Rearrangements of Cyclobutenones. Synthesis of Benzoquinones from 4-Alkenyl-4-hydroxycyclobutenones

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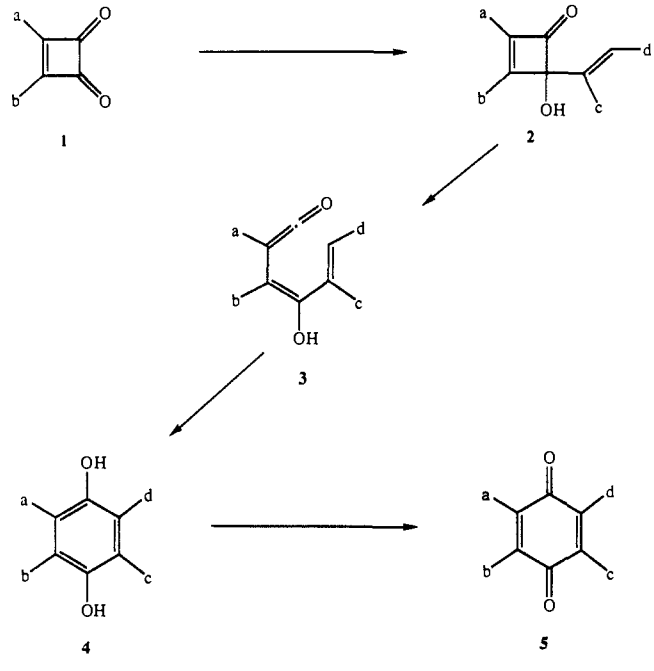
Abstract: The rearrangement of 4-alkenyl-4-hydroxycyclobutenones to quinones and related aromatic compounds is described. This rearrangement is complimentary to the previously reported ring expansions of 4-aryl- and 4-alkynyl-4-hydroxycyclobutenones. The synthetic scope and utility of the reaction are discussed. It is employed as a key step in the synthesis of a number of benzoquinones as well as in the total synthesis of the natural product, (±)-*O*-methylperezone and its regioisomer, (±)-*O*-methylisoperezone as well as coenzyme Q_0 and aurantiogliocladin.

Reported here are the details of a versatile synthetic route to benzoquinones and related compounds (Scheme I).[1] This methodology involves the ring expansion of 4-alkenyl-4-hydroxycyclobutenones to hydroquinones. The starting materials initiate from cyclobutenediones **1** which are readily converted to the corresponding 4-alkenyl-4-hydroxycyclobutenones **2** upon treatment with the appropriate alkenyllithium reagent. The resulting cyclobutenones undergo a remarkably stereoselective electrocyclic ring opening upon thermolysis to generate the intermediate dienylketenes **3**.[2,3] These ketenes then undergo electrocyclic ring closure and subsequent tautomerism to give the hydroquinones **4** which can be easily converted to the corresponding quinones **5** upon oxidative workup. The reaction is general in scope and complimentary to the previously reported ring expansions of 4-aryl- and 4-alkynyl-4-hydroxycyclobutenones to respectively annelated hydroquinones and benzoquinones.[4-8] Since the starting cyclobutenediones **1** are common to all of these ring expansions and they are now available in a variety of substitution patterns, a very versatile regioselective route to highly substituted quinones and related aromatic compounds is now available.[9-11]

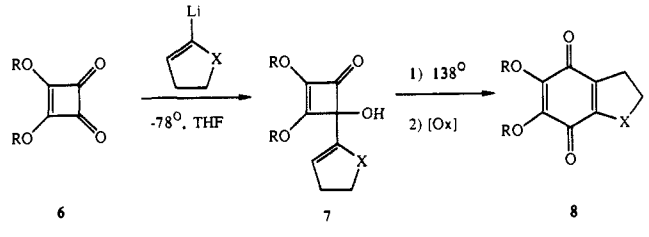
Scheme I



General Synthetic Scope

Specific examples illustrating the synthetic utility of this method are given in Schemes II and III. Those in Scheme II illustrate a route to annelated quinones **8a-f** from the ring expansion of cyclobutenones **7a-f** upon thermolysis in refluxing *p*-xylene (138°) followed by an oxidative workup with CAN. The starting material for these transformations is either dimethyl or diethyl squarate **6** which were easily converted to the cyclobutenones **7a-f** upon treatment with the corresponding ethenyllithium reagent at −78 °C in THF. The examples given illustrate the utility of the method to prepare heterocyclic as well as carbocyclic examples in which the annelated ring size was varied, in selected cases, between five- and seven-membered. Scheme III illustrates an extension of the

Scheme II



	R	X	% YIELD 7	% YIELD 8
a	CH_3	CH_2	73	71
b	CH_2CH_3	O	43	82
c	CH_3	CH_2CH_2	86	76
d	CH_2CH_3	CH_2CH_2	--	55
e	CH_2CH_3	OCH_2	45	71
f	CH_3	$CH_2CH_2CH_2$	55	72

(1) For a preliminary account of this work, see: Perri, S. T.; Dyke, H. J.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 2032.

(2) The selective conrotatory electrocyclic ring opening of the cyclobutenones reported here is in analogy to the more extensively studied ring opening of cyclobutenes. For a computational study accounting for the observed preferred opening in which the more electron-donating group at C-3 of the cyclobutene rotates outward, see: Randan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. For experimental studies on the stereochemistry of cyclobutene opening, see: Curry, M. J.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391. Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 409 and 415. Dolbier, W. R.; Koroniak, H.; Burton, D. J.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 1871. Kirmse, W.; Randan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

(3) For other very interesting routes to dienylketenes, see: Danheiser, R. L.; Gee, S. K.; Perez, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 806. Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1672. Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc.* **1982**, *104*, 7670.

(4) Perri, S. T.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 996.

(5) The synthesis of quinones from 4-aryl-4-hydroxycyclobutenones was independently discovered. See: (a) Leibeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065. (b) Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *Ibid.* **1986**, *51*, 3067.

(6) Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989.

(7) Reed, M. W.; Moore, H. W. *J. Org. Chem.* **1988**, *52*, 4166.

(8) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(9) Reed, M.; Pollart, D.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477.

(10) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

(11) Benzocyclobutenediones are also now easily prepared, see: Liebeskind, L. S.; Lescosky, L. J.; McSwain, C. M., Jr. *J. Org. Chem.* **1989**, *54*, 1435.

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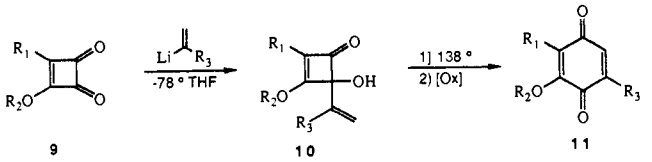
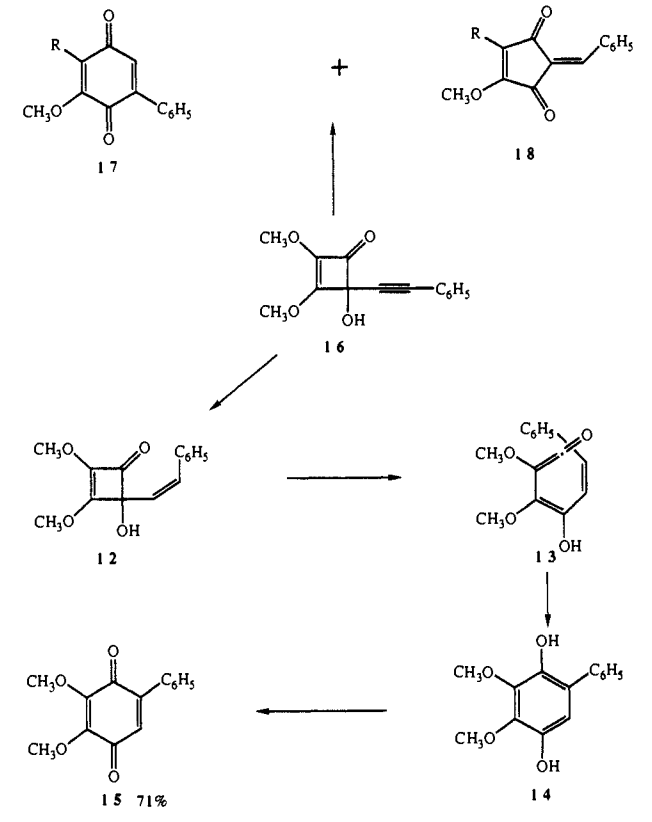
Scheme III

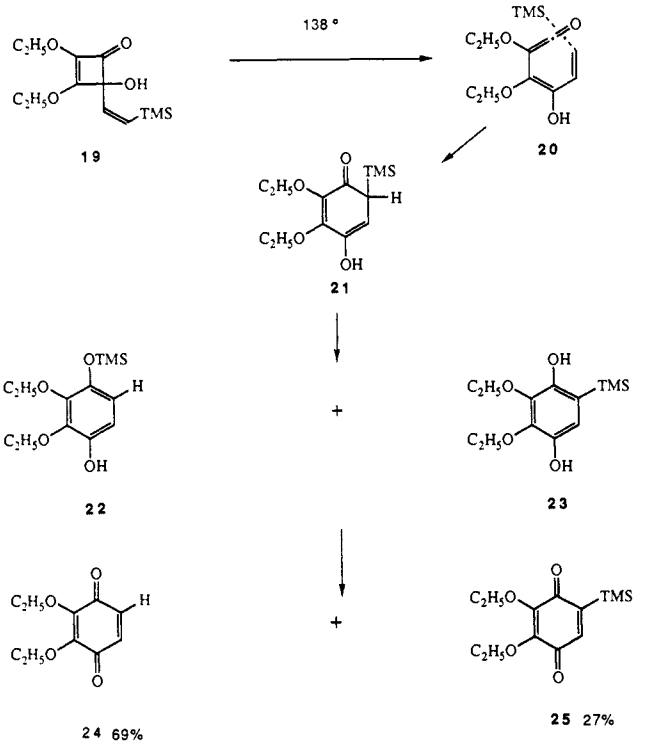


	R_1	R_2	R_3	% Yield 10	% Yield 11
a	C_6H_5	CH_3	n-C_4H_9	78	87
b	C_6H_5	CH_3CH_2	n-C_4H_9	71	82
c	C_6H_5	CH_3CH_2	$CH_2C_6H_5$	71	76
d	C_6H_5	CH_3CH_2	C_6H_5	55	71
e	C_6H_5	CH_3	CH_3	87	68
f	C_6H_5	CH_3	OCH_2CH_3	46	55
g	$C{\equiv}CC_6H_5$	CH_3	n-C_4H_9	48	80
h	$C{\equiv}CC_6H_5$	CH_3	$CH_2C_6H_5$	57	69
i	$C{\equiv}CC_6H_5$	CH_3	C_6H_5	51	72
j	n-C_4H_9	CH_3	$CH_2C_6H_5$	59	86
k	n-C_4H_9	CH_3	n-C_4H_9	56	83

Scheme IV



Scheme V



methodology to include monocyclic examples in which the quinones possess a 2,5-dialkylated substitution pattern. Here, the cyclobutenediones **9a–k** were employed as starting materials and converted to the cyclobutenones **10a–k** upon treatment with the appropriate alkenyllithium agent. Thermolysis then resulted in ring expansion to the substituted benzoquinones **11a–k**.

It was of interest to see if the stereochemistry of the 4-alkenyl moiety of the starting cyclobutenones had any influence on the course of the rearrangement. That is, it seemed possible that the cis isomer might not readily undergo ring expansion since the ketene intermediates could suffer appreciable steric interaction as shown in **13** (Scheme IV). It is of interest to note that this does not appear to be a problem since the desired ring expansion of **12** to **14** was observed to be a facile transformation. That is, the cyclobutenone **12** was prepared from the 4-phenylethynyl derivative **16** (Lindlar reduction) and subjected to thermolysis in the usual manner.[1] The hydroquinone product **14** was not purified but subjected directly to oxidative conditions (CAN on SiO_2) to give **15** in 71% purified yield.

The ring expansion of **12** to **14** is of further synthetic note since it represents a potentially general route to aryl benzoquinones and these are not readily available by any other general route. The reaction is also of interest in comparison to the ring expansion of 2,3-dimethoxy-4-(phenylethynyl)-4-hydroxycyclobutenone (**16**) which could conceivably also provide a route to **15**. However, we have previously shown that 4-(arylethynyl)-4-hydroxycyclobutenones give both the benzoquinone **17** and the cyclopentenedione **18** upon thermolysis.[8] Thus, the ring expansion of 4-(arylethenyl)-4-hydroxycyclobutenones to arylbenzoquinones is clearly the method of choice. Also, since unsymmetrical cyclobutenediones are now readily available, regioselectivity in the synthesis of variously substituted quinones can be envisaged, i.e., 1-aryl-1-lithio- as well as 1-aryl-2-lithioalkenes are easily generated by a variety of methods.[12]

An additional example illustrating the independence of the stereochemistry of the 4-alkenyl moiety on the ring expansion is given in Scheme V. Here the cyclobutenone **19** was prepared from the corresponding alkynyl derivative (Lindlar reduction).[8,13] Even though the ring expansion proceeded smoothly, an unanticipated product was observed. Specifically, trimethylsilyl as well as proton tautomerism took place from the cyclohexadienone **21** to give, respectively, the hydroquinones **22** and **23**. These were converted to the quinones **24** (69%) and **25** (27%) upon oxidation. In spite of the competitive formation of **24** this method illustrates a complimentary procedure to the thermolysis of 4-alkynyl-4-((trimethylsilyl)oxy)cyclobutenones as a route to trimethylsilylquinones.[8,14]

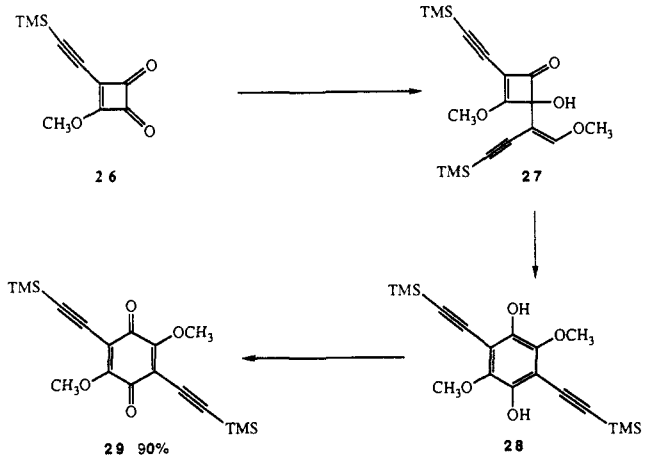
Finally, one last example concerning the stereochemical independence of the alkenyl side chain is given in Scheme VI. Here, the cyclobutenone **27** was prepared from 2-((trimethylsilyl)-

(12) For an excellent discussion of the synthesis of organolithium reagents, see: Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry 1*; Springer-Verlag, Berlin, Heidelberg, 1987.

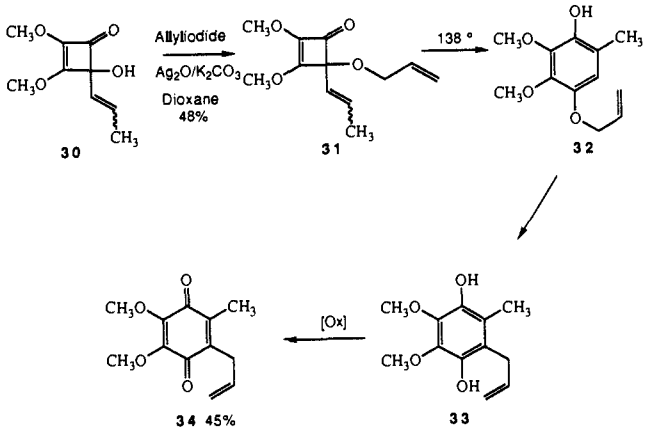
(13) The stereochemistry of the alkenyl group is based upon the H–H coupling constant of $J = 14.9$ Hz which is in excellent agreement with the assigned *Z* isomer, see: Hobgood, R. T.; Goldstein, J. H.; Reddy, G. S. *J. Chem. Phys.* **1961**, *33*, 2038.

(14) Trimethylsilylquinones are rare, see: Bock, H.; Alt, H. *Angew. Chem., Int. Ed. Engl.* **1967**, 941. Hashimoto, T. *Yakugaku Zasshi* **1967**, *87*, 535. Razuvaeav, G. A.; Vasileiskaya, N. S.; Gorbunova, L. V.; Chevnikova, G. V.; Bornikov, G. N. *Izv. Akad. Nauk. USSR Ser. Khim.* **1971**, *20*, 2392. Vasileiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Bortnikov, N. G. *Izv. Akad. Nauk. USSR Ser. Khim.* **1972**, *21*, 2755. Vasileiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Makarenko, N. P.; Bortnikov, G. N. *Izv. Akad. Nauk. USSR Ser. Khim.* **1976**, *24*, 2770.

Scheme VI



Scheme VII



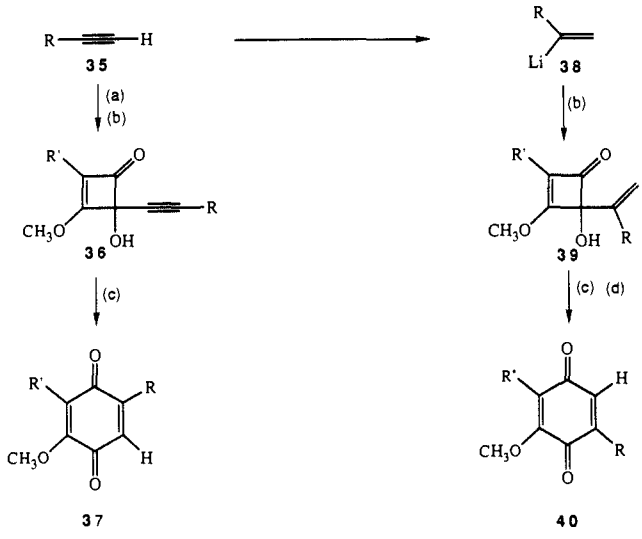
ethynyl)-3-methoxycyclobutenedione **26** and Zweifel's enyne.[15] Thermolysis of **27** in refluxing *p*-xylene gave the hydroquinone **28** which was converted to the quinone **29**, a compound of interest as a monomer to potential polyacetylenic quinones and hydroquinones.

The scope of this rearrangement was further probed to investigate the possibility of incorporating a tandem Claisen rearrangement into the ring expansion methodology. This was successfully advanced as outlined in Scheme VII. Specifically, the cyclobutenone **30** was allylated to give **31**. This was then subjected to thermolysis in refluxing *p*-xylene at 138 °C for 29 h. Under these conditions the quinone **34** was realized directly in 45% isolated yield. The transformation is assumed to proceed via the allyl ether **32** which suffers a Claisen rearrangement to **33** and this undergoes oxidation under the reaction conditions to give the quinone **34**.

One of the particularly interesting points concerning the methodology reported here is the regiochemical control it offers as compared to that of the previously reported ring expansion of 4-alkynyl-4-hydroxycyclobutenone.[8] Together these two methods are complimentary for the regiospecific synthesis of highly substituted quinones (Scheme VIII). For example, the 4-alkynyl-4-hydroxycyclobutenones starts with the conversion of the alkyne **35** into the corresponding lithium acetylide which is then treated with a cyclobutenedione. When the dione is unsymmetrical the resulting cyclobutenone **36** is formed regiospecifically by addition of the alkyne anion to the more electrophilic carbonyl group. Thermolysis of **36** in refluxing *p*-xylene then leads directly to the benzoquinone **37**. As described above, the 4-alkenyl-4-hydroxycyclobutenones can be employed to prepare **40**, the regioisomer of **37**. This involves generation of the vinyllithium reagent **38** which can be accomplished from a variety of precursors including

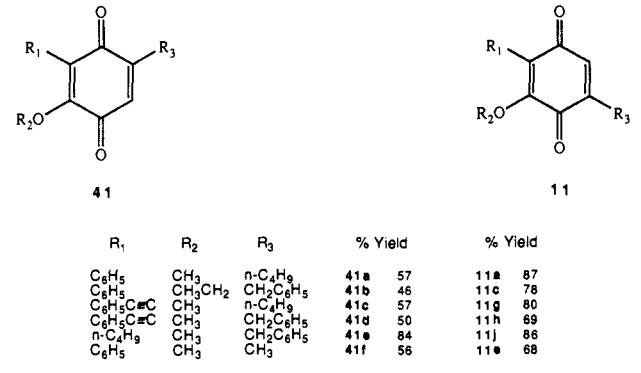
(15) Zwiefel, G.; Rajagopalan, S. *J. Am. Chem. Soc.* **1985**, *107*, 700.

Scheme VIII[a]



[a] Reagents: (a) BuLi, THF, −78 °C; (b) a cyclobutenedione; (c) *p*-xylene, 138 °C; (d) oxidation.

Scheme IX



R_1	R_2	R_3	% Yield		% Yield	
C_6H_5	CH_3	n-C_4H_9	**41a**	57	**11a**	87
C_6H_5	CH_3CH_2	$CH_2C_6H_5$	**41b**	46	**11c**	78
$C_6H_5C{\equiv}C$	CH_3	n-C_4H_9	**41c**	57	**11g**	80
$C_6H_5C{\equiv}C$	CH_3	$CH_2C_6H_5$	**41d**	50	**11h**	69
n-C_4H_9	CH_3	$CH_2C_6H_5$	**41e**	84	**11j**	86
C_6H_5	CH_3	CH_3	**41f**	56	**11e**	68

the alkyne **35**.[16,17] Conversion of **38** to the cyclobutenone **39** and subsequent thermolysis in refluxing *p*-xylene results in the formation of the benzoquinone **40** after an oxidative workup.

Several specific examples illustrating the above noted regiocontrol are given in Scheme IX. Specifically, the regioisomeric pairs of benzoquinones **41** and **11** were prepared from the respective alkoxycyclobutenedione and a suitable lithium reagent. For each pair the first member was prepared from the appropriate lithioalkyne and the second from the proper vinyllithium reagent which were generally prepared from the corresponding alkyne.[16,17]

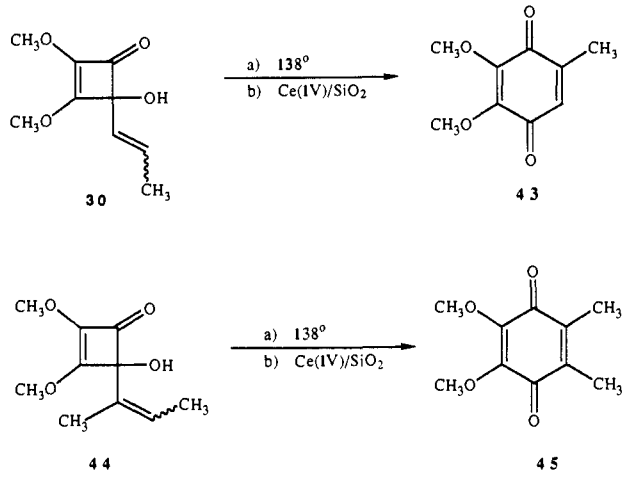
Specific Synthetic Utility

As final illustrations of the synthetic utility of the 4-alkenyl-4-hydroxycyclobutenone/benzoquinone rearrangement, efficient synthesis of coenzyme Q_0, aurantiogliocladin, (±)-*O*-methylperezone, and (±)-*O*-methylisoperezone are described herein.

Coenzyme Q_0, **43**, is the synthetic starting point for a wide variety of natural polyisoprenoidquinones.[18] Its synthesis as outlined in Scheme X represents the best available route to this compound.[19] It entails the addition of 1-lithio-1-propene to dimethyl squarate **6** to give the cyclobutenone **30**. Thermolysis of this in refluxing *p*-xylene and subsequent oxidation gave **43** in 84% isolated yield. In an analogous manner aurantiogliocladin **45** was obtained in 67% overall yield from dimethyl squarate **6** via the cyclobutenone **44** as outlined in Scheme X.[20] This syn-

(16) Peirs, E.; Chong, M. *J. Chem. Soc., Chem. Commun.* **1983**, 934.
(17) Cousseau, J. *Synthesis* **1980**, 805.
(18) Thomson, R. H. *Naturally Occurring Quinones*, 2nd ed.; Chapman and Hall: New York, 1987.
(19) For a leading reference concerning the conversion of coenzyme Q_0 to higher homologs, see: Keinan, E.; Eren, D. *J. Org. Chem.* **1987**, *52*, 3827.

Scheme X



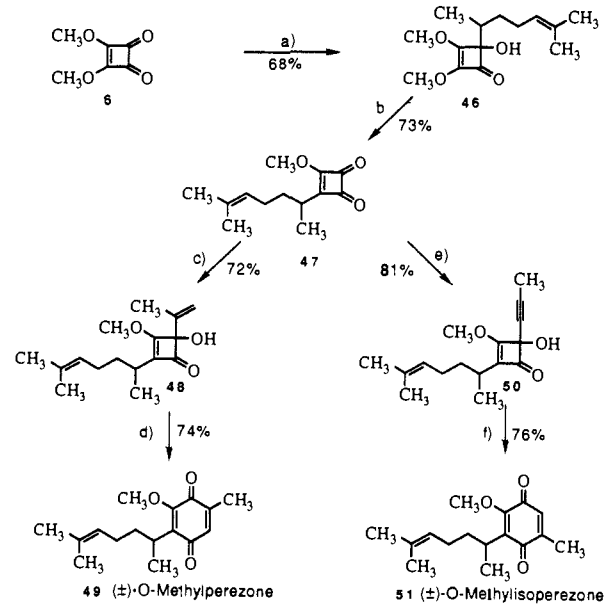
thesis also represents the best available method.

Of particular note is the synthesis of the naturally occurring sesquiterpene quinone, (±)-*O*-methylperezone, **49**. This quinone has been reported to occur in the aerial parts of *Coreopsis fasciculata*, and its synthesis was previously reported.[21-23] The synthesis described here involves treatment of dimethyl squarate **6** with 6-lithio-2-methyl-2-heptene to furnish the cyclobutenone **46** in 68% purified yield.[24] Hydrolysis of **46** upon treatment with trifluoroacetic anhydride and pyridine gave the cyclobutenedione **47** in 73% yield. Addition of 2-lithiopropene to **47** then provided the cyclobutenone **48** in 72% yield. Thermolysis of **48** followed by oxidation provided *d,l*-*O*-methylperezone (**49**) in 74% yield. Comparison of the ^{13}C NMR and ^{1}H NMR spectral data obtained for this synthetic product with those reported for the natural product showed them to be identical. This synthesis constitutes a 27% overall yield of the racemic natural product from dimethyl squarate in four steps as compared to the previously reported synthesis which provided a slightly lower overall yield (21%) from 2,3-dimethoxytoluene in eight steps.

As final documentation of the regiocontrol available from the ring expansions of 4-alkenyl- vs 4-alkynyl-4-hydroxycyclobutenones, (±)-*O*-methylisoperezone (**51**) was also prepared. Treatment of the cyclobutenedione **47** with 1-lithiopropyne furnished the cyclobutenone **50** in 81% yield. Thermolysis of **50** in refluxing acetonitrile then provided (±)-*O*-methylisoperezone (**51**) in 76% yield.[25]

In conclusion, it is shown that 4-alkenyl-4-hydroxycyclobutenones undergo ring expansion to benzohydroquinones upon thermolysis. This ring expansion is complimentary to the previously reported rearrangement of the 4-aryl analogues to annelated hydroquinones and the ring expansion of 4-alkynyl-4-hydroxycyclobutenones to benzoquinones.[1-8] Comparison of the methodology reported here with the ring expansion of 4-alkynyl-4-hydroxycyclobutenones is of particular note since together these rearrangements provide a powerful method for controlling the regiochemistry in the synthesis of highly substituted quinones.

Scheme XI[a]



[a] Reagents: (a) $CH_3CHLi(CH_2)_2CH{=}C(CH_3)_2$, hexane; (b) trifluoroacetic anhydride, pyridine, ether; (c) 2-lithiopropene, ether/THF; (d) (i) benzene, reflux, 2 h; (ii) Ce^{IV}, CH_2Cl_2; (e) 1-lithiopropyne, THF; (f) acetonitrile, reflux.

Experimental Section

Proton and carbon NMR were recorded on a Bruker WM-250, a General Electric QE 300 NMR, or a General Electric 500 NMR spectrometer. Chemical shifts were referenced relative to internal solvent resonances and are reported relative to TMS in $CDCl_3$ solvent, relative to $CHCl_3$ for carbon NMR in $CDCl_3$ solvent, or relative to DMSO for carbon NMR in DMSO-d_6 solvent. Infrared were recorded on a Perkin-Elmer spectrometer (double beam) by using $CHCl_3$ as the solvent and the reference solvent in a set of matched solution cells (Perkin-Elmer). Low-resolution mass spectra (MS) were determined on a Finnigan 4000 spectrometer; high-resolution mass spectra (HRMS) were measured with a VG Analytic 7070E spectrometer. Elemental analyses were performed by the Robertson Laboratory, Inc. of Madison, NJ. Melting points were uncorrected.

Reactions were performed in flame-dried glassware under a positive pressure of argon unless stated otherwise. Reaction mixtures were stirred magnetically. Air-sensitive solutions were transferred via cannulae and were introduced into the reaction vessels through rubber septa. Butyllithium was introduced to the reaction vessels via syringe. Reaction solutions were concentrated by using a Buchi rotary evaporator at 15–30 mmHg, and *p*-xylene was removed in the same manner with a bath temperature of 50–60 °C. Column chromatography was performed by using E. Merck silica gel (230–400) mesh, with hexane and ethyl acetate as the eluants.

Butyllithium in hexane was purchased from Aldrich Chem. Co. Commercial grade solvents were used without purification except as stated below. Tetrahydrofuran and diethyl ether were distilled prior to use from sodium benzophenone ketyl. Dimethoxyethane was distilled from lithium aluminum hydride. Benzene, *p*-xylene, and acetonitrile were distilled from calcium hydride prior to use.

General Procedure for the Preparation of 4-Alkenyl-4-hydroxy-2-cyclobuten-1-ones. As a typical example, the 1,2-addition of 1-lithiocyclopentene from 1-bromopentene to dimethyl squarate was carried out in the following manner.

4-(1-Cyclopentenyl)-2,3-dimethoxy-4-hydroxy-2-cyclobuten-1-one, 7a. A solution containing 0.40 g (2.74 mmol) of 1-bromocyclopentene in 25 mL of dry THF was cooled to −78 °C under argon. The solution was treated with 3.40 mL (5.48 mmol) of 1.60 M *tert*-butyllithium and stirred for 2 h. The resulting solution was then transferred via a cannula to a solution containing 0.37 g (2.61 mmol) of dimethyl squarate **6** in 125 mL of dry THF at −78 °C under argon. The reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of

(20) Previously, the most efficient synthesis of aurantiogliocladin was reported to be a five-step synthesis starting with 3,4,5-trimethoxybenzaldehyde, see: Aquila, H. *Liebigs Ann. Chem.* **1969**, 220.

(21) Bohlmann, F.; Ahmed, M.; Grenz, M.; King, R. M.; Robinson, H. *Phytochem.* **1983**, *22*, 2858.

(22) Sanchez, I. H.; Larraza, M. I.; Basurto, F.; Yanez, R.; Avila, S.; Tovar, R.; Joseph-Nathan, P. *Tetrahedron* **1985**, *41*, 2355.

(23) Sas', J. M.; Liobera, A. *Tetrahedron Lett.* **1987**, 5045.

(24) The lithium reagent was prepared according to Oppolzer et al. (Oppolzer, W.; Zutterman, F.; Battig, K. *Helv. Chem. Acta* **1983**, *66*, 522). Preparation of the lithium reagent requires specific conditions. It was necessary to use lithium sand containing 2% sodium (lithium containing 1% sodium did not work) and to employ sonication conditions.

(25) This synthesis also illustrates a potentially general route to a variety of analogues which will be of interest in a forthcoming study of the scope of the perezone/pipitzol rearrangement. For results of this rearrangement, see: (a) Walls, F.; Padilla, J.; Joseph-Nathan, P.; Giral, F.; Escobar, M.; Romo, J. *Tetrahedron* **1966**, *22*, 2387. (b) Sanchez, I. H.; Basurto, F.; Joseph-Nathan, P. *J. Nat. Prod.* **1984**, *47*, 382. (c) Joseph-Nathan, P.; Mendoza, V.; Garcia, E. *Tetrahedron* **1977**, *33*, 1573.

(26) Joseph-Nathan, P.; Abramo-bruno, D.; Ortega, D. A. *Org. Magn. Reson.* **1981**, *15*, 311.

5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over solid K_2CO_3 for 5 min. Filtration followed by concentration of the filtrate in vacuo afforded an oil. The oil was purified by column chromatography (3.5:1 hexane–ethyl acetate) which provided 0.40 g (73%) of **7a** as a pale yellow oil: IR (neat) 3400, 2960, 1772, 1635, 1415, 1342, 1050, 870, and 786 cm^{-1}; ^1H NMR ∂ 1.92 (quint, 2 H), 2.38 (m, 4 H), 3.93 (s, 3 H), 4.09 (s, 3 H), 4.11 (s, 1 H), 5.89 (t, J = 2.1 Hz, 1 H); MS (EI) 210 (85), 195 (59), 167 (33), 154 (39), 139 (82), 124 (34), 111 (36), 95 (100), 67 (82); HRMS m/e calcd for $C_{11}H_{14}O_4$ (M^+) 210.0892, found 210.0886.

2,3-Diethoxy-4-(2,3-dihydro-5-furanyl)-4-hydroxy-2-cyclobuten-1-one, 7b: 43% yield; colorless oil; IR (neat) 3425, 2998, 1784, 1669, 1630, 1387, 1335, and 1068 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.31 (t, J = 7.1 Hz, 3 H), 1.41 (t, J = 7.0 Hz, 3 H), 2.72 (m, 2 H), 3.09 (s, 1 H), 4.32 (q, J = 7.1 Hz, 2 H), 4.42 (m, 4 H), 5.11 (t, J = 2.5 Hz, 1 H); MS (EI) 240 (100), 211 (34), 183 (22), 165 (9), 155 (51), 137 (10), 110 (18); MS (CI) 241 (100); HRMS m/e calcd for $C_{12}H_{16}O_5$ (M^+) 240.0998, found 240.1003.

4-(1-Cyclohexenyl)-2,3-dimethoxy-4-hydroxy-2-cyclobuten-1-one, 7c: 86% yield; yellow oil; IR (neat) 3420, 2950, 1780, 1638, 1475, 1348, 1150, 1045, and 995 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.64 (m, 4 H), 2.05 (m, 4 H), 2.69 (s, 1 H), 3.96 (s, 3 H), 4.09 (s, 3 H), 6.01 (quint, 1 H); MS (EI) 224 (100), 209 (16), 192 (29), 181 (17), 165 (11), 136 (35), 121 (33), 109 (13), 91 (31); MS (CI) 225 (100); HRMS m/e calcd for $C_{12}H_{16}O_4$ (M^+) 224.1048, found 224.1032.

2,3-Diethoxy-4-(3,4-dihydro-2*H*-pyran-6-yl)-4-hydroxy-2-cyclobuten-1-one, 7e: 45% yield; yellow oil; IR (neat) 3400, 2997, 1786, 1678, 1635, 1482, 1330, 1050, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.31 (t, J = 7.1 Hz, 3 H), 1.41 (t, J = 7.1 Hz, 3 H), 1.85 (m, 2 H), 2.08 (m, 2 H), 3.14 (s, 1 H), 4.05 (m, 2 H), 4.33 (m, 2 H), 4.42 (m, 2 H), 5.03 (t, J = 3.8 Hz, 1 H); MS (EI) 254 (36), 226 (18), 197 (27), 169 (43), 151 (53), 124 (98), 83 (61); MS (CI) 255 (42), 209 (100); HRMS m/e calcd for $C_{13}H_{18}O_5$ (M^+) 254.1155, found 254.1150.

4-(1-Cycloheptenyl)-2,3-dimethoxy-4-hydroxy-2-cyclobuten-1-one, 7f. A solution of 0.15 g (21.4 mmol) of lithium metal (2% Na) cut into $^1/_4$-in. pieces (rinsed in hexanes) in 12 mL of freshly distilled ether was placed under argon. A neat solution of 0.69 g (5.28 mmol) of 1-chlorocycloheptene was added over a period of 20 min. The grey mixture was stirred for 18 h at ambient temperature and then transferred via cannulae to another solution containing 0.48 g (3.38 mmol) of dimethyl squarate **6** in 125 mL of dry THF at −78 °C under argon. The resulting solution was stirred 15 min, and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over solid K_2CO_3 for 5 min. Filtration followed by concentration in vacuo afforded an oil. The oil was purified by column chromatography (4:1 hexane–ethyl acetate) which provided 0.44 g (55%) of **7f** as a colorless oil: IR (neat) 3400, 2930, 1772, 1625, 1470, 1340, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.50 (m, 4 H), 1.78 (m, 2 H), 2.18 (m, 2 H), 2.23 (m, 2 H), 2.46 (s, 1 H), 3.98 (s, 3 H), 4.16 (s, 3 H), 6.19 (t, J = 8.5 Hz, 1 H); MS (EI) 238 (15), 206 (15), 163 (11), 150 (30), 107 (32), 91 (61), 79 (99), 67 (100); HRMS m/e calcd for $C_{13}H_{18}O_4$ (M^+) 238.1205, found 238.1197.

General Procedure for the Thermolysis of and Oxidation of 4-Alkenyl-4-hydroxy-2-cyclobuten-1-ones. Method A. 5,6-Dimethoxy-4,7-dioxobenzocyclopentane, 8a. A 318-mg (1.52 mmol) portion of **7a** was dissolved in 75 mL of freshly distilled *p*-xylene and heated at reflux for 2 h under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 45 °C. The residue was dissolved in 50 mL of dry ether followed by the addition of 0.84 g (6.08 mmol) of K_2CO_3 and 1.41 g (6.08 mmol) of Ag_2O. The reaction mixture was stirred for 2 h and then vacuum filtered through a bed of Celite. The filtrate was concentrated in vacuo which resulted in an orange solid. Recrystallization from ether afforded 225 mg (71%) of the benzoquinone as orange needles: mp 66–67 °C; IR ($CHCl_3$) 2980, 1660, 1598, 1460, 1436, 1385, 1310, 1006, and 882 cm^{-1}; ^1H NMR ∂ 2.04 (quint, 2 H), 2.77 (t, J = 7.7 Hz, 4 H), 3.99 (s, 6 H); MS (EI) 208 (78), 193 (29), 179 (15), 163 (75), 147 (12), 137 (28), 122 (68), 109 (25), 94 (63), 77 (20), 66 (100); HRMS m/e calcd for $C_{11}H_{12}O_4$ (M^+) 208.0735, found 208.0730. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.44; H, 5.83. Found: C, 63.18; H, 5.59.

General Procedure for the Thermolysis and Oxidation of 4-Alkenyl-4-hydroxy-2-cyclobuten-1-ones. Method B. 7,8-Dimethoxy-6,9-dioxobenzocycloheptane, 8f. A 210-mg (0.88 mmol) portion of **7f** was dissolved in 70 mL of freshly distilled *p*-xylene and heated at reflux for 2 h under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 45 °C. The crude residue was dissolved in 70 mL of CH_2Cl_2, and 8.76 g (2.64 mmol) of 20% Ce^{IV}/SiO_2[4] was added and stirred 30 min. The solution was filtered and then concentrated in vacuo to afford an orange solid. The solid was purified by column chromatography (4:1 hexane–ethyl acetate) which provided 0.15 g (72%) of the benzoquinone as orange needles after recrystallization from ether: mp 79–80 °C; ^1H NMR ($CDCl_3$) ∂ 1.53 (quint, 4 H), 1.83 (m, 2 H), 2.68 (t, J = 5.4 Hz, 4 H), 3.99 (s, 6 H); MS (EI) 236 (61), 221 (29), 193 (19), 175 (15), 165 (18), 137 (30), 105 (27), 91 (52), 79 (100); HRMS m/e calcd for $C_{13}H_{16}O_4$ (M^+) 236.1048, found 236.1025. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.82. Found: C, 65.91; H, 6.86.

5,6-Diethoxy-4,7-dioxobenzo-2,3-dihydrofuran, 8b: method A; 82% yield; red needles (ether); mp 61–62.5 °C; IR ($CHCl_3$) 2998, 1667, 1658, 1591, 1493, 1478, 1271, 1241, and 1028 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.36 (t, J = 7.2 Hz, 3 H), 1.39 (t, J = 7.1 Hz, 3 H), 3.05 (t, J = 9.7 Hz, 2 H), 4.15 (q, J = 7.0 Hz, 2 H), 4.36 (q, J = 7.1 Hz, 2 H), 4.73 (t, J = 9.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) ∂ 180.40, 176.80, 158.48, 146.95, 142.40, 118,83, 74.07, 70.01, 69.99, 27.09, 15.87, 15.68; MS (EI) 238 (100), 224 (28), 210 (47), 195 (23), 126 (32), 98 (33); MS (CI) 239 (100); HRMS m/e calcd for $C_{12}H_{14}O_5$ (M^+) 238.0841, found 238.0865. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.48; H, 5.92. Found: C, 60.52; H, 6.07.

6,7-Dimethoxy-5,8-dioxobenzocyclohexane, 8c: method A; 76% yield; red needles (ether); mp 79.5–81 °C; IR ($CHCl_3$) 2955, 1665, 1620, 1308, 1275, 1240, 1155, 1075, and 992 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.67 (quint, 4 H), 2.40 (quint, 4 H), 3.99 (s, 6 H); MS (EI) 222 (100), 207 (39), 189 (11), 177 (53), 161 (17), 151 (20), 123 (22), 108 (33), 79 (47); HRMS m/e calcd for $C_{12}H_{14}O_4$ (M^+) 222.0892, found 222.0890. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.34. Found: C, 64.94; H, 6.40.

6,7-Diethoxy-5,8-dioxobenzocyclohexane, 8d. A solution of 0.15 g (21.4 mmol) of lithium metal (2% Na) cut into $^1/_4$-in. pieces (rinsed in hexanes) in 12 mL of freshly distilled ether was placed under argon. A neat solution of 0.95 mL (8.53 mmol) of 1-chlorocyclohexene was added over a period of 20 min. The grey mixture was stirred for 18 h at ambient temperature and then transferred via cannulae to another solution containing 0.85 g (5.00 mmol) of diethyl squarate 6 in 125 mL of dry THF at −78 °C under argon. The resulting solution was stirred 15 min, and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over solid K_2CO_3 for 5 min. Filtration followed by concentration in vacuo afforded an inseparable mixture of product and starting material. The crude mixture was dissolved in 125 mL of freshly distilled *p*-xylene and heated at reflux for 2 h under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 45 °C. The crude residue was dissolved in 150 mL of CH_2Cl_2, and 26.56 g (8.00 mmol) of 20% Ce^{IV}/SiO_2 was added and stirred 20 min. The solution was filtered and then concentrated in vacuo to afford a red oil. The oil was purified by column chromatography (6:1 hexane–ethyl acetate) which provided 0.69 g (55%) of the benzoquinone as orange needles after recrystallization from ether: mp 50–51.5 °C; IR ($CHCl_3$) 2950, 1660, 1612, 1390, 1350, 1300, 1270, 1235, 1170, 1075, and 1018 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.37 (t, J = 7.0 Hz, 6 H), 1.67 (quint, 4 H), 2.39 (quint, 4 H), 4.25 (q, J = 7.0 Hz, 4 H); MS (EI) 250 (100), 221 (57), 207 (29), 194 (20), 177 (20), 166 (59), 91 (19), 79 (48); HRMS m/e calcd for $C_{14}H_{18}O_4$ (M^+) 250.1205, found 250.1207. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.24. Found: C, 67.09; H, 7.08.

6,7-Diethoxy-5,8-dioxobenzo-3,4-dihydro-2*H*-pyran, 8e: method A; 71% yield; orange needles (ether); mp 77.5–79 °C; IR ($CHCl_3$) 2994, 1671, 1650, 1610, 1267, 1121, 1065, and 968 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.35 (t, J = 7.0 Hz, 3 H), 1.37 (t, J = 7.0 Hz, 3 H), 1.93 (m, 2 H), 2.40 (t, J = 6.3 Hz, 2 H), 4.17 (q, J = 7.1 Hz, 2 H), 4.25 (t, J = 5.2 Hz, 2 H), 4.33 (q, J = 7.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) ∂ 183.49, 179.44, 152.55, 145.41, 142.07, 116.41, 69.81, 68.07, 20.74, 17.87, 15.83, 15.68; MS (EI) 252 (81), 237 (13), 223 (57), 209 (31), 196 (33), 179 (14), 168 (100), 152 (15), 140 (46), 83 (28); MS (CI) 253 (100); HRMS m/e calcd for $C_{13}H_{16}O_5$ (M^+) 252.0998, found 252.1005. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.68; H, 6.36.

4-(1-*n*-Butylethenyl)-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one, 10a: 78% yield; colorless oil; IR (neat) 3390, 2960, 1744, 1628, 1596, 1497, 1425, 1365, 915, and 797 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.87 (t, J = 7.2 Hz, 3 H), 1.32 (sext, 2 H), 1.47 (sext, 2 H), 2.10 (t, J = 7.2 Hz, 2 H), 4.13 (s, 1 H), 4.17 (s, 3 H), 5.15 (d, J = 0.7 Hz, 1 H), 5.43 (s, 1 H), 7.30 (m, 3 H), 7.72 (m, 2 H); MS (EI) 272 (100), 229 (65), 215 (28), 201 (55), 183 (18), 170 (17), 155 (10), 141 (22), 129 (37), 115 (25); HRMS m/e calcd for $C_{17}H_{20}O_3$ (M^+) 272.1412, found 272.1407.

4-(1-*n*-Butylethenyl)-3-ethoxy-4-hydroxy-2-phenyl-2-cyclobuten-1-one, 10b: 71% yield; pale yellow oil; IR (neat) 3380, 2960, 1745, 1628, 1596, 1495, 1455, 1364, 915, and 598 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.87 (t, J = 7.2 Hz, 3 H), 1.32 (m, 2 H), 1.47 (m, 3 H), 2.09 (t, J = 7.2 Hz, 2 H), 3.60 (s, 1 H), 4.42 (m, 2 H), 4.56 (m, 2 H), 5.15 (d, J = 0.7 Hz, 1 H),

5.43 (d, J = 0.6 Hz, 1 H), 7.25–7.40 (m, 3 H), 7.70–7.75 (m, 2 H); MS (EI) 286 (90), 257 (17), 243 (14), 215 (100), 197 (37), 187 (41), 169 (18), 155 (12), 141 (32), 129 (55), 115 (52), 91 (47); HRMS m/e calcd for $C_{18}H_{22}O_3$ (M^+) 286.1569, found 286.1563.

3-Ethoxy-4-hydroxy-2-phenyl-4-(1-(phenylmethyl)ethenyl)-2-cyclobuten-1-one, 10c: 71%; pale yellow oil; IR (neat) 3380, 3040, 1750, 1625, 1600, 1498, 1412, 1384, 1352, 1012, 920, 758, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3 H), 3.35 (d, J = 15.3 Hz, 1 H), 3.53 (d, J = 15.2 Hz, 1 H), 3.56 (s, 1 H), 4.10 (m, 1 H), 4.40 (m, 1 H), 5.11 (d, J = 1.0 Hz, 1 H), 5.54 (s, 1 H), 7.10–7.40 (m, 8 H), 7.65 (m, 2 H); MS (EI) 320 (17), 291 (3), 227 (2), 214 (15), 202 (5), 157 (2), 139 (4), 128 (11), 115 (23), 91 (100); HRMS m/e calcd for $C_{21}H_{20}O_3$ (M^+) 320.1412, found 320.1403.

3-Ethoxy-4-hydroxy-2-phenyl-4-(1-phenylethenyl)-2-cyclobuten-1-one, 10d: 51% yield; pale yellow oil; analysis of the crude ^{1}H NMR revealed a mixture of the cyclobutenone and the corresponding hydroquinone in a 9/1 ratio, respectively. Spectral properties of the cyclobutenone: IR (neat) 3390, 1750, 1630, 1605, 1496, 1400, 1348, 1289, 1046, 1018, 919, 762, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (t, J = 7.1 Hz, 3 H), 4.10 (s, 1 H), 4.53 (m, 1 H), 4.63 (m, 1 H), 5.42 (s, 1 H), 5.58 (s, 1 H), 7.20–7.35 (m, 6 H), 7.45 (m, 2 H), 7.67 (m, 2 H).

4-Hydroxy-3-methoxy-4-(1-methylethenyl)-2-phenyl-2-cyclobuten-1-one, 10e: 87% yield; yellow oil; IR (neat) 3400, 2966, 1749, 1631, 1597, 1495, 1370, 910, 769, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3 H), 3.32 (s, 1 H), 4.19 (s, 3 H), 5.17 (s, 1 H), 5.37 (s, 1 H), 7.32 (m, 3 H), 7.71 (d, J = 9.0 Hz, 2 H); MS (EI) 230 (100), 215 (28), 197 (42), 187 (22), 170 (22), 141 (47), 129 (66), 115 (52), 89 (58), 77 (31), 69 (47), MS (Cl) 231 (100); HRMS m/e calcd for $C_{14}H_{14}O_3$ (M^+) 230.0943, found 230.0940.

4-(1-Ethoxyethenyl)-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one, 10f. A solution of 0.48 g (6.65 mmol) of ethyl vinyl ether in 10 mL of THF was cooled to −78 °C under nitrogen. The solution was treated with 3.33 mL (5.32 mmol) of 1.60 M *tert*-butyllithium followed by warming to −25 °C for 15 min (CCl_4/dry ice) while stirring. The solution was cooled again to −78 °C and then transferred via cannula to a solution containing 1.00 g (5.32 mmol) of 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione (**9f**) in 150 mL of THF at −78 °C under nitrogen. The reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo afforded a yellow oil. The oil was purified by column chromatography (5:1 hexane–ethyl acetate) to afford 0.64 g (46%) of **10f** as a yellow oil: IR (neat) 3400, 2989, 1758, 1637, 1601, 1498, 1464, 1452, and 1370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (t, J = 3.1 Hz, 1 H), 3.54 (s, 1 H), 3.83 (m, 2 H), 4.19 (s, 3 H), 4.27 (d, J = 3.1 Hz, 1 H), 4.55 (d, J = 3.0 Hz, 1 H), 7.35 (m, 3 H), 7.76 (m, 2 H); MS EI 260 (28), 199 (19), 189 (22), 161 (47), 149 (63), 118 (35), 89 (19); MS (CI) 261 (100), 187 (30); HRMS m/e calcd for $C_{15}H_{16}O_4$ (M^+) 260.1048, found 260.1039.

4-(1-*n*-Butylethenyl)-4-hydroxy-3-methoxy-2-(phenylethynyl)-2-cyclobuten-1-one, 10g: 48% yield; pale yellow oil; IR (neat) 3400, 2960, 1762, 1670, 1592, 1492, 1455, 1365, 1160, 1058, 990, 760, and 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3 H), 1.37 (sext, 2 H), 1.49 (sext, 2 H), 2.13 (t, J = 7.2 Hz, 2 H), 2.94 (s, 1 H), 4.39 (s, 3 H), 5.13 (d, J = 1.5 Hz, 1 H), 5.38 (s, 1 H), 7.34 (m, 3 H), 7.44 (m, 2 H); MS (EI) 296 (45), 253 (100), 239 (38), 225 (9), 210 (11), 165 (13), 153 (17), 105 (16); HRMS m/e calcd for $C_{19}H_{20}O_3$ (M^+) 296.1412, found 296.1394.

4-Hydroxy-3-methoxy-4-(1-(phenylmethyl)ethenyl)-2-(phenylethynyl)-2-cyclobuten-1-one, 10h: 57% yield; orange oil; analysis of the ^{1}H NMR revealed a mixture of the cyclobutenone and the corresponding hydroquinone in a 6/1 ratio, respectively (orange oil). Spectral properties of the cyclobutenone: IR (neat) 3400, 1762, 1617, 1596, 1494, 1455, 1365, 1060, 990, 758, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.01 (s, 1 H), 3.41 (d, J = 15.7 Hz, 1 H), 3.58 (d, J = 15.9 Hz, 1 H), 4.11 (s, 3 H), 5.08 (s, 1 H), 5.52 (s, 1 H), 7.20–7.45 (m, 10 H); MS (EI) 330 (52), 315 (13), 297 (14), 209 (39), 165 (18), 152 (33), 115 (96), 105 (100), 91 (92).

4-Hydroxy-3-methoxy-4-(1-phenylethenyl)-2-(phenylethynyl)-2-cyclobuten-1-one, 10i: 51% yield; orange oil; analysis of the ^{1}H NMR revealed a mixture of the cyclobutenone and the corresponding hydroquinone in an 8/1 ratio, respectively. Spectral properties of the cyclobutenone: IR (neat) 2400, 1764, 1620, 1594, 1492, 1360, 1218, 988, 911, 757, 701, and 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.57 (s, 1 H), 4.38 (s, 3 H), 5.43 (s, 1 H), 5.57 (s, 1 H), 7.27–7.55 (m, 10 H).

2-*n*-Butyl-4-hydroxy-3-methoxy-4-(1-(phenylmethyl)ethenyl)-2-cyclobuten-1-one, 10j: 59% yield; colorless oil; analysis of the ^{1}H NMR revealed a mixture of the cyclobutenone and the corresponding hydroquinone in a 7/1 ratio, respectively. Spectral properties of the cyclobutenone: IR (neat) 3370, 2960, 1749, 1615, 1497, 1457, 1360, 1056, 999, 752, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.33 (m, 2 H), 1.50 (m, 2 H), 2.07 (t, J = 8.0 Hz, 2 H), 3.34 (d, J = 15.9 Hz, 1 H), 3.50 (d, J = 15.8 Hz, 1 H), 3.42 (s, 1 H), 3.87 (s, 3 H), 4.98 (d, J = 0.9 Hz, 1 H), 5.47 (d, J = 0.6 Hz, 1 H), 7.18–7.35 (m, 5 H); MS (EI) 286 (13), 243 (7), 197 (2), 181 (2), 165 (26), 153 (12), 128 (8), 115 (22), 105 (6), 91 (100).

2-*n*-Butyl-4-(1-*n*-butylethenyl)-4-hydroxy-3-methoxy-2-cyclobuten-1-one, 10k: 56% yield; colorless oil: IR (neat) 3400, 1750, 1640, 1468, 1360, 1420, 1049, 988, 902, and 758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (two overlapping t, J = 7.1 Hz, 6 H), 1.30–1.60 (m, 8 H), 2.05 (t, J = 7.90 Hz, 2 H), 2.12 (dt, J = 2.2, 7.30 Hz, 2 H), 3.31 (s, 1 H), 4.05 (s, 3 H), 5.10 (d, J = 0.8 Hz, 1 H), 5.35 (s, 1 H); MS (EI) 252 (28), 209 (39), 153 (38), 125 (32), 107 (15), 79 (28), 55 (100); HRMS m/e calcd for $C_{15}H_{24}O_3$ (M^+) 252.1725, found 252.1720.

5-*n*-Butyl-3-methoxy-2-phenyl-2,5-cyclohexadiene-1,4-dione, 11a: method B; 87% yield; orange oil; IR (neat) 2960, 1658, 1652, 1598, 1498, 1447, 1325, 1280, 1160, 1057, 765, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3 H), 1.42 (sext, 2 H), 1.53 (sext, 2 H), 2.48 (dt, J = 1.4, 7.4 Hz, 2 H), 3.74 (s, 3 H), 6.58 (t, J = 1.5 Hz, 1 H), 7.25 (m, 2 H), 7.40 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.63, 28.60, 29.99, 61.49, 128.07, 128.40, 128.79, 130.40, 130.71, 132.58, 147.86, 155.40, 184.20, 187.66; MS (EI) 270 (31), 228 (100), 213 (40), 196 (37), 181 (29), 171 (23), 157 (79), 141 (17), 128 (38), 115 (23), 89 (54); HRMS m/e calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, found 270.1251.

5-*n*-Butyl-3-ethoxy-2-phenyl-2,5-cyclohexadiene-1,4-dione, 11b: method B; 82% yield; orange oil; IR (neat) 2960, 1660, 1594, 1325, 1270, 1176, 1052, 758, and 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.1 Hz, 3 H), 1.18 (t, J = 7.1 Hz, 3 H), 1.42 (sext, 2 H), 1.53 (m, 2 H), 2.47 (t, J = 7.0 Hz, 2 H), 3.99 (q, J = 7.1 Hz, 2 H), 6.58 (t, J = 1.4 Hz, 1 H), 7.30 (m, 3 H), 7.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.06, 15.77, 22.66, 28.67, 30.05, 69.97, 128.00, 128.70, 129.64, 130.49, 130.68, 132.62, 147.90, 154.96, 184.43, 187.79; MS (EI) 284 (18), 269 (34), 242 (27), 227 (12), 213 (100), 196 (14), 185 (27), 171 (35), 157 (11), 141 (14), 129 (44), 115 (27); HRMS m/e calcd for $C_{18}H_{20}O_3$ (M^+) 284.1412, found 284.1424.

3-Ethoxy-2-phenyl-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 11c: method B; 76% yield; orange needles (ether/hexane); mp 110–112 °C; IR ($CHCl_3$) 3020, 1665, 1652, 1591, 1498, 1447, 1312, 1171, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7.1 Hz, 3 H), 3.80 (s, 2 H), 4.00 (q, J = 7.0 Hz, 2 H), 6.38 (t, J = 1.5 Hz, 1 H), 7.20–7.40 (m, 10 H); MS (EI) 318 (8), 289 (5), 271 (9), 225 (3), 203 (14), 189 (6), 128 (23), 115 (78), 89 (100), 77 (50); HRMS m/e calcd for $C_{21}H_{18}O_3$ (M^+) 318.1256, found 318.1244. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.72. Found: C, 78.96; H, 5.49.

2,5-Diphenyl-3-ethoxy-2,5-cyclohexadiene-1,4-dione, 11d: method B; 71% yield; orange needles (CH_2Cl_2/ether); mp 119–120 °C; IR ($CHCl_3$) 3020, 1669, 1647, 1590, 1497, 1448, 1328, 1262, 1100, 902, and 697 cm^{-1}; ^{1}H NMR ($CHCl_3$) δ 1.22 (t, J = 7.1 Hz, 3 H), 4.07 (q, J = 7.1 Hz, 2 H), 6.90 (s, 1 H), 7.30–7.60 (m, 10 H); MS (EI) 304 (35), 289 (34), 276 (26), 247 (25), 219 (19), 191 (95), 165 (12), 129 (23), 102 (74), 89 (100); HRMS m/e calcd for $C_{20}H_{16}O_3$ (M^+) 304.1099, found 304.1081. Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.91; H, 5.31. Found: C, 78.65; H, 5.41.

3-Methoxy-5-methyl-2-phenyl-2,5-cyclohexadiene-1,4-dione, 11e: method A; 68% yield; orange needles (CH_2Cl_2/ether); mp 87.5–89 °C; IR ($CHCl_3$) 3001, 2950, 1661, 1609, 1593, 1493, 1444, 1353, 1320, 1285, 1001, 967, and 885 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.10 (d, J = 1.4 Hz, 3 H), 3.75 (s, 3 H), 6.63 (d, J = 1.6 Hz, 1 H), 7.29 (m, 2 H), 7.41 (m, 3 H); MS (EI) 228 (31), 210 (30), 185 (39), 129 (100), 89 (78), 77 (21), 68 (20), 63 (42), 51 (22), MS (CI) 229 (100); HRMS m/e calcd for $C_{14}H_{12}O_3$ (M^+) 228.0786, found 228.0768. Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.65; H, 5.30. Found: C, 73.43; H, 5.26.

5-Ethoxy-3-methoxy-2-phenyl-2,5-cyclohexadiene-1,4-dione, 11f: method A; 55% yield; yellow needles (ether); mp 93–95 °C; IR ($CHCl_3$) 3047, 3001, 2951, 1688, 1646, 1598, 1448, and 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50 (t, J = 7.0 Hz, 3 H), 3.75 (s, 3 H), 4.04 (q, J = 6.9 Hz, 2 H), 5.93 (s, 1 H), 7.28 (m, 2 H), 7.40 (m, 3 H); MS (EI) 258 (73), 240 (12), 229 (11), 215 (46), 201 (41), 183 (39), 145 (31), 131 (39), 102 (18), 89 (43), 69 (100); MS (CI) 259 (100); HRMS m/e calcd for $C_{15}H_{14}O_4$ (M^+) 258.0890, found 258.0895. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.74; H, 5.46. Found: C, 69.61; H, 5.64.

5-*n*-Butyl-3-methoxy-2-(phenylethynyl)-2,5-cyclohexadiene-1,4-dione, 11g: method B; 80% yield; red flakes (ether); mp 79.5–81 °C; IR ($CHCl_3$) 3020, 2960, 2210, 1658, 1601, 1588, 1492, 1450, 1330, 1286, 1201, and 1072 cm^{-1}; ^{1}H NMR δ 0.93 (t, J = 7.2 Hz, 3 H), 1.40 (sext, 2 H), 1.50 (sext, 2 H), 2.44 (t, J = 8.0 Hz, 2 H), 4.42 (s, 3 H), 6.55 (t, J = 1.4 Hz, 1 H), 7.38 (m, 3 H), 7.55 (m, 2 H); MS (EI) 294 (99), 251 (100), 237 (9), 223 (100), 209 (19), 195 (18), 165 (24), 153 (21), 113 (32); HRMS m/e calcd for $C_{19}H_{18}O_3$ (M^+) 294.1256, found 294.1252.

Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.51; H, 6.16. Found: C, 77.18; H, 6.16.

3-Methoxy-2-(phenylethynyl)-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 11h: method B; 69% yield; red needles (CH_2Cl_2/ether): mp 112.5–114 °C; IR ($CHCl_3$) 2960, 1660, 1600, 1581, 1491, 1455, 1448, 1330, 1275, 1208, 1074, 763, 718, 702, and 694 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 3.74 (d, J = 1.5 Hz, 2 H), 4.40 (s, 3 H), 6.34 (t, J = 1.6 Hz, 1 H), 7.2–7.4 (m, 8 H), 7.56 (m, 2 H); MS (EI) 328 (12), 313 (18), 239 (14), 228 (36), 202 (9), 165 (6), 142 (11), 126 (14), 115 (100), 105 (47), 91 (49); HRMS m/e calcd for $C_{22}H_{16}O_3$ (M^+) 328.1100, found 328.1083. Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.46; H, 4.91. Found: C, 80.32; H, 4.67.

3-Methoxy-5-phenyl-2-(phenylethynyl)-2,5-cyclohexadiene-1,4-dione, 11i: method B; 72% yield; red needles (CH_2Cl_2/ether); mp 147.5–149 °C; IR ($CHCl_3$) 3020, 1676, 1650, 1600, 1584, 1490, 1447, 1330, 1272, 1138, 1075, 902, 703, and 689 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 4.47 (s, 3 H), 6.87 (s, 1 H), 7.39 (m, 3 H), 7.47 (m, 5 H), 7.56 (m, 2 H); MS (EI) 314 (45), 257 (6), 226 (13), 215 (70), 113 (100), 102 (82); HRMS m/e calcd for $C_{21}H_{14}O_3$ (M^+) 314.0943, found 314.0939. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.23; H, 4.49. Found: C, 79.95; H, 4.21.

2-*n*-Butyl-3-methoxy-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 11j: method B; 86% yield; yellow oil; IR (neat) 2965, 1658, 1650, 1602, 1497, 1455, 1384, 1217, 1043, 929, and 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.1 Hz, 3 H), 1.34 (m, 4 H), 2.40 (t, J = 7.5 Hz, 2 H), 3.71 (d, J = 1.5 Hz, 2 H), 3.98 (s, 3 H), 6.24 (t, J = 1.6 Hz, 1 H), 7.20–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) ∂ 14.11, 23.11, 31.28, 35.06, 61.24, 127.12, 127.16, 129.03, 129.53, 129.58, 133.45, 136.79, 146.83, 156.06, 183.74, 188.42; MS (EI) 284 (32), 242 (43), 227 (22), 209 (6), 181 (12), 165 (14), 152 (18), 141 (19), 128 (14), 115 (62), 91 (100); HRMS m/e calcd for $C_{18}H_{20}O_3$ (M^+) 284.1412, found 284.1411.

2,5-Di-*n*-butyl-3-methoxy-2,5-cyclohexadiene-1,4-dione, 11k: method B; 83% yield; yellow oil; IR (neat) 2960, 2930, 1652, 1607, 1418, 1452, 1284, 1217, 1140, 1042, 928, 888, and 759 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.93 (two overlapping t, 6 H), 1.30–1.55 (m, 8 H), 2.42 (m, 4 H), 3.97 (s, 3 H), 6.44 (t, J = 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) ∂ 14.04, 14.12, 22.64, 23.10 (two coincidental carbons), 28.51, 30.09, 31.32, 61.21, 132.43, 133.31, 147.76, 156.83, 184.07, 188.61; MS (EI) 250 (23), 208 (21), 179 (18), 166 (100), 151 (13), 137 (19), 123 (19), 109 (15), 91 (23); HRMS m/e calcd for $C_{15}H_{22}O_3$ (M^+) 250.1560, found 250.1570.

2,3-Dimethoxy-4-(2-phenyl-(*Z*)-ethenyl)-4-hydroxy-2-cyclobuten-1-one, 12. A solution containing 1.19 g (11.7 mmol) of phenylacetylene in 50 mL of dry THF was cooled to −78 °C under nitrogen. The solution was treated with 6.82 mL (10.9 mmol) of 1.60 M *n*-butyllithium in hexanes and stirred for 15 min. This solution was then transferred via cannula to a solution containing 1.50 g (10.9 mmol) of dimethyl squarate in 100 mL of THF at −78 °C under nitrogen. After 10 min of stirring, the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration of the filtrate in vacuo afforded 2.08 g (80%) of the intermediate 2,3-dimethoxy-4-hydroxy-4-(phenylethynyl)-2-cyclobuten-1-one (**16**) as a yellow oil: IR (neat) 3390, 3015, 2960, 2213, 1783, 1640, 1472, 1350, 1072, 1031, 883, 758, and 688 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 3.44 (s, 1 H), 3.99 (s, 3 H), 4.24 (s, 3 H), 7.34 (m, 3 H), 7.43 (m, 2 H); MS (EI) 243 (14), 229 (11), 215 (23), 199 (3), 158 (10), 145 (26), 129 (100), 113 (28), 75 (22); MS (CI) 245 (100), 227 (19), 213 (25); HRMS m/e calcd for $C_{14}H_{12}O_4$ (M^+) 244.0735, found 244.0733. The phenyl acetylene adduct was reduced to the *cis*-olefin by dissolving 0.25 g (1.02 mmol) of the adduct in 100 mL of ethyl acetate in the presence of 0.03 g (12%) of 5% $Pd/CaCO_3$ and 0.11 g (44%) of quinoline. The reaction was stirred under an atmosphere of hydrogen for 1.5 h and then filtered through a bed of Celite. The ethyl acetate extract was washed with 50 mL of 0.5 M HCl, two times with brine, and then dried over $MgSO_4$. Filtration followed by concentration of the filtrate in vacuo afforded 0.25 g (99%) of **12** as a clear oil: IR (neat) 3400, 3011, 2957, 1768, 1634, 1469, 1435, 1342, 1030, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 2.87 (s, 1 H), 3.78 (s, 3 H), 3.92 (s, 3 H), 5.71 (d, J = 12.0 Hz, 1 H), 6.71 (d, J = 12.0 Hz, 1 H), 7.24 (m, 3 H), 7.40 (m, 2 H); MS (EI) 246 (12), 203 (9), 189 (7), 171 (10), 157 (20), 131 (90), 115 (100), 103 (54), 91 (40), 77 (51); MS (CI) 247 (100), 229 (29), 215 (38): HRMS m/e calcd for $C_{14}H_{14}O_4$ (M^+) 246.0892, found 246.0889.

2,3-Dimethoxy-5-phenyl-2,5-cyclohexadiene-1,4-dione, 15: method A; 71% yield; orange needles (CH_2Cl_2/hexane); mp 90–91.5 °C; IR ($CHCl_3$) 3001, 2947, 1658, 1593, 1452, 1444, 1333, 1263, 1097, and 890 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 4.04 (s, 3 H), 4.09 (s, 3 H), 6.70 (s, 1 H), 7.45 (s, 5 H); MS (EI) 244 (37), 225 (8), 215 (9), 199 (50), 173 (16), 145 (58), 115 (26), 102 (100), 76 (22), MS (CI) 245 (100); HRMS m/e calcd for $C_{14}H_{12}O_4$ (M^+) 244.0735, found 244.0728.

2,3-Diethoxy-4-(2-(trimethylsilyl)-(*Z*)-ethenyl)-2-cyclobuten-1-one, 19. A solution containing 0.30 g (3.06 mmol) of trimethylsilylacetylene in 45 mL of distilled THF was colled to −78 °C under argon. The solution was treated with 2.19 mL (3.00 mmol) of 1.37 M *n*-butyllithium in hexanes and stirred for 20 min. The resulting solution was then transferred via a cannula to a solution containing 0.50 g (2.94 mmol) of diethyl squarate in 100 mL of THF at −78 °C under argon. The reaction mixture was stirred for 10 min, and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo provided a white solid. Recrystallization from ether afforded 0.52 g (66%) of the alkynylcyclobutenone as white plates: mp 79.5–81.5 °C; IR ($CHCl_3$) 3690, 2160, 1782, 1645, 1415, 1384, 1332, 1100, 1035, 865, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.18 (s, 9 H), 1.32 (t, J = 7.1 Hz, 3 H), 1.46 (t, J = 7.1 Hz, 3 H), 2.92 (s, 1 H), 4.32 (q, J = 7.1 Hz, 2 H), 4.53 (q, J = 7.1 Hz, 2 H); MS (EI) 268 (7), 253 (20), 239 (16), 225 (42), 211 (100), 197 (52), 183 (13), 165 (26), 127 (59), 99 (66), 75 (72); MS (CI) 269 (100); HRMS m/e calcd for $C_{13}H_{20}O_4Si$ (M^+) 268.1130, found 268.1114.

A 0.18-g (0.67 mmol) portion of the alkynylcyclobutenone prepared above was placed in 50 mL of ethyl acetate. To the solution was added 0.03 g (15%) of $Pd/CaCO_3$ and two drops of quinoline, and the reaction mixture was stirred under an atmosphere of hydrogen for 10 h. The reaction mixture was filtered through Celite and rinsed with ethyl acetate. The clear filtrate was washed with cold dilute HCl, saturated $NaHCO_3$, and brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo provided an oil. The oil was purified by column chromatography on silica gel (5:1 hexane–ethyl acetate) to afford 65 mg (36%) of the cyclobutenone as a colorless oil: IR (neat) 3430, 2980, 1780, 1625, 1485, 1385, 1330, 1110, 1040, 936, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.16 (s, 9 H), 1.30 (t, J = 7.1 Hz, 3 H), 1.40 (t, J = 7.1 Hz, 3 H), 2.98 (s, 1 H), 4.30 (q, J = 7.1 Hz, 2 H), 4.42 (m, 2 H), 5.91 (d, J = 14.9 Hz, 1 H), 6.25 (d, J = 14.9 Hz, 1 H); MS (EI) 270 (37), 255 (4), 226 (9), 209 (9), 197 (79), 181 (47), 169 (23), 99 (10), 73 (100); MS (CI) 271 (100); HRMS m/e calcd for $C_{13}H_{22}O_4Si$ (M^+) 270.1287, found 270.1271.

2,3-Diethoxy-5-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 25, and 2,3-Diethoxy-2,5-cyclohexadiene-1,4-dione, 24. A 62.2-mg (0.23 mmol) portion of **19** was dissolved in 20 mL of freshly distilled *p*-xylene and heated at reflux for 4 h under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 45 °C. The resulting yellow oil was dissolved in 50 mL of CH_2Cl_2, and 3.05 g (0.91 mmol) of 20% Ce^{IV}/SiO_2 was added and stirred 15 min. The reaction mixture was filtered and then concentrated in vacuo to afford a red oil. Analysis of the crude ^1H NMR revealed a 2:1 mixture of products with the desilylated quinone as the major product. The oil was purified by column chromatography on silica gel (7:1 hexane–ethyl acetate) to afford 17 mg (27%) of the desired quinone and 31 mg (69%) of the desilylated quinone. **2,3-Diethoxy-5-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 25**: IR (neat) 2995, 1662, 1585, 1315, 1260, 1200, 1125 and 825 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.23 (s, 9 H), 1.39 (two overlapping triplets, J = 7.0 Hz, 6 H), 4.27 (two overlapping quartets, J = 7.0 Hz, 4 H), 6.71 (s, 1 H); MS (EI) 268 (97), 252 (75), 224 (94), 209 (40), 197 (82), 179 (68), 155 (11), 140 (26), 112 (15), 99 (11), 83 (66), 73 (100); HRMS m/e calcd for $C_{13}H_{20}O_4Si$ (M^+) 268.1130, found 268.1120. **2,3-Diethoxy-2,5-cyclohexadiene-1,4-dione, 24**: mp 34–35 °C; IR ($CHCl_3$) 2995, 1666, 1592, 1300, 1285, 1075, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 1.38 (t, J = 7.1 Hz, 6 H), 4.30 (q, J = 7.1 Hz, 4 H), 8.60 (s, 2 H); MS (EI) 196 (19), 168 (29), 153 (23), 140 (5), 123 (8), 112 (100), 94 (6), 84 (15); HRMS m/e calcd for $C_{10}H_{12}O_4$ (M^+) 196.0735, found 196.0733.

4-Hydroxy-3-methoxy-4-[2-methoxy-1-((trimethylsilyl)ethynyl)-(*E*)-ethenyl]-2-((trimethylsilyl)ethynyl)-2-cyclobuten-1-one, 27. A solution containing 0.44 g (2.86 mmol) of (*Z*)-4-(trimethylsilyl)-1-methoxybut-1-en-3-yne in 8 mL of freshly distilled dimethoxyethane (from LAH) was cooled to −78 °C under argon. The solution was treated with 2.04 mL (2.86 mmol) of 1.40 M *n*-butyllithium in hexanes and stirred for 25 min. The resulting solution was then transferred via a cannula to a solution containing 0.54 g (2.60 mmol) of 3-methoxy-4-((trimethylsilyl)ethynyl)-3-cyclobutene-1,2-dione in 125 mL of dry THF at −78 °C under argon. The resulting solution was stirred for 45 min and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo provided a dark oil. The oil was purified by column chromatography on silica gel (5:1 hexane–ethyl acetate) to afford 0.54 g (57%) of the cyclobutenone as an orange oil: IR (neat) 3520, 2960, 2145, 1750, 1618, 1455, 1352, 1252, 1150, 988, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) ∂ 0.17 (s, 9 H), 0.18 (s, 9 H), 3.78 (s, 3 H), 4.31 (s, 3 H), 4.42 (s, 1 H), 6.67 (s, 1 H); MS (EI)

362 (43), 347 (82), 332 (25), 319 (50), 302 (20), 287 (4), 215 (5), 123 (5), 109 (6), 89 (20), 73 (100); HRMS *m/e* calcd for $C_{18}H_{26}O_4Si_2$ (M^+) 362.1369, found 362.1354.

2,5-Dimethoxy-3,6-bis((trimethylsilyl)ethynyl)-2,5-cyclohexadiene-1,4-dione, 29: method B; 90% yield; orange needles (CH_2Cl_2/ether); mp 120.5–121.5 °C; IR ($CHCl_3$) 2960, 2150, 1670, 1588, 1452, 1305, 1288, 1252, 1055, and 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 18 H), 4.37 (s, 6 H); MS (EI) 360 (20), 345 (29), 330 (14), 317 (14), 287 (13), 272 (3), 229 (8), 165 (34), 151 (19), 122 (15), 89 (17), 73 (100); MS (CI) 361 (32), 105 (100); HRMS *m/e* calcd for $C_{18}H_{24}O_4Si_2$ (M^+) 360.1213, found 360.1189. Anal. Calcd for $C_{18}H_{24}O_4Si_2$: C, 59.97; H, 6.71. Found: C, 59.69; H, 6.48.

2,3-Dimethoxy-4-hydroxy-4-(1-propenyl)-2-cyclobuten-1-one, 30. A solution of 0.46 g (3.77 mmol) of 1-bromo-1-propene in 18 mL of 4:1:1 THF/pentane/ether was cooled to −120 °C (liquid N_2/ligroin/isopropyl alcohol/acetone). The solution was treated with 4.86 mL (7.53 mmol) of 1.55 M *tert*-butyllithium in hexanes and stirred for 80 min. The solution was warmed to −78 °C, stirred for 20 min, and then transferred via a cannula to another flask containing 0.50 g (3.52 mmol) of dimethyl squarate in 125 mL of THF at −78 °C under argon. After stirring for 20 min, the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over solid K_2CO_3 (5 min). Filtration followed by concentration in vacuo provided an oil. The oil was purified by column chromatography on silica gel (3:1 hexane–ethyl acetate) to afford 440 mg (68%) of **30** as an 8:5 mixture of trans/cis isomers, respectively (pale yellow oil): IR (neat) 3420, 1780, 1640, 1470, 1350, 1035, and 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (s, 2 H), 1.68 (dd, J = 1.7, 2.1 Hz, 3 H), 1.85 (dd, J = 1.7, 2.1 Hz, 3 H), 3.96 (s, 3 H), 3.97 (s, 3 H), 4.13 (s, 3 H), 4.19 (s, 3 H), 5.60 (m, 2 H), 5.80 (m, 1 H), 5.98 (m, 1 H); MS (EI) 184 (36), 169 (23), 156 (12), 96 (27), 81 (57), 69 (67), 53 (100); MS (CI) 185 (62), 167 (53), 153 (100); HRMS *m/e* calcd for $C_9H_{12}O_4$ (M^+) 184.0735, found 184.0736.

2,3-Dimethoxy-4-(1-propenyl)-4-(2-propenyloxy)-2-cyclobuten-1-one, 31. A 151-mg (0.82 mmol) portion of **30** was dissolved in 8 mL of dioxane under argon. The flask was wrapped with aluminum foil to reduce the exposure to light, 1.60 g (6.90 mmol) of Ag_2O, 0.95 g (6.90 mmol) of K_2CO_3, and 0.63 mL (6.90 mmol) of allyl iodide were added, and the reaction mixture was stirred at ambient temperature for 4 days. The reaction mixture was vacuum filtered through Celite and rinsed with ether. The filtrate was concentrated in vacuo to yield a yellow oil. The oil was purified by column chromatography on silica gel (5.5:1 hexane–ethyl acetate) to afford 87 mg (48%) of **31** as an 8/5 mixture of trans/cis isomers, respectively (pale yellow oil): IR (neat) 2980, 1785, 1650, 1605, 1472, 1350, and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (dd, J = 1.7, 2.1 Hz, 3 H), 1.82 (dd, J = 1.7, 2.1 Hz, 3 H), 3.54 (d, J = 6.9 Hz, 2 H), 3.96 (s, 3 H), 3.97 (s, 3 H), 3.98 (s, 3 H), 4.29 (m, 2 H), 4.05 (d, J = 6.9 Hz, 2 H), 4.16 (s, 3 H), 5.18 (dd, J = 1.3, 10.4 Hz, 2 H), 5.30 (d, J = 17.2 Hz, 2 H), 5.95 (m, 4 H); MS (EI) 223 (3), 181 (55), 163 (5), 153 (11), 137 (16), 125 (33), 107 (9), 91 (14), 79 (29), 67 (100); MS (CI) 224 (11), 181 (24), 165 (100); HRMS *m/e* calcd for $C_{12}H_{16}O_4$ (M^+) 224.1048, found 222.0897 (converted to quinone **34**).

2,3-Dimethoxy-6-methyl-5-(2-propenyl)-2,5-cyclohexadiene-1,4-dione, 34. An 80-mg (0.36 mmol) portion of **31** was dissolved in 35 mL of freshly distilled *p*-xylene and heated at reflux for 29 h under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 55 °C. Analysis of the crude ^1H NMR spectrum of the residual oil revealed complete conversion of the cyclobutenone to the corresponding quinone. The oil was purified by column chromatography on silica gel (7:1 hexane–ethyl acetate) to afford 36 mg (45%) of the benzoquinone as a red oil: IR (neat) 2960, 1670, 1620, 1460, 1372, 1205, 1160, 1100, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02 (s, 3 H), 3.24 (d, J = 6.3 Hz, 2 H), 3.99 (s, 3 H), 4.00 (s, 3 H), 5.03 (m, 2 H), 5.73 (m, 1 H); MS (EI) 222 (100), 207 (75), 189 (13), 179 (33), 108 (23), 79 (65); HRMS *m/e* calcd for $C_{12}H_{14}O_4$ (M^+) 222.0892, found 222.0891.

2,3-Dimethoxy-5-methyl-2,5-cyclohexadiene-1,4-dione [Coenzyme Q_0], 43. A 262-mg (1.42 mmol) portion of **42** was dissolved in 40 mL of freshly distilled *p*-xylene and heated at reflux for 75 min under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 45 °C. The resulting red oil was dissolved in 50 mL of CH_2Cl_2, 7.90 g (2.38 mmol) of 20% Ce^{IV}/SiO_2 was added, and the reaction mixture was stirred for 20 min. The reaction mixture was filtered then the filtrate concentrated in vacuo to afford red needles. Recrystallization from diisopropyl ether afforded 220 mg (84%) of the benzoquinone as red needles: mp 57–58 °C (lit.[19] 59 °C); IR ($CHCl_3$) 1665, 1608, 1425, 1380, 1040, and 882 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (d, J = 1.6 Hz, 3 H), 4.00 (s, 3 H), 4.02 (s, 3 H), 6.44 (q, J = 1.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.70, 61.42, 61.49, 131.50, 144.26, 144.26, 145.03, 145.22, 184.42; MS (EI) 182 (88), 167 (36), 153 (14), 139 (19), 137 (100), 111, (19), 83 (49); (CI) 183 (15), 73 (100); HRMS *m/e* calcd for $C_9H_{10}O_4$ (M^+) 182.0579, found 182.0565.

2,3-Dimethoxy-4-hydroxy-4-(1-methyl-1-propenyl)-2-cyclobuten-1-one, 44. A solution of 0.51 g (3.77 mmol) of 2-bromo-2-butene in 35 mL of dry ether was cooled to −78 °C. The solution was treated with 4.71 mL (7.54 mmol) of 1.60 M *tert*-butyllithium in hexanes and stirred for 30 min. The solution was warmed to 0 °C, stirred for 90 min, and then cooled again to −78 °C. The resulting solution was transferred via a cannula to a flask containing 1.00 g (5.88 mmol) of dimethyl squarate in 125 mL of THF at −78 °C under argon. After stirring for 20 min, the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 20 mL of ether. The aqueous layer was extracted twice with 15-mL portions of ether, and the organic phases were combined, washed with brine, and dried over K_2CO_3 (5 min). Filtration followed by concentration in vacuo provided an oil. The oil was purified by column chromatography on silica gel (3:1 hexane–ethyl acetate) to afford 0.58 g (83%) of **44** as a 7/1 mixture of E/Z isomers, respectively (colorless oil): IR (neat) 3420, 1780, 1635, 1470, 1342, 1050, 1025, 980, and 832 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer, δ 1.79 (d, J = 1.5 Hz, 3 H), 1.85 (m, 3 H), 2.83 (s, 1 H), 3.97 (s, 3 H), 4.14 (s, 3 H), 5.55 (dq, J = 1.5, 5.8 Hz, 1 H); MS (EI) 198 (60), 183 (73), 155 (32), 95 (54), 83 (34), 67 (100); MS (CI) 198 (100); HRMS *m/e* calcd for $C_{10}H_{14}O_4$ (M^+) 198.0892, found 198.0907.

2,3-Dimethoxy-5,6-dimethyl-2,5-cyclohexadiene-1,4-dione, [Auran-tiogliocladin] 45. A 386-mg (1.95 mmol) portion of **44** was dissolved in 40 mL of freshly distilled *p*-xylene and heated at reflux for 90 min under argon. The solution was cooled to ambient temperature and then concentrated in vacuo at a bath temperature of 45 °C. The yellow residue was dissolved in 65 mL of CH_2Cl_2, 13.60 g (4.10 mmol) of 20% Ce^{IV}/SiO_2 was added, and the reaction mixture was stirred for 20 min. The reaction mixture was filtered, and then the filtrate was concentrated in vacuo to afford orange needles. Recrystallization from hexanes/CH_2Cl_2 afforded 310 mg (81%) of the benzoquinone as orange needles: mp 62.5–63.5 °C (lit.[20] 62–62.5 °C); IR ($CHCl_3$) 2950, 1652, 1612, 1450, 1325, 1255, 1160, and 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (s, 6 H), 3.99 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 12.33, 61.35, 139.10, 144.54, 184.50; MS (EI) 196 (100), 181 (46), 153 (31), 151 (96), 125 (32), 104 (29), 97 (65); MS (CI) 197 (100); HRMS *m/e* calcd for $C_{10}H_{12}O_4$ (M^+) 196.0735, found 196.0732.

(±)-2,3-Dimethoxy-4-(1,5-dimethyl-4-hexenyl)-4-hydroxy-2-cyclobuten-1-one, 46. A solution containing 1.50 g (64 mmol) of a mineral oil suspension containing Li/Na (98:2, 30% dispersion) in 35 mL of distilled hexanes was placed under an atmosphere of argon. A solution containing 1.50 g (10.3 mmol) of (±)-6-chloro-2-methyl-2-heptene in 15 mL of hexanes was added to the lithium suspension, and the resulting suspension was immersed in a sonicating cleaning bath for 4 h. The salts were allowed to settle to the bottom of the flask after standing for a few minutes. Then 10-mL aliquots of the solution were transferred with the aid of a syringe pump (0.75 mL/min) to a solution containing 1.05 g (7.4 mmol) of dimethyl squarate in 125 mL of dry THF at −78 °C. The solution was stirred for 20 min, and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 120 mL of 5% NH_4Cl and 75 mL of ether. The aqueous layer was separated from the organic and extracted three times with ether. The organic layers were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo provided a pale yellow oil. The oil was purified by column chromatography (3.5:1 hexane–ethyl acetate) to afford 1.28 g (68%) of the alcohol as a colorless oil: (mixture of diastereomers 1:1) IR (neat) 3500, 2970, 1768, 1630, 1469, 1340, 1058, 1030, and 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (d, J = 7.2 Hz, 3 H; diastereomer 1), 1.03 (d, J = 7.2 Hz, 3 H; diastereomer 2), 1.22 (m, 4 H), 1.60 (s, 6 H), 1.68 (s, 6 H), 1.90 (m, 4 H), 2.10 (m, 2 H), 2.58 (br s, 2 H), 3.95 (s, 6 H), 4.12 (s, 6 H), 5.09 (br t, J = 5.1 Hz, 2 H); MS (EI) 254 (0.1), 236 (0.3), 222 (0.4), 207 (4), 194 (0.6), 171 (6), 151 (3), 139 (6), 125 (6), 109 (7), 97 (13), 83 (17), 69 (100); HRMS *m/e* calcd for $C_{14}H_{22}O_4$ (M^+) 254.1518, found 254.1528.

(±)-4-(1,5-Dimethyl-4-hexenyl)-3-methoxy-3-cyclobutene-1,2-dione, 47. A solution containing 1.11 g (4.37 mmol) of **46** in 100 mL of distilled ether was cooled to 0 °C under argon. A 0.42-mL (5.24 mmol) portion of pyridine was added via a syringe, and the resulting solution was stirred for 10 min. A 0.74-mL (5.24 mmol) portion of trifluoroacetic anhydride was added, and the resulting solution was stirred for 15 min. The solution was then partitioned between 75 mL of ethyl acetate and 20 mL of water. The aqueous layer was extracted six times with ether, and the organics were combined, washed with saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo gave a yellow oil. The oil was purified by column chromatography (8:1 hexane–ethyl acetate) to afford 0.71 g (73%) of the dione as a pale yellow oil: IR

(neat) 2960, 2940, 1795, 1762, 1600, 1465, 1380, 1325, and 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (d, J = 7.5 Hz, 3 H), 1.58 (d, J = 4.1 Hz, 3 H), 1.60 (m, 1 H), 1.68 (br s, 3 H), 1.80 (m, 1 H), 1.99 (q, J = 7.7 Hz, 2 H), 2.92 (sext, 1 H), 4.43 (s, 3 H), 5.07 (m, 1 H); MS (CI) 235 (5); MS (EI) 222 (0.3), 207 (10), 179 (11), 151 (3), 140 (4), 119 (6), 97 (14); HRMS m/e calcd for $C_{13}H_{18}O_3$ (M^+) 222.1256, found 222.1248.

(±)-2-(1,5-Dimethyl-4-hexenyl)-4-hydroxy-3-methoxy-4-(1-methylethenyl)-2-cyclobuten-1-one, 48. A 50-mL portion of ether was cooled to −78 °C under argon, and a 132-μL (1.46 mmol) portion of 2-bromopropene was introduced to the flask via a syringe. A 1.82-mL (2.92 mmol) portion of 1.6 M *tert*-butyllithium in hexanes was added, and the resulting solution was stirred for 30 min and then transferred by cannulae to a solution containing 270 mg (1.22 mmol) of **47** in 125 mL of dry THF at −78 °C. The solution was stirred for 20 min, and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 25 mL of ether. The aqueous layer was separated from the organic and extracted six times with ether. The organic layers were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo provided a colorless oil. The oil was purified by column chromatography on silica gel (3.5:1 hexane–ethyl acetate) to afford 230 mg (72%) of the alcohol as a colorless oil: (mixture of diastereomers 1:1) IR (neat) 3380, 2970, 2930, 1750, 1618, 1465, 1375, 996, 908, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (d, J = 4.5 Hz, 3 H; diastereomer 1), 1.14 (d, J = 4.5 Hz, 3 H; diastereomer 2), 1.42 (m, 2 H), 1.58 (br s, 6 H), 1.62 (m, 2 H), 1.67 (br s, 6 H), 1.81 (br s, 6 H), 1.99 (m, 4 H), 2.42 (m, 2 H), 3.20 (br s, 2 H), 4.03 (s, 3 H; diastereomer 1), 4.04 (s, 3 H; diastereomer 2), 5.09 (m, 2 H), 5.14 (d, J = 1.4 Hz, 2 H), 5.31 (d, J = 1.4 Hz, 2 H); MS (EI) 264 (8), 232 (2), 181 (30), 167 (10), 154 (44), 139 (6), 125 (17), 107 (9), 95 (29), 69 (89); HRMS m/e calcd for $C_{16}H_{24}O_3$ (M^+) 264.1725, found 264.1725.

(±)-2-(1,5-Dimethyl-4-hexenyl)-3-methoxy-5-methyl-2,5-cyclohexadiene-1,4-dione [(±)-O-Methylperezone], 49. A 230-mg (0.87 mmol) portion of **48** was dissolved in 125 mL of freshly distilled benzene and heated at reflux for 2 h under argon. The clear solution was cooled to ambient temperature and then concentrated in vacuo to provide a colorless oil. The resulting oil was dissolved in 100 mL of CH_2Cl_2, 8.66 g (2.61 mmol) of 20% Ce^{IV}/SiO_2 was added, and the reaction mixture was stirred for 30 min. The reaction mixture was filtered, and the filtrate was concentrated in vacuo to afford an orange oil. The oil was purifed by column chromatography on silica gel (9:1 hexane–ethyl acetate) to afford 172 mg (74%) of (±)-*O*-methylperezone which had spectral properties in accord with thosee reported in the literature:[26] IR (neat) 2960, 1660, 1600, 1445, 1366, 1272, 1205, 1058, 926, and 888 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (d, J = 7.1 Hz, 3 H), 1.54 (br s, 3 H), 1.65 (d, J = 0.9 Hz, 3 H), 1.60–1.74 (m, 2 H), 1.89 (m, 2 H), 2.02 (d, J = 1.4 Hz, 3 H), 3.08 (sext, 1 H), 3.94 (s, 3 H), 5.05 (tqq, 1 H), 6.47 (q, J = 1.6 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 187.80, 183.51, 156.37, 143.73, 134.82, 132.86, 130.79, 124.33, 60.58, 34.29, 29.00, 26.23, 25.49, 18.85, 17.49, 14.78; ^{13}C NMR ($CDCl_3$) δ 188.25, 184.39, 156.50, 143.51, 136.98, 133.89, 131.67, 124.60, 61.04, 34.89, 29.94, 26.97, 25.87, 19.11, 17.83, 15.36; MS (EI) 262 (4), 219 (12), 180 (57), 165 (37), 147 (15), 137 (28), 119 (7), 109 (14), 91 (22); HRMS m/e calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1570.

(±)-2-(1,5-Dimethyl-4-hexenyl)-4-hydroxy-3-methoxy-4-(1-propynyl)-2-cyclobuten-1-one, 50. A solution containing 0.68 mL (1.54 mmol) of 2.25 M *n*-butyllithium in hexanes in 60 mL of dry THF at −78 °C was treated with propyne gas by condensing the gas in the cold solution for 4 min. The resulting solution was stirred for 25 min then transferred by cannulae to a solution containing 310 mg (1.40 mmol) of **47** in 125 mL of dry THF at −78 °C. The solution was stirred for 15 min, and then the reaction was quenched by pouring the cold solution into a separatory funnel containing 20 mL of 5% NH_4Cl and 25 mL of ether. The aqueous layer was separated from the organic and extracted two times with ether. The organic layers were combined, washed with brine, and dried over $MgSO_4$. Filtration followed by concentration in vacuo provided a pale yellow oil. The oil was purified by column chromatography (3.5:1 hexane–ethyl acetate) to afford 300 mg (81%) of the alcohol as a pale yellow oil: (mixture of diastereomers 1:1) IR (neat) 3380, 2970, 2920, 2240, 1752, 1620, 1468, 1375, 1320, and 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (d, J = 7.2 Hz, 3 H; diastereomer 1), 1.14 (d, J = 7.2 Hz, 3 H; diastereomer 2), 1.42 (m, 2 H), 1.59 (br s, 6 H), 1.63 (m, 2 H), 1.70 (br s, 6 H), 1.92 (br s, 6 H), 1.97 (m, 4 H), 2.38 (sext, 2 H), 3.28 (br s, 2 H), 4.22 (s, 3 H; diastereomer 1), 4.23 (s, 3 H; diastereomer 2), 5.08 (tqq, 2 H); MS (EI) 262 (2), 219 (7), 180 (13), 165 (19), 152 (9), 137 (8), 199 (8), 109 (12), 91 (28), 77 (21), 67 (100); HRMS m/e calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1557.

(±)-3-(1,5-Dimethyl-4-hexenyl)-2-methoxy-5-methyl-2,5-cyclohexadiene-1,4-dione [(±)-O-Methylisoperezone], 51. A 250-mg (0.95 mmol) portion of **50** was dissolved in 100 mL of dry acetonitrile and heated at reflux for 2 h under argon. The yellow solution was cooled to ambient temperature and then concentrated in vacuo to provide an orange oil. The oil was purified by column chromatography on silica gel (5:1 hexane–ethyl acetate) to afford 192 mg (76%) of the quinone as an orange oil: IR (neat) 2970, 2940, 1668, 1650, 1601, 1450, 1318, 1215, 1136, 988, and 885 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (d, J = 7.1 Hz, 3 H), 1.54 (br s, 3 H), 1.64 (d, J = 1.1 Hz, 3 H), 1.62 (m, 1 H), 1.74 (m, 1 H), 1.88 (m, 2 H), 2.02 (d, J = 1.7 Hz, 3 H), 3.12 (sext, 1 H), 3.96 (s, 3 H), 5.06 (tqq, 1 H), 6.43 (q, J = 1.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 188.42, 184.23, 156.16, 146.35, 137.09, 131.73, 131.51, 124.72, 61.16, 34.89, 30.24, 27.04, 25.92, 19.12, 17.87, 16.21; MS (EI) 262 (4), 219 (7), 180 (46), 165 (26), 147 (15), 137 (22), 109 (12), 91 (18), 69 (50); HRMS m/e calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1564.

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Registry No. 6a, 5222-73-1; **6b**, 5231-87-8; **7a**, 124602-91-1; **7b**, 124602-92-2; **7c**, 124602-93-3; **7e**, 124602-94-4; **7f**, 124618-66-2; **8a**, 124602-96-6; **8b**, 124602-97-7; **5c**, 124602-98-8; **8d**, 124602-99-9; **8e**, 124603-00-5; **8f**, 124603-01-6; **9a**, 711-78-4; **9b**, 22118-95-2; **9g**, 113976-82-2; **9j**, 102683-52-3; **10a**, 124603-02-7; **10b**, 124603-03-8; **10c**, 119908-14-4; **10d**, 119908-13-3; **10e**, 124603-04-9; **10f**, 124603-05-0; **10g**, 124603-06-1; **10h**, 124603-07-2; **10i**, 124603-08-3; **10j**, 124603-09-4; **10k**, 124603-10-7; **11a**, 124603-11-8; **11b**, 124603-12-9; **11c**, 119908-06-4; **11d**, 119908-07-5; **11e**, 124603-13-0; **11f**, 124603-14-1; **11g**, 124603-15-2; **11h**, 124603-16-3; **11i**, 124603-17-4; **11j**, 124603-18-5; **11k**, 124603-19-6; **12**, 124618-60-6; **13**, 118042-05-0; **16**, 113976-70-8; **19**, 124603-21-0; **19** (alkynyl derivative), 124603-20-9; **24**, 124603-23-2; **25**, 124603-22-1; **27**, 124618-67-3; **29**, 124603-24-3; (*Z*)-**30**, 124603-25-4; (*E*)-**30**, 124603-26-5; (*Z*)-**31**, 124603-27-6; (*E*)-**31**, 124603-28-7; **34**, 67913-13-7; **41a**, 118041-95-5; **41b**, 118041-97-7; **41c**, 118041-96-6; **41d**, 118042-01-6; **41e**, 118042-00-5; **41f**, 124603-38-9; **43**, 605-94-7; (*E*)-**44**, 124603-29-8; (*Z*)-**44**, 124603-30-1; **45**, 483-54-5; (*R*,R**)-**46**, 124603-32-3; (*R*,S**)-**46**, 124603-33-4; **47**, 119908-09-7; (*R*,R**)-**48**, 124603-34-5; (*R*,S**)-**48**, 124603-35-6; **49**, 100761-40-8; (*R*,R**)-**50**, 124603-36-7; (*R*,S**)-**50**, 124603-37-8; **51**, 119908-12-2; *n*-$C_4H_9C{\equiv}CH$, 693-02-7; $C_6H_5CH_2C{\equiv}CH$, 10147-11-2; $C_6H_5C{\equiv}CH$, 536-74-3; $CH_3C{\equiv}CH$, 74-99-7; $CH_3CH_2OC{\equiv}CH$, 109-92-2; (*Z*)-TMS-$C{\equiv}CCH{=}CHOCH_3$, 93782-17-3; (±)-$CH_3(Cl)CHCH_2CH_2(CH_3)C{=}CH_2$, 124603-31-2; 1-bromocyclopentene, 1192-04-7; 2-bromo-4,5-dihydrofuran, 124602-95-5; 1-chlorocyclohexene, 930-66-5; 2-chloro-5,6-dihydro-4*H*-pyran, 40446-77-3; 1-chlorocycloheptene, 13294-30-9; trimethylsilylacetylene, 1066-54-2; 3-methoxy-4-[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione, 113976-89-9; 1-bromo-1-propene, 590-14-7; 2-bromo-2-butene, 13294-71-8; 2-bromopropene, 557-93-7.