distillation (90 °C (0.1 Torr)) afforded 51 mg (23%) of **32a** as a clear oil.

A solution of **28a**[5] (91 mg, 0.79 mmol), methylenecyclopentane (65 mg, 0.79 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (423 mg, 1.58 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (143 mg, 0.79 mmol), and TFA (450 mg, 3.95 mmol) in 8 mL of ethanol was stirred at 25 °C for 28 h. Workup as above afforded 174 mg (92%) of crude **32a** free of **39**. Evaporative distillation (90 °C (0.1 Torr)) afforded 96 mg (51%) of **32a** as a clear oil and 65 mg (35%) of uncharacterizable oligomeric material as residue of the distillation.

Methyl 7-Acetyl-10-oxospiro[4.5]decane-7-carboxylate (32b) and Methyl α-Acetyl-γ-cyano-α-(cyclopentylmethyl)-1-cyclopentene-1-pentanoate (36b). A solution of **28b**[6] (115 mg, 0.67 mmol), methylenecyclopentane (55 mg, 0.67 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (361 mg, 1.34 mmol) in 7 mL of ethanol was stirred at 25 °C for 6 h. Workup as described above for **20a** afforded 160 mg (98%) of a mixture of **32b** and **36b**. Flash chromatography on silica gel (5:1 hexane–EtOAc) afforded 24 mg (21%) of **36b** as a 1:1 mixture of diastereomers, followed by 66 mg (39%) of **32b**.

Data for **32b**: ^{1}H NMR 3.80 (s, 3), 2.81 (dd, 1, J = 7.2, 17.1), 2.77 (dd, 1, J = 5.0, 14.7), 2.51 (dd, 1, J = 2.2, 14.6), 2.26 (d, 1, J = 14.6), 2.53–2.45 (m, 2), 2.19 (s, 3), 2.06–1.95 (m, 1), 1.80 (ddd, 1, J = 4.8, 7.9, 11.8), 1.68–1.48 (m, 4), 1.43 (ddd, 1, J = 2.2, 4.5, 12), 1.24 (ddd, 1, J = 8, 8, 13); ^{13}C NMR 212.9, 203.4, 172.6, 59.3, 55.0, 52.7, 41.1, 36.3, 35.7, 35.3, 29.9, 25.6, 25.0, 24.2; IR (neat) 2960, 1750, 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.66; H, 8.02.

Data for **36b**: ^{1}H NMR 5.56 (br s, 1), 3.79 (s, 0.5 × 3), 3.78 (s, 0.5 × 3), 2.22 (s, 0.5 × 3), 2.16 (s, 0.5 × 3), 2.68–2.52 (m, 1), 2.50–2.39 (m, 1), 2.39–1.96 (m, 8), 1.96–1.80 (m, 2), 1.80–1.40 (m, 8), 1.14–0.98 (m, 2); ^{13}C NMR 204.8 (C), 204.4 (C), 172.2 (2 C), 138.9 (C), 138.7 (C), 128.9 (CH), 128.6 (CH), 121.9 (C), 121.4 (C), 62.3 (2 C), 52.6 (2 CH_3), 39.3 (CH_2), 37.1 (CH_2), 36.0 (CH), 35.9 (CH), 35.7 (CH_2), 35.6 (CH_2), 34.8 (2 CH_2), 34.7 (CH_2), 33.9 (CH_2), 33.8 (2 CH_2), 33.7 (CH_2), 33.5 (CH_2), 32.5 (2 CH_2), 27.3, 26.6, 26.0, and 25.2 (2 CH and 2 CH_3), 24.8 (3 CH_2), 24.7 (CH_2), 23.5 (CH_2), 23.4 (CH_2); MS (EI) m/z (rel intensity) 331 (1, M^+), 313 (11), 254 (39), 198 (14), 169 (65), 129 (100); IR (neat) 2925, 2230, 1750, 1715 cm^{-1}.

Acknowledgment. We are grateful to the National Science Foundation for generous financial support.

Registry No. 14, 59529-68-9; **15a**, 137393-41-0; **15b**, 137393-42-1; **20a**, 137393-43-2; **20b**, 137393-44-3; **21**, 71203-73-1; **22a**, 137393-45-4; **22b**, 137393-46-5; **24a**, 137393-47-6; **24b**, 137393-48-7; **25b**, 137393-49-8; **28a**, 137393-50-1; **28b**, 105630-56-6; **32a**, 137393-51-2; **32b**, 137393-52-3; **36b** (isomer 1), 137393-53-4; **36b** (isomer 2), 137393-54-5; **39**, 137393-55-6; bromoacetonitrile, 590-17-0; acrylonitrile, 107-13-1; methylenecyclopentane, 1528-30-9.

Supplementary Material Available: ^{1}H NMR spectrum for **22b** and ^{1}H and ^{13}C NMR spectra for **36b** (3 pages). Ordering information is given on any current masthead page.

Synthesis of *p*-Chlorophenols (and -naphthols) from the Thermal Rearrangement of 4-Chlorocyclobutenones

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Received April 23, 1991

A systematic study of the reaction of 4-hydroxycyclobutenones with thionyl chloride is reported. A useful model evolves from this study which allows the prediction of the site of chlorination for unsymmetrical examples. The chlorination is envisaged to involve the corresponding homoaromatic carbocation, and the site of chlorination takes place preferentially at the position substituted with the greater cation-stabilizing substituent. Specifically, this follows the general order of allyl > benzyl > alkyl > propargyl. The 4-chlorocyclobutenones prepared in this study were shown to be useful synthetic precursors to highly substituted chlorophenols and chloronaphthols.

Introduction

Reported here are details of the ring expansions of 4-aryl(or alkenyl or alkynyl)-4-chlorocyclobutenones to chlorophenols (Scheme I).[1] These rearrangements provide useful syntheses of highly substituted aromatic compounds and are mechanistically related to the ring expansions of 4-aryl(or alkenyl or alkynyl)-4-hydroxycyclobutenones to hydroquinones and quinones.[2,3]

The generalized transformations outlined here have their genesis in the chemistry of dimethylsquarate (1), a readily available cyclobutenedione that is easily converted to the regioisomeric cyclobutenones **2** and **3** by known methods.[4,5] Surprisingly, these then give the same 4-chloro derivative **4** upon treatment with thionyl chloride/pyridine in methylene chloride. Finally, thermolysis of **4** in refluxing *p*-xylene results in stereoselective ring opening to the conjugated ketene **5** and then to the chlorophenols (or naphthols) **6** upon electrocyclic ring closure.

Formation of **4** from both **2** and **3** suggests the homoaromatic carbocation **7** to be a common intermediate.[6,7] Furthermore, consideration of the substituent effects on the selectivity of the transformation presents a useful paradigm for predicting the site of chlorination of unsymmetrically substituted cyclobutenones. *Specifically, chlorination takes place preferentially at the position*

(1) For a preliminary account of this work, see: Xu, S. L.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 4024.

(2) (a) Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392. (b) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1988**, *111*, 975.

(3) (a) Moore, H. W.; Perri, S. T. *J. Org. Chem.* **1988**, *53*, 996. (b) Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067. (c) Liebeskind, L. S.; Jewell, C. F.; Iyer, S. *J. Org. Chem.* **1986**, *51*, 3065.

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

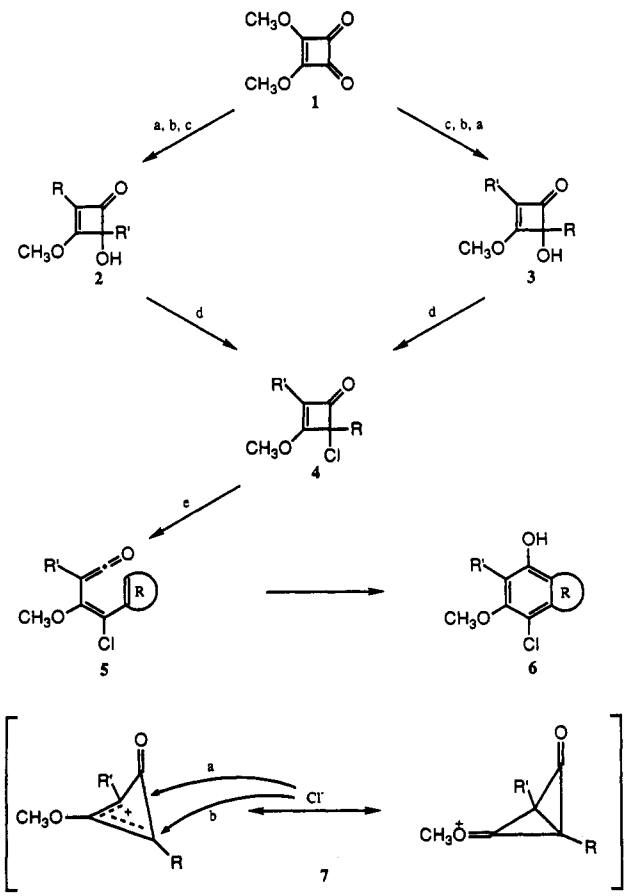
(5) Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477.

(6) For analogies to this intermediate, see: (a) Olah, G. A.; Staral, J. S. *J. Am. Chem. Soc.*, **1976**, *98*, 6290. (b) Sprenger, H. E.; Ziegenbein, *Angew. Chem. Internat Edit.*, **1968**, *7*, 530.

(7) (a) Olah, G. A.; Bollinger, J. M.; White, A. M. *J. Am. Chem. Soc.*, **1969**, *91*, 3667. (b) Prakash, G. K. S.; Krishnamurthy, V. V.; Gergas, R.; Bau, R.; Yuan, H.; Olah, G. A. *Ibid.* **1986**, *108*, 836. (c) Jespersen, K. K.; Schleyer, P.; Pople, J. A.; Cremer, D. *Ibid.* **1978**, *100*, 4301. (d) Olah, G. A.; Mateescu, G. D. *Ibid.* **1970**, *92*, 1430. (e) Clark, T.; Wilhelm, D.; Schleyer, P. *Tetrahedron Lett.*, **1982**, 3547.

0022-3263/92/1957-0326$03.00/0

Scheme I[a]



[a] Reagents: (a) RLi, THF, −78 °C; (b) TFAA/H^+; (c) R'Li, THF, −78 °C; (d) $SOCl_2$/pyridine, CH_2Cl_2, 0 °C; (e) *p*-xylene, 138 °C.

better able to stabilize the positive charge (allyl > benzyl > alkyl > propargyl).[8] In general, 4-hydroxycyclobutenones bearing an alkenyl group at position 2 or 4 always gave the corresponding allylic chloride. Those having a phenyl group in competition with groups other than an allyl moiety, e.g., alkyl or alkynyl, undergo benzylic chlorination, and when an alkynyl group is competing with an alkyl substituent only chlorination at the position adjacent to the alkyl group was observed. Chlorination next to an alkynyl group was observed to be most difficult and could only be accomplished with 2,4-dialkynyl-4-hydroxycyclobutenones. Selected examples of these transformations are described below.

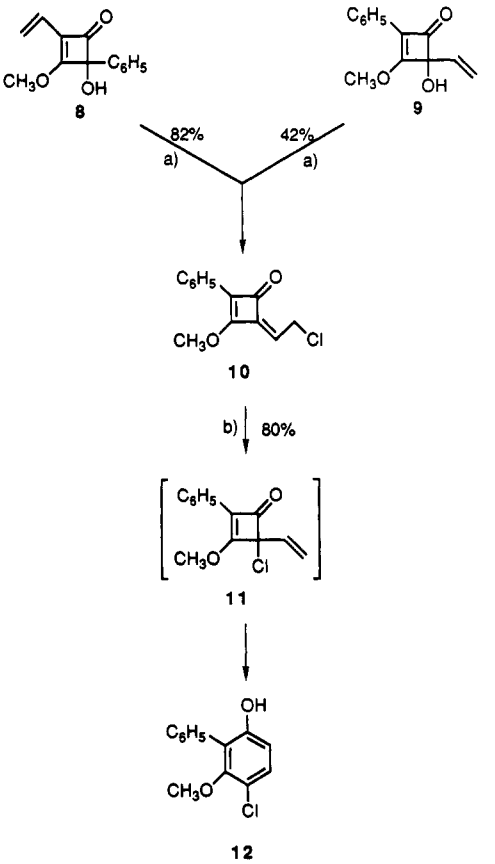
Results and Discussion

Synthesis of substituted chlorophenols from 4-hydroxycyclobutenones bearing alkenyl and phenyl substituents are given in Schemes II and III. Treatment of **8** or **9** with thionyl chloride in the presence of pyridine gave (*Z*)-4-(2-chloroethylidene)-3-methoxy-2-phenylcyclobutenone (**10**) in isolated yields of, respectively, 82% and 42%. The lower efficiency of **9** as a precursor to **10** is due to its propensity to rearrange to the corresponding hydroquinone even at ambient temperature, and this competes with the chlorination reaction.[3]

Upon thermolysis (refluxing *p*-xylene), **10** rearranged to the *p*-chlorophenol **12** (80%) presumably via the isomeric 4-chloro-4-ethenylcyclobutenone **11**. Once formed, **11** undergoes ring opening to the corresponding dienylketene

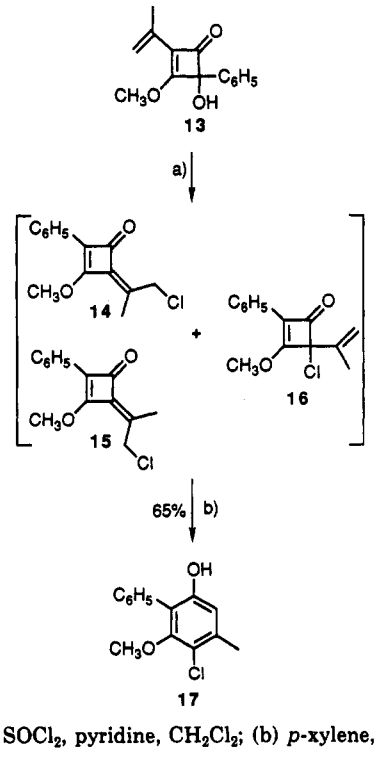
(8) Vogel, P. Carbocation Chemistry; Elsevier Science Publishers B. V.: New York, 1985.

Scheme II[a]



[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b) *p*-xylene, 138 °C, 3 h.

Scheme III[a]

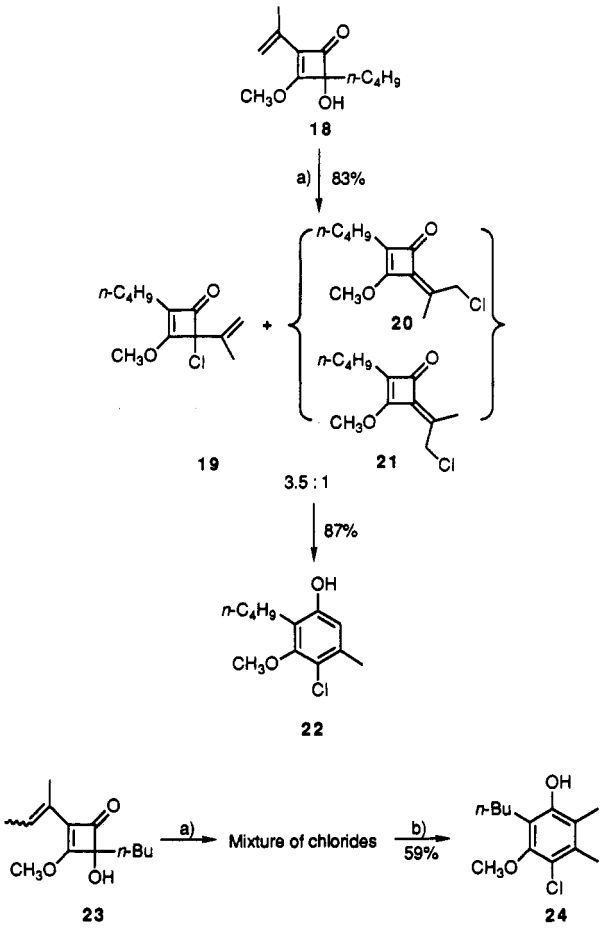


[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b) *p*-xylene, 138 °C, 24 h.

and this gives **12** upon electrocyclic ring closure. This rearrangement is of particular note since, to our knowledge, such ring expansions of alkylidenecyclobutenones have not previously been reported.

The structure assignments of **10** and **12** are based on characteristic spectral data. For example, compound **10**

Scheme IV[a]



[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b) *p*-xylene, 138 °C, 20 h.

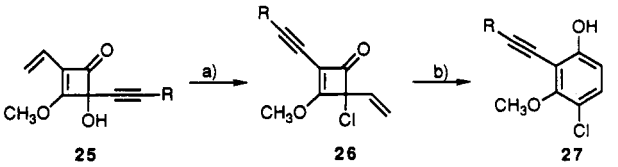
shows an intense carbonyl stretch around 1760 cm^{-1} and its ^1H NMR spectrum reveals a triplet at 5.61 ppm (J = 8.0 Hz) for the vinylic proton and a doublet at 4.60 ppm (J = 8.0 Hz) for the ethylidene group. The Z stereochemistry of the alkylidene substituent was substantiated by difference NOE experiments which showed an enhancement of 5% for the vinylic proton absorption at 5.61 ppm upon preirradiation of the methoxy absorption at 4.39 ppm.

The IR spectrum of **12** shows an intense phenolic hydroxyl absorption at 3450 cm^{-1} and no carbonyl stretching vibration. Absorptions for the phenyl substituent and two sets of doublets (6.75 and 7.27 ppm) for the two adjacent protons on the phenol ring are evident in the ^1H NMR spectrum.

In a related study, a mixture of the stereoisomers **14** and **15** as well as the regioisomer **16** were obtained from **13** (Scheme III). This mixture was subjected directly to thermolysis to give the chlorophenol **17** (65%), the only significant product detected by ^1H NMR analysis of the crude reaction mixture.

The hydroxycyclobutenones **18** and **23** having an alkenyl/alkyl substitution pattern were also treated with thionyl chloride (Scheme IV). On the basis of the above results, the alkenyl group was anticipated, and in fact observed, to have the greater influence on controlling the regiochemistry of chlorination. Thus, treatment of **18** with thionyl chloride gave a mixture of the alkylidenecyclobutenones **20** and **21** along with the 4-chloro-4-(1-methylethenyl)cyclobutenone **19** in a ratio of 1:3.5 (83%) as revealed by ^1H NMR analysis of the crude reaction mixture. Thermolysis of this mixture afforded chlorophenol **22** in 87% isolated yield. When **19** and **20/21** mixture were independently subjected to the thermolysis conditions **22** was also realized in high yield. Thus, the conversion to **20** and **21** to **19** and its subsequent ring expansion to **22** is a reasonable mechanistic pathway.

Scheme V[a]



	R	% 25	% 26	% 27
a	n-C_4H_9	89	80*	48
b	C_6H_5	78	44*	45

* crude yield

[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b) *p*-xylene, 138 °C.

Similarly, chlorination of **23** gave a mixture of chlorides which give the *p*-chlorophenol **24** in an overall yield of 59% upon thermolysis. This transformation is analogous to those described above, but is particularly noteworthy since it demonstrates that this method can even be used for the regiospecific construction of hexasubstituted benzene derivatives.

Still other examples illustrating the important influence of alkenyl groups in controlling the site of chlorination of unsymmetrical 4-hydroxycyclobutenones is outlined in Scheme V. Here, **25a,b** furnished the chlorocyclobutenones **26a,b** in 44–80% yields. Subsequent thermolysis of these chloro derivatives gave *p*-chlorophenol **27a,b** (45–48%).

The structure assignments of **27a,b** are based on characteristic spectral data which include alkyne and phenolic hydroxyl absorptions in the infrared spectra and two proton AB patterns in the aromatic region of their ^1H NMR spectra.

The synthesis and thermolysis of chlorocyclobutenones bearing phenyl/alkyl substituents are illustrated in Scheme VI. Only one respective regioisomer **30a–c** was obtained for each regioisomeric pair **28a–c** and **29a–c**. That the chloro and phenyl groups in **30** are at position 4 is consistent with the fact that they gave naphthols **31a–c** along with methylene cyclobutenones **32a–c** upon thermolysis.

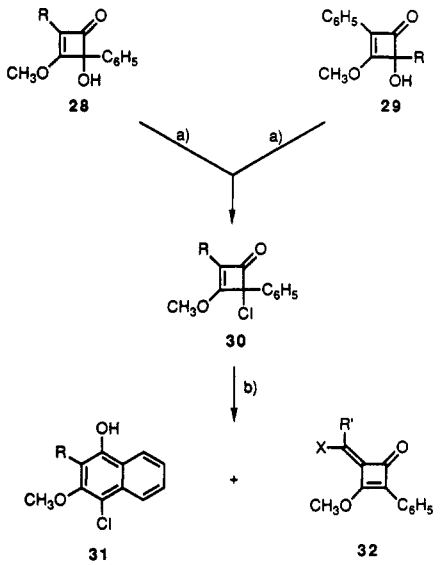
The Z stereochemistry of the alkylidene group in **32a** was determined by difference NOE studies; i.e., preirradiation of the methoxy absorption at 4.35 ppm resulted in enhancement of the vinylic proton (X = H) absorption at 5.46 ppm.

Syntheses of substituted alkynylnaphthols **36a,b** from hydroxycyclobutenones bearing phenyl and alkynyl substituents are given in Scheme VII. Chlorination of the regioisomeric pairs **33a,b** and **34a,b** provides the expected **35a,b** as single regioisomers. Thermolysis of these in refluxing *p*-xylene then gave the respective alkynylnaphthols **36a,b** in good yields.

Chlorination of the cyclobutenone **37** having an alkyl and an alkynyl substituent was also studied (Scheme VIII). In this case, the site of chlorination was not obvious beforehand since alkynyl and alkyl groups have similar abilities to stabilize an adjacent cationic center.[9] In any regard, the reaction again showed useful selectivity and the product obtained was 4-chloro-2-(1-hexynyl)-3-meth-

(9) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P.v. R. *J. Am. Chem. Soc.* **1976**, 98, 10.

Scheme VI[a]

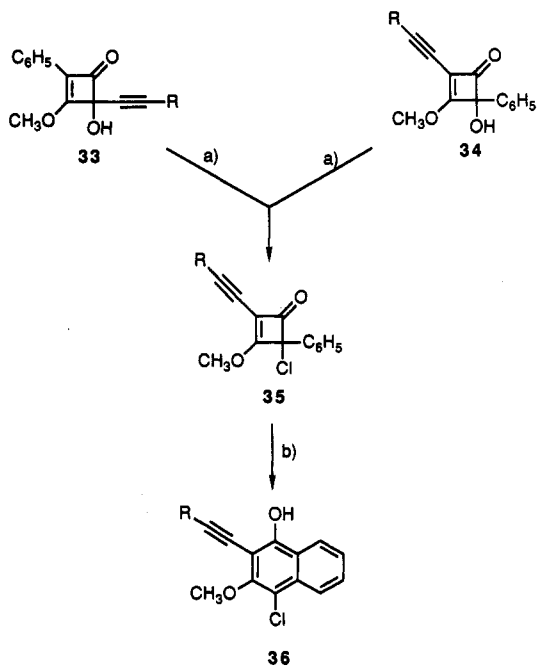


	R	R'	X	% 30	% 31	% 32
a	n-C_4H_9	n-C_3H_7	H	81 (91)	62	20
b	CH_3	H	H	73 (77)	34	21
c	s-C_4H_9	C_2H_5	CH_3	93	80	Trace

* ( )=yield from **29**

[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b) *p*-xylene, 138 °C.

Scheme VII[a]



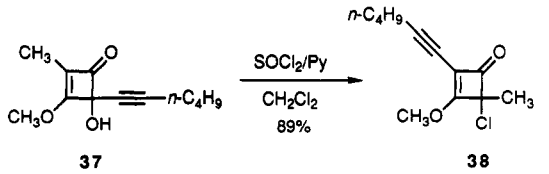
	R	%33	% 34	%35*	% 36
a	C_6H_5	75	76	59 (49)	76
b	n-C_4H_9	82	76	74 (64)	78

* ( )=yield from **34**

[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b)*p*-xylene, 138 °C, 3 h.

oxy-4-methylcyclobutenone (**38**) whose assigned structure is in accord with its observed spectroscopic properties. The most revealing is the ^{13}C NMR spectrum which shows a polarized conjugated alkyne moiety as evidenced by the large difference in the chemical shifts of the alkyne carbon

Scheme VIII



atoms (δ 78.21 and 96.19) and the C-4 methyl absorption at δ 21.49. For comparison, the analogous chemical shifts for **37** are, respectively, δ 82.32, 90.79, and 5.98. Also, it is of note that **38**, unlike the other chlorocyclobutenones studied, is stable in refluxing *p*-xylene for up to 2 days.

Mechanistic Considerations

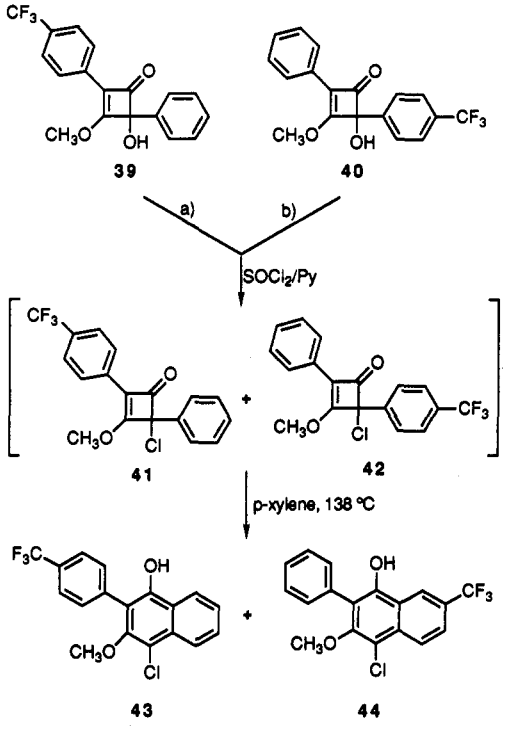
Since the regioisomeric hydroxycyclobutenone pairs **8**/**9**, **28**/**29**, and **33**/**34** gave the same respective 4-chlorocyclobutenone derivative, a common intermediate is suggested to be involved in the chlorination reaction. As noted earlier, this is most likely the corresponding cyclobutenyl cation generally represented as **7** (Scheme I). Such an intermediate is reasonable on the basis of the above data and is consistent with literature precedents.[6,7,10]

The site of chlorination of compounds **8**, **9**, and **13** occurs at the allylic rather than the benzylic position. Similarly, compounds **18** and **23** react with thionyl chloride at the allylic rather than the alkyl position, and chlorination of **25a,b** takes place at the allylic rather than the propargylic position. The chlorination preference for benzylic over alkyl and propargylic positions is illustrated by **28**, **29** and **33**, **34**, respectively. Finally, chlorination was shown to occur at the alkyl rather than the propargylic site for the cyclobutenone **37**. These results are in agreement with the intermediacy of carbocations such as **7** and the mechanistic paradigm presented earlier.

To further probe this mechanistic rationale, an experiment was designed to study the site of chlorination of hydroxycyclobutenones carrying substituents at the 2- and 4-position that differ only slightly in electron density. To this end, regioisomeric 2-[4-(trifluoromethyl)phenyl]-4-hydroxy-3-methoxy-4-phenyl-2-cyclobutenone (**39**) and [4-(trifluoromethyl)phenyl]-4-hydroxy-3-methoxy-2-phenyl-2-cyclobutenone (**40**) were prepared by adding phenyllithium and 4-(trifluoromethyl)phenyllithium to 3-methoxy-4-[4-(trifluoromethyl)phenyl]-3-cyclobutene-1,2-dione and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione, respectively (Scheme IX). When **39** and **40** were independently subjected to the same chlorination conditions, mixtures of 4-chloro derivatives were obtained and these were directly subjected to thermolysis. Naphthols **43** and **44** were isolated in each case in a respective ratio of 2:1 (71%) from the former (**39**) and 3:1 (70%) from the latter (**40**). Compound **43** and **44** are readily distinguishable from characteristic patterns in their ^1H NMR spectra. The fact that **43** is the major product in each case indicates that 4-chloro-3-methoxy-4-phenyl-2-[4-(trifluoromethyl)-phenyl]-2-cyclobutenone **41** rather than its regioisomer **42**

(10) For leading references, see: (a) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967; pp 122–127. (b) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430. (c) Pittman, C. U., Jr.; Kress, A.; Kispert, L. D. *J. Org. Chem.* **1974**, *39*, 378. (d) Jespersen, K. K.; Schleyer, P.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301. (e) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 5489. (f) Treibs, A.; Jacob, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *77*, 680. (g) Sprenger, H.-E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *79*, 581. (h) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530. (i) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530. (j) Schmidt, A. H.; Reid, W.; Gildemeister, H. *Liebigs Ann. Chem.* **1976**, 705–715.

Scheme IX[a]



[a] Key: (a) 71%, **43**:**44** = 2:1; (b) 70%, **43**:**44** = 3:1.

is the major chlorocyclobutenone formed. These results are consistent with the prediction noted above that chlorination is favored at the site bearing the most cation-stabilizing group.

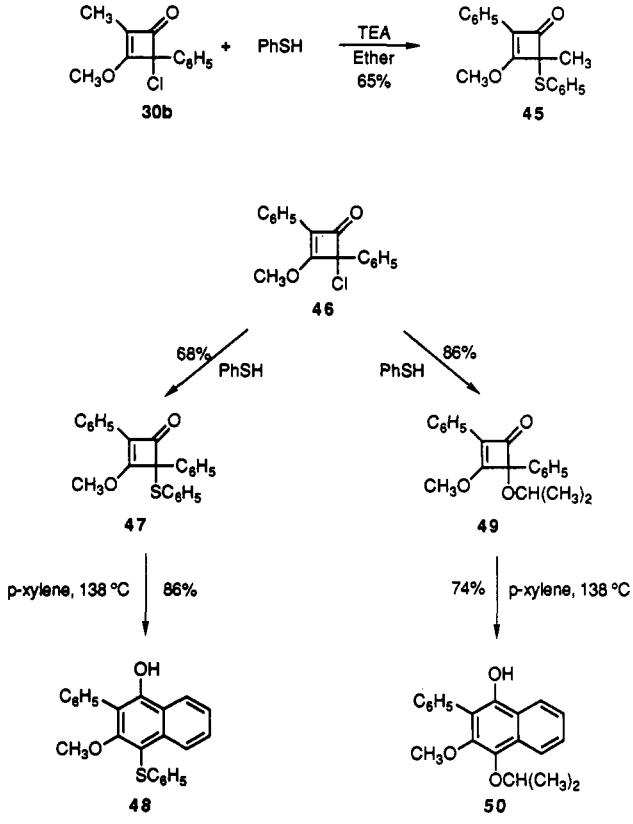
Other Synthetic Applications

Many of the 4-chlorocyclobutenones described here were found to readily hydrolyze to their precursor 4-hydroxycyclobutenones. This prompted a study directed to the possibility of introducing different functional groups at the 4-position of the cyclobutenones through nucleophilic displacement of the chloro substituent. Thus, when **30b** was treated with thiophenol in ether in the presence of triethylamine, **45** was obtained in 65% yield (Scheme X). The structure assignment of **45** is based on its spectroscopic data and the fact that it does not ring expand when subjected to the usual thermolysis conditions (refluxing p-xylene). A characteristic strained carbonyl stretch at 1765 cm^{-1} was observed in the infrared spectrum, and the presence of the thiophenyl moiety is evident from both the ^1H NMR and mass spectra.[11]

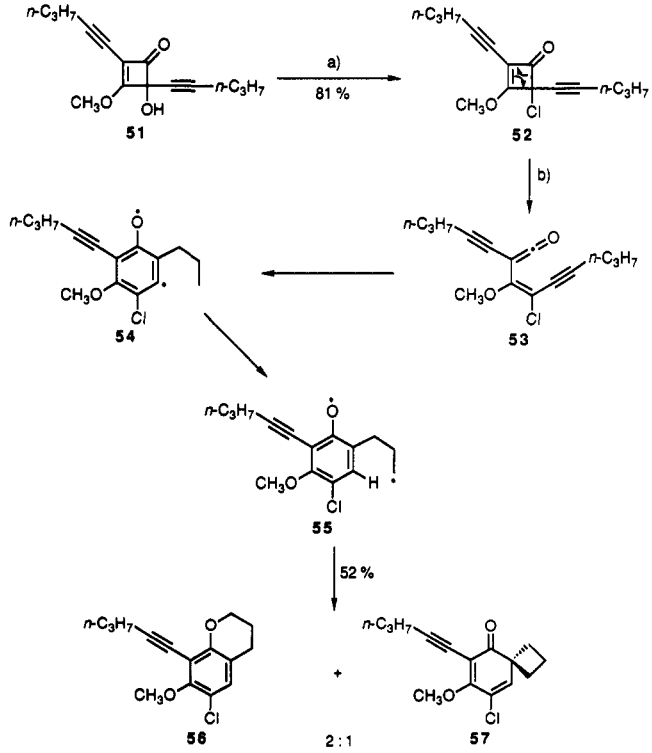
When 4-chloro-2,4-diphenyl-2-cyclobuten-1-one **46** was treated with thiophenol under the same conditions, the thio ether **47** was realized in 68% yield. Its thermolysis in refluxing *p*-xylene gave **48** in 86% isolated yield (Scheme X). Also, conversion of **46** to **49** (89%) upon treatment with 2-propanol in the presence of silver(I) oxide was accomplished, and this compound also rearranged upon thermolysis to gave the naphthol **50** in 74% yield.

A final area of study involves the thermal chemistry of 4-alkynyl-4-chlorocyclobutenones. This is of particular interest since the eneynylketenes resulting from electrocyclic ring opening of the cyclobutenones would be expected to ring close to unusual diradical intermediates.[2] However, the synthesis of 4-alkynyl-4-chlorocyclobutenones from 4-alkynyl-4-hydroxycyclobutenones is not

Scheme X



Scheme XI[a]



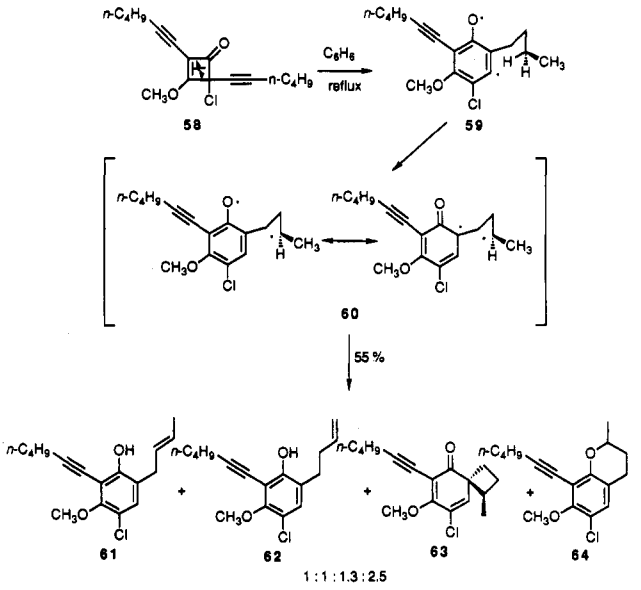
[a] Key: (a) $SOCl_2$, pyridine, CH_2Cl_2; (b) *p*-xylene, 138 °C, 3 h.

trivial by the methods outlined here since, as noted above, chlorination at the propargylic position as opposed to a nonpropargylic site of **7** is the least favorable. As a result it was necessary to start with 2,4-dialkynyl-4-hydroxycyclobutenones.

Thermolysis of 4-chloro-4-alkynylcyclobutenone **52** (prepared from the cyclobutenone **51**) resulted in **56** and

(11) For an analogy, see: (a) Jenny, E. F.; Druey, J. *J. Am. Chem. Soc.* **1960**, *82*, 3111. (b) Caserio, M. C.; Simmons, H. E., Jr.; Johnson, A. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 3102.

Scheme XII



57 which are viewed as arising from the intermediates 53–55 (Scheme XI).

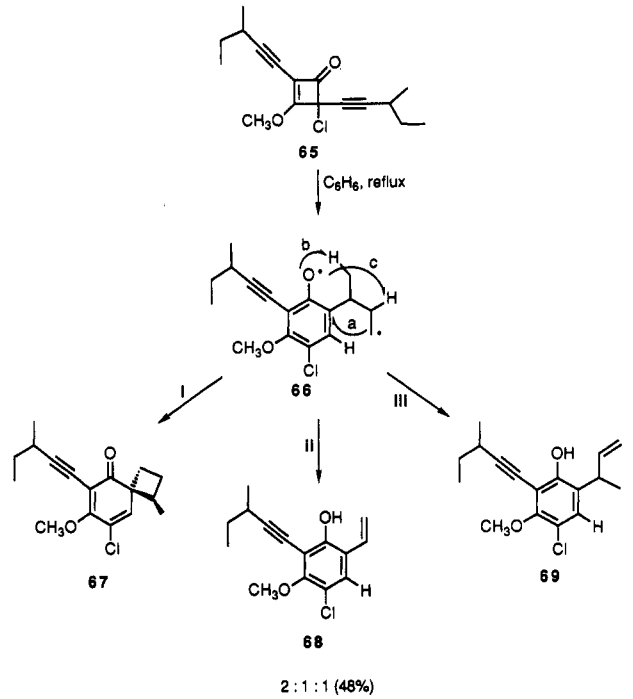
Formation of the spiro compound 57 is particularly interesting and unanticipated since closure of the diradical 55 to a four-membered ring would not normally be expected to compete with six-membered-ring formation, particularly since chromanol formation maintains aromatic character.[12] Formation of 57 is rationalized as arising via a mechanism involving an intramolecular hydrogen atom abstraction in 54 to give 55. This is formed having an initial conformation of the side chain such that ring closure to 57 is entropically favored over 56 in spite of the fact that aromatic stabilization is thus voided.

This study was extended to include the dialkynylcyclobutenones 58 and 65. Compound 58 was prepared (84%) from its 4-hydroxy precursor and observed to give the phenols 61 and 62 along with the spiro ketone 63 and the chromanol 64 in a respective ratio of 1:1:1.3:2.5 when thermolyzed in refluxing benzene (Scheme XII).

The phenols are envisaged to arise via intramolecular hydrogen atom abstraction involving six-membered ring transition states. The spiro ketone 63 is of interest since it appears to be a single diastereoisomer (^{1}H NMR and ^{13}C NMR). The stereochemistry is tentatively assigned on the assumption that intramolecular hydrogen atom abstraction from 59 proceeds via the chair conformer, thus placing the methyl group in an equatorial position.[13] This then leads to 60 whose collapse to the spiro ketone 63 competes with chromanol 64 formation.

Thermolysis of 65 presents still another unusual picture. Here, the products are the spiro ketone 67 and the alkenes 68 and 69, formed in a ratio of 2:1:1 (48%) (Scheme XIII). These are again are viewed as arising from a diradical intermediate 66 via the respective pathways (i), (ii), and (iii). It is of interest that no chromanol was detected in this reaction. This is not necessarily unexpected since the required bond rotation in the diradical intermediate 66 would be retarded in comparison to the analogous rotation in the less hindered diradicals 55 and 60. Formation of 68 is of particular note since this involves a fragmentation process, i.e., hydrogen atom abstraction from the methyl

Scheme XIII



group by the phenoxy radical and concomitant loss of ethene.

Conclusions

In conclusion, we wish to note the following points: (1) 4-chlorocyclobutenones are readily available from their 4-hydroxy counterparts upon treatment with thionyl chloride/pyridine; (2) the site of chlorination depends upon the substitution pattern of the starting 4-hydroxycyclobutenone and in general takes place at the position bearing the more cation-stabilizing group; (3) thermolyses of the 4-chlorocyclobutenones thus obtained provide general routes to highly substituted p-chlorophenols and chloronaphthols; (4) thermolyses of 4-chloro-4-alkynylcyclobutenones lead to products steming from unusual diradical intermediates.

Experimental Section

General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of argon. Reaction mixtures were stirred magnetically. Air-sensitive solutions were transferred via a cannula and were introduced into the reaction vessels through rubber septa. Butyllithium was introduced to the reaction mixture vessels via syringe. Reaction solutions were concentrated using a Buchi rotary evaporator at 15–20 mmHg. Column chromatography was performed by using E. Merck silica gel (230–400 mesh), with hexanes and ethyl acetate as the eluants.

The new compounds reported here were greater than 90% pure as evidenced by NMR elemental and/or NMR analysis. The NMR spectra are available as supplementary material.

Materials. Commercial-grade solvents were used without further purification except as indicated below. Tetrahydrofuran was distilled from sodium–benzophenone ketyl. Benzene and p-xylene were also distilled from calcium hydride.

General Procedure for the Synthesis of Hydroxycyclobutenones. 2-Ethenyl-4-hydroxy-3-methoxy-4-phenyl-2-cyclobuten-1-one (8). A solution of 0.200 g (1.45 mmol) of 3-ethenyl-4-methoxy-3-cyclobutene-1,2-dione in 40 mL of THF was cooled to −78 °C under a positive Ar pressure. To the solution was added dropwise via a syringe 0.80 mL (1.6 mmol) of 2.0 M PhLi. The solution turned orange during the addition of PhLi and turned brownish orange while the last few drops of PhLi were added. The solution was allowed to stay at −78 °C for 15 min

(12) For an excellent review of the synthetic utility of free radical intermediates, see: Curran, D. P. *Synthesis* **1988**, 417.

(13) For a review on free-radical intramolecular hydrogen abstraction, see: Heusler, K.; Kalvoda, J. *Angew. Chem., Ind. Ed. Engl.* **1964**, *3*, 525.

and then quenched by pouring into a separatory funnel containing 5 mL of 5% NH_4Cl and 20 mL of ether. The layers were separated, and the organic phase was washed with brine (2 × 5 mL) and dried ($MgSO_4$). Removal of the volatiles in vacuo gave an orange oil which was chromatographed (3:1 Hex–EtOAc) to afford 0.235 g (75%) of **8** as a pale yellow oil: IR (film) 3360, 2960, 1750, 1700, 1640, 1600, 1580, 1500, 1450, 1400, 1360, 1200, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.38 (s, 1 H), 4.06 (s, 3 H), 5.45 (dd, J = 11.0, 1.8 Hz, 1 H), 5.98 (dd, J = 17.6, 2.0 Hz, 1 H), 6.23 (dd, J = 17.6, 11.0 Hz, 1 H), 7.33–7.42 (m, 3 H), 7.49–7.52 (m, 2 H); MS (CI), 217 (MH^+); MS (EI), m/z (rel intensity) 216 (14), 201 (15), 185 (16), 173 (7), 155 (9), 145 (7), 128 (50), 117 (13), 105 (100), 77 (76), 63 (6), 51 (28). HRMS calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0791.

4-Ethenyl-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one (9). The general procedure above was followed using vinyllithium as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatograhy (3:1 Hex-EtOAc) gave 0.328 g (71%) of **9** as a pale yellow oil: IR (film) 3400, 3070, 3040, 2970, 1750, 1650, 1630, 1600, 1500, 1470, 1450, 1370, 1340, 1320, 1200, 1150, 990, 930, 820, 780, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 1 H), 4.22 (s, 3 H), 5.45 (d, J = 10.5 Hz, 1 H), 5.64 (d, J = 17.1 Hz, 1 H), 6.11 (dd, J = 17.4, 10.8 Hz, 1 H), 7.28–7.39 (m, 3 H), 7.22–7.74 (m, 2 H); MS (CI), 217 (MH^+); MS (EI) m/z (rel intensity) 216 (14), 201 (4), 183 (5), 173 (6), 156 (6), 129 (26), 115 (17), 89 (26), 77 (16), 63 (26). HRMS calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0782.

General Procedure for the Synthesis of Chlorocyclobutenones. (*Z*)-4-(2-Chloroethylidene)-3-methoxy-2-phenyl-2-cyclobuten-1-one (10). A solution of 0.11 g (0.51 mmol) of **8** and 0.41 mL (5.1 mmol) dry pyridine in 2 mL of CH_2Cl_2 was cooled to 0 °C under Ar. To the solution was added via a syringe 0.13 mL (1.8 mmol) of distilled thionyl chloride. The orange solution thus obtained was stirred for 10 min and transferred to a short silica gel column saturated with 10:1 Hex–EtOAc. The column was flushed with 10:1 Hex–EtOAc (80 mL). Removal of the volatiles in vacuo gave a white solid which was triturated with hexanes to give 98 mg (82%) of **10** as a white solid. Following a similar procedure, **10** was also obtained from **9** (42%): mp 151–154 °C dec; IR ($CHCl_3$) 3030, 1760, 1680, 1580, 1500, 1450, 1380, 1210, 1040, 730, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.39 (s, 3 H), 4.60 (d, J = 8.0 Hz, 2 H), 5.61 (t, J = 8.0 Hz, 1 H), 7.24–7.40 (m, 3 H), 7.73–7.79 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.9 (CH_3), 60.2 (CH_2), 111.71 (CH), 126.7 (CH), 128.5 (CH), 128.7 (C), 128.8 (CH), 137.7 (C), 148.6 (C), 180.0 (C), 183.0 (C) (carbon editing based on DEPT data); MS (EI) m/z (rel intensity) 236 (M + 2, 18), 234 (53), 199 (98), 171 (100), 139 (13), 128 (43), 114 (10), 102 (8), 89 (9), 77 (9), 63 (14), 51 (9); HRMS calcd for $C_{13}H_{11}ClO_2$ 234.0448, found 234.0454. Anal. Calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.35; H, 4.76.

General Procedure for the Synthesis of Chlorophenols. 4-Chloro-3-methoxy-2-phenylphenol (12). A solution of 90 mg of **10** in 40 mL of freshly distilled *p*-xylene was heated at reflux for 3 h. During the thermolysis, the originally colorless solution turned yellow. The xylene was removed in vacuo to give a yellow oil which was purified by chromatography (20:1 Hex–EtOAc) to afford 71.8 mg (80%) of **12** as a slightly yellow oil: IR (film) 3456, 3030, 2940, 1610, 1580, 1465, 1440, 1410, 1330, 1290, 1220, 1170, 1060, 1040, 950, 810, 760, 710, 660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.47 (s, 3 H), 4.99 (s, 1 H), 6.75 (d, J = 8.8 Hz, 1 H), 7.27 (d, J = 8.8 Hz, 1 H), 7.38–7.52 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) 60.6 (CH_3), 112.1 (CH), 119.2 (C), 123.8 (C), 128.5 (CH), 129.2 (CH), 129.6 (CH), 130.2 (CH), 131.6 (C), 152.4 (C), 153.7 (C) (peak editing based on DEPT data); MS (EI) m/z (rel intensity) 236 (M + 2, 32), 234 (100), 219 (12), 198 (5), 184 (64), 168 (4), 155 (11), 139 (14), 128 (16), 115 (3), 102 (6), 89 (4), 77 (9), 63 (9), 51 (6). HRMS calcd for $C_{13}H_{11}ClO_2$ 234.0448, found 234.0454.

4-Hydroxy-3-methoxy-4-phenyl-2-(2-propenyl)-2-cyclobuten-1-one (13). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-methoxy-4-(2-propenyl)-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) gave a white solid. The solid was recrystallized from ether/hexanes to provide 0.261 g (74%) of **13** as white crystals: mp 139–141 °C; IR ($CHCl_3$) 3350, 3000, 2960, 1750, 1740, 1640, 1610, 1590, 1470, 1450, 1380, 1150, 1035, 1020, 900, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 3.48 (s, 1 H), 3.94 (s, 3 H), 5.13 (t, J = 1.7 Hz, 1 H), 5.62 (s, 1 H), 7.33–7.43 (m, 3 H), 7.48–7.51 (m, 2 H); MS (CI), 231 (MH^+); MS (EI) m/z (rel intensity) 230 (55), 215 (48), 213 (13), 187 (15), 142 (16), 141 (15), 105 (100); HRMS calcd for $C_{14}H_{14}O_3$ 230.0943, found 230.0931. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.74; H, 5.95.

4-Chloro-3-methoxy-5-methyl-2-phenylphenol (17). Hydroxycyclobutenone **13** was converted to a mixture of chlorides (**14–16**) following the procedure described for the synthesis of **10**. This mixture was taken into 100 mL of freshly distilled *p*-xylene. The solution was then heated at reflux for 24 h. Removal of the xylene in vacuo gave an orange oil which was purified by chromatography (20:1 Hex–EtOAc) to give 113 mg (65% from **13**) of **17** as a yellow oil: IR (film) 3400, 2940, 2860, 1620, 1580, 1460, 1390, 1340, 1300, 1200, 1170, 1080, 1010, 940, 850, 750, 700, 660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3 H), 3.46 (s, 3 H), 4.96 (s, 1 H), 6.72 (s, 1 H), 7.38–7.54 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.3 (CH_3), 60.4 (CH_3), 113.2 (CH), 119.7 (C), 121.1 (C), 128.3 (CH), 129.1 (CH), 130.3 (CH), 131.9 (C), 137.5 (C), 151.4 (C), 153.6 (C) (carbon editing based on DEPT data); MS (CI) 249 (MH^+); MS (EI) m/z (rel intensity) 250 (M + 2, 46), 248 (100), 233 (6), 198 (65), 169 (15), 152 (15), 141 (23), 115 (31), 77 (17), 63 (22). HRMS calcd for $C_{14}H_{13}ClO_2$ 248.0604, found 248.0622.

4-(1-Butyl)-4-hydroxy-3-methoxy-2-(2-propenyl)-2-cyclobuten-1-one (18). The procedure described for the synthesis of **8** was followed using *n*-butyllithium as the anion and 3-methoxy-4-(2-propenyl)-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) gave 0.280 g (81%) of **18** as a colorless clear oil: IR (film) 3480, 2960, 2940, 2870, 1750, 1640, 1610, 1600, 1470, 1380, 1280, 1080, 1000, 900, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 6.8 Hz, 3 H), 1.25–1.41 (m, 4 H), 1.79–1.90 (m, 1 H), 1.92 (m, 3 H), 2.03–2.12 (m, 1 H), 3.18 (s, 1 H), 4.16 (s, 3 H), 5.05 (m, 1 H), 5.52 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 20.1, 22.6, 27.3, 33.2, 59., 92.2, 116.6, 125.6, 132.2, 181.9, 191.9; MS (EI) m/z (rel intensity) 210 (20), 195 (4), 167 (30), 149 (5), 139 (13), 125 (22), 108 (11), 97 (40), 93 (51), 83 (41), 67 (29), 57 (100). Exact mass calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1253.

2-(1-Butyl)-4-chloro-3-methoxy-4-(1-methylethenyl)-2-cyclobuten-1-one (19) and (*E*,*Z*)-2-(1-Butyl)-4-(2-chloro-1-methylethylidene)-3-methoxy-2-cyclobuten-1-one (20/21). Hydroxycyclobutenone **18** was converted to a mixture of chlorocyclobutenones **19** and **20/21** (245 mg, 83%) following the procedure described for the synthesis of **10**. The ratio of **19** and **20/21** was revealed by ^1H NMR analysis to be 3.4:1. Isomers **19** and **20/21** can be separated by flash chromatography. A portion of 272 mg of the mixture was subjected to flash chromatography (20:1 Hex–EtOAc, 2 drops of pyridine/100 mL eluant). Compounds **19** and **20/21** were obtained in the amounts of 195 mg and 63 mg, respectively. Compound **19** (colorless oil): IR (film) 2970, 2940, 2890, 1770, 1640, 1620, 1600, 1470, 1390, 1360, 1290, 1180, 1150, 1010, 910, 680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 3 H), 1.30–1.48 (m, 4 H), 1.91 (s, 3 H), 2.08–2.13 (m, 1 H), 2.25–2.34 (m, 1 H), 4.22 (s, 3 H), 5.10–5.11 (m, 1 H), 5.57–5.58 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 20.1, 22.4, 28.1, 36.6, 59.4, 83.0, 118.4, 125.3, 131.9, 176.1, 182.2; MS (EI) m/z (rel intensity) 230 (M + 2, 12), 228 (33), 193 (66), 185 (52), 165 (93), 157 (33), 151 (29), 143 (37), 135 (21), 121 (38), 109 (21), 105 (27), 91 (100), 79 (70), 77 (9), 67 (41), 65 (52), 53 (71); exact mass calcd for $C_{12}H_{17}ClO_2$ 228.0917, found 228.0922. Compound **20/21** (slightly yellow oil): IR (film) 2960, 2940, 2875, 1770, 1710, 1590, 1455, 1375, 1270, 1260, 1220, 1110, 1040, 990, 920, 795, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 6 H), 1.31–1.41 (m, 4 H), 1.53–1.62 (m, 4 H), 1.87 (s, 3 H), 2.01 (s, 3 H), 2.35 (t, J = 7.5 Hz, 4 H), 4.16 (s, 3 H), 4.17 (s, 3 H), 4.19 (s, 2 H), 4.43 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 14.6, 15.1, 22.6, 23.8, 31.0, 31.1, 44.6, 44.7, 59.5, 59.6, 117.6, 117.8, 138.9, 139.0, 142.1, 142.6, 182.3, 182.6, 187.6, 187.9; MS (EI) m/z (rel intensity) 230 (M + 2, 14), 228 (M, 40), 193 (64), 185 (24), 179 (100), 165 (91), 157 (13), 151 (32), 137 (17), 121 (31), 109 (31), 105 (25), 91 (89), 79 (66), 77 (87), 67 (36), 65 (43), 55 (45), 53 (60); exact mass calcd for $C_{12}H_{17}ClO_2$ 228.0917, found 228.0920.

2-(1-Butyl)-4-chloro-3-methoxy-5-methylphenol (22). A solution of 200 mg of a mixture of **19** and **20/21** (3.4:1) in 60 mL of *p*-xylene was heated at reflux for 20 h. The slightly yellow

solution obtained was cooled to ambient temperature. Removal of the solvent gave a yellow oil which was chromatographed (30:1 Hex–EtOAc) to afford 173 mg of a slightly yellow oil. The oil solidified upon refrigeration. Recrystallization with hexanes yielded 163 mg (82%) of **22** as colorless crystals: mp 49–50 °C; IR 3420, 2960, 2940, 2870, 1610, 1580, 1460, 1400, 1330, 1210, 1170, 1110, 1060, 1010, 950, 915, 845, 650, 610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3 H), 1.37–1.59 (m, 4 H), 2.29 (s, 3 H), 2.61 (t, J = 7.5 Hz, 2 H), 3.82 (s, 3 H), 4.61 (s, 1 H), 6.48 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 20.0, 22.3, 24.1, 31.9, 60.3, 113.2, 119.8, 121.7, 134.9, 152.5, 154.7; MS (EI) m/z (rel intensity) 230 (M + 2, 8), 229 (M + 1, 3), 228 (M, 25), 187 (34), 185 (100), 155 (25), 127 (8), 107 (8), 91 (26), 79 (8), 77 (24), 65 (14), 55 (16), 51 (24); exact mass calcd for $C_{12}H_{17}ClO_2$ 228.0917, found 228.0920. Anal. Calcd for $C_{12}H_{17}ClO_2$: C, 63.02; H, 7.49. Found: C, 62.95; H, 7.68.

2-[2-(2-Butenyl)]-4-butyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one (23). The procedure described above for the synthesis of **8** was followed using n-butyllithium as the anion and (E/Z)-3-(2-buten-2-yl)-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (3:1 Hex–EtOAc) provided 0.71 g (81%) of **23** (a 6:1 mixture of E/Z stereoisomers) as a colorless oil: IR (film) 3360, 2960, 2940, 2870, 1750, 1665, 1620, 1470, 1370, 1320, 1170, 1140, 1120, 1090, 1010 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, major isomer) δ 0.90 (t, J = 6.0 Hz, 3 H), 1.30–1.38 (m, 4 H), 1.67–1.73 (m, 3 H), 1.80–1.86 (m, 4 H), 1.96–2.07 (m, 1 H), 2.90 (s, 1 H), 4.13 (s, 3 H), 5.43–5.51 (m, 1 H); MS (EI) m/z (rel intensity) 224 (10), 181 (58), 139 (14), 107 (61), 85 (31), 77 (46), 67 (39), 57 (100), 55 (66), 53 (48). Exact mass calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1419.

2-(1-Butyl)-4-chloro-3-methoxy-5,6-dimethylphenol (24). Similar to the procedure described for the synthesis of **17**, hydroxycyclobutenone **23** was converted to a mixture of chlorides then thermolyzed to give 117 mg (59% from **23**) of **24** as a colorless oil: IR (film) 3500, 2940, 2880, 1570, 1460, 1410, 1330, 1215, 1200, 1110, 1070 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.0 Hz, 3 H), 1.40–1.57 (m, 4 H), 2.17 (s, 3 H), 2.32 (s, 3 H), 2.63 (t, J = 8.0 Hz, 2 H), 3.80 (s, 3 H), 4.66 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.6, 13.9, 16.8, 22.9, 24.3, 31.9, 60.9, 119.1, 120.22, 120.6, 133.4, 150.6, 152.3; MS (EI) m/z (rel intensity) 244 (M + 2, 10), 242 (32), 201 (31), 199 (100), 169 (19), 141 (11), 135 (12), 105 (14), 91 (29), 77 (29), 65 (22), 55 (21), 53 (19); exact mass calcd for $C_{13}H_{19}ClO_2$ 242.1073, found 242.1077.

2-Ethenyl-4-hexynyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one (25a). The procedure described above for the synthesis of **8** was followed using the lithium acetylide generated from 1-hexyne and n-butyllithium as the anion and 3-ethenyl-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (3:1 Hex–EtOAc) afforded 0.357 g (89%) of **25a** as a pale yellow oil: IR (film) 3360, 2960, 2940, 2880, 2240, 1760, 1650, 1610, 1590, 1470, 1410, 1360, 1250, 1140, 990, 930, 900, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.40 (sextet, J = 6.9 Hz, 2 H), 1.44–1.55 (m, 2 H), 2.28 (t, J = 7.2 Hz, 2 H), 3.10 (s, 1 H), 4.29 (s, 3 H), 5.42 (dd, J = 11.1, 1.8 Hz, 1 H), 5.90 (dd, J = 17.7, 2.1 Hz, 1 H), 6.12 (dd, J = 17.7, 11.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.4, 18.5, 21.8, 30.2, 60.0, 74.0, 83.1, 91.8, 121.5, 121.6, 125.2, 178.0, 185.4; MS (EI) m/z (rel intensity) 220 (7), 205 (10), 191 (5), 177 (14), 163 (15), 149 (11), 131 (10), 119 (12), 111 (31), 95 (31), 91 (42), 79 (69), 67 (56). Exact mass calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1091.

2-Ethenyl-4-hydroxy-3-methoxy-4-(phenylethynyl)-2-cyclobuten-1-one (25b). The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from phenylacetylene and n-butyllithium as the anion and 3-ethenyl-4-methoxy-2-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography yielded 0.342 g (78%) of **25b** as a yellow oil: IR 3360, 3050, 2960, 2220, 1750, 1630, 1490, 1455, 1405, 1350, 1075, 985, 755, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.35 (s, 3 H), 5.45 (dd, J = 11.1, 1.5 Hz, 1 H), 5.95 (dd, J = 17.7, 2.1 Hz, 1 H), 6.16 (dd, J = 17.7, 11.1 Hz, 1 H), 7.31–7.47 (m, 5 H); MS (EI) m/z (rel intensity) 240 (20), 225 (7), 211 (7), 197 (6), 183 (4), 169 (9), 152 (16), 141 (30), 129 (98), 115 (23), 102 (27), 95 (47), 75 (44); exact mass calcd for $C_{15}H_{12}O_3$ 240.0786, found 240.0788.

4-Chloro-4-ethenyl-2-(1-hexynyl)-3-methoxy-2-cyclobuten-1-one 26a. Following the procedure described for the synthesis of **10**, **26a** (167 mg, 80%, ^1H NMR shows purity greater than 80%) was obtained from **25a** as a yellow oil: IR (film) 2970, 2940, 2880, 2240, 1790, 1625, 1590, 1460, 1375, 980, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 3 H), 1.37–1.56 (m, 4 H), 2.36 (t, J = 6.9 Hz, 2 H), 4.39 (s, 3 H), 5.40 (d, J = 10.8 Hz, 1 H), 5.59 (d, J = 16.5 Hz, 1 H), 6.02 (dd, J = 17.1, 10.5 Hz, 1 H); MS (EI) m/z (rel intensity) 240 (M + 2, 4), 238 (14), 223 (3), 203 (15), 195 (24), 175 (41), 161 (75), 149 (15), 131 (22), 115 (42), 103 (54), 89 (85), 77 (100), 63 (90), 55 (62); exact mass calcd for $C_{13}H_{15}ClO_2$ 238.0761, found 238.0744.

4-Chloro-4-ethenyl-3-methoxy-2-(phenylethynyl)-2-cyclobuten-1-one (26b). Following the procedure described for the synthesis of **10**, **26b** (62 mg, 44%, ^1H NMR showed purity greater than 60%) was obtained from **25b** as a yellow oil: IR (film) 3060, 2950, 1780, 1620, 1580, 1490, 1455, 1440, 1370, 980, 850, 755, 690, 620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.48 (s, 3 H), 5.44 (d, J = 10.5 Hz, 1 H), 5.63 (d, J = 18.9 Hz, 1 H), 6.06 (dd, J = 17.4, 10.5 Hz, 1 H), 7.34–7.47 (m, 5 H); MS (EI) m/z (rel intensity) 258 (39), 243 (39), 223 (26), 195 (61), 165 (23), 152 (100), 126 (21), 105 (14), 76 (51), 63 (37); exact mass calcd for $C_{15}H_{11}ClO_2$ 258.0448, found 258.0443.

4-Chloro-2-(1-hexynyl)-3-methoxyphenol (27a). Following the procedure described for the synthesis of **12**, 160 mg of **26a** was thermolyzed to give a brown oil. Purification by flash chromatography (3:1 Hex–EtOAc) provided 77 mg (48%) of **27a** as a colorless clear oil: IR (film) 3480, 2940, 2870, 2220, 1570, 1465, 1415, 1340, 1300, 1220, 1180, 1055, 950, 810, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 3 H), 1.45–1.70 (m, 4 H), 2.55 (t, J = 7.2 Hz, 2 H), 3.95 (s, 3 H), 5.81 (s, 1 H), 6.66 (d, J = 8.7 Hz, 1 H), 7.18 (d, J = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.4 (CH_3), 19.4 (CH_2), 21.9 (CH_2), 30.5 (CH_2), 60.8 (CH_3), 70.5 (C), 102.8 (C), 106.5 (C), 110.6 (CH), 118.3 (C), 129.8 (CH), 156.2 (C), 156.4 (C) (carbon editing based on DEPT data); MS (EI) m/z (rel intensity) 240 (17), 238 (47), 223 (17), 209 (11), 195 (100), 181 (44), 160 (21), 141 (19), 132 (21), 115 (21), 103 (35), 89 (72), 77 (61), 63 (67); exact mass calcd for $C_{13}H_{18}ClO_2$ 238.0761, found 238.0750.

4-Chloro-3-methoxy-2-(phenylethynyl)phenol (27b). Following the procedure described for the synthesis of **12**, 50 mg of **26b** was thermolyzed to give a brownish orange oil. Purification by chromatography (30:1 Hex–EtOAc) yielded 22.6 mg (45%) of **27b** as a yellow oil: IR (film) 3400, 2950, 1600, 1570, 1500, 1470, 1420, 1350, 1310, 1230, 1200, 1055, 960, 900, 810, 760, 710, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.03 (s, 3 H), 5.85 (s, 1 H), 6.72 (d, J = 8.1 Hz, 1 H), 7.25 (d, J = 8.1 Hz, 1 H), 7.39–7.43 (m, 3 H), 7.56–7.59 (m, 2 H); MS (EI) m/z (rel intensity) 260 (M + 2, 12), 258 (51), 243 (100), 152 (75), 126 (11), 105 (6), 76 (41), 58 (38); exact mass calcd for $C_{15}H_{11}ClO_2$ 258.0448, found 258.0440.

2-(1-Butyl)-4-hydroxy-3-methoxy-4-phenyl-2-cyclobuten-1-one (28a). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-(1-butyl)-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (6:1 Hex–EtOAc) provided a solid. After triturating with hexanes, 0.290 g (59%) of **28a** was obtained as a white solid: mp 59–61 °C; IR ($CHCl_3$) 3350, 3000, 2960, 2930, 2870, 1750, 1620, 1460, 1370, 1320, 1045, 1020, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, J = 7.1 Hz, 3 H), 1.38 (sextet, J = 7.6 Hz, 2 H), 1.58 (quintet, J = 7.4 Hz, 2 H), 2.21 (t, J = 7.6 Hz, 2 H), 3.31 (s, 1 H), 3.97 (s, 3 H), 7.32–7.42 (m, 3 H), 7.47–7.50 (m, 2 H); MS (EI) m/z (rel intensity) 246 (10), 231 (3), 189 (6), 175 (3), 157 (5), 143 (15), 115 (24), 105 (100), 77 (88), 51 (36); HRMS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1263. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.13; H, 7.37. Found: C, 73.13; H, 7.29.

4-Hydroxy-3-methoxy-2-methyl-4-phenyl-2-cyclobuten-1-one (28b). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-methoxy-4-methyl-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (3:1 Hex–EtOAc) gave 0.293 g (72%) of **28b** as a colorless clear oil: IR (film) 3360, 2960, 1755, 1620, 1460, 1390, 1340, 1180, 1050, 1000, 860, 790, 720, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.74 (s, 3 H), 3.95 (s, 3 H), 5.04 (s, 1 H), 7.28–7.47 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.04, 59.4, 91.9, 124.6, 125.4, 127.7, 128.2, 136.8, 182.6, 191.4; MS (EI) m/z (rel intensity) 204 (31), 189 (50), 161 (18), 143 (15), 131 (8), 115 (30), 105 (100), 77 (91), 67 (47), 55 (45). HRMS calcd for $C_{12}H_{12}O_3$ 204.0786, found 204.0804.

2-(2-Butyl)-4-hydroxy-3-methoxy-4-phenyl-2-cyclobuten-1-one (28c). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-(2-butyl)-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) afforded a solid which was triturated with hexanes to give 0.290 g (59%) of **28c** as a white solid: mp 84–85 °C; IR ($CHCl_3$) 3350, 3020, 2980, 2940, 2880, 1755, 1630, 1620, 1470, 1380, 1370, 1320, 1215, 1040, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.4 Hz, 3 H), 0.96 (t, J = 7.4 Hz, 3 H), 1.20 (d, J = 7.2 Hz, 3 H), 1.22 (d, J = 7.2 Hz, 3 H), 1.48–1.74 (m, 4 H), 2.42 (sextet, J = 7.2 Hz, 2 H), 3.91 (s, 3 H), 3.92 (s, 3 H), 7.30–7.52 (m, 10 H); MS (CI), 247 (MH^+); MS (EI) m/z (rel intensity) 246 (5), 189 (18), 157 (7), 129 (18), 115 (7), 105 (100), 91 (8), 77 (80), 69 (12), 51 (33); HRMS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1243. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.13; H, 7.37. Found: C, 73.39; H, 7.61.

4-(1-Butyl)-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one (29a). The procedure described for the synthesis of **8** was followed using *n*-butyllithium as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) afforded a colorless oil. To the oil was added 2 mL of hexanes and the mixture was allowed to stay in the freezer (−30 °C) overnight to give 0.22 g (68%) of **29a** as white crystals: mp 78–80 °C; IR (CCl_4) 3580, 3350, 3010, 2960, 2940, 2880, 1750, 1630, 1595, 1495, 1460, 1450, 1375, 1330, 1315, 1070, 1000, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 6.0 Hz, 3 H), 1.33–1.39 (m, 4 H), 1.89–1.94 (m, 1 H), 2.05–2.14 (m, 1 H), 3.14 (s, 1 H), 4.26 (s, 3 H), 7.28–7.37 (m, 3 H), 7.70–7.73 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.4, 182.2, 128.4, 128.3, 127.9, 126.8, 124.0, 92.9, 59.7, 33.4, 27.5, 22.7, 13.8; MS (CI) m/z 247 (MH^+); MS (EI) m/z (rel intensity) 246 (55), 218 (28), 203 (28), 189 (8), 176 (28), 161 (25), 144 (36), 129 (100), 118 (64), 102 (26), 85 (32), 77 (17); HRMS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1237. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.13; H, 7.37. Found: C, 73.32; H, 7.29.

4-Hydroxy-3-methoxy-4-methyl-2-phenyl-2-cyclobuten-1-one (29b). The procedure described for the synthesis of **8** was followed using methyllithium as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by chromatography provided a pale yellow oil. To the oil was added 2 mL of hexanes, and the mixture was kept in a freezer overnight (−30 °C) to form 0.407 g (83%) of **29b** as white crystals: mp 72–75 °C; IR ($CHCl_3$) 3350, 3010, 2980, 1880, 1750, 1630, 1600, 1500, 1460, 1370, 1335, 1320, 1135, 1100, 990, 870, 820, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, 3 H), 4.32 (s, 3 H), 7.24–7.36 (m, 3 H), 7.71 (d, J = 8.1 Hz, 2 H); MS (EI) m/z (rel intensity) 204 (14), 176 (16), 145 (13), 129 (100), 118 (35), 105 (20), 89 (44), 77 (20), 63 (45), 55 (46); HRMS calcd for $C_{12}H_{12}O_3$ 204.0786, found 204.0799. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.41; H, 5.75.

2-(1-Butyl)-4-chloro-3-methoxy-4-phenyl-2-cyclobuten-1-one (30a). Following the procedure described for the synthesis of **10**, 94 mg of **29a** was converted to 91.5 mg (91%) of **30a** as a colorless oil. Similarly, **30a** was also obtained from **28a** (81%): IR (film) 2960, 2940, 2880, 1780, 1640, 1600, 1500, 1460, 1450, 1370, 1340, 1320, 1150, 1000, 770, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.1 Hz, 3 H), 1.34–1.45 (m, 4 H), 2.17–2.24 (m, 1 H), 2.34–2.45 (m, 1 H), 4.33 (s, 3 H), 7.30–7.40 (m, 3 H), 7.72–7.75 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 176.3, 128.6, 128.5, 127.8, 127.1, 123.6, 83.4, 59.7, 36.7, 28.1, 22.4, 13.7; MS (CI) m/z 265 (MH^+); MS (EI) m/z (rel intensity) 266 (M + 2, 18), 265 (M + 1, 5), 264 (51), 229 (37), 228 (21), 223 (20), 221 (64), 201 (63), 195 (11), 193 (25), 187 (26), 178 (12), 171 (21), 169 (27), 163 (22), 158 (24), 143 (17), 129 (43), 128 (62), 127 (37), 115 (100), 102 (14), 91 (26), 89 (41), 77 (26), 63 (27), 55 (14), 51 (17); exact mass calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0906.

4-Chloro-3-methoxy-2-methyl-4-phenyl-2-cyclobuten-1-one (30b). Following the procedure described for the synthesis of **10**, 0.239 g of **29b** was converted to 201 mg (77%) of **30b** as a pale yellow oil. Similarly, **30b** was also obtained from **28b** (73%): IR (film) 3060, 2980, 2960, 2860, 1970, 1775, 1640, 1600, 1500, 1460, 1450, 1380, 1365, 1335, 1150, 1100, 1060, 980, 870, 780, 750, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 3 H), 4.38 (s, 3 H), 7.30–7.39 (m, 3 H), 7.71–7.74 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.6, 59.7, 79.3, 122.3, 127.1, 127.8, 128.49, 128.6, 177.2, 182.2; MS (EI) m/z (rel intensity) 224 (M + 2, 17), 222 (48), 187 (25), 163 (14), 159 (100), 128 (20), 115 (81), 89 (21), 77 (10), 63 (24), 51 (21). HRMS calcd for $C_{12}H_{11}ClO_2$ 222.0448, found 222.0441.

2-(2-Butyl)-4-chloro-3-methoxy-4-phenyl-2-cyclobuten-1-one (30c). Following the procedure described for the synthesis of **10**, 150 mg of **28c** was converted to 150 mg (93%) of **30c** as a colorless clear oil: IR (film) 2980, 2880, 1770, 1640, 1600, 1500, 1470, 1455, 1370, 1340, 1320, 1070, 1000, 910, 760, 700, 610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.2 Hz, 3 H), 0.99 (t, J = 7.2 Hz, 3 H), 1.09 (d, J = 7.2 Hz, 3 H), 1.20–1.70 (m, 4 H), 1.33 (d, J = 6.9 Hz, 3 H), 2.10–2.24 (m, 2 H), 4.30 (s, 3 H), 4.31 (s, 3 H), 7.27–7.40 (m, 6 H), 7.69–7.73 (m, 4 H); MS (EI) m/z (rel intensity) 264 (18), 235 (50), 229 (44), 207 (22), 201 (16), 169 (21), 153 (15), 141 (44), 129 (77), 128 (78), 115 (63), 102 (22), 89 (71), 77 (66), 63 (89), 59 (54); HRMS calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0909.

3-(1-Butyl)-1-chloro-4-hydroxy-2-methoxynaphthalene (31a) and (*Z*)-3-Methoxy-2-phenyl-4-(1-propylmethylene)-2-cyclobuten-1-one (32a). Following the procedure described for the synthesis of **12**, 80 mg of **30a** was thermolyzed to give a yellow oil. Purification by flash chromatography (30:1 Hex–EtOAc) provided 66 mg (82%) of a light yellow oil (homogeneous by TLC analysis using different solvents). ^1H NMR revealed that the yellow oil was a mixture of **31a** and **32a** (3:1 based on integration). After protection of the hydroxy group of **31a** with a TBDMS group, **32a** was separated from the protected phenol by column chromatography (30:1 Hex–EtOAc). Deprotection of the protected phenol gave pure **31a**: IR (film) 3500, 2960, 2940, 2860, 1630, 1590, 1570, 1500, 1450, 1390, 1345, 1260, 1210, 1120, 1060, 990, 930, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3 H), 1.45 (m, 2 H), 1.60 (m, 2 H), 2.79 (t, J = 7.5 Hz, 2 H), 3.94 (s, 3 H), 7.46 (t, J = 7.5 Hz, 1 H), 7.55 (t, J = 7.5 Hz, 1 H), 8.10 (d, J = 8.1 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H); MS (CI) m/z 265 (MH^+); MS (EI) m/z (rel intensity) 266 (M + 2, 32), 265 (M + 1, 15), 264 (100), 221 (85), 191 (40), 186 (87), 155 (23), 143 (46), 128 (73), 115 (67), 101 (11), 89 (16), 77 (17), 63 (21), 51 (13); exact mass calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0912. Compound **32a**: IR (film) 3050, 2960, 2920, 2860, 1755, 1680, 1585, 1490, 1450, 1370, 1310, 1060, 1010, 790, 750, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.4 Hz, 3 H), 1.47 (sextet, J = 7.4 Hz, 2 H), 2.50 (q, J = 7.4 Hz, 2 H), 4.35 (s, 3 H), 5.46 (t, J = 7.9 Hz, 1 H), 7.21–7.37 (m, 3 H), 7.73 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5 (CH_3), 23.1 (CH_2), 29.9 (CH_2), 59.9 (CH_3), 118.0 (CH), 126.1 (CH), 127.7 (CH), 128.4 (CH), 129.4 (C), 133.3 (C), 144.9 (C), 181.7 (C), 185.6 (C) (peak editing based on DEPT data); MS (CI), m/z 229 (MH^+); MS (EI) m/z (rel intensity) 228 (57), 200 (33), 185 (39), 171 (95), 157 (39), 141 (36), 128 (100), 115 (73), 105 (41), 89 (76), 77 (47), 55 (42); HRMS calcd for $C_{15}H_{16}O_2$ 228.1149, found 228.1149.

1-Chloro-4-hydroxy-2-methoxy-3-methylnaphthalene (31b) and 3-Methoxy-4-methylene-2-phenyl-2-cyclobuten-1-one (32b). Following the procedure described for the synthesis of **12**, 145 mg of **30b** was thermolyzed to give a yellow oil. Purification by flash chromatography (20:1 Hex–EtOAc) gave 49 mg of **31b** (34%, white solid) and 25 mg of **32b** (21%, white solid). Compound **31b**: mp 75–77 °C; IR ($CHCl_3$) 3600, 3000, 2940, 1630, 1600, 1570, 1500, 1460, 1390, 1380, 1350, 1280, 1270, 1200, 1110, 1010, 990, 930, 870, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 3.90 (s, 3 H), 7.47 (t, J = 6.9 Hz, 1 H), 7.56 (t, J = 7.9 Hz, 1 H), 8.10 (d, J = 8.3 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H); MS (CI), 223 (MH^+); MS (EI) m/z (rel intensity) 224 (M + 2, 13), 222 (23), 179 (69), 143 (13), 128 (18), 115 (100), 89 (23), 75 (20); HRMS calcd for $C_{12}H_{11}ClO_2$ 222.0448, found 222.0444. Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98. Found: C, 64.49; H, 5.11. Compound **32b**: mp 67–70 °C; IR ($CHCl_3$) 3020, 2960, 2940, 2880, 1780, 1750, 1670, 1590, 1500, 1460, 1450, 1370, 1340, 1320, 1130, 1110, 1005, 1000, 880, 800, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.41 (s, 3 H), 4.94 (d, J = 2.1 Hz, 1 H), 5.16 (d, J = 2.0 Hz, 1 H), 7.28–7.39 (m, 3 H), 7.77 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.3, 96.2, 126.6, 128.5, 128.7, 128.9, 136.9, 152.8, 181.5, 184.3; MS (CI), 187 (MH^+); MS (EI) m/z (rel intensity) 186 (15), 129 (31), 119 (18), 115 (100), 89 (19), 75 (13); HRMS calcd for $C_{12}H_{10}O_2$ 186.0681, found 186.0666.

3-(2-Butyl)-1-chloro-4-hydroxy-2-methoxynaphthalene (31c). Following the procedure described for the synthesis of **12**, 145 mg of **30c** was thermolyzed to give a yellow oil which was

purified by chromatography (30:1 Hex–EtOAc) to provide, along with a trace amount of **32c**, 116 mg of **31c** as a colorless oil: IR (film) 3460, 2980, 2960, 2880, 1630, 1600, 1500, 1460, 1420, 1390, 1350, 1290, 1250, 1190, 1130, 1090, 1070, 990, 930, 760, 670, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 3 H), 1.46 (d, J = 7.2 Hz, 3 H), 1.80–1.97 (m, 2 H), 3.39 (sextet, J = 7.5 Hz, 1 H), 3.92 (s, 3 H), 5.41 (s, 1 H), 7.46 (t, J = 8.1 Hz, 1 H), 7.55 (t, J = 7.8 Hz, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H); MS (EI) m/z (rel intensity) 266 (M + 2, 12), 164 (41), 235 (100), 220 (49), 200 (14), 185 (8), 170 (12), 152 (21), 141 (27), 128 (52), 115 (42), 89 (22), 77 (36), 63 (50), 51 (50); exact mass calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0899.

4-Hydroxy-3-methoxy-2-phenyl-4-(phenylethynyl)-2-cyclobuten-1-one (33a). The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from phenylacetylene and n-butyllithium as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) gave 0.46 g (75%) of **33a** as a sticky yellow oil: IR (CCl_4) 3320, 3060, 2960, 2220, 1760, 1635, 1600, 1495, 1465, 1450, 1370, 1335, 1320, 1240, 1100, 1070, 990, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.48 (s, 3 H), 7.31–7.38 (m, 6 H), 7.44–7.47 (m, 2 H), 7.76 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.4, 82.8, 83.7, 90.5, 121.5, 126.0, 127.0, 128.2, 128.2, 128.3, 128.4, 128.9, 131.7, 178.0, 184.8; MS (CI) m/z 291 (MH^+); MS (EI) m/z (rel intensity) 308 (M + H_2O, 4), 292 (M + 2, 3), 291 (M + 1, 8), 290 (38), 261 (15), 231 (14), 202 (35), 191 (43), 158 (33), 145 (50), 129 (63), 117 (32), 102 (36), 89 (100), 77 (28), 63 (27), 51 (18); exact mass calcd for $C_{19}H_{14}O_3$ 290.0943, found 290.0948.

4-Hydroxy-4-(1-hexynyl)-3-methoxy-2-phenyl-2-cyclobuten-1-one (33b). The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from 1-hexyne and n-butyllithium as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (3:1 Hex–EtOAc) provided a white solid. Trituration of the white solid with hexanes gave 0.47 g (82%) of **33b**: mp 115–119 °C dec; IR ($CHCl_3$) 3340, 3020, 2980, 2950, 2890, 2240, 1770, 1640, 1600, 1500, 1470, 1380, 1340, 1320, 1230, 1160, 1080, 1010, 1000, 900, 820, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3 H), 1.38–1.55 (m, 4 H), 2.29 (t, J = 6.9 Hz, 2 H), 4.40 (s, 3 H), 7.29–7.39 (m, 3 H), 7.72–7.75 (m, 2 H); MS (CI) m/z 271 (MH^+); MS (EI) m/z (rel intensity) 270 (20), 241 (21), 185 (18), 161 (45), 129 (44), 105 (37), 89 (81), 77 (70), 67 (64), 63 (59); exact mass calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1242. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.52; H, 6.72. Found: C, 75.29; H, 6.61.

4-Hydroxy-3-methoxy-4-phenyl-2-(phenylethynyl)-2-cyclobuten-1-one (34a). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-(phenylethynyl)-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (5:1 Hex–EtOAc) afforded 0.53 g (76%) of **34a** as a sticky yellow oil: IR ($CHCl_3$) 3590, 3070, 3040, 2255, 1775, 1730, 1720, 1630, 1600, 1500, 1455, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.27 (s, 1 H), 4.39 (s, 3 H), 7.35–7.57 (m, 10 H); MS (CI) m/z 291 (MH^+); MS (EI) m/z (rel intensity) 290 (21), 275 (36), 202 (31), 189 (26), 137 (27), 105 (100), 94 (49), 77 (92), 63 (19), 51 (28); exact mass calcd for $C_{19}H_{14}O_2$ 290.0943, found 290.0929.

2-(1-Hexynyl)-4-hydroxy-3-methoxy-4-phenyl-2-cyclobuten-1-one (34b). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-(1-hexynyl)-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) yielded 0.272 g (76%) of **34b** as a pale yellow oil: IR (film) 3400, 2960, 2940, 2880, 2240, 1770, 1620, 1500, 1460, 1370, 1210, 1050, 1000, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.37–1.56 (m, 4 H), 2.36 (t, J = 7.1 Hz, 2 H), 3.00 (s, 1 H), 4.31 (s, 3 H), 7.34–7.41 (m, 3 H), 7.50–7.53 (m, 2 H); MS (CI) m/z 271 (MH^+); MS (EI) m/z (rel intensity) 270 (5), 255 (5), 228 (5), 213 (5), 181 (9), 167 (8), 154 (8), 139 (12), 128 (9), 105 (66), 91 (8), 77 (100), 55 (15); exact mass for $C_{17}H_{18}O_3$ 270.1256, found 270.1264.

4-Chloro-3-methoxy-4-phenyl-2-(phenylethynyl)-2-cyclobuten-1-one (35a). Following the procedure described for the synthesis of **10**, 0.16 g of **33a** was converted to 0.13 g of slightly orange oil. ^1H NMR analysis revealed that 26% of it was CH_2Cl_2 (product not stable without certain amount of solvent present), therefore, the actual yield was 59%. Similarly, compound **35a** was also generated from **34a** (49%): IR (film) 3060, 2960, 2940, 2860, 2210, 1790, 1630, 1600, 1495, 1450, 1370, 1220, 1120, 1070, 985, 925, 850, 790, 760, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.53 (s, 3 H), 7.33–7.40 (m, 6 H), 7.42–7.47 (m, 2 H), 7.59–7.62 (m, 2 H); MS (CI) m/z 309 (MH^+); MS (EI) m/z (rel intensity) 310 (M + 2, 6), 309 (M + 1, 4), 308 (20), 293 (11), 265 (15), 245 (50), 230 (16), 213 (12), 202 (93), 150 (8), 113 (16), 101 (100), 88 (28), 77 (15), 63 (18), 51 (8); exact mass calcd for $C_{19}H_{13}ClO_2$ 308.0604, found 308.0615.

4-Chloro-2-(1-hexynyl)-3-methoxy-4-phenyl-2-cyclobuten-1-one (35b). Following the procedure described for the synthesis of **10**, 0.250 g of **33b** was converted to 0.214 g (74%) of **35b** as a pale yellow oil. Similarly, **35b** was also generated from **34b** (64%): IR (film) 2960, 2940, 2880, 2240, 1790, 1630, 1500, 1450, 1375, 990, 885, 810, 730, 700, 680, 660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.39–1.55 (m, 4 H), 2.35 (t, J = 7.1 Hz, 2 H), 4.44 (s, 3 H), 7.34–7.39 (m, 3 H), 7.55–7.58 (m, 2 H); MS (EI) m/z (rel intensity) 290 (M + 2, 2), 288 (7), 273 (5), 253 (12), 245 (23), 225 (26), 211 (18), 195 (13), 178 (19), 165 (51), 152 (56), 139 (89), 126 (26), 115 (34), 105 (40), 89 (59), 77 (90), 69 (43), 63 (84), 55 (81); exact mass calcd for $C_{17}H_{17}ClO_2$ 288.0917, found 288.0909.

1-Chloro-4-hydroxy-2-methoxy-3-(phenylethynyl)-naphthalene (36a). Following the procedure described for the synthesis of **12**, 99 mg of **35a** was thermolyzed to give an orange oil. The oil was purified by column chromatography (40:1 Hex–EtOAc) to give a slightly yellow oil which solidified upon refrigeration. The solid was recrystallized from hexanes to give 75.3 mg (76%) of **36a** as slightly pale yellow crystals: mp 80–82 °C; IR (CCl_4) 3520, 3080, 2950, 1630, 1595, 1575, 1500, 1470, 1430, 1400, 1355, 1310, 1290, 1240, 1220, 1100, 995, 940 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.08 (s, 3 H), 6.46 (s, 1 H), 7.40–7.65 (m, 7 H), 8.17–8.20 (d, J = 9.0 Hz, 1 H), 8.21–8.24 (d, J = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.2 (CH_3), 79.6 (C), 100.7 (C), 100.7 (C), 114.7 (C), 121.2 (C), 122.1 (C), 122.7 (CH), 124.0 (CH), 125.3 (CH), 128.5 (CH), 128.8 (CH), 129.0 (CH), 2 × 131.5 (C and CH, overlapping peaks revealed by attached proton test (APT) program), 152.3 (C), 153.7 (C) (peak editing based on DEPT data); MS (CI) m/z 309 (MH^+); MS (EI) m/z (rel intensity) 308 (100), 310 (50), 295 (17), 293 (53), 267 (17), 265 (52), 231 (10), 230 (49), 202 (70), 201 (25), 200 (34), 154 (11), 146 (18), 133 (22), 115 (32), 105 (31), 101 (63), 100 (32), 88 (26), 77 (31); exact mass calcd for $C_{19}H_{13}ClO_2$ 308.0604, found 308.0589.

1-Chloro-3-(1-hexynyl)-4-hydroxy-2-methoxynaphthalene (36b). Following the procedure described for the synthesis of **12**, 270 mg of **35b** was thermolyzed to give an orange oil. Purification by flash chromatography (30:1 Hex–EtOAc) provided a yellow oil which upon refrigeration turned into a yellow solid. Recrystallization of the solid gave 210 mg (78%) of **36b** as slightly yellow needles: mp 52–53 °C; IR ($CHCl_3$) 3500, 3020, 2970, 2940, 2870, 2220, 1630, 1600, 1580, 1500, 1465, 1430, 1395, 1300, 1230, 1210, 1130, 1100, 1020, 990, 920, 670, 645 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 0.98 (t, J = 7.2 Hz, 3 H), 1.50–1.58 (m, 2 H), 1.64–1.71 (m, 2 H), 2.60 (t, J = 7.1 Hz, 2 H), 4.01 (s, 3 H), 6.39 (s, 1 H), 7.44–7.49 (m, 1 H), 7.56–7.62 (m, 1 H), 8.15–8.20 (m, 2 H); MS (EI) m/z (rel intensity) 290 (M + 2, 35), 288 (M, 72), 273 (27), 245 (98), 230 (61), 167 (21), 152 (52), 139 (72), 89 (25), 76 (51), 69 (39), 63 (59), 55 (100); HRMS calcd for $C_{17}H_{17}ClO_2$ 288.0917, found 288.0900. Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.81; H, 5.98. Found: C, 70.96; H, 5.98.

4-(1-Hexynyl)-4-hydroxy-3-methoxy-2-methyl-2-cyclobuten-1-one (37). The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from 1-hexyne and n-butyllithium as the anion and 3-methyl-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) yielded 0.59 g (89%) of **37** as a colorless oil: IR (film) 3350, 2980, 2950, 2880, 2240, 1750, 1660, 1540, 1380, 1340, 1140, 980 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.0 Hz, 3 H), 1.35–1.53 (m, 4 H), 1.69 (s, 3 H), 2.27 (t, J = 6.0 Hz, 2 H), 4.23 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.98 (CH_3), 13.2 (CH_3), 18.3 (CH_2), 21.6 (CH_2), 30.0 (CH_2), 59.3 (CH_3), 74.2 (C), 82.3 (C), 90.7 (C), 124.2 (C), 181.5 (C), 188.7 (C) (carbon editing based on DEPT data); MS (CI) m/z 209 (MH^+); MS (EI) m/z (rel intensity) 208 (39), 193 (11), 179 (74), 166 (36), 151 (29), 137 (36), 123 (45), 109 (32), 99 (19), 95 (25), 91 (33), 83

(100), 79 (39), 67 (77), 55 (54), 43 (78); exact mass calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1095.

4-Chloro-2-(1-hexynyl)-4-methyl-3-methoxy-2-cyclobuten-1-one (38). Following the procedure described for the synthesis of **10**, 200 mg of **37** was converted to 142 mg (65%) of **38** as a clear light yellow oil: IR (film) 2960, 2940, 2880, 2860, 2230, 1795, 1625, 1460, 1370, 1270, 1115, 1065, 960, 720, 660, 640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.36–1.55 (m, 4 H), 1.77 (s, 3 H), 2.35 (t, J = 6.9 Hz, 2 H), 4.39 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.3 (CH_3), 18.9 (CH_2), 21.4 (CH_3), 21.7 (CH_2), 30.0 (CH_2), 61.0 (CH_3), 66.5 (C), 78.2 (C), 96.1 (C), 105.6 (C), 181.3 (C), 182.8 (C) (carbon editing based on DEPT data); MS (CI) m/z 227 (MH^+); MS (EI) m/z (rel intensity) 228 (M + 2, 10), 227 (4), 226 (32), 191 (8), 163 (100), 156 (4), 131 (2), 115 (3), 105 (11), 91 (17), 77 (21), 63 (10), 51 (12); exact mass calcd for $C_{12}H_{15}ClO_2$ 226.0761, found 226.0752.

4-Hydroxy-3-methoxy-4-phenyl-2-[1-(4-trifluoromethyl)-phenyl]-2-cyclobuten-1-one (39). The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-methoxy-4-(1-(4-trifluoromethyl)phenyl]-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (3:1 Hex–EtOAc) gave 0.138 g (47%) of **39** as a sticky yellow oil: IR ($CHCl_3$) 3360, 1740, 1630, 1610, 1515, 1495, 1460, 1450, 1370, 1340, 1330, 1170, 1130, 1065, 1010, 900, 850, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.09 (s, 3 H), 7.35–7.43 (m, 3 H), 7.51–7.54 (m, 2 H), 7.60 (d, J = 8.3 Hz, 2 H), 7.86 (d, J = 8.2 Hz, 2 H); MS (EI) m/z (rel intensity) 334 (10), 273 (3), 246 (6), 205 (4), 197 (9), 157 (5), 105 (100), 77 (80); HRMS calcd for $C_{18}H_{13}F_3O_3$ 334.0817, found 334.0818.

4-Hydroxy-3-methoxy-2-phenyl-4-[1-(4-trifluoromethyl)-phenyl]-2-cyclobuten-1-one (40). The procedure described for the synthesis of **8** was followed using the aryllithium generated from *p*-bromobenzotrifluoride and *n*-BuLi as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) provided a white solid. The solid was recrystallized from CH_2Cl_2/hexanes to give 0.424 g (57%) of **40** as white crystals: mp 140–143 °C; IR ($CHCl_3$) 3300, 1775, 1630, 1595, 1450, 1390, 1370, 1320, 1170, 1110, 1070, 970, 870, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (s, 3 H), 4.21 (s, 1 H), 7.33–7.41 (m, 3 H), 7.67 (s, 4 H0, 7.64–7.80 (m, 2 H); MS (CI), 335 (MH^+); MS (EI) m/z (rel intensity) 334 (10), 306 (6), 275 (6), 246 (17), 173 (72), 165 (19), 145 (89), 129 (100), 118 (51), 105 (28), 89 (84), 75 (42), 63 (59); HRMS calcd for $C_{18}H_{13}F_3O_3$ 334.0817, found 334.0843. Anal. Calcd for $C_{18}H_{13}F_3O_3$: C, 64.67; H, 3.92. Found: C, 64.47; H, 3.75.

1-Chloro-4-hydroxy-2-methoxy-3-[1-(4-trifluoromethyl)-phenyl]naphthalene (43) and 1-Chloro-4-hydroxy-2-methoxy-3-phenyl-6-(trifluoromethyl)naphthalene (44). Following the procedure described for the synthesis of **10**, 270 mg of **39** was converted to a pale yellow oil which was taken into 120 mL of freshly distilled *p*-xylene. The solution was heated at reflux for 4.5 h. Removal of the xylene gave an orange oil. Analysis of the crude ^1H NMR revealed a 2:1 mixture of products. The oil was purified by chromatography (30:1 Hex–EtOAc) to yield 141 mg (50%) of **43** and 60 mg (21%) of **44**. Compound **43**: white solid, mp 124–126 °C; IR ($CHCl_3$) 3560, 3010, 2940, 1630, 1620, 1600, 1500, 1410, 1390, 1330, 1295, 1280, 1190, 1140, 1080, 1075, 1055, 1030, 990, 925, 870, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.55 (s, 3 H), 5.45 (s, 1 H), 7.53 (t, J = 7.9 Hz, 1 H), 7.64–7.69 (m, 3 H), 7.84 (d, J = 8.5 Hz, 2 H), 8.24–8.27 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.85, 115.53, 117.14, 112.36, 122.77, 122.84, 123.89, 125.43, 126.33, 126.35, 128.34, 131.37, 131.56, 136.14, 148.08, 151.20; MS (EI) m/z (rel intensity) 354 (M + 2, 50), 352 (100), 333 (5), 302 (9), 289 (42), 273 (19), 257 (14), 145 (11), 225 (30), 205 (15), 189 (14), 176 (49), 151 (9), 127 (13), 113 (29), 88 (26), 75 (23), 69 (78), 58 (30); HRMS calcd for $C_{18}H_{12}ClO_2F_3$ 352.0478, found 352.0463. Compound **44**: slightly yellow solid, mp 115–118 °C; IR ($CHCl_3$) 3540, 3020, 2940, 1635, 1610, 1470, 1435, 1390, 1320, 1290, 1195, 1170, 1130, 1100, 990, 930, 910, 830, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 3 H), 5.74 (s, 1 H), 7.46–7.62 (m, 5 H), 7.77 (dd, J = 9.0, 3.0 Hz, 1 H), 8.34 (d, J = 9.0 Hz, 1 H), 8.56 (s, 1 H); MS (EI) 354 (M + 2, 45), 352 (100), 309 (16), 273 (45), 257 (27), 245 (28), 225 (25), 205 (18), 189 (19), 176 (42), 168 (16), 151 (14), 137 (17), 123 (17), 98 (23), 77 (33), 69 (64); HRMS calcd for $C_{18}H_{12}ClO_2F_3$ 352.0478, found 352.0463. Anal. Calcd for $C_{18}H_{12}ClO_2F_3$: C, 61.29; H, 3.43. Found: C, 61.23; H, 3.27.

3-Methoxy-4-methyl-2-phenyl-4-(phenylthio)-2-cyclobuten-1-one (45). A solution of 98 mg (0.44 mmol) of **30b**, 0.067 mL (0.66 mmol) of thiophenol, and 0.15 mL (1.1 mmol) of triethylamine in 5 mL of diethyl ether was stirred at ambient temperature for 10 h. The white suspension obtained was filtered through a pad of alumina. Removal of the volatiles afforded a white paste which was recrystallized from ether/hexanes to give 84 mg (65%) of **45** as white crystals: mp 80–82 °C; IR ($CHCl_3$) 3060, 3010, 2960, 1765, 1630, 1600, 1500, 1450, 1380, 1360, 1340, 1150, 1100, 1070, 990, 860, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3 H), 4.38 (s, 3 H), 7.18–7.26 (m, 6 H), 7.36–7.39 (m, 2 H), 7.47–7.51 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3 (CH_3), 59.4 (CH_3), 71.5 (C), 121.9 (C), 126.7 (CH), 127.5 (CH), 128.0 (C), 128.1 (CH), 128.7 (CH), 129.2 (CH), 130.0 (C), 136.1 (CH), 177.7 (C), 185.6 (C); MS (EI) m/z (rel intensity) 296 (10), 187 (40), 159 (100), 115 (29), 89 (6), 77 (8), 59 (15); exact mass calcd for $C_{18}H_{16}SO_2$ 296.0871, found 296.0854. Anal. Calcd for $C_{18}H_{16}SO_2$: C, 72.95; H, 5.44. Found: C, 73.19; H, 5.57.

2,4-Diphenyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one. The procedure described for the synthesis of **8** was followed using phenyllithium as the anion and 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione as the electrophile. Purification by chromatography (3:1 Hex–EtOAc) yielded a slightly yellow solid. Trituration with hexanes afforded 0.284 g (80%) of the title compound as a white solid: mp 135–139 °C; IR ($CHCl_3$) 3350, 3080, 3020, 1750, 1640, 1600, 1500, 1460, 1455, 1370, 1340, 1320, 1070, 1010, 900, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 1 H), 4.05 (s, 3 H), 7.31–7.43 (m, 6 H), 7.53–7.56 (m, 2 H), 7.77–7.81 (m, 2 H); MS (EI) m/z (rel intensity) 266 (21), 251 (4), 205 (9), 178 (19), 161 (7), 129 (24), 118 (13), 105 (100), 89 (30), 77 (97), 63 (18), 57 (7); exact mass calcd for $C_{17}H_{14}O_3$ 266.0943, found 266.0924. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.66; H, 5.30. Found: C, 76.38; H, 5.34.

4-Chloro-2,4-diphenyl-3-methoxy-2-cyclobuten-1-one (46). Following the procedure described for the synthesis of **10**, 159 mg of 2,4-diphenyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one was converted to 126 mg (74%) of **46** as a slightly yellow oil: IR (film) 3060, 1770, 1640, 1600, 1500, 1450, 1370, 1340, 1320, 1045, 1020, 870, 775, 760, 730, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.20 (s, 3 H), 7.34–7.44 (m, 6 H), 7.59–7.62 (m, 2 H), 7.80–7.82 (m, 2 H); MS (EI) m/z (rel intensity) 286 (M + 2, 16), 284 (34), 266 (4), 249 (10), 225 (20), 221 (32), 205 (11), 189 (22), 178 (47), 149 (11), 129 (9), 105 (37), 94 (33), 89 (100), 76 (49), 63 (42); exact mass calcd for $C_{17}H_{13}ClO_2$ 284.0604, found 284.0591.

3-Methoxy-2,4-diphenyl-4-(phenylthio)-2-cyclobuten-1-one (47). Following the procedure described for the synthesis of **45**, 180 mg of **46** was converted to 154 mg (68%) of **47** as a white solid: mp 111–113 °C; IR ($CHCl_3$) 3060, 3000, 1760, 1630, 1600, 1500, 1450, 1360, 1330, 1315, 1135, 1070, 1050, 1020, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.26 (s, 3 H), 7.17–7.46 (m, 11 H), 7.57–7.68 (m, 4 H); MS (EI) m/z (rel intensity) 358 (7), 249 (51), 222 (17), 221 (100), 189 (11), 178 (42), 165 (8), 152 (7), 139 (3), 121 (20), 105 (9), 89 (9), 77 (23), 65 (11), 50 (39); exact mass calcd for $C_{23}H_{18}SO_2$ 358.1027, found 358.1030. Anal. Calcd for $C_{23}H_{18}SO_2$: C, 77.07; H, 5.07. Found: C, 76.77; H, 4.93.

1-Hydroxy-3-methoxy-2-phenyl-4-(phenylthio)-naphthalene (48). Following the procedure described for the synthesis of **12**, 105 mg of **47** was thermolyzed to give a clear oil. Purification by chromatography (20:1 Hex–EtOAc) yielded 90 mg (86%) of **48** as a waxy solid: IR ($CHCl_3$) 3540, 3070, 3010, 2940, 1620, 1585, 1560, 1495, 1480, 1415, 1380, 1295, 1275, 1095, 910, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.43 (s, 3 H), 5.86 (s, 1 H), 7.03–7.06 (m, 3 H), 7.13–7.18 (m, 2 H), 7.46–7.60 (m, 7 H), 8.43 (d, J = 8.3 Hz, 1 H), 8.47 (d, J = 8.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 61.5, 111.3, 118.4, 122.5, 122.9, 124.6, 124.9, 125.8, 125.9, 128.2, 128.5, 128.7, 129.5, 130.7, 132.3, 135.8, 139.1, 151.4, 159.6; MS (EI) m/z (rel intensity) 360 (M + 2, 6), 359 (M + 1, 22), 358 (100), 315 (23), 265 (9), 253 (7), 248 (4), 237 (48), 221 (15), 205 (54), 189 (28), 176 (87), 165 (69), 151 (34), 121 (20), 105 (22), 91 (16), 77 (64); exact mass calcd for $C_{23}H_{18}SO_2$ 358.1027, found 358.1030.

4-Isopropoxy-3-methoxy-2,4-diphenyl-2-cyclobuten-1-one (49). A solution of 0.130 g (0.457 mmol) of **46** and 0.30 g (1.3 mmol) of Ag_2O in 10 mL of isopropyl alcohol was stirred at ambient temperature for 12 h. The reaction mixture was then filtered through a pad of Celite. The Celite was rinsed with 20

mL of diethyl ether. Concentration gave a slightly yellow oil which was purified by chromatography (20:1 Hex–EtOAc) to afford 107 mg (76%) of **49** as a colorless clear oil: IR (film) 3060, 2980, 2940, 1760, 1640, 1600, 1500, 1450, 1370, 1360, 1320, 1185, 1100, 1070, 1015, 990, 770, 750, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (d, J = 6.0 Hz, 3 H), 1.37 (d, J = 6.0 Hz, 3 H), 4.04 (s, 3 H), 4.24 (septet, J = 6.0 Hz, 1 H), 7.29–7.43 (m, 6 H), 7.51–7.54 (m, 2 H), 7.85–7.88 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.6, 23.9, 60.1, 68.2, 98.7, 125.6, 127.0, 127.6, 128.1, 128.2, 128.4, 128.5, 128.5, 137.1, 179.8, 187.4; MS (CI), 309 (MH^+); MS (EI) m/z (rel intensity) 308 (1), 266 (36), 265 (30), 233 (2), 223 (2), 221 (4), 205 (3), 194 (12), 178 (14), 166 (4), 165 (7), 145 (2), 129 (6), 106 (8), 105 (100), 89 (17), 77 (56), 51 (15); exact mass calcd for $C_{20}H_{20}O_3$ 308.1412, found 308.1428.

1-Hydroxy-4-isopropoxy-3-methoxy-2-phenylnaphthalene (50). Following the procedure described for the synthesis of **12**, 90 mg of **49** was thermolyzed to give a yellow oil. Purification by chromatography (20:1 Hex–EtOAc) afforded 78 mg (86%) of **50** as a colorless clear oil: IR (film) 3550, 2980, 2940, 1630, 1600, 1500, 1460, 1450, 1420, 1385, 1300, 1285, 1215, 1110, 1070, 1050, 1020, 950, 770, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.37 (d, J = 6.3 Hz, 6 H), 3.69 (s, 3 H), 4.61 (septet, J = 6.3 Hz, 1 H), 5.35 (s, 1 H), 7.40–7.60 (m, 7 H), 8.14 (d, J = 8.7 Hz, 1 H), 8.17 (d, J = 9.3 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8 (CH_3), 60.4 (CH_3), 75.6 (CH), 118.2 (C), 121.4 (C), 122.1 (CH), 122.2 (CH), 124.4 (CH), 126.3 (CH), 128.2 (CH), 129.3 (CH), 130.3 (C), 130.6 (CH), 132.8 (C), 138.4 (C), 144.5 (C), 146.9 (C); MS (EI) m/z (rel intensity) 309 (M + 1, 6), 308 (M, 32), 267 (15), 266 (81), 265 (61), 251 (19), 237 (13), 233 (100), 222 (12), 205 (63), 189 (12), 177 (29), 176 (59), 164 (15), 163 (13), 152 (10), 151 (19), 129 (15), 105 (51), 89 (25), 82 (17), 77 (57), 76 (37), 63 (16), 51 (21); exact mass calcd for $C_{20}H_{20}O_3$ 308.1412, found 308.1409.

4-Hydroxy-3-methoxy-2,4-di-1-pentynyl-2-cyclobuten-1-one (51). The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from 1-pentyne and n-butyllithium as the anion and 3-methoxy-4-(1-pentynyl)-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (3:1 Hex–EtOAc) gave 0.37 g (87%) of **51** as a golden oil: IR (film) 3400, 2970, 2940, 2880, 2240, 1770, 1620, 1465, 1360, 1170, 1070, 990 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.4 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.50–1.60 (m, 4 H), 2.24 (t, J = 7.2 Hz, 2 H), 2.32 (t, J = 7.2 Hz, 2 H), 2.87 (s, 1 H), 4.36 (s, 3 H); MS (EI) m/z (rel intensity) 246 (10), 231 (3), 217 (8), 203 (13), 189 (18), 175 (14), 161 (14), 147 (13), 128 (32), 115 (35), 105 (29), 95 (49), 91 (53), 77 (100), 67 (68), 53 (94); HRMS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1244.

4-Chloro-2,4-di-1-pentynyl-3-methoxy-2-cyclobuten-1-one (52). Following the procedure described for the synthesis of **10**, 90 mg of **51** was converted to 74 mg (81%) of **52** as an orange oil: IR (film) 2980, 2940, 2880, 2240, 1795, 1625, 1460, 1370, 985, 670, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3 H), 0.97 (t, J = 7.3 Hz, 3 H), 1.53–1.61 (m, 4 H), 2.27 (t, J = 6.9 Hz, 2 H), 2.34 (t, J = 6.9 Hz, 2 H), 4.42 (s, 3 H); MS (EI) m/z (rel intensity) 266 (M + 2, 3), 264 (M, 10), 235 (5), 229 (12), 201 (34), 185 (12), 157 (15), 141 (34), 128 (83), 115 (74), 99 (22), 87 (37), 77 (100), 63 (40); HRMS calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0908.

6-Chloro-8-(1-pentynyl)-7-methoxy-1,2,3,4-tetrahydro-1-oxonaphthalene (56) and 8-Chloro-7-methoxy-5-oxo-6-(1-pentynyl)spiro[3.5]-6,8-nonadiene (57). A solution of 250 mg of **52** in 200 mL of freshly distilled benzene was heated at reflux for 3 h. During the thermolysis, the originally light yellow solution turned golden. Removal of the solvent resulted in a golden oil which was chromatographed (30:1 Hex–EtOAc) to give 91 mg (36%) of **56** and 32 mg (13%) of **57**. Compound **56** (colorless oil): IR (film) 2980, 2960, 2880, 2240, 1570, 1470, 1435, 1385, 1350, 1275, 1265, 1220, 1110, 1090, 1030, 1005, 960, 940, 890, 800, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, J = 7.2 Hz, 3 H), 1.68 (sextet, J = 7.2 Hz, 2 H), 1.95–2.01 (m, 2 H), 2.51 (t, J = 7.2 Hz, 2 H), 2.69 (t, J = 6.6 Hz, 2 H), 3.91 (s, 3 H), 4.26 (t, J = 5.1 Hz, 2 H), 6.96 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 13.4, 21.6, 21.9, 22.1, 24.4, 60.6, 67.0, 72.0, 99.7, 108.2, 118.2, 118.7, 129.2, 154.8, 155.8; MS (EI) m/z (rel intensity) 266 (M + 2, 32), 264 (100), 249 (5), 235 (12), 221 (25), 207 (46), 193 (14), 172 (7), 157 (5), 141 (7), 128 (23), 115 (37), 101 (14), 87 (11), 77 (30), 63 (23), 55 (25). HRMS calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0917. Compound **57** (yellow solid): mp 38–40 °C; IR ($CHCl_3$) 3020, 2980, 2950, 2880, 1670, 1560, 1460, 1355, 1295, 1010, 860, 800 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, J = 7.5 Hz, 3 H), 1.63 (sextet, J = 7.2 Hz, 2 H), 2.02–2.20 (m, 4 H), 2.45 (t, J = 6.9 Hz, 2 H), 2.63–2.70 (m, 2 H), 4.37 (s, 3 H), 6.90 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6 (CH_3), 15.2 (CH_2), 21.9 (CH_2), 22.0 (CH_2), 32.7 (CH_2), 51.8 (C), 60.7 (CH_3), 72.5 (C), 100.9 (C), 103.2 (C), 123.7 (C), 140.4 (CH), 165.4 (C), 198.9 (C=O) (peak assignment based on DEPT data); MS (EI) m/z (rel intensity 266 (M + 2, 12), 264 (27), 249 (9), 235 (19), 221 (10), 207 (22), 201 (64), 193 (29), 185 (12), 171 (11), 157 (12), 149 (9), 141 (18), 128 (48), 115 (67), 101 (25), 87 (22), 77 (70), 63 (51). HRMS calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0911.

2,4-Di-1-hexynyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one. The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from 1-hexyne and n-butyllithium as the anion and 3-(1-hexynyl)-4-methoxy-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) afforded 0.305 g (88%) of the title compound as a golden oil: IR (film) 2960, 2940, 2880, 2240, 1775, 1620, 1460, 1360, 1160, 1110, 1070, 1040, 980 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3 H), 0.91 (t, J = 7.2 Hz, 3 H), 1.34–1.55 (m, 8 H), 2.26 (t, J = 6.9 Hz, 2 H), 2.35 (t, J = 6.9 Hz, 2 H), 4.36 (s, 3 H); MS (CI) m/z 275 (MH^+); MS (EI) m/z (rel intensity) 274 (9), 233 (10), 217 (11), 203 (11), 189 (22), 175 (14), 161 (13), 147 (14), 128 (17), 115 (26), 91 (50), 79 (100); HRMS calcd for $C_{17}H_{12}O_3$ 274.1569, found 274.1563.

4-Chloro-2,4-di-1-hexynyl-3-methoxy-2-cyclobuten-1-one (58). Following the procedure described for the synthesis of **10**, 0.260 g of 2,4-di-1-hexynyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one was converted to 0.233 g (84%) of **58** as an orange oil: IR (film) 2960, 2930, 2860, 2220, 1790, 1620, 1450, 1430, 1360, 1320, 1270, 1140, 1100, 970, 880, 790, 670, 640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3 H), 0.91 (t, J = 7.2 Hz, 3 H), 1.36–1.60 (m, 8 H), 2.29 (t, J = 7.2 Hz, 2 H), 2.36 (t, J = 6.9 Hz, 2 H), 4.41 (s, 3 H); MS (CI) m/z 293 (MH^+); MS (EI) m/z (rel intensity) 294 (M + 2, 14), 292 (M, 26), 257 (17), 251 (15), 229 (28), 207 (23), 199 (18), 187 (19), 171 (19), 155 (28), 141 (33), 128 (72), 115 (86), 91 (68), 81 (92), 77 (100); HRMS calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1225.

6-[1′-(3′-Butenyl)]-4-chloro-2-(1-hexynyl)-3-methoxyphenol (61), 6-[1′-(2′-Butenyl)]-4-chloro-2-(1-hexynyl)-3-methoxyphenol (62), 8-Chloro-6-(1-hexynyl)-7-methoxy-1-methyl-5-oxospiro[3.5]-6,8-nonadiene (63), and 6-Chloro-8-(1-hexynyl)-7-methoxy-2-methyl-1,2,3,4-tetrahydro-1-oxonaphthalene (64). Following the procedure described for the thermolysis of **52**, 250 mg of **58** was thermolyzed to afford, after purification, 49 mg (20%) of a mixture of **61** and **62**, 29 mg (12%) of **63**, and 65 mg (26%) of **64**. Compounds **61** and **62** (slightly yellow oil): IR (film) 3500, 2970, 2940, 2880, 2230, 1480, 1430, 1340, 1210, 1115, 1095, 1070, 975, 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.5 Hz, 3 H), 0.97 (t, J = 7.3 Hz, 3 H), 1.48–1.67 (m, 8 H), 1.69 (d, J = 4.6 Hz, 3 H), 2.33 (q, J = 7.5 Hz, 2 H), 2.54 (t, J = 6.9 Hz, 2 H), 2.55 (t, J = 6.9 Hz, 2 H), 2.62–2.67 (m, 2 H), 3.25 (d, J = 4.5 Hz, 2 H), 3.915 (s, 3 H), 3.919 (s, 3 H), 4.97–5.08 (m, 2 H), 5.53–5.56 (m 2 H), 5.79–5.93 (m, 1 H), 5.89 (s, 1 H), 5.90 (s, 1 H), 7.04 (s, 2 H); MS (EI) m/z (rel intensity) 294 (M + 2, 11), 292 (23), 235 (4), 221 (3), 209 (9), 193 (15), 183 (17), 153 (8), 141 (7), 128 (12), 115 (23), 101 (10), 91 (15), 81 (56), 77 (24), 55 (100); HRMS calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1225. Compound **63** (yellow oil): IR (film) 2970, 2880, 2240, 1660, 1560, 1460, 1360, 1300, 1060, 1040, 1020, 975, 820 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3 H), 0.94 (d, J = 7.1 Hz, 3 H), 1.41–1.49 (m, 2 H), 1.56–1.63 (m, 2 H), 1.78–1.89 (m, 2 H), 2.14–2.20 (m, 1 H), 2.47 (t, J = 6.9 Hz, 2 H), 2.57–2.64 (m, 1 H), 3.00 (sextet, J = 6.9 Hz, 1 H), 4.37 (s, 3 H), 6.87 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6 (CH_3), 17.9 (CH_3), 19.7 (CH_2), 22.1 (CH_2), 23.7 (CH_2), 28.6 (CH_2), 30.5 (CH_2), 43.9 (CH), 56.6 (C), 60.7 (CH_3), 72.4 (C), 101.0 (C), 103.4 (C), 124.8 (C), 138.4 (CH), 165.2 (C), 198.6 (C=O) (peak assignment based on DEPT data); MS (EI) m/z (rel intensity) 294 (M + 2, 4), 292 (14), 277 (4), 251 (15), 235 (24), 208 (29), 193 (50), 169 (16), 128 (31), 115 (65), 91 (23), 81 (46), 63 (36), 55 (100); HRMS calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1213. Compound **64** (white solid): mp 44–45 °C; IR ($CHCl_3$) 3020, 2960, 2940, 2880, 2240, 1570, 1470, 1440, 1430, 1420, 1390, 1350, 1260, 1230, 1120, 1070, 990, 910, 880, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3 H), 1.44

(d, J = 6.3 Hz, 3 H), 1.50–1.75 (m, 5 H), 1.93–2.02 (m, 1 H), 2.53 (t, J = 6.9 Hz, 2 H), 2.61–2.83 (m, 2 H), 3.90 (s, 3 H), 4.13–4.24 (m, 1 H), 6.96 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 19.6, 21.0, 21.8, 24.4, 28.5, 30.7, 60.7, 72.0, 72.9, 99.9, 108.2, 118.0, 118.4, 128.9, 155.2, 155.7; MS (EI) m/z (rel intensity) 294 (M + 2, 7), 292 (15), 251 (9) 235 (12), 221 (7), 207 (14), 193 (17), 183 (8), 169 (6), 153 (6), 141 (8), 128 (20), 115 (51), 101 (20), 91 (20), 77 (34), 63 (31); HRMS calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1209. Anal. Calcd for $C_{17}H_{21}ClO_2$: C, 69.73; H, 7.23. Found: C, 69.94; H, 7.43.

2,4-Bis(3-methyl-1-pentynyl)-4-hydroxy-3-methoxy-2-cyclobuten-1-one. The procedure described for the synthesis of **8** was followed using the lithium acetylide generated from 3-methyl-1-pentyne and n-butyllithium as the anion and 3-methoxy-4-(3-methyl-1-pentynyl)-3-cyclobutene-1,2-dione as the electrophile. Purification by flash chromatography (4:1 Hex–EtOAc) gave 0.322 g (90%, the ^{1}H NMR spectrum showed purity greater than 90%) of the title compound as an orange oil: IR (film) 3380, 2980, 2940, 2880, 2240, 1770, 1620, 1460, 1360, 1140, 980, 900, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.16 (d, J = 7.2 Hz, 3 H), 1.18 (d, J = 7.0 Hz, 3 H), 1.43–1.56 (m, 4 H), 2.44 (sextet, J = 6.9 Hz, 1 H), 2.53 (sextet, J = 6.9 Hz, 1 H), 2.70 (s, 1 H), 4.36 (s, 3 H); MS (CI), 275 (MH^+); MS (EI) m/z (rel intensity) 274 (2), 259 (2), 245 (2), 231 (2), 217 (4), 189 (2), 159 (3), 141 (5), 128 (9), 115 (15), 105 (11), 91 (32), 77 (55), 65 (35), 53 (100); exact mass calcd for $C_{17}H_{22}O_3$ 274.1569, found 274.1569.

2,4-Bis(3-methyl-1-pentynyl)-4-chloro-3-methoxy-2-cyclobuten-1-one (65). Following the procedure described for the synthesis of **10**, 0.320 g of 2,4-bis(3-methyl-1-pentynyl)-4-hydroxy-3-methoxy-2-cyclobuten-1-one was converted to 0.298 g (87%) of **65** as a yellow oil: IR (film) 2980, 2940, 2880, 2230, 1810, 1790, 1630, 1460, 1370, 980, 870, 790, 670, 650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3 H), 0.99 (t, J = 7.4 Hz, 3 H), 1.16 (d, J = 7.0 Hz, 3 H), 1.19 (d, J = 7.1 Hz, 3 H), 1.43–1.55 (m, 4 H), 2.42–2.58 (m, 2 H), 4.42 (s, 3 H); MS (EI) m/z (rel intensity) 294 (M + 2, 1), 292 (M, 8), 263 (8), 257 (24), 229 (9), 213 (8), 199 (8), 185 (11), 169 (10), 155 (18), 141 (37), 128 (40), 115 (44), 105 (15), 91 (59), 77 (100), 63 (55), 55 (78); exact mass calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1234.

8-Chloro-7-methoxy-1-methyl-6-(3-methyl-1-pentynyl)-5-oxospiro[3.5]-6,8-nonadiene (67), 4-Chloro-6-ethenyl-2-(3-methyl-1-pentynyl)-3-methoxyphenol (68), and 6-[2′-(3′-Butenyl)]-4-chloro-2-(3-methyl-1-pentynyl)-3-methoxyphenol (69). Following the procedure described for the thermolysis of **52**, 180 mg of **65** was thermolyzed to give, after purification, 41 mg (23%) of **67**, 25 mg (14%) of **68**, and 20 mg (11%) of **69**. Compound **67** (yellow oil): IR (film) 2980, 2940, 2880, 2230, 1660, 1560, 1460, 1355, 1300, 1060, 1040, 85 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ, 0.95 (d, J = 6.9 Hz, 3 H), 1.05 (t, J = 6.9 Hz, 3 H), 1.24 (d, J = 7.2 Hz, 3 H), 1.55 (quintet, J = 7.2 Hz, 2 H), 1.76–1.91 (m, 2 H), 2.12–2.21 (m, 1 H), 2.55–2.69 (m, 2 H), 2.95–3.07 (m, 1 H), 4.37 (s, 3 H), 6.86 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 11.8 (CH_3), 17.9 (CH_3), 20.0 (CH_3), 23.7 (CH_2), 28.6 (CH), 28.7 (CH_2), 29.6 (CH_2), 43.7 (CH), 43.8 (CH), 56.5 (C), 60.7 (CH_3), 72.7 (C), 103.4 (C), 105.1 (C), 124.8 (C), 138.3 (CH), 169.0 (C), 198.42 (C) (carbon editing based on DEPT data); MS (EI) m/z (rel intensity) 294 (M + 2, 7), 292 (M, 23), 277 (6), 263 (20), 235 (27), 221 (33), 207 (33), 193 (15), 181 (7), 169 (7), 141 (12), 128 (29), 115 (38), 91 (19), 77 (41), 63 (30); exact mass calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1231. Compound **68** (colorless oil): IR (film) 3490, 2970, 2940, 2880, 2220, 1630, 1600, 1475, 1430, 1410, 1340, 1290, 1210, 1080, 1020, 990, 970, 915, 825 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, J = 7.5 Hz, 3 H), 1.31 (d, J = 6.9 Hz, 3 H), 1.57–1.64 (m, 2 H), 2.73 (sextet, J = 6.8 Hz, 1 H), 3.96 (s, 3 H), 5.29 (dd, J = 11.0, 1.0 Hz, 1 H), 5.72 (dd, J = 18.0, 1.0 Hz, 1 H), 6.04 (s, 1 H), 6.86 (dd, J = 17.5, 11.0 Hz, 1 H), 7.36 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8, 20.5, 28.6, 29.7, 60.8, 70.8, 106.3, 107.5, 115.1, 118.6, 120.6, 129.8, 153.1, 155.6; MS (EI) m/z (rel intensity) 266 (M + 2, 39), 264 (87), 249 (21), 237 (30), 235 (100), 222 (12), 220 (39), 128 (11), 115 (8); exact mass calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0906. Compound **69** (colorless oil): IR (film) 3500, 2980, 2940, 2880, 2230, 1640, 1610, 1480, 1430, 1340, 1325, 1210, 1070, 970, 920, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, J = 7.2 Hz, 3 H), 1.307 (d, J = 6.9 Hz, 3 H), 1.309 (d, J = 6.9 Hz, 3 H), 1.56–1.64 (m, 2 H), 2.72 (sextet, J = 6.9 Hz, 1 H), 3.79 (quintet, J = 6.9 Hz, 1 H), 3.93 (s, 3 H), 5.04–5.12 (m, 2 H), 5.93 (s, 1 H), 5.92–6.05 (m, 1 H), 7.05 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (CH_3), 18.9 (CH_3), 20.6 (CH_3), 28.6 (CH), 29.7 (CH_2), 35.9 (CH), 60.8 (CH_3), 71.1 (C), 106.0 (C), 106.9 (C), 113.6 (CH_2), 118.1 (C), 127.6 (C), 128.2 (CH), 141.5 (CH), 153.1 (C), 154.42 (C) (carbon editing based on DEP data); MS (EI) m/z (rel intensity) 294 (M + 2, 28), 292 (M, 100), 277 (33), 265 (39), 263 (78), 242 (25), 235 (16), 213 (52), 193 (24), 185 (15), 141 (14), 128 (18), 115 (25), 81 (35), 73 (34), 55 (79); exact mass calcd for $C_{17}H_{21}ClO_2$ 292.1230, found 292.1227.

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Registry No. **8**, 122745-86-2; **9**, 122745-87-3; **10**, 137394-83-3; **12**, 122745-93-1; **13**, 137394-84-4; **17**, 137394-85-5; **18**, 122745-89-5; **19**, 122745-97-5; **20**, 137394-86-6; **21**, 137394-87-7; **22**, 122745-98-6; (*E*)-**23**, 137394-88-8; (*Z*)-**23**, 137394-89-9; **24**, 137394-90-2; **25a**, 122745-88-4; **25b**, 137394-91-3; **26a**, 122745-94-2; **26b**, 137394-92-4; **27a**, 122745-95-3; **27b**, 137394-93-5; **28a**, 122745-91-9; **28b**, 102808-46-8; **28c**, 137394-94-6; **29a**, 122745-90-8; **29b**, 137394-95-7; **29c**, 137394-96-8; **30a**, 122745-99-7; **30b**, 137394-97-9; **30c**, 137394-98-0; **31a**, 122746-00-3; **31b**, 137394-99-1; **31c**, 137395-00-7; **32a**, 137433-35-3; **32b**, 137395-01-8; **32c**, 137395-02-9; **33a**, 137395-03-0; **33b**, 118041-91-1; **34a**, 137395-04-1; **34b**, 122745-92-0; **35a**, 137395-05-2; **35b**, 122746-02-5; **36a**, 137395-06-3; **36b**, 122746-03-6; **37**, 111238-88-1; **38**, 137395-07-4; **39**, 137395-08-5; **40**, 137395-09-6; **43**, 137395-10-9; **44**, 137395-11-0; **45**, 137395-12-1; **46**, 122746-04-7; **47**, 122746-07-0; **48**, 122746-08-1; **49**, 122746-05-8; **50**, 122746-06-9; **51**, 137395-13-2; **52**, 137395-14-3; **56**, 137395-15-4; **57**, 137395-16-5; **58**, 137395-17-6; **61**, 137395-18-7; **62**, 137395-19-8; **63**, 137395-20-1; **64**, 137395-21-2; **65**, 137395-22-3; **67**, 137395-23-4; **68**, 137395-24-5; **69**, 137395-25-6; PhLi, 591-51-5; PhSH, 108-98-5; vinyllithium, 917-57-7; n-butyllithium, 109-72-8; 1-hexyne, 693-02-7; phenylacetylene, 536-74-3; methyllithium, 917-54-4; p-bromobenzotrifluoride, 402-43-7; 1-pentyne, 627-19-0; 3-methyl-1-pentyne, 922-59-8; 3-ethenyl-4-methoxy-3-cyclobutene-1,2-dione, 124022-02-2; 3-methoxy-4-(2-propenyl)-3-cyclobutene-1,2-dione, 137395-26-7; 3-[(*E*)-2-buten-2-yl]-4-methoxy-3-cyclobutene-1,2-dione, 137395-27-8; 3-[(*Z*)-2-buten-2-yl]-4-methoxy-3-cyclobutene-1,2-dione, 137395-28-9; 3-(1-butyl)-4-methoxy-3-cyclobutene-1,2-dione, 102683-52-3; 3-methoxy-4-methyl-3-cyclobutene-1,2-dione, 29769-77-5; 3-(2-butyl)-4-hydroxy-3-cyclobutene-1,2-dione, 137395-29-0; 3-(1-hexynyl)-4-methoxy-3-cyclobutene-1,2-dione, 124022-03-3; 3-(phenylethynyl)-4-methoxy-3-cyclobutene-1,2-dione, 113976-82-2; 3-methoxy-4-[1-(4-trifluoromethyl)phenyl]-3-cyclobutene-1,2-dione, 137395-30-3; 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione, 711-78-4; 3-methoxy-4-(1-pentynyl)-3-cyclobutene-1,2-dione, 137395-31-4; 3-methoxy-4-(3-methyl-1-pentynyl)-3-cyclobutene-1,2-dione, 137395-32-5; 2,4-diphenyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one, 137395-33-6; 2,4-di-1-hexynyl-4-hydroxy-3-methoxy-2-cyclobuten-1-one, 137395-34-7; 2,4-bis(3-methyl-1-pentynyl)-4-hydroxy-3-methoxy-2-cyclobuten-1-one, 137395-35-8.

Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra for all compounds (121 pages). Ordering information is given on any current masthead page.