.37; Cl, 12.8; S, 42.8.

2,5-Bis(bis(methylthio)methylene)-7-nitrobenzo[1,2-*d*:3,4-*d'*]bis[1,3]dithiole (8): from 2 g (10.2×10^{-3} mol) of 2,3,4-trichloro-1,5-dinitrobenzene[15] in 20 mL of DMF; eluant, toluene/cyclohexane, 20/80 (v/v); 0.87 g (65%) of a red compound melting at 133 °C is obtained. ^{1}H NMR (CD_2Cl_2): 2.35 (s, 12 H), 7.8 (s, 1 H). ^{13}C NMR (CD_2Cl_2): 16.67 (SCH_3), 113.93-114.23, 135.32-135.59 (tetrathioethylene carbons), 113.32, 130.93, 133.96, 139.21, 192.11, 144.42 (ring carbons). Anal. Calcd for $C_{14}H_{13}NO_2S_8$: C, 34.7; H, 2.69; N, 2.89; O, 6.62; S, 53.0. Found: C, 35.11; H, 3.01; N, 2.86; O, 6.3; S, 52.72. MS *m/z*: 485 (MH^+).

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Regiospecific Preparation of Cyclobutenedione Monoacetals

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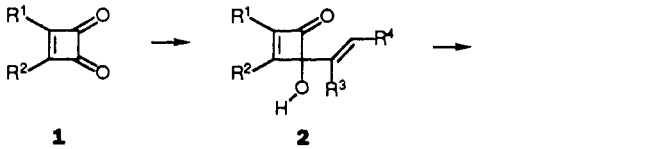
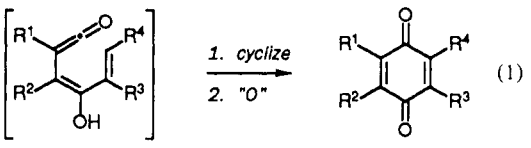
Treatment of 2,3-diisopropoxy-4-hydroxy-4-organyl-2-cyclobuten-1-ones, prepared by addition of nucleophiles (H^-, C-sp^3, C-sp^2, C-sp) to diisopropyl squarate, with $Me_3SiOCH_2CH_2OSiMe_3$ and catalytic trimethylsilyl triflate in THF induces a regiospecific monoacetalization, providing the 3-isopropoxy-4-organyl-3-cyclobutene-1,2-dione 2-(ethylene acetal) in high yield. These compounds react with a wide range of nucleophiles to give 1,2-adducts that can be converted into 3,4-disubstituted-3-cyclobutene-1,2-dione-2-ethylene acetals under mild conditions. By changing the order of introduction of substituents, this sequence of reactions provides access to a variety of isomeric cyclobutenedione monoacetals in a regiodefined fashion.

Introduction

Two powerful new methods for the synthesis of highly substituted quinones based on the thermolysis of 4-hydroxycyclobutenones bearing sp^2- and sp-hydridized substituents at the 4-position were uncovered within the last few years (eqs 1 and 2).[2] The 4-alkynyl-4-hydroxy-





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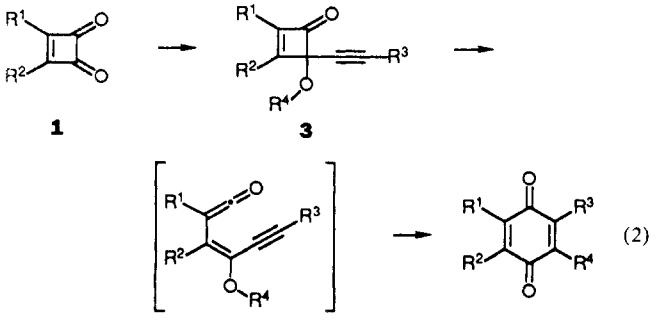
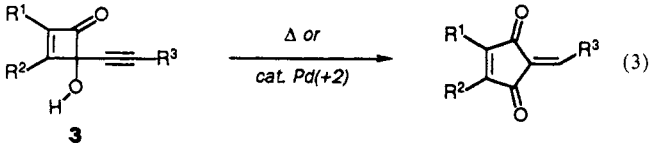


(2)

(1) Camille and Henry Dreyfus Teacher-Scholar, 1985-1990.

cyclobutenones also serve as precursors to alkylidenecyclopentenone derivatives, either via thermolysis[2a,j] or more efficiently via metal-catalyzed ring expansion (eq 3).[3]



(3)

The thermal processes are presumed to proceed via ring opening of the cyclobutenone to an unsaturated vinylketene intermediate. Unsymmetrically substituted quinones and alkylidenecyclopentenones can be prepared by these methods, but because the placement of substituents in the products is established in the initial addition of the unsaturated nucleophile to the cyclobutenedione (**1** → **2**, **1** → **3**), regiochemical control in the quinone synthesis and stereochemical control in the alkylidenecyclopentenone

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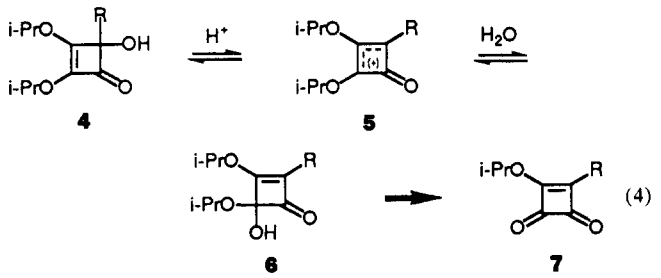
synthesis is limited to cyclobutenediones that show differing reactivities of the two carbonyl groups. Accordingly, all of the examples of unsymmetrical quinone synthesis and stereoselective alkylidenecyclopentenone synthesis published to date rely on nucleophilic additions to alkoxy-substituted cyclobutenediones (1, R^1 or R^2 = OR), the vinylogous ester carbonyl group exhibiting diminished reactivity. Ultimately, a truly general synthesis of the indicated compounds via the cyclobutenedione route will be realized if two requirements can be met: (1) broadly applicable methods for the placement of functionalized substituents at the 3- and 4-position of the cyclobutenedione must be developed and (2) an efficient differentiation of the two carbonyl groups that does not rely on electronic or steric effects imparted by cyclobutenedione ring substituents must be perfected to allow the regiospecific transformations inferred by the conversion of 1 into 2 and 3 shown in eqs 1 and 2. The goal of establishing simple routes to substituted cyclobutenediones has been met, in part, by the nucleophilic functionalization of squaric acid esters recently described,[4] and in the following paper we substantially extend the scope of substituted cyclobutenedione synthesis via the palladium-catalyzed cross-coupling of organic electrophiles with 3-stannylcyclobutenediones.[5] In this paper, we describe a solution to the second requirement listed above, the development of a simple synthetic method that provides cyclobutenedione monoacetals, regiospecifically, regardless of the substituents introduced at the 3- and 4-positions of the cyclobutenedione ring. We will describe, at a later date, how these cyclobutenedione monoacetals react with carbon nucleophiles, and, after mild hydrolysis of the acetal, furnish 4-hydroxy-4-unsaturated cyclobutenones primed for conversion into quinones by one of the two methods mentioned above, establishing a general synthesis of unsymmetrically substituted quinones.[6] Utilization of the cyclobutenedione monoacetals in the stereospecific synthesis of alkylidenecyclopentenedione monoacetals is also feasible.

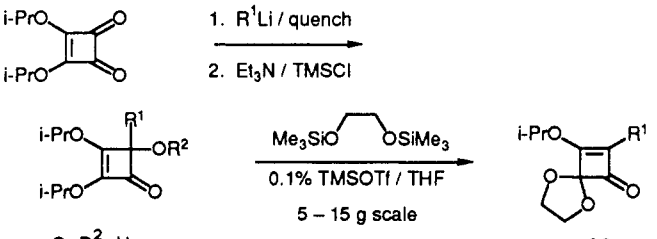
Results and Discussion

Addition of nucleophiles (H^-, C-sp^3, C-sp^2, C-sp) to diisopropyl squarate occurs to provide the corresponding mono-1,2-adducts 4 in high isolated yields.[2] Addition of acid effects loss of *i*-PrOH with formation of the organylisopropoxycyclobutenedione 7, presumably by acid-catalyzed allylic equilibration of the tertiary allylic alcohol to a hemiacetal (4 → 6) that collapses to the observed product (eq 4). We reasoned that it should be



possible to trap the presumed carbocationic intermediate 5 in this reaction with ethylene glycol and through a series of reversible steps specifically generate a cyclobutenedione monoacetal. This premise was verified. The 4-substituted-4-(trimethylsiloxy)cyclobutenones **9a–f** were prepared by addition of the corresponding organolithium reagents to diisopropyl squarate followed by protection of the resulting alcohols 8 as the trimethylsilyl ethers (Me_3SiCl/Et_3N, ether, room temperature). Treatment of (trimethylsiloxy)cyclobutenones **9a–f** with ethylene glycol bis(trimethylsilyl ether)[7] in THF in the presence of 0.1% trimethylsilyl triflate at room temperature effected clean conversion to the monoacetals **10a–f** in 76–99% isolated yields (Table I). The monoacetals were easily purified by recrystallization or chromatography. The success of the acetal formation depended on the use of rigorously dry reaction conditions and pure trimethylsilyl triflate. Prolonged reaction times led to the formation of impurities.

Table I. Synthesis of 3-Isopropoxy-4-substituted-3-cyclobutene-1,2-dione 2-(Ethylene acetals)



R^1	comp, %	comp, %	comp, %
H (as *i*-Bu_2AlH)	**8a**, 89	**9a**, 90	**10a**, 76
Me	**8b**, 99	**9b**, 99	**10b**, 99
n-Bu	**8c**, 80	**9c**, 92	**10c**, 87
t-Bu	**8d**, 83	**9d**, 97	**10d**, 85
Ph	**8e**, 93	**9e**, 92	**10e**, 80
C≡C-*n*-C_4H_9	**8f**, 99	**9f**, 95	**10f**, 80

The monoacetals **10** were treated in THF solution at −78 °C with a variety of carbon nucleophiles (and *i*-Bu_2AlH in ether at −23 °C), furnishing the tertiary allylic alcohols **11** in high yields, in most cases, after purification by chromatography (Table II). While most organolithium reagents added to **10** in a 1,2-fashion without complication, acetylides reacted very slowly at −78 °C and on warming produced 1,4-adducts admixed with products of multiple addition. By reversing the addition and adding the acetal to a solution of the acetylide in ether at 0–25 °C, 1,2-adducts from acetylides were obtained almost exclusively. Conversion of the 3-isopropoxyallylic alcohol moiety of **11** into the cyclobutenones **12**, without perturbing the acetal, was accomplished in most cases by a mild hydrolysis with 2 N HCl in THF. The resulting disubstituted cyclobutenedione monoacetals were formed in good isolated yields within minutes. Where R^1 or R^2 = H (entries 1–4), even milder conditions were required to prevent concomitant acetal hydrolysis. This was accomplished by using the conditions of allylic rearrangement worked out earlier by Moore (for **12a** and **12c**, where R^1 = H, trifluoroacetic anhydride quench of the alkoxide followed by treatment with aqueous $NaHCO_3$; for **12b** and **12d**, where R^2 = H, isolation of the alcohol **11** followed by treatment with trifluoroacetic anhydride/base).[2a] Both compounds **11** and **12** were purified by silica gel chromatography and were stable on refrigerated storage. The generality of the synthesis of cyclobutenedione monoacetals is exemplified by the employment of nucleophiles of widely ranging steric and electronic demands. The regiospecific nature of this

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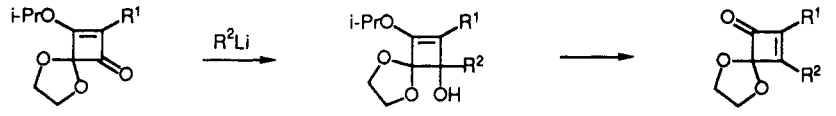
Table II. Synthesis of Regioisomeric Cyclobutenedione Monoacetals



10 **11** **12**

entry	R^1	R^2	comp, %	conditions	comp, %
1	H	Me	**11a**, not isol.	$TFAA/NaHCO_3$	**12a**, 91
2	Me	H (as i-Bu_2AlH)	**11b**, 78	$TFAA/Et_3N$	**12b**, 76
3	H	t-Bu	**11c**, not isol.	$TFAA/NaHCO_3$	**12c**, 78
4	t-Bu	H (as i-Bu_2AlH)	**11d**, 95	TFAA/DMAP	**12d**, 92
5	Me	n-Bu	**11e**, 99	2 N HCl	**12e**, 99
6	n-Bu	Me	**11f**, 99	2 N HCl	**12f**, 96
7	n-Bu	t-Bu	**11g**, 73	2 N HCl	**12g**, 99
8	t-Bu	n-Bu	**11h**, 97	2 N HCl	**12h**, 98
9	n-Bu	C≡C-n-Bu	**11i**, 70	2 N HCl	**12i**, 97
10	C≡C-n-Bu	n-Bu	**11j**, 93	2 N HCl	**12j**, 90
11	C≡C-n-Bu	t-Bu	**11k**, 90	2 N HCl	**12k**, 99
12	t-Bu	C≡C-n-Bu	**11l**, 69	2 N HCl	**12l**, 86
13	t-Bu	Ph	**11m**, 98	2 N HCl	**12m**, 94
14	Ph	t-Bu	**11n**, 97	2 N HCl	**12n**, 99
15	Ph	C≡C-n-Bu	**11o**, 62	2 N HCl	**12o**, 90
16	C≡C-n-Bu	Ph	**11p**, 61	2 N HCl	**12p**, 65

cyclobutenedione monoacetal synthesis is conclusively demonstrated by the preparation of the numerous regioisomeric cyclobutenedione monoacetals shown in Table II (compare consecutive entries).

Conclusions

In summary, an efficient and regiocontrolled synthesis of cyclobutenedione monoacetals has been developed. The use of these compounds in the general preparation of substituted quinones and 5-alkylidene-2-cyclopentenones will be described in forthcoming articles.

Experimental Section

General Information. All starting materials were obtained from the Aldrich Chemical Company. Ether and tetrahydrofuran were freshly distilled from sodium and bezophenone for use in reactions generating compounds 8–11. All other solvents used were reagent-grade solvents purchased from Fisher. Triethylamine and trimethylsilyl chloride were distilled from calcium hydride. Freshly opened 99% trimethylsilyl triflate obtained from Aldrich was suitable for use, providing care was taken to prevent exposure to moisture. Thin layer chromatography was performed with E. Merck silica gel 60F-245 glass plates of 0.25-mm thickness, using UV light and phosphomolybdic acid in methanol for visualization. Flash grade silica gel was obtained from EM Science (230–400 mesh). Separations were done via radial chromatography using a Model 7924T Chromatotron purchased from Harrison Research on rotors coated with Merck PF254 silica gel. All melting points were taken in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Mass spectra were obtained on a VG 70S high resolution instrument. All compounds gave the expected nominal mass via low resolution EI mass spectra. Infrared spectra were recorded on a Perkin-Elmer Model 1420 spectrometer. ^1H NMR spectra were recorded on a Nicolet 360-MHz spectrometer (frequency = 361.00 MHz) or a G.E. QE 300-MHz spectrometer (frequency = 300.15 MHz). ^{13}C NMR spectra were taken on the QE 300 (frequency = 75.4808 MHz). All compounds **8b–f** were prepared according to the literature procedure.[4b] Compound **8a** was prepared by a slight modification of the literature procedure.[8]

Preparation of 2,3-Diisopropoxy-4-substituted-4-(trimethylsiloxy)-2-cyclobuten-1-ones 9. Typical Experimental Procedure: 2,3-Diisopropoxy-4-methyl-4-(trimethylsiloxy)-2-cyclobuten-1-one (9b). 2,3-Diisopropoxy-4-hydroxy-4-methyl-2-cyclobuten-1-one (**8b**) (10.19 g, 47.56 mmol) in a 250-mL round-bottomed flask was dissolved in 100 mL of anhydrous diethyl ether. The magnetically stirred solution was treated with triethylamine (20.0 mL, 14.4 g, 143 mmol, 3 equiv) followed by rapid addition of chlorotrimethylsilane (9.1 mL, 7.8 g, 72 mmol, 1.5 equiv.). The solution was stirred overnight (16 h) and then quenched with 20 mL of H_2O. After the salts dissolved, the ether phase was decanted and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic extracts were briefly dried with Na_2SO_4 and concentrated at 35 mmHg on a rotary evaporator. The resulting triethylamine-containing liquid was dissolved in 200 mL of hexanes and dried with Na_2SO_4. The liquid was then vacuum filtered through a 60-mL course-frit sintered-glass funnel containing 0.25-in. Celite and 2-in. flash SiO_2 using a 150-mL hexane rinse. The hexanes and triethylamine were removed at 35 mmHg and residual solvents removed at 0.2 mmHg to give analytically pure **9b** (13.46 g, 47.00 mmol, 99%) as a colorless liquid: IR (CH_2Cl_2) 2980, 2935, 2890, 2860, 1765, 1630, 1468, 1455, 1387, 1378, 1325, 1290, 1250, 1190, 1140, 1105, 1048, 1000, 928, 914, 868, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.83 (hept, J = 6 Hz, 1 H), 4.82 (hept, J = 6 Hz, 1 H), 1.39 (s, 3 H), 1.36 (d, J = 6 Hz, 3 H), 1.34 (d, J = 6 Hz, 3 H), 1.24 (d, J = 6 Hz, 3 H), 1.21 (d, J = 6 Hz, 3 H), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 186.52, 168.20, 129.74, 83.81, 75.97, 72.41, 22.19, 22.10, 21.83, 21.73, 20.18, 0.70 (3 C). Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.52; H, 9.12.

2,3-Diisopropoxy-4-(trimethylsiloxy)-2-cyclobuten-1-one (9a). A solution of 2,3-diisopropoxy-4-hydroxy-2-cyclobuten-1-one (**8a**) (5.108 g, 25.51 mmol) in 80 mL of dry Et_2O was treated with 3 equiv of triethylamine (10.7 mL, 7.74 g, 76.5 mmol) and then 1.5 equiv of chlorotrimethylsilane (4.86 mL, 4.16 g, 38.3 mmol). The white slurry was stirred overnight. The solution was quenched with 15 mL of H_2O, extracted with Et_2O (2 × 50 mL), and worked up in an identical fashion as compound **9b**. Compound **9a** was obtained as a colorless liquid (6.255 g, 22.96 mmol, 90%): IR (CH_2Cl_2) 2965, 2945, 2875, 2230, 1778, 1636, 1625, 1466, 1403, 1390, 1380, 1326, 1258, 1190, 1170, 1150, 1104, 1035, 988, 962, 906, 885, 852, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.87–4.71 (m, 2 H), 4.76 (s, 1 H), 1.33 (d, J = 6 Hz, 6 H), 1.22 (d, J = 6 Hz, 3 H), 1.20 (d, J = 7 Hz, 3 H), 0.112 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 182.24, 164.29, 131.38, 77.33, 75.99, 72.59, 22.09, 21.88, –0.51. Anal. Calcd for $C_{13}H_{24}O_4Si$: C, 57.32; H, 8.88. Found: C, 57.42; H, 8.92.

4-n-Butyl-2,3-diisopropoxy-4-(trimethylsiloxy)-2-cyclobuten-1-one (9c). A solution of 4-n-butyl-2,3-diisopropoxy-4-hydroxy-2-cyclobuten-1-one (**8c**) (6.70 g, 26.2 mmol) in 40 mL of dry Et_2O was treated with triethylamine (11.0 mL, 7.99 g, 78.9 mmol) and chlorotrimethylsilane (5.0 mL, 4.3 g, 39 mmol) in an

(8) Treatment of a 1 M THF solution of diisopropyl squarate (18.00 g, 90.81 mmol) with 100 mL of a 1 M THF solution of lithium tri-*tert*-butoxyaluminum hydride at –20 °C and quenching with 125 mL of H_2O after TLC analysis indicated consumption of starting material, followed by extraction with 8 × 100 mL ether, drying (Na_2SO_4), filtration through a plug of SiO_2, and removal of solvent, gave pure **8a** in 73% yield (13.2 g, 66.02 mmol).

identical fashion as compound **9b**. Compound **9c** was obtained as a colorless liquid (7.93 g, 24.1 mmol, 92%): IR (CH_2Cl_2) 2970, 2940, 2890, 1770, 1618, 1470, 1390, 1378, 1370, 1312, 1040, 1183, 1126, 1090, 1010, 1000, 970, 908, 868, 840, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.80 (octet, 2 overlapping heptets, J = 6 Hz, 2 H), 1.77–1.59 (m, 2 H), 1.34–1.12 (m, 4 H), 1.33 (d, J = 5 Hz, 3 H), 1.31 (d, J = 5 Hz, 3 H), 1.21 (d, J = 6 Hz, 3 H), 1.18 (d, J = 6 Hz, 3 H), 0.86 (t, J = 7 Hz, 3 H), 0.11 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 186.24, 167.22, 130.77, 87.04, 75.88 (2 C), 72.32, 33.28, 26.38, 22.15, 22.06, 21.90, 21.65, 13.24, 0.69 (3 C). Anal. Calcd for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 62.25; H, 9.85.

4-*tert*-Butyl-2,3-diisopropoxy-4-(trimethylsiloxy)-2-cyclobuten-1-one (9d). A solution of 4-*tert*-butyl-2,3-diisopropoxy-4-hydroxy-2-cyclobuten-1-one (**8d**) (9.500 g, 37.06 mmol) in 75 mL of dry ether was treated consecutively with triethylamine (15.5 mL, 11.2 g, 111 mmol), chlorotrimethylsilane (7.0 mL, 6.0 g, 55 mmol), and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) (0.1 g, 0.8 mmol). After 24 h the reaction mixture was worked up in an identical fashion as compound **9b**. Compound **9d** was obtained pure as a white solid (11.84 g, 36.03 mmol, 97%): mp 31.5–32.0 °C; IR (CH_2Cl_2) 2970, 2940, 2910, 2880, 1768, 1622, 1467, 1389, 1378, 1320, 1250, 1190, 1160, 1145, 1100, 1050, 1035, 990, 963, 920, 900, 890, 850, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.87 (hept, J = 6 Hz, 1 H), 4.82 (hept, J = 6 Hz, 1 H), 1.36 (d, J = 6 Hz, 6 H), 1.25 (d, J = 6 Hz, 3 H), 1.22 (d, J = 6 Hz, 3 H), 0.95 (s, 9 H), 0.09 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 187.03, 167.23, 131.12, 91.24, 75.82, 72.26, 35.72, 25.24, 22.39, 22.23, 22.11, 21.72, 0.63. Anal. Calcd for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 62.26; H, 9.88.

2,3-Diisopropoxy-4-phenyl-4-(trimethylsiloxy)-2-cyclobuten-1-one (9e). A solution of 2,3-diisopropoxy-4-hydroxy-4-phenyl-2-cyclobuten-1-one (**8e**) (6.315 g, 22.85 mmol) in 40 mL of dry ether was treated consecutively with triethylamine (10.0 mL, 7.26 g, 7.17 mmol) and chlorotrimethylsilane (4.5 mL, 3.8 g, 35 mmol). After 12 h the reaction mixture was worked up in an identical fashion with compound **9b**. Compound **9e** was obtained pure as a colorless oil (7.305 g, 20.96 mmol, 92%): IR (CH_2Cl_2) 3010, 2970, 2925, 2890, 2865, 1765, 1620, 1490, 1462, 1442, 1380, 1370, 1313, 1242, 1205, 1172, 1150, 1137, 1091, 1058, 1022, 948, 878, 840, 820, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.45–7.42 (m, 2 H), 7.35–7.22 (m, 3 H), 4.93 (hept, J = 6 Hz, 1 H), 4.88 (hept, J = 6 Hz, 1 H), 1.38 (d, J = 6 Hz, 3 H), 1.32 (d, J = 6 Hz, 3 H), 1.31 (d, J = 6 Hz, 3 H), 1.28 (d, J = 6 Hz, 3 H), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 183.33, 165.08, 138.29, 132.71, 127.58, 127.05, 125.32, 88.10, 76.42, 72.92, 22.28, 22.19, 21.94, 21.73, 0.67. Anal. Calcd for $C_{19}H_{28}O_4Si$: C, 65.48; H, 8.10. Found: C, 65.58; H, 8.15.

2,3-Diisopropoxy-4-(1-hexynyl)-4-(trimethylsiloxy)-2-cyclobuten-1-one (9f). A solution of 2,3-diisopropoxy-4-(1-hexynyl)-4-hydroxy-2-cyclobuten-1-one (**8f**) (10.27 g, 36.62 mmol) in 100 mL of dry ether was treated consecutively with triethylamine (15.3 mL, 11.1 g, 110 mmol) and chlorotrimethylsilane (7.0 mL, 5.97 g, 54.9 mmol). After 12 h the reaction mixture was worked up in an identical fashion with compound **9b**. Compound **9f** was obtained pure as a light yellow oil (12.09 g, 34.30 mmol, 94%): IR (CH_2Cl_2) 2965, 2945, 2880, 2230, 1777, 1638, 1625, 1466, 1403, 1390, 1380, 1326, 1248, 1190, 1170, 1150, 1103, 1035, 987, 962, 903, 885, 852, 820, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.94 (hept, J = 6 Hz, 1 H), 4.84 (hept, J = 6 Hz, 1 H), 2.23 (t, J = 7 Hz, 2 H), 1.57–1.32 (m, 4 H), 1.40 (d, J = 6 Hz, 3 H), 1.39 (d, J = 6 Hz, 3 H), 1.27 (d, J = 6 Hz, 3 H), 1.26 (d, J = 6 Hz, 3 H), 0.882 (t, J = 7 Hz, 3 H), 0.201 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 180.64, 165.22, 132.40, 88.86, 78.73, 76.51, 75.29, 72.96, 29.65, 22.07, 21.87, 21.87, 21.82, 21.28, 18.01, 12.88, 0.59. Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.08. Found: C, 64.84; H, 9.16.

Preparation of 3-Isopropoxy-4-substituted-3-cyclobutene-1,2-dione 2-(Ethylene acetals) 10. Typical Experimental Procedure: 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (10b). 2,3-Diisopropoxy-4-methyl-4-(trimethylsiloxy)-2-cyclobuten-1-one (**9b**) (13.46 g, 47.00 mmol) was placed in a dry 100-mL airless-ware flask under argon and dissolved in 25 mL of anhydrous THF. The magnetically stirred solution was treated first with bis(trimethylsiloxy)ethane (11.6 mL, 9.80 g, 47.5 mmol, 1.01 equiv) and then a catalytic amount of fresh trimethylsilyl triflate (44 μL, 51 mg, 0.23 mmol). The reaction was complete in 4 h and was poured through a plug of flash silica gel using an ether wash. Removal of the solvents at 35 mmHg followed by removal of residual solvents at 0.2 mmHg gave **10b** (9.20 g, 46.4 mmol, 99%) as a pale translucent oil, which solidified to an analytically pure white crystalline solid upon refrigeration: mp 50.0–50.5 °C; IR (CH_2Cl_2) 2990, 2950, 2900, 1769, 1630, 1615, 1470, 1408, 1390, 1345, 1327, 1216, 1144, 1106, 1060, 1030, 1010, 970, 952, 908 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.73 (hept, J = 6 Hz, 1 H), 4.21–4.02 (m, 4 H), 1.72 (s, 3 H), 1.41 (d, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 192.66, 181.37, 130.78, 116.94, 76.36, 65.38 (2 C), 21.91 (2 C), 6.18. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.58; H, 7.16.

3-Isopropoxy-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (10a). A solution of 2,3-diisopropoxy-4-(trimethylsiloxy)-2-cyclobuten-1-one (**8a**) (11.54 g, 57.63 mmol) in 50 mL of dry methylene chloride was treated with bis(trimethylsiloxy)ethane (14.2 mL, 12.0 g, 57.9 mmol, 1.01 equiv) and then a catalytic amount of fresh trimethylsilyl triflate (50 μL, 58 mg, 0.25 mmol). The reaction was complete in 14 h and was poured through a plug of flash silica gel using an ether wash. Removal of the solvents at 35 mmHg followed by removal of residual solvents at 0.2 mmHg gave an impure solid mass, which was redissolved in small amount of ether and treated with hexanes at −10 °C. The resulting solid was filtered and triturated with a small volume of hexanes to give white crystalline **10a** (8.089 g, 43.91 mmol, 76%): mp 68.5–69.0 °C; IR (CH_2Cl_2) 2990, 2940, 2910, 1770, 1585, 1578, 1470, 1455, 1392, 1380, 1365, 1330, 1222, 1182, 1145, 1104, 1075, 1053, 1020, 972, 952, 907, 843, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 5.54 (s, 1 H), 4.54 (hept, J = 6 Hz, 1 H), 4.18–4.07 (m, 4 H), 1.42 (d, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 190.61, 186.83, 118.57, 116.83, 78.41, 65.75, 20.79. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.79; H, 6.59.

4-*n*-Butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (10c). A solution of 4-*n*-butyl-2,3-diisopropoxy-4-(trimethylsiloxy)-2-cyclobuten-1-one (**9c**) (5.263 g, 16.02 mmol) in 20 mL of dry THF was treated with bis(trimethylsiloxy)ethane (4.0 mL, 3.4 g, 16 mmol, 1.01 equiv), and then a catalytic amount of fresh trimethylsilyl triflate (10 μL, 12 mg, 0.05 mmol). The reaction was complete in 6–10 h and was worked up in the same manner as **10b**. The product required chromatography on silica gel (30% ether in hexanes) to obtain **10c** as a yellow oil (3.338 g, 13.89 mmol, 87%): IR (CH_2Cl_2) 2950, 2925, 2885, 2865, 1760, 1615, 1463, 1450, 1393, 1385, 1372, 1340, 1320, 1260, 1222, 1180, 1138, 1100, 1025, 1000, 925, 905, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.66 (hept, J = 6 Hz, 1 H), 4.17–3.97 (m, 4 H), 2.06 (t, J = 7.5 Hz, 2 H), 1.51–1.41 (m, 2 H), 1.32–1.20 (m, 2 H), 1.36 (d, J = 6 Hz, 6 H), 0.83 (t, J = 7 Hz, 3 H), ^{13}C NMR ($CDCl_3$, 300 MHz) δ 192.59, 180.85, 135.91, 117.13, 76.37, 65.34 (2 C), 28.11, 21.99 (2 C), 21.88, 21.47, 13.02. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.81; H, 8.42.

4-*tert*-Butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (10d). A solution of 4-*tert*-butyl-2,3-diisopropoxy-4-(trimethylsiloxy)-2-cyclobuten-1-one (**9d**) (3.075 g, 9.359 mmol) in 10 mL of dry THF was treated with bis(trimethylsiloxy)ethane (2.3 mL, 1.9 g, 9.4 mmol, 1.01 equiv) and then a catalytic amount of fresh trimethylsilyl triflate (10 μL, 12 mg, 0.05 mmol). The reaction was complete in 6–10 h and was worked up in the same manner as **10b**. The product required chromatography on silica gel (30% ether in hexanes) to obtain **10d** as a white solid (1.919 g, 7.984 mmol, 85%): mp 68.5–70.0 °C; IR (CH_2Cl_2) 2970, 2900, 1756, 1615, 1477, 1400, 1380, 1365, 1345, 1265, 1210, 1140, 1100, 1025, 1008, 950, 918, 885, 852, 808 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.64 (hept, J = 6 Hz, 1 H), 4.21–3.97 (m, 4 H), 1.36 (d, J = 6 Hz, 6 H), 1.45 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 191.38, 178.85, 143.90, 117.22, 76.45, 65.17, 30.76, 27.14, 22.12. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.96; H, 8.37.

3-Isopropoxy-4-phenyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (10e). A solution of 2,3-diisopropoxy-4-phenyl-4-(trimethylsiloxy)-2-cyclobuten-1-one (**9e**) (3.225 g, 9.253 mmol) in 10 mL of dry THF was treated with bis(trimethylsiloxy)ethane (2.3 mL, 1.9 g, 9.4 mmol, 1.01 equiv), and then a catalytic amount of fresh trimethylsilyl triflate (10 μL, 12 mg, 0.05 mmol, 0.7% equiv). The reaction was complete in 6 h and was worked up in the same manner as **10b**. The product required chromatography on silica gel (30% ether in hexanes) to obtain **10e** (1.926 g, 7.401 mmol, 80%) as a white solid: mp 121.5–122.5 °C; IR (CH_2Cl_2)

2985, 2940, 2900, 1760, 1630, 1608, 1598, 1498, 1404, 1356, 1350, 1322, 1290, 1200, 1150, 1122, 1090, 1020, 950, 913, 824, 783 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.80–7.77 (m, 2 H), 7.38–7.26 (m, 3 H), 4.85 (hept, J = 6 Hz, 1 H), 4.30–4.07 (m, 4 H), 1.49 (d, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 190.06, 178.64, 131.56, 128.07, 127.88, 127.84 (2 C), 126.63 (2 C), 117.68, 77.93, 65.48 (2 C), 22.35 (2 C). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.02. Found: C, 68.92; H, 6.24.

4-(1-Hexynyl)-3-isopropoxy-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (10f). A solution of 2,3-diisopropoxy-4-(1-hexynyl)-4-(trimethylsiloxy)-2-cyclobuten-1-one (**9f**) (1.253 g, 3.56 mmol) was dissolved in 2 mL of dry THF and treated with bis(trimethylsiloxy)ethane (0.92 mL, 0.77 g, 3.7 mmol, 1.05 equiv), and then a catalytic amount of fresh trimethylsilyl triflate (4 μL, 5 mg, 0.02 mmol, 0.6% equiv) was added. The flask was then placed in a 50 °C oil bath and monitored for disappearance of starting material (SiO_2, 30% ether in hexanes). After 8 h the reaction mixture was worked up in the same manner as **10b**. The product required chromatography on silica gel (30% ether in hexanes) to obtain **10f** (0.755 g, 2.86 mmol, 80%) as a colorless oil: IR (CH_2Cl_2) 2990, 2955, 2915, 2885, 2235, 1780, 1620, 1475, 1460, 1420, 1400, 1393, 1340, 1308, 1235, 1215, 1190, 1150, 1110, 1080, 1058, 1024, 960, 910, 826, 794 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 5.12 (hept, J = 6 Hz, 1 H), 4.14–4.05 (m, 4 H), 2.33 (t, J = 7 Hz, 2 H), 1.54–1.30 (m, 4 H), 1.43 (d, J = 6 Hz, 6 H), 0.86 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 189.31, 181.94, 117.21, 115.42, 97.81, 78.20, 66.65, 65.82 (2 C), 29.69, 21.66 (2 C), 21.28, 18.63, 12.87. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.10; H, 7.67.

Preparation of 3,4-Disubstituted-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetals 11. Typical Experimental Procedure: 4-*n*-Butyl-4-hydroxy-2-isopropoxy-3-methyl-2-cyclobuten-1-one Ethylene Acetal (11e). 3-Isopropoxy-4-methyl-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10b**) (2.500 g, 12.61 mmol) in a dry 25-mL round-bottomed flask under argon was dissolved in 10 mL of anhydrous THF and cooled to −78 °C. *n*-Butyllithium (4.1 mL, 13 mmol, 3.1 M in hexanes, 1.01 equiv) was added dropwise from a syringe. After 30 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 20 mL), dried with Na_2SO_4, filtered through a plug of flash silica gel with an ether rinse, and concentrated. Removal of residual solvent at 0.2 mmHg gave pure **11e** (3.232 g, 12.60 mmol, 99.9%) as a pale yellow oil: IR (CH_2Cl_2) 3550, 2950, 2930, 2890, 2865, 1687, 1467, 1452, 1384, 1320, 1243, 1225, 1191, 1140, 1110, 1052, 1036, 1000, 960, 950, 900, 882, 650 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.39 (hept, J = 6 Hz, 1 H), 4.08–3.88 (m, 4 H), 2.19 (s, 1 H), 1.68 (s, 3 H), 1.72–1.40 (m, 2 H), 1.38–1.25 (m, 4 H), 1.28 (d, J = 5 Hz, 3 H), 1.27 (d, J = 5 Hz, 3 H), 0.91 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.67; H, 9.50.

4-Hydroxy-2-isopropoxy-3-methyl-2-cyclobuten-1-one Ethylene Acetal (11b). A solution of 3-isopropoxy-4-methyl-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10b**) (634 mg, 3.20 mmol) in 3 mL of dry Et_2O at −23 °C was treated with 1.1 equiv of diisobutylaluminum hydride (3.5 mL, 1 M in hexanes) via syringe. The reaction was followed for disappearance of starting material (TLC, SiO_2, 50% ether in hexanes) and was complete in 10 min. H_2O (1 mL) was added and the product was extracted into ether (3 × 5 mL). The ether was dried (Na_2SO_4) and concentrated to give **11b** (502 mg, 0.250 mmol, 78%) as a colorless oil: IR (CH_2Cl_2) 3450 (br), 2980, 2920, 2890, 1705, 1685, 1384, 1339, 1260, 1198, 1140, 1115, 1090, 1044, 990, 968, 950, 935 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.42 (hept, J = 6 Hz, 1 H), 4.14 (d, J = 10 Hz, 1 H), 4.08–3.94 (m, 4 H), 1.75 (d, J = 10 Hz, 1 H), 1.72 (s, 3 H), 1.28 (d, J = 6 Hz, 3 H), 1.27 (d, J = 6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 144.74, 119.07, 109.68, 76.45, 71.10, 64.34, 63.86, 21.94, 21.76, 8.93; M^+ calcd for $C_{10}H_{16}O_4$ 200.1048, found 200.1056.

3-*tert*-Butyl-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11d). A solution of 4-*tert*-butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10d**) (510 mg, 2.12 mmol) in 4 mL of anhydrous Et_2O was cooled to −78 °C and treated with 1.04 equiv of diisobutylaluminum hydride (2.2 mL, 1 M in hexanes). The reaction was complete in 30 min (TLC, 50% ether in hexanes, SiO_2) and was carefully quenched with 1 mL of H_2O. The aluminum solids separated out after several minutes of stirring and the ether layer was decanted. The solids were washed with ether (3 × 5 mL) and the combined organic layers were concentrated and chromatographed on a 2-mm silica gel rotor (30% ether in hexanes) to give **11d** (486 mg, 2.01 mmol, 95%) as a pure white solid: mp 53.5–54.5 °C (recrystallized from cold hexanes; sublimes at 1 mmHg); IR (CH_2Cl_2) 3560, 2980, 2900, 1680, 1476, 1397, 1386, 1347, 1285, 1227, 1193, 1137, 1113, 1050, 1036, 990, 948, 927, 874, 845 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.32 (hept, J = 6 Hz, 1 H), 4.21 (d, J = 10 Hz, 1 H), 4.02–3.91 (m, 4 H), 1.74 (d, J = 10 Hz, 1 H), 1.22 (d, J = 6 Hz, 3 H), 1.20 (d, J = 6 Hz, 3 H), 1.10 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 142.69, 135.39, 110.54, 74.96, 71.33, 64.06, 63.63, 31.00, 28.17 (3 C), 22.28, 22.11. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.51; H, 9.16.

3-*n*-Butyl-4-hydroxy-3-isopropoxy-4-methyl-2-cyclobutenone Ethylene Acetal (11f). A solution of 4-*n*-butyl-3-isopropoxy-3-cyclobutene,1,2-dione 2-ethylene acetal (**10c**) (341 mg, 1.42 mmol) in 1 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. Methyllithium (1.2 mL, 1.7 mmol, 1.4 M in hexanes, 1.2 equiv) was added dropwise from a syringe. After 15 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (30% ether in hexanes) and removal of solvent at reduced pressure gave pure **11f** (363 mg, 1.42 mmol, 99.7%) as a colorless oil: IR (CH_2Cl_2) 3560, 2955, 2920, 2885, 2865, 1692, 1675, 1464, 1450, 1370, 1330, 1316, 1212, 1176, 1136, 1105, 1038, 1005, 990, 940, 900, 880, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.29 (hept, J = 6 Hz, 1 H), 4.02–3.87 (m, 4 H), 2.22 (s, 1 H), 2.09–1.92 (m, 2 H), 1.49–1.39 (m, 2 H), 1.33–1.16 (m, 2 H), 1.24 (s, 3 H), 1.19 (d, J = 6 Hz, 6 H), 0.83 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 143.38, 127.93, 111.64, 79.19, 71.09, 64.43, 63.52, 29.41, 22.56, 22.25, 22.01, 21.88, 18.50, 13.14. Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.71; H, 9.48.

3-*n*-Butyl-4-*tert*-butyl-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11g). A solution of 4-*n*-butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10c**) (254 mg, 1.10 mmol) in 1 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. *tert*-Butyllithium (1.0 mL, 1.7 mmol, 1.7 M in hexanes, 1.5 equiv) was added dropwise from a syringe. After 5 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (30% ether in hexanes) and removal of solvent at reduced pressure gave pure **11g** (238 mg, 0.799 mmol, 73%) as a colorless oil: IR (CH_2Cl_2) 3525, 2955, 2930, 2885, 2870, 1690, 1675, 1480, 1463, 1380, 1370, 1353, 1335, 1317, 1240, 1208, 1176, 1135, 1110, 1090, 1068, 1030, 975, 960, 910, 878 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.30 (hept, J = 6 Hz, 1 H), 4.06–3.96 (m, 2 H), 3.94–3.86 (m, 1 H), 3.81–3.73 (m, 1 H), 2.33 (s, 1 H), 2.22–1.98 (m, 2 H), 1.61–1.45 (m, 2 H), 1.38–1.21 (m, 2 H), 1.23 (d, J = 6 Hz, 3 H), 1.22 (d, J = 6 Hz, 3 H), 0.99 (s, 9 H), 0.86 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 144.80, 128.76, 112.99, 86.68, 71.06, 64.83, 63.10, 34.66, 29.14, 25.93, 24.75, 22.31, 22.16, 21.97, 13.19. Anal. Calcd for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.38; H, 10.15.

4-*n*-Butyl-3-*tert*-butyl-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11h). A solution of 4-*tert*-butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10d**) (110 mg, 0.458 mmol) in 1 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. *n*-Butyllithium (200 μL, 5.0 mmol, 2.5 M in hexanes, 1.1 equiv) was added dropwise from a syringe. After 5 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (30% ether in hexanes) and removal of solvent at reduced pressure gave pure **11h** (133 mg, 0.446 mmol, 97%) as a colorless oil: IR (CH_2Cl_2) 3560, 2950, 2885, 2860, 1672, 1473, 1460, 1390, 1380, 1370, 1358, 1337, 1222, 1180, 1133, 1105, 1032, 990, 976, 960, 946, 903, 870 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.25 (hept, J = 6 Hz, 1 H), 4.04–3.78 (m, 4

H), 2.18 (s, 1 H), 1.82–1.72 (m, 1 H), 1.63–1.53 (m, 1 H), 1.50–1.37 (m, 2 H), 1.31–1.21 (m, 2 H), 1.182 (d, J = 6 Hz, 3 H), 1.180 (d, J = 6 Hz, 3 H), 1.10 (s, 9 H), 0.85 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 142.78, 137.82, 112.58, 82.64, 71.09, 64.65, 63.18, 33.62, 31.63, 28.64 (3 C), 26.57, 22.77, 22.25, 22.14, 13.44. Anal. Calcd for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.53; H, 10.17.

3-*n*-Butyl-4-hydroxy-4-(1-hexynyl)-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11i). A solution of 4-*n*-butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10c**) (276 mg, 1.15 mmol) in 2 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. Approximately 1.5 equiv of *n*-butyl acetylide, formed by treating 1-hexyne (170 μL, 114 mg, 1.39 mmol) in 1 mL of dry THF at −78 °C with *n*-butyllithium (550 mL, 1.38 mmol, 2.5 M in hexanes) and stirring 1 h, was added through a cannula. After 5 min the reaction mixture was allowed to warm to room temperature. After 20 min the reaction was judged complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (10% ether in hexanes) and removal of solvent at reduced pressure gave pure **11i** (258 mg, 0.800 mmol, 70%) as a yellow oil: IR (CH_2Cl_2) 3520, 2960, 2935, 2900, 2875, 2240, 1698, 1582, 1468, 1383, 1344, 1328, 1220, 1182, 1140, 1110, 1085, 1030, 998, 950, 928, 883, 870, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.35 (hept, J = 6 Hz, 1 H), 4.14–3.92 (m, 4 H), 2.43 (s, 1 H), 2.22 (t, J = 7 Hz, 2 H), 2.11 (t, J = 8 Hz, 2 H), 1.60–1.27 (m, 8 H), 1.22 (d, J = 6 Hz, 6 H), 0.85 (t, J = 7 Hz, 3 H), 0.85 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 145.07, 126.66, 110.25, 86.50, 76.17, 75.59, 71.61, 64.06, 63.68, 30.09, 28.91, 23.06, 22.22, 21.98, 21.93, 21.24, 18.03, 13.18, 12.95. Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.52; H, 9.30.

4-*n*-Butyl-3-(1-hexynyl)-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11j). A solution of 4-(1-hexynyl)-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10f**) (1.063 g, 4.022 mmol) in 4 mL of anhydrous Et_2O in a dry 10-mL round-bottomed flask under argon was cooled to −20 °C. *n*-Butyllithium (1.35 mL, 4.03 mmol, 3.1 M in hexane, 1.0 equiv) was added dropwise from a syringe. After 5 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −20 °C with H_2O. The product was extracted into ether (2 × 5 mL), dried with Na_2SO_4, and passed through a plug of flash silica gel. Removal of solvent at reduced pressure gave pure **11j** (1.211 g, 3.757 mmol, 93%) as a light yellow oil: IR (CH_2Cl_2) 3560, 2960, 2940, 2900, 2880, 1660, 1468, 1376, 1331, 1230, 1183, 1142, 1108, 1038, 1022, 1008, 990, 970, 953 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 4.78 (hept, J = 6 Hz, 1 H), 4.10–4.00 (m, 2 H), 3.98–3.89 (m, 2 H), 2.46 (s, 1 H), 2.33 (t, J = 7 Hz, 2 H), 1.79–1.68 (m, 1 H), 1.68–1.58 (m, 2 H), 1.54–1.46 (m, 2 H), 1.45–1.28 (m, 5 H), 1.32 (d, J = 6 Hz, 3 H), 1.31 (d, J = 6 Hz, 3 H), 0.90 (t, J = 7 Hz, 3 H), 0.896 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 150.16, 111.07, 105.76, 94.27, 82.35, 72.66, 71.17, 65.36, 64.12, 33.15, 30.08, 25.87, 22.74, 21.72, 21.54, 21.27, 18.73, 13.45, 12.91. Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.85; H, 9.39.

4-*tert*-Butyl-3-(1-hexynyl)-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11k). A solution of 4-(1-hexynyl)-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10f**) (270 mg, 1.02 mmol) in 1.5 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. *tert*-Butyllithium (720 μL, 1.22 mmol, 1.7 M in hexane, 1.2 equiv) was added dropwise from a syringe. After 5 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (10% ether in hexanes) and removal of solvent at reduced pressure gave pure **11k** (295 mg, 0.914 mmol, 90%) as a white solid: mp 48.0–49.5 °C; IR (CH_2Cl_2) 3535, 2965, 2940, 2900, 2875, 1660, 1462, 1380, 1375, 1332, 1244, 1228, 1210, 1120, 1141, 1108, 1064, 1038, 1018, 998, 955, 882 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.82 (hept, J = 6 Hz, 1 H), 4.11–3.97 (m, 3 H), 3.87–3.75 (m, 1 H), 2.63 (s, 1 H), 2.31 (t, J = 7 Hz, 2 H), 1.54–1.35 (m, 4 H), 1.30 (d, J = 6 Hz, 6 H), 1.07 (s, 9 H), 0.87 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 150.77, 111.88, 104.62, 94.78, 87.33, 72.35, 72.06, 65.54, 63.76, 35.13, 30.06, 25.44, 21.73, 21.50, 21.29, 18.77, 12.91. Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.91; H, 9.43.

3-*tert*-Butyl-4-(1-hexynyl)-4-hydroxy-2-isopropoxy-2-cyclobutenone Ethylene Acetal (11l). A solution of 4-*tert*-butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10d**) (108 mg, 0.448 mmol) in 2 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. *n*-Butyl acetylide (600 μL, 0.504 mmol, 0.84M in THF) was added by syringe. After 30 min the reaction mixture was brought to room temperature. After 10 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (10% ether in hexanes) gave **11l** (100 mg, 0.311 mmol, 69%), a white solid: mp 43.5–45.5 °C (sublimes at 1 mmHg); IR (CH_2Cl_2) 3535, 2960, 2925, 2900, 2865, 1675, 1475, 1392, 1383, 1370, 1360, 1340, 1185, 1125, 1100, 1022, 997, 970, 945, 925 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.35 (hept, J = 6 Hz, 1 H), 4.12–4.02 (m, 3 H), 3.95 (q, J = 7 Hz, 1 H), 2.41 (s, 1 H), 2.24 (t, J = 7 Hz, 2 H), 1.53–1.36 (m, 4 H), 1.23 (d, J = 7 Hz, 3 H), 1.22 (d, J = 6 Hz, 3 H), 1.19 (s, 9 H), 0.87 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 143.94, 136.25, 110.73, 86.58, 75.05, 71.74 (2 C), 63.84, 63.44, 31.81, 30.08, 28.35 (3 C), 22.32, 22.14, 21.31, 18.06, 12.96. Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.86; H, 9.37.

3-*tert*-Butyl-4-hydroxy-2-isopropoxy-4-phenyl-2-cyclobutenone Ethylene Acetal (11m). A solution of 4-*tert*-butyl-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10d**) (164 mg, 0.682 mmol) in 1 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. PhLi (1.0 mL, 0.70 mmol, 0.70M in Et_2O) was added by syringe. After 15 min the reaction was complete by TLC (SiO_2, 50% Et_2O in hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (30% ether in hexanes) followed by removal of solvent at reduced pressure gave **11m** (214 mg, 0.673 mmol, 99%) as a colorless oil: IR (CH_2Cl_2) 3545, 2960, 2890, 1674, 1490, 1474, 1460, 1445, 1390, 1382, 1368, 1357, 1340, 1198, 1180, 1134, 1102, 1048, 1027, 1000, 977, 945, 935, 872, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56–7.53 (m, 2 H), 7.32–7.19 (m, 3 H), 4.41 (hept, J = 6 Hz, 1 H), 3.96–3.83 (m, 2 H), 3.78–3.71 (m, 1 H), 3.25 (q, J = 7 Hz, 1 H), 2.80 (s, 1 H), 1.30 (d, J = 6 Hz, 6 H), 1.05 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 144.55, 139.60, 136.20, 126.56 (2 C), 126.38 (2 C), 125.82, 111.78, 83.59, 71.67, 63.29, 63.08, 31.64, 28.77 (3 C), 22.43, 22.25. Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.40; H, 8.39.

4-*tert*-Butyl-4-hydroxy-2-isopropoxy-3-phenyl-2-cyclobutenone Ethylene Acetal (11n). A solution of 3-isopropoxy-4-phenyl-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10e**) (147 mg, 0.564 mmol) in 2 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. *tert*-Butyllithium (0.50 mL, 0.85 mmol, 1.7M in Et_2O) was added by syringe, producing a dark yellow solution. After 5 min the reaction was complete by TLC (SiO_2, 50% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was worked up using the general procedure for **11e** to obtain a white crystalline solid, **11n** (174 mg, 0.548 mmol, 97%): mp 103–105 °C; IR (CH_2Cl_2) 3555, 2980, 2965, 2940, 2895, 1680, 1490, 1378, 1340, 1230, 1196, 1144, 1138, 1100, 1036, 1025, 1000, 973, 956 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.58–7.55 (m, 2 H), 7.28–7.14 (m, 3 H), 4.45 (hept, J = 6 Hz, 1 H), 4.10 (m, 2 H), 4.00–3.84 (m, 2 H), 2.74 (s, 1 H), 1.28 (d, J = 6 Hz, 3 H), 1.25 (d, J = 6 Hz, 3 H), 1.02 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 145.42, 132.87, 127.49 (2 C), 127.18 (2 C), 126.04, 125.11, 113.04, 87.81, 72.00, 64.98 (2 C), 63.20, 35.67, 26.41 (3 C), 22.34. Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.46; H, 8.31.

4-(1-Hexynyl)-4-hydroxy-2-isopropoxy-3-phenyl-2-cyclobutenone Ethylene Acetal (11o). A solution of 3-isopropoxy-4-phenyl-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10e**) (250 mg, mmol) was added to an ethereal solution of 1.1 equiv of *n*-butyl acetylide (0.53 M in ether) at room temperature. After 20 min the reaction mixture turned clear and was complete by TLC (SiO_2, 50% Et_2O/hexanes). The reaction mixture was quenched with 1 mL of H_2O and extracted into ether (3 × 5 mL), and the organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting oil was chromatographed on a 2-mm

silica gel rotor (5% ether in hexanes) to give **11o** (204 mg, 0.596 mmol, 74%) as a yellow oil: IR (CH_2Cl_2) 3530, 2965, 2940, 2900, 2870, 2230, 1680, 1492, 1465, 1388, 1355, 1288, 1185, 1145, 1133, 1102, 1020, 1013, 979, 948, 926, 828, 814 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.69 (d, J = 7 Hz, 2 H), 7.32 (t, J = 7.5 Hz, 2 H), 7.21 (t, J = 7 Hz, 1 H), 4.59 (hept, J = 6 Hz, 1 H), 4.24–4.00 (m, 4 H), 2.65 (s, 1 H), 2.24 (t, J = 7 Hz, 2 H), 1.54–1.3 (m, 4 H), 1.34 (d, J = 6 Hz, 6 H), 0.86 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 145.43, 129.90, 127.62 (2 C), 126.75 (2 C), 126.61, 124.24, 110.91, 86.79, 76.62, 74.80, 73.16 (2 C), 64.22, 63.78, 30.08, 22.50, 21.24, 18.08, 12.98. Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.52; H, 7.73. Small amounts of **12o** (33.4 mg, 0.118 mmol, 12%) and an undetermined amount of a double addition product (from 1,4 addition followed by 1,2 addition to the carbonyl) were also obtained.

3-(1-Hexynyl)-4-hydroxy-2-isopropoxy-4-phenyl-2-cyclobutenone Ethylene Acetal (11p). A solution of 4-(1-hexynyl)-3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10f**) (276 mg, 1.04 mmol) in 1.5 mL of anhydrous THF in a dry 10-mL round-bottomed flask under argon was cooled to −78 °C. Phenyllithium (1.7 mL, 1.3 mmol, 0.74 M in Et_2O, 1.2 equiv) was added dropwise from a syringe. After 1 h the reaction was complete by TLC (SiO_2, 30% Et_2O/hexanes) and was quenched at −78 °C with 1 mL of H_2O. The product was extracted into ether (3 × 10 mL), dried with Na_2SO_4, filtered, and concentrated. Radial chromatography on a 2-mm SiO_2 rotor (10% ether in hexanes) and removal of solvent at reduced pressure gave pure **11p** (327 mg, 0.955 mmol, 91%) as a light yellow solid: mp 58.5–59.5 °C; IR (CH_2Cl_2) 3525, 2940, 2905, 2850, 1668, 1495, 1468, 1450, 1398, 1390, 1380, 1340, 1213, 1182, 1142, 1110, 1075, 1038, 1030, 1013, 955, 932, 877 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.52 (d, J = 7 Hz, 2 H), 7.37–7.24 (m, 3 H), 4.96 (hept, J = 6 Hz, 1 H), 4.06–3.96 (m, 2 H), 3.88–3.81 (m, 1 H), 3.52 (q, J = 7 Hz, 1 H), 3.07 (s, 1 H), 2.27 (t, J = 7 Hz, 2 H), 1.50–1.25 (m, 4 H), 1.41 (d, J = 6 Hz, 3 H), 1.40 (d, J = 6 Hz, 3 H), 0.86 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 151.31, 137.92, 127.09 (2 C), 126.62, 126.50 (2 C), 111.26, 104.11, 94.05, 84.60, 73.10, 70.75, 64.41, 64.24, 30.02, 21.77, 21.70, 21.26, 18.73, 12.92. Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.48; H, 7.68.

Preparation of Cyclobutenedione Monoacetals 12. 3-Methyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12a). A solution of 3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10a**) (3.360 g, 18.24 mmol) in 20 mL of anhydrous THF was cooled to −78 °C and treated with 1.01 equiv of methyllithium (13.1 mL, 18.3 mmol, 1.4 M in Et_2O) via syringe. The reaction was followed for disappearance of starting material (TLC, SiO_2, 50% ether in hexanes) and was quenched with 1.05 equiv of TFAA (2.7 mL, 4.02 g, 19.1 mmol) after 15 min.[6b] The reaction mixture was stirred for 4 h at −78 °C and was then carefully quenched with 10 mL of $NaHCO_3$ solution (aqueous, saturated) and warmed to room temperature. The mixture was diluted with 50 mL of ether and washed with $NaHCO_3$ solution until the trifluoroacetic acid was all removed. After a wash with 20 mL of H_2O, the solvent was dried over Na_2SO_4 and removed at 35 mmHg. The resulting yellow oil was purified by simple distillation to obtain pure **12a** (2.34 g, 16.7 mmol, 91%) as a light yellow oil: bp 44–48.5 °C/0.5 mmHg; IR (CH_2Cl_2) 2995, 2965, 2905, 1775, 1600, 1472, 1433, 1371, 1318, 1222, 1150, 1090, 1055, 1028, 1005, 955, 914, 882, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.46 (s, 1 H), 4.14–4.03 (m, 4 H), 2.18 (d, J = 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 194.45, 184.93, 145.63, 119.93, 65.78 (2 C), 11.30; M^+ calcd for $C_7H_8O_3$ 140.0473, found, 140.0477.

4-Methyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12b). A solution of 4-hydroxy-2-isopropoxy-3-methyl-2-cyclobuten-1-one ethylene acetal (**11b**) (427 mg, 2.13 mmol) in 3 mL of dry Et_2O was treated with 3 equiv of triethylamine (0.90 mL, 653 mg, 6.46 mmol) and then 1.3 equiv of TFAA (0.40 mL, 595 mg, 2.83 mmol) and stirred at room temperature for 1 h. The reaction mixture was treated with 5 mL of $NaHCO_3$ solution (aqueous, saturated), stirred for 30 min, then diluted with 30 mL ether, and washed with H_2O (3 × 10 mL). The ether layer was dried (Na_2SO_4) and concentrated at 35 mmHg. The product was then distilled (0.2 mmHg, bp 44–46 °C) through a short path into a dry-ice cooled flask to obtain **12b** (227 mg, 1.62 mmol, 76%) as a light yellow oil, which was stored in the freezer to slow down decomposition: IR (CH_2Cl_2) 2980, 2900, 1775, 1591, 1310, 1246, 1216, 1170, 1110, 1078, 1048, 1025, 950, 865 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.13 (s, 1 H), 4.10–4.00 (m, 4 H), 1.85 (s, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 197.32, 164.46, 162.94, 120.16, 65.44 (2 C), 9.19; M^+ calcd for $C_7H_8O_3$ 140.0473, found 140.0478. Anal. Calcd for $C_7H_8O_3$: C, 60.00; H, 5.75. Found: C, 59.76; H, 5.79.

3-*tert*-Butyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12c). A solution of 3-isopropoxy-3-cyclobutene-1,2-dione 2-(ethylene acetal) (**10a**) (300 mg, 1.63 mmol) in 5 mL of anhydrous THF was cooled to −78 °C and treated with 1.2 equiv of *tert*-butyllithium (1.2 mL, 2.0 mmol, 1.7 M in hexanes). The reaction was followed for disappearance of starting material (TLC, SiO_2, 50% ether in hexanes) and was quenched with 1.4 equiv of TFAA (320 μL, 476 mg, 2.27 mmol) after 20 min. The reaction mixture was warmed to room temperature and after 30 min was quenched with 2 mL of H_2O followed by a slow addition of 5 mL of $NaHCO_3$ solution (aqueous, saturated). The mixture was stirred for 30 min, extracted into ether (3 × 10 mL), and washed with 10 mL of H_2O. The solvent was dried over Na_2SO_4 and removed at 35 mmHg. The product was purified by sublimation at 0.2 mmHg onto a dry-ice cooled coldfinger with a bath temperature of 45 °C. Pure **12c** (230 mg, 1.26 mmol, 78%) was obtained as a white solid: mp 36.0–38.5 °C; IR (CH_2Cl_2) 2990, 2940, 2910, 1770, 1575, 1470, 1456, 1366, 1307, 1220, 1192, 1107, 1068, 1050, 1022, 953, 906, 890, 783 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.45 (s, 1 H), 4.15–4.05 (m, 4 H), 1.24 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 196.59, 195.24, 142.61, 119.86, 65.51 (2 C), 33.88, 27.63 (3 C); M^+ calcd for $C_{10}H_{14}O_3$ 182.0943, found 182.0941.

4-*tert*-Butyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12d). A solution of 4-*tert*-butyl-4-hydroxy-2-isopropoxy-2-cyclobutenone ethylene acetal (**11d**) (312 mg, 1.29 mmol) in 5 mL of anhydrous Et_2O was treated with 1.5 equiv of (dimethylamino)pyridine (DMAP) (240 mg, 1.96 mmol) and stirred until the DMAP was fully dissolved. Trifluoroacetic anhydride (1.1 equiv, 200 μL, 297 mg, 1.42 mmol) was syringed into the solution to produce a white suspension. Monitoring by ^1H NMR for disappearance of starting material showed the reaction to be complete after 2 h. The suspension was treated with 1 mL of H_2O, 5 mL of $NaHCO_3$ solution (aqueous, saturated, carefully added) and then stirred for 30 min. The product was extracted into ether (3 × 20 mL), and the organic phase washed with $CuSO_4$ solution (aqueous, saturated) to remove DMAP and then with 10 mL of H_2O. The solvent was dried over Na_2SO_4 and removed at 35 mmHg. The product was purified by sublimation at 0.2 mmHg onto a dry-ice-cooled coldfinger with a bath temperature of 45 °C. Warming to room temperature gave pure **12d** (216 mg, 1.18 mmol, 92%) as a colorless oil: IR (CH_2Cl_2) 2985, 2915, 2880, 1770, 1675, 1605, 1595, 1473, 1460, 1397, 1367, 1344, 1313, 1285, 1223, 1210, 1173, 1138, 1100, 1046, 1020, 954, 876, 865, 797, 778 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.98 (s, 1 H), 4.13–4.01 (m, 4 H), 1.15 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 195.65, 175.73, 159.20, 119.18, 65.43, 26.73, 31.80. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.03; H, 7.77.

3-*n*-Butyl-4-methyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12e). 4-*n*-Butyl-4-hydroxy-2-isopropoxy-3-methyl-2-cyclobutenone ethylene acetal (**11e**) (2.008 g, 7.833 mmol) was dissolved in 5 mL of reagent-grade CH_2Cl_2 in a 25-mL round-bottomed flask open to the atmosphere and at room temperature. This was stirred with 5 mL of 2 N HCl and was closely followed by TLC until the reaction was complete (about 15 min). The reaction mixture was extracted with 50 mL of CH_2Cl_2 and washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated, and the residual solvent was removed at 0.2 mmHg to obtain pure **12e** (1.504 g, 7.664 mmol, 98%): IR (CH_2Cl_2) 2960, 2940, 2900, 1768, 1635, 1470, 1382, 1325, 1230, 1210, 1112, 1030, 1009, 951, 920, 867 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.17–4.03 (m, 4 H), 2.52 (dt, J = 7.7, 0.5 Hz, 2 H), 1.79 (d, J = 0.5 Hz, 3 H), 1.63 (pent, J = 8 Hz, 2 H), 1.40 (hextet, J = 7 Hz, 2 H), 0.94 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 196.22, 181.34, 155.73, 120.0, 65.47, 28.0, 24.94, 22.19, 13.05, 7.48. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.21; H, 8.26. Regulating the reaction time is important to avoid overhydrolysis. THF has been found to be the preferred solvent for hydrolysis. It provides a one-phase system, which gives more reproducible results.

4-*n*-Butyl-3-methyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12f). A solution of 3-*n*-butyl-4-hydroxy-3-isopropoxy-

4-methyl-2-cyclobutenone ethylene acetal (**11f**) (156 mg, 0.610 mmol) in 2 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 0.5 mL of 2 N HCl and closely followed by TLC until the reaction was complete (about 20 min). The reaction mixture was extracted with 50 mL of Et_2O and washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4 and then passed through a plug of flash silica gel. The solvent was removed to obtain pure **12f** (115 mg, 588 mmol, 96%) as a clear oil: IR (CH_2Cl_2) 2960, 2935, 2890, 2870, 1765, 1630, 1465, 1430, 1380, 1336, 1313, 1295, 1285, 1225, 1209, 1148, 1105, 1040, 1010, 990, 950, 912, 865, 832 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.13–4.01 (m, 4 H), 2.16 (t, J = 7 Hz, 2 H), 2.07 (s, 3 H), 1.49 (pent, J = 7 Hz, 2 H), 1.34–1.18 (m, 2 H), 0.85 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 195.74, 177.02, 160.20, 119.75, 65.59 (2 C), 27.82, 22.57, 21.93, 13.02, 9.41. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.15; H, 8.26.

4-*n*-Butyl-3-*tert*-butyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12g). A solution of 3-*n*-butyl-4-*tert*-butyl-4-hydroxy-2-isopropoxy-2-cyclobutenone ethylene acetal (**11g**) (144 mg, 0.482 mmol) in 2 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 0.5 mL of 2 N HCl and closely followed by TLC until the reaction was complete, about 20 min. The reaction mixture was extracted with 50 mL of Et_2O and washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4 and then passed through a plug of flash silica gel. The solvent was removed to obtain pure **12g** (114 mg, 0.478 mmol, 99%) as a white solid: mp 40.5–41.0 °C; IR (CH_2Cl_2) 2960, 2930, 2895, 2865, 1760, 1610, 1474, 1460, 1393, 1363, 1338, 1315, 1228, 1208, 1193, 1090, 1035, 1020, 1000, 950 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.12–4.00 (m, 4 H), 2.27 (t, J = 7 Hz, 2 H), 1.55–1.45 (m, 2 H), 1.39–1.28 (m, 2 H), 1.26 (s, 9 H), 0.86 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 197.07, 186.10, 158.45, 120.09, 65.27 (3 C), 34.22, 28.62, 28.03 (2 C), 23.70, 22.12, 13.13. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.47; H, 9.31.

3-*n*-Butyl-4-*tert*-butyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12h). A solution of 4-*n*-butyl-3-*tert*-butyl-4-hydroxy-2-isopropoxy-2-cyclobutenone ethylene acetal (**11h**) (178 mg, 0.595 mmol) in 5 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 0.5 mL of 2 N HCl and closely followed by TLC until the reaction was complete (about 20 min). The reaction mixture was extracted with 50 mL of Et_2O and washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4 and then passed through a plug of flash silica gel. The solvent was removed to obtain pure **12h** (139 mg, 0.583 mmol, 98%) as a white solid: mp 27–29 °C; IR (CH_2Cl_2) 2970, 2960, 2900, 2880, 1765, 1620, 1480, 1470, 1400, 1370, 1343, 1330, 1300, 1210, 1135, 1395, 1030, 1010, 953, 915, 866, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.12–4.00 (m, 4 H), 2.57 (t, J = 8 Hz, 2 H), 1.62–1.52 (m, 2 H), 1.38 (hextet, J = 7 Hz, 2 H), 1.19 (s, 9 H), 0.91 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 195.39, 177.00, 166.36, 119.55, 65.44 (3 C), 32.29, 29.18, 27.34 (2 C), 25.74, 22.47, 13.16. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.45; H, 9.34.

4-*n*-Butyl-3-(1-hexynyl)-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12i). A solution of 3-*n*-butyl-4-hydroxy-4-(1-hexynyl)-2-isopropoxy-2-cyclobutenone ethylene acetal (**11i**) (160 mg, 0.496 mmol) in 4 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 1 mL of 2 N HCl and closely followed by TLC until the reaction was complete (about 20 min). The reaction mixture was extracted with 50 mL of Et_2O and washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4 and then passed through a plug of flash silica gel. The solvent was removed to obtain pure **12i** (126 mg, 0.481 mmol, 97%) as a yellow oil: IR (CH_2Cl_2) 2960, 2940, 2900, 2875, 2220, 1765, 1610, 1470, 1382, 1345, 1228, 1153, 1088, 1050, 1030, 1012, 954, 912, 885, 847 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.10–4.05 (m, 4 H), 2.50 (t, J = 7 Hz, 2 H), 2.22 (t, J = 7.5 Hz, 2 H), 1.59–1.49 (m, 4 H), 1.46–1.16 (m, 4 H), 0.87 (t, J = 7 Hz, 3 H), 0.84 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 197.36, 164.18, 160.26, 119.99, 117.44, 69.76, 65.75 (2 C), 29.40, 27.36, 23.64, 21.83, 21.24, 19.62, 12.96, 12.84. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.19; H, 8.49.

3-*n*-Butyl-4-(1-hexynyl)-3-cyclobutene-1,2-dione 2-(Ethylene Acetal) acetal) (12j). A solution of 4-*n*-butyl-3-(1-hexynyl)-4-hydroxy-2-isopropoxy-2-cyclobutenone ethylene acetal (**11j**) (234 mg, 0.726 mmol) in 4 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 0.5 mL of 2 N HCl and closely followed by TLC (30% ether in hexanes, SiO_2) until the reaction was complete (about 15 min). The reaction mixture was extracted with 50 mL of Et_2O and washed with H_2O (3 × 15 mL). The organic phase was dried with Na_2SO_4 and concentrated. The product was chromatographed on a 2-mm silica gel rotor (30% ether in hexanes) to obtain pure **12j** (172 mg, 0.654 mmol, 90%) as a yellow oil: IR (CH_2Cl_2) 2960, 2940, 2900, 2880, 2330, 2230, 1775, 1612, 1468, 1280, 1230, 1210, 1090, 1039, 1015, 952, 815 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.17–4.05 (m, 4 H), 2.59 (t, J = 7.5 Hz, 2 H), 2.41 (t, J = 7 Hz, 2 H), 1.71 (pent, J = 7.5 Hz, 2 H), 1.54 (pent, J = 7 Hz, 1 H), 1.54 (pent, J = 7.6 Hz, 1 H), 1.42 (heptet, J = 7 Hz, 4 H), 0.94 (t, J = 7 Hz, 3 H), 0.91 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 192.30, 184.67, 140.45, 120.55, 102.98, 67.44, 65.72 (2 C), 29.52, 27.53, 25.98, 22.08, 21.26, 18.78, 13.01, 12.86. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.32; H, 8.50.

3-*tert*-Butyl-4-(1-hexynyl)-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12k). A solution of 4-*tert*-butyl-3-(1-hexynyl)-4-hydroxy-2-isopropoxy-2-cyclobutenone ethylene acetal (**11k**) (187 mg, 0.580 mmol) in 4 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 0.5 mL of 2 N HCl. Analysis by ^1H NMR after 5 min showed that all starting material had reacted. The reaction mixture was extracted with Et_2O (2 × 20 mL) and washed with 30 mL of H_2O. The organic phase was dried with Na_2SO_4 and concentrated. The product was chromatographed on a 2-mm silica gel rotor (30% ether in hexanes) to obtain pure **12k** (151 mg, 0.576 mmol, 99%) as a colorless oil: IR (CH_2Cl_2) 2965, 2940, 2900, 2870, 2220, 1770, 1600, 1475, 1458, 1388, 1362, 1334, 1204, 1100, 1042, 1027, 1015, 1000, 950, 924, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.14–4.04 (m, 4 H), 2.39 (t, J = 7 Hz, 2 H), 1.57–1.46 (m, 2 H), 1.46–1.33 (m, 2 H), 1.30 (s, 9 H), 0.88 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 192.93, 190.57, 138.85, 120.75, 104.21, 67.96, 65.51 (2 C), 34.74, 29.50, 27.47 (3 C), 21.28, 18.88, 12.87. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.20; H, 8.49.

4-*tert*-Butyl-3-(1-hexynyl)-3-cyclobuten-1-one 2-(Ethylene acetal) (12l). A solution of 3-*tert*-butyl-4-(1-hexynyl)-4-hydroxy-2-isopropoxy-2-cyclobutenone ethylene acetal (**11l**) (150 mg, 0.467 mmol) in 5 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 2 mL of 2 N HCl. The reaction was complete after 1 h by TLC analysis. The reaction mixture was extracted with Et_2O (2 × 20 mL) and washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4 and concentrated. The product was chromatographed on a 2-mm silica gel rotor (10% ether in hexanes) to obtain pure **12l** (106 mg, 0.403 mmol, 86%) as a yellow oil, which will slowly evaporate at 0.2 mmHg if left on the pump: IR (CH_2Cl_2) 2960, 2935, 2900, 2860, 2215, 1764, 1604, 1579, 1478, 1467, 1400, 1370, 1340, 1228, 1207, 1129, 1108, 1046, 1025, 952, 872, 802 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.16–4.06 (m, 4 H), 2.52 (t, J = 7 Hz, 2 H), 1.62–1.52 (m, 2 H), 1.48–1.34 (m, 2 H), 1.22 (s, 9 H), 0.90 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 196.23, 170.69, 156.80, 119.41, 117.31, 70.31, 65.79, 32.66, 29.40, 26.91 (2 C), 21.28, 19.66, 12.86. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.44; H, 8.48.

4-*tert*-Butyl-3-phenyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12m). A solution of 3-*tert*-butyl-4-hydroxy-3-isopropoxy-4-phenyl-2-cyclobutenone ethylene acetal (**11m**) (210 mg, 0.660 mmol) in 5 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 2 mL of 2 N HCl. The reaction was complete after 45 min by TLC analysis. Et_2O (50 mL) was added and the organic phase was washed with H_2O (3 × 10 mL). The organic phase was dried with Na_2SO_4 and concentrated. The product was chromatographed on a 2-mm silica gel rotor (30% ether in hexanes) to obtain pure **12m** (161 mg, 0.623 mmol, 94%) as a white crystalline solid: mp 138.5 °C dec; IR (CH_2Cl_2) 2970, 2900, 1763, 1620, 1596, 1476, 1400, 1370, 1340, 1228, 1210, 1130, 1027, 1010, 953, 870, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.52–7.49 (m, 2 H), 7.41–7.39

(m, 3 H), 4.18–3.98 (m, 4 H), 1.25 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 194.90, 171.54, 166.54, 129.94, 129.29, 127.71 (2 C), 127.53 (2 C), 119.74, 65.71 (3 C), 32.50, 27.66 (2 C). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.31; H, 7.02.

3-*tert*-Butyl-4-phenyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12n). A solution of 4-*tert*-butyl-4-hydroxy-2-isopropoxy-3-phenyl-2-cyclobutenone ethylene acetal (**11n**) (169 mg, 0.530 mmol) in 5 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 1 mL of 2 N HCl. The reaction was complete after 10 min by TLC analysis. Et_2O (50 mL) was added and the organic phase was washed with H_2O (3 × 5 mL). The organic phase was dried with Na_2SO_4 and concentrated. Removal of residual solvent at reduced pressure gave pure **12n** (137 mg, 0.530 mmol, 99.8%) as a white crystalline solid: mp 66–67 °C; IR (CH_2Cl_2) 2975, 2940, 2900, 1767, 1630, 1594, 1495, 1480, 1460, 1448, 1423, 1400, 1370, 1335, 1220, 1210, 1095, 1037, 1020, 1005, 952, 900, 825 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47–7.44 (m, 2 H), 7.40–7.32 (m, 3 H), 4.22–4.12 (m, 4 H), 1.33 (s, 9 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 194.90, 185.88, 154.87, 128.47, 128.21, 128.06 (2 C), 127.72 (2 C), 120.22, 65.49 (2 C), 34.47, 28.18 (3 C). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.18; H, 7.04.

3-(1-Hexynyl)-4-phenyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12o). A solution of 4-(1-hexynyl)-4-hydroxy-2-isopropoxy-3-phenyl-2-cyclobutenone ethylene acetal (**11o**) (211 mg, 0.616 mmol) in 3 mL of reagent-grade THF was stirred for 30 min with 1 mL of 2 N HCl. The reaction was complete by TLC (SiO_2, 30% ether in hexanes). After addition of 50 mL of Et_2O, the reaction mixture was washed with water (3 × 10 mL), dried with Na_2SO_4, and concentrated. The yellow oil was chromatographed on a 2-mm silica gel rotor (10% ether in hexanes), and the first band was collected and concentrated to give **12o** (156 mg, 0.553 mmol, 90%) as a pure yellow solid: mp 53.0–54.0 °C; IR (CH_2Cl_2) 2950, 2920, 2885, 2855, 2205, 1766, 1603, 1582, 1483, 1469, 1440, 1355, 1308, 1220, 1150, 1088, 1062, 1042, 1013, 9948, 812, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.02–7.99 (m, 2 H), 7.40 (t, J = 3 Hz, 3 H), 4.19 (brs, 4 H), 2.66 (t, J = 7 Hz, 2 H), 1.67 (pent, J = 7 Hz, 2 H), 1.50 (hextet, J = 7 Hz, 2 H), 0.95 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 195.39, 155.36, 154.73, 130.31 (2 C), 128.05 (2 C), 127.40 (2 C), 120.08 (2 C), 71.60, 65.98 (2 C), 29.48, 21.41, 20.03, 12.93. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.42; H, 6.49.

4-(1-Hexynyl)-3-phenyl-3-cyclobutene-1,2-dione 2-(Ethylene acetal) (12p). A solution of 3-(1-hexynyl)-4-hydroxy-2-isopropoxy-4-phenyl-2-cyclobutenone ethylene acetal (**11p**) (109 mg, 0.319 mmol) in 4 mL of reagent-grade THF in a 25-mL round-bottomed flask open to the atmosphere at room temperature was stirred with 0.5 mL of 2 N HCl. The reaction was complete after 10 min by TLC analysis. Et_2O (50 mL) was added and the organic phase was washed with H_2O (3 × 5 mL). The organic phase was dried with Na_2SO_4 and concentrated. Chromatography on a 2-mm silica gel rotor (10% ether in hexanes) gave pure **12p** (89.3 mg, 0.316 mmol, 99%) as a pale yellow oil: IR (CH_2Cl_2) 2960, 2935, 2895, 2870, 2220, 1770, 1615, 1570, 1360, 1304, 1225, 1180, 1160, 1075, 1038, 1012, 948, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (dd, J = 8 Hz, 2 Hz, 2 H), 7.52–7.42 (m, 3 H), 4.26 (brs, 4 H), 2.52 (t, J = 7 Hz, 2 H), 1.66–1.57 (m, 2 H), 1.53–1.41 (m, 2 H), 0.93 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 192.09, 172.46, 135.92, 131.90, 128.46, 128.33 (2 C), 128.20 (2 C), 120.29, 106.34, 69.17, 65.87 (2 C), 29.57, 21.40, 19.21, 12.94. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.66; H, 6.44.

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Registry No. **8a**, 114094-60-9; **8b**, 114094-61-0; **8c**, 114094-62-1; **8d**, 114094-63-2; **8e**, 114094-64-3; **8f**, 128242-33-1; **9a**, 128242-34-2; **9b**, 128242-35-3; **9c**, 128242-36-4; **9d**, 128242-37-5; **9e**, 128242-38-6; **9f**, 128242-39-7; **10a**, 128242-40-0; **10b**, 128242-41-1; **10c**, 128242-42-2; **10d**, 128242-43-3; **10e**, 128242-44-4; **10f**, 128242-45-5; **11b**, 128242-46-6; **11d**, 128242-47-7; **11e**, 128242-48-8; **11f**, 128242-49-9; **11g**, 128242-50-2; **11h**, 128242-51-3; **11i**, 128242-52-4; **11j**, 128242-53-5; **11k**, 128242-54-6; **11l**, 128242-55-7; **11m**, 128242-56-8; **11n**, 128242-57-9; **11o**, 128242-58-0; **11p**, 128242-59-1; **12a**, 128242-60-4; **12b**, 128242-61-5; **12c**, 128242-62-6; **12d**, 128242-63-7; **12e**, 128242-64-8; **12f**, 128242-65-9; **12g**, 128242-66-0; **12h**, 128242-67-1; **12i**, 128242-68-2; **12j**, 128242-69-3; **12k**, 128242-70-6; **12l**, 128242-71-7; **12m**, 128242-72-8; **12n**, 128242-73-9; **12o**, 128242-74-0; **12p**, 128269-79-4; PhLi, 591-51-5; bis(trimethylsiloxy)ethane, 7381-30-8; 1-hexyne, 693-02-7; *n*-butyl acetylide, 1942-46-7; diisopropyl squarate, 61699-62-5.