2,3-Dihalo-1-(phenylsulfonyl)-1-propenes as Versatile Reagents for the Synthesis of Annulated Furans and Cyclopentenones

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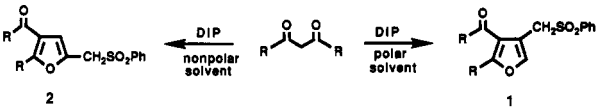
Received September 10, 1991

2,3-Dihalo-1-(phenylsulfonyl)-1-propenes (DBP and DIP) are conveniently prepared by treating 1-(phenylsulfonyl)-1,2-propadiene with the appropriate halogen. These novel reagents undergo reaction with a variety of simple β-dicarbonyl anions to give substituted and annulated furans. When the reaction is carried out in polar solvents, 2,3,4-trisubstituted furans are formed. The reaction proceeds by an initial addition–elimination of the carbanion onto the vinyl carbon of the unsaturated sulfone which is followed by intramolecular ring closure on the enolate oxygen atom. When sodium methoxide is used as the base, the initially produced adduct undergoes deacylation and subsequent cyclization to give a 2,4-disubstituted furan. The synthetic utility of the method is demonstrated by a synthesis of (*R*)-menthofuran. Treatment of DIP with various trimethylsilyl enol ethers in the presence of silver tetrafluoroborate give alkylation products derived from S_N2 displacement of the terminal halide. These compounds readily cyclize with base to produce an isomeric set of furans. Anions derived from 1,3-dicarbonyls substituted in the C-2 position are found to induce a complete reversal in the mode of ring closure. The major products obtained are 3-[(phenylsulfonyl)methyl]-substituted cyclopentenones. The internal displacement reaction leading to the furan ring apparently encounters an unfavorable $A^{1,3}$-interaction in the transition state when a substituent group is present at the 2-position of the dicarbonyl compound. This steric interaction is not present in the transition state leading to the cyclopentenone ring. An efficient synthesis of *cis*-jasmone was carried out using this methodology.

The furan nucleus, a ubiquitous structural unit in diverse classes of biologically active molecules,[1-7] can be found in a variety of commercially important pharmaceuticals,[8] flavor and fragrance compounds,[9] insect[10] and fish antifeedants,[11] as well as anti-leukemic agents.[12] Various types of sesqui- and diterpenes contain an annulated furan ring as a common structural unit.[13-15] Furthermore, furans are also useful synthetic intermediates for the preparation of a wide range of cyclic and acyclic compounds.[16] Certainly, there is no paucity in the variety or quantity of approaches by which this heterocyclic ring has been prepared.[17-39] Even though numerous synthetic routes to furans are known, single-step convergent annulation approaches still remain scarce. As described in the preceding paper, we developed an efficient route to a variety of (phenylsulfonyl)methyl-substituted furan derivatives starting from (phenylsulfonyl)allene.[40-42] As an extension of this work, we set out to investigate the scope of the methodology and its application as a means of synthesizing a variety of annulated furans and cyclopentenones. In this paper we report the results of these studies.

Results and Discussion

Furan Formation. In the previous article, 2,3-dihalo-1-(phenylsulfonyl)-1-propenes were shown to react with a variety of heteronucleophiles and carbon nucleophiles to give substituted vinyl sulfones with predictable regiochemical control.[42] In the case of carbonyl enolate adducts, the sequence could be extended to furan formation via an O-alkylative ring closure. In practice, diactivated carbonyl compounds such as β-diketones, β-keto esters, and malonates are preferable to simple ketones for use as nucleophiles, since simple enolates induced decomposition of the 2,3-dihalo sulfones. Other mechanistic considerations are also immediately evident. For example, the regiochemistry of the first step determines which furan isomer is formed. Polar solvents lead to an addition–elimination mode of attack on the vinyl carbon of DIP producing the 2,3,4-trisubstituted furan 1. When the reaction was performed



2 1

in non-polar solvents, the enolate anion selectively dis-

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‡C.L.M. is pleased to acknowledge the NIH for a postdoctoral fellowship (CA-08845-01).

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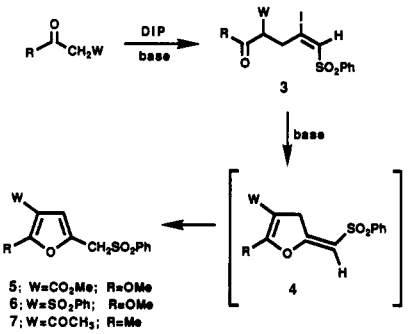
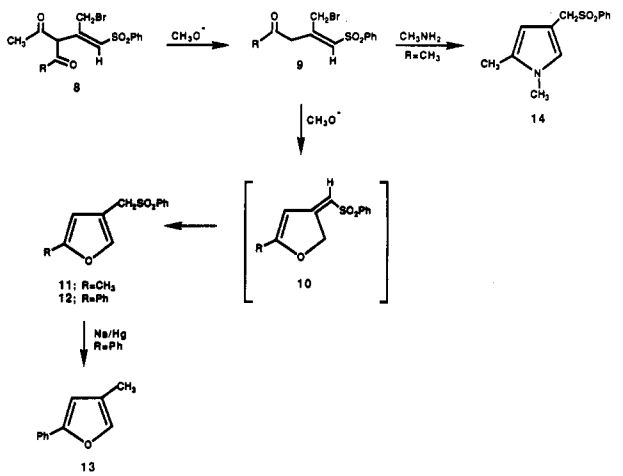
placed the allylic halide and the resulting halosulfone underwent a subsequent 5-*exo-trig* addition–elimination[43] reaction to give the 2,3,5-trisubstituted furan **2**.[44]

Formation of furans from dicarbonyl compounds and DIP (or DBP) is operationally quite straightforward. Deprotonation of the β-dicarbonyl compound was accomplished with one equivalent of sodium hydride in THF at 0 °C. After addition of DIP, the reaction mixture was allowed to stir at 0 °C for several hours before workup, which led to the smooth formation of furans **5–7**. By



carrying out the reaction for short periods of time, it was possible to isolate the halovinyl sulfones **3**. Because 2 equiv of base is required for the alkylation and cyclization, a reaction employing an equivalent mixture of base, dicarbonyl compound and dihalide led to the clean but incomplete (ca. 50%) conversion to the furan. Complete conversion to the furan could be effected by using two equivalents of the dicarbonyl carbanion. The activating functionality (W) need not be exclusively a carbonyl group. Phenylsulfonyl acetate, for example, was deprotonated and alkylated with DIP. The resulting adduct **3** was treated with potassium *tert*-butoxide in *tert*-butyl alcohol to give furan **6**.

Changing the base/solvent system to methoxide/methanol led to two remarkable alterations in the course of the reaction. First, initial alkylation took place not at the allylic position, but rather at the vinyl bromide site. Furthermore, the intermediate substituted β-dicarbonyl substrate did not immediately cyclize to the furan, but rather first underwent a base-catalyzed deacetylation (i.e. **8** → **9**). Longer exposure to sodium methoxide led to



cyclization and formation of a 2,4-disubstituted furan. In this fashion, 2,4-pentanedione was converted to furan **11** in 95% yield. Benzoylacetone also was transformed into furan **12** in 82% yield, which was desulfonylated with sodium amalgam to afford a sample of the known 2-phenyl-4-methylfuran (**13**).[45] This protocol is not limited to the preparation of furans only. Under the appropriate conditions, intermediate **9** could be modified to incorporate another heteroatom. For example, treatment of an equimolar mixture of 2,4-pentanedione and DBP with 1 equiv of methanolic sodium methoxide followed by an excess of aqueous methylamine resulted in the clean formation of pyrrole **14** in high yield.

Annulated Furan Formation. Our new methodology also proved to be amenable to the synthesis of 2,3-fused bicyclic furans. To realize this goal, we used cyclic diketones as nucleophiles. The second activating carbonyl group was either incorporated into the ring (e.g. 1,3-cyclohexanedione) or attached to the ring (e.g. 2-formylcyclohexanone). For this method, both approaches are successful, but with strikingly divergent regiochemical outcomes. Thus, treatment of DBP with 1,3-cyclohexanedione (**15**) in the presence of sodium methoxide produced tetrahydrobenzofuranone **18** in 85% yield. The initial step most likely involves O-alkylation to give **16** as a transient species,[46] which in the presence of base undergoes spontaneous cyclization and aromatization. On the other hand, treatment of DBP with the sodium salt of 2-formyl-6-methylcyclohexanone (**19**) in methanol resulted in addition and subsequent deformylation to give **20**, which produced the annulated furan **21** upon treatment with *t*-BuOK.

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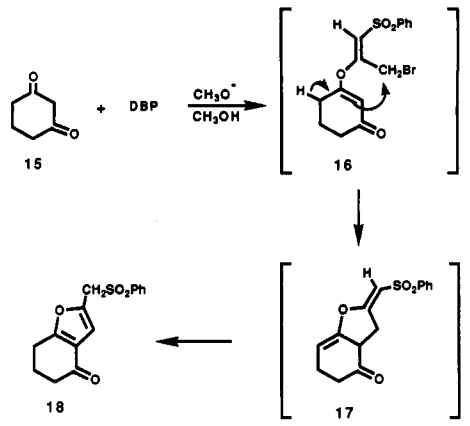
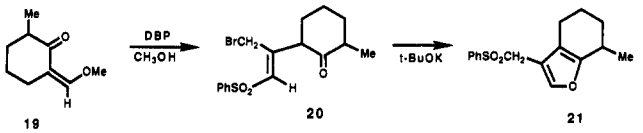
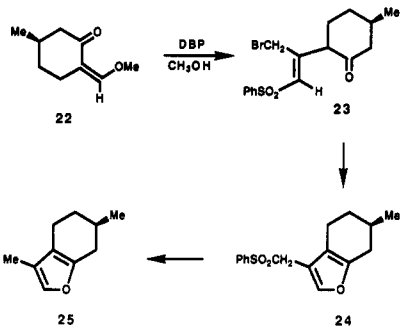


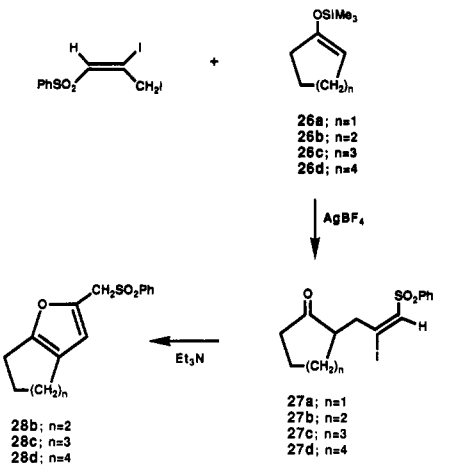
We sought to demonstrate the utility of this approach further as an entry into the vast number of 3-methyl furanoterpenoids[47] by employing DBP in the total synthesis of (*R*)-menthofuran (**25**).[48] (Phenylsulfonyl)menthofuran

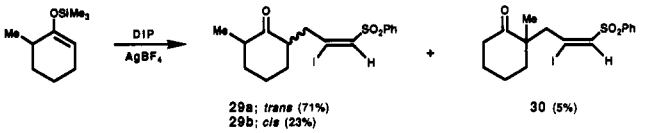




(**24**) was prepared in the same fashion as **21**, using the commercially available (*R*)-3-methylcyclohexanone. This compound was then treated with sodium amalgam to give (*R*)-menthofuran (**25**) in 85% overall yield.

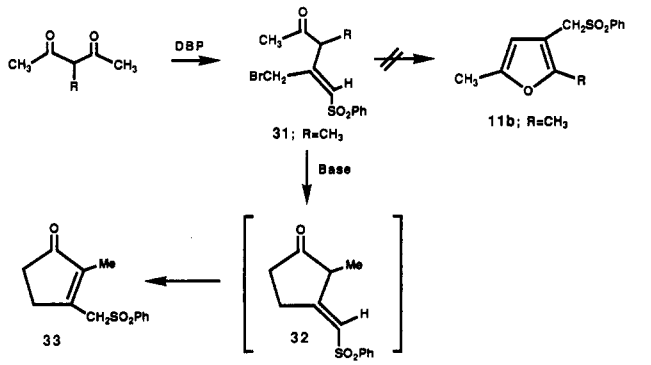
Our next goal was to explore the possibility of regiochemical crossover in this annulated series. As previously mentioned, our choice of nucleophile was limited by the action of strong base on the dihalosulfones. However, the ability to work under essentially nonbasic conditions with silyl enol ethers brought these substrates into examination. After some investigation, $AgBF_4$ was found to be the ideal reagent. Thus, treatment of DIP and **26a** at 25 °C in methylene chloride (0.05 M) with 2.0 equiv of $AgBF_4$ produced **27a** in 82% yield after chromatographic purification. A related set of reactions took place with the silyl enol ethers derived from cyclohexanone (**27b**, 71%), cycloheptanone (**27c**, 88%) and cyclooctanone (**27d**, 81%). Treatment of iodo phenylsulfonyl ketones **27b–d** with triethylamine in THF at 25 °C proceeded smoothly to give the 2-[(phenylsulfonyl)methyl]-substituted furans **28b–d** in 65%, 76%, and 86% yield, respectively. Further investigation of this reaction with the silyl enol ether derived from 2-methylcyclohexanone revealed that the alkylation occurred from the kinetically produced enolate. Thus, the major product obtained was a 71:23 mixture of the geometric isomers **29a** and **29b** with only a trace of the 2,2-dialkylated ketone **30** (<5%). The regioselectivity of





alkylation using these conditions nicely complements that encountered with β-dicarbonyl anions which gives products derived from vinyl displacement. By altering the experimental conditions, it is possible to prepare either 2,3,4-(**24**) or 2,3,5-substituted (**28**) furans.

Cyclopentenone Formation. We have shown how the regiochemistry of the initial alkylation reaction can be controlled to give a choice of substitution about the furan nucleus. But what about the regiochemistry of the ring closure itself? If closure could be induced to occur on the methyl carbon rather than the oxygen atom of the carbonyl group, the expansion of this methodology into the synthesis of carbocycles could be realized. This would provide a simple and direct route to the cyclopentenone moiety, a structural unit found in many natural products, such as the jasmonoids[49] and prostaglandins[50], and for which new routes continue to be developed.[51] *Indeed, we have found that substitution of the β-dicarbonyl compound at the C_2-position induces a complete reversal in the mode of ring closure.* Thus, treatment of DBP with 3-methyl-2,4-pentanedione in methanolic sodium methoxide produced keto sulfone **31** by the familiar addition–deacylation sequence. However, further reaction of **31** with base re-



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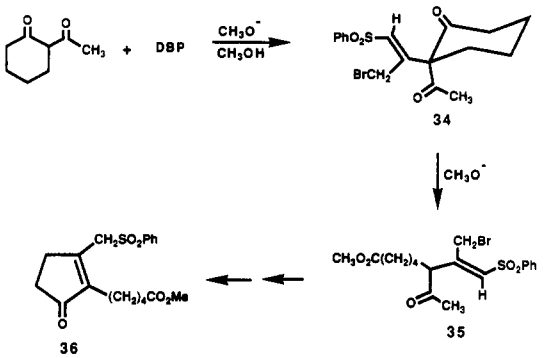
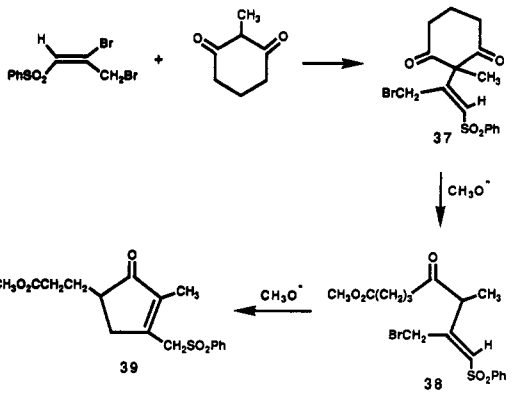
sults in cyclization not to furan **11b**, but to the substituted cyclopentenone **33**. This latter transformation proceeds by an initial cyclization producing **32** as a transient species which rapidly isomerizes to the isolated cyclopentenone.

One explanation which could account for this divergent mode of cyclization follows. When a substituent group is present (R = CH_3; **31**), the internal displacement leading to the furan ring encounters an unfavorable $A^{1,3}$-interaction in the transition state. This interaction is absent in the alternative transition state leading to the cyclopentenone ring. Though the origin of this remarkable crossover has not yet been established, its potential application in synthesis is immediately evident. The cyclopentenone nucleus is found in numerous natural products of biological and commercial importance; therefore, new methods to prepare such compounds continue to attract attention. In order to extend the generality of the above method, we sought to examine additional systems which would afford cyclopentenones with substituents in the 2- and 5-positions of the ring. Our initial efforts focused on modification of the 2-substituent. Toward this end, reaction of DBP with 2-acetylcyclohexanone using methanolic sodium methoxide as the base resulted in the formation of dione **34**. Addition of a further equivalent of base induced a ring-opening reaction, presumably as a consequence of the stability of the resultant anion,[52] giving rise to keto ester **35**. Further exposure of **35** to sodium methoxide effected ring closure to give the long-chain cyclopentenone **36** in 52% overall yield, thus demonstrating the generality of this protocol in regard to substitution at the 2-position of the cyclopentenone ring.

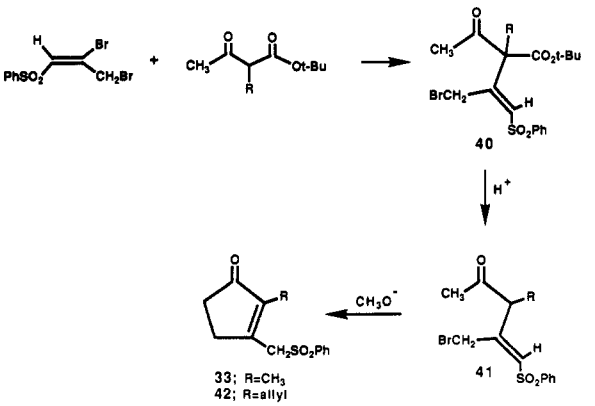


Attention next was turned toward the introduction of substituents in the 5-position of the cyclopentenone ring. A similar approach was used for this protocol. A solution of DBP and 2-methyl-1,3-cyclohexanedione in DMF was treated with an equivalent of sodium hydride at 0 °C, resulting in the formation of dione adduct **37**. This sterically compromised cyclic dione underwent facile deacylative ring opening under the methanolic sodium methoxide conditions to give the open-chain keto ester **38**. S_N2 displacement using another equivalent of sodium methoxide afforded cyclopentenone **39** in 69% overall yield.

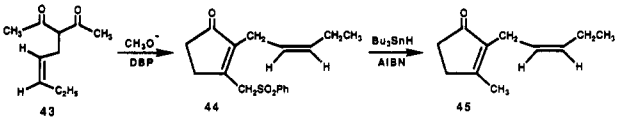
In addition to 1,3-diketones, substituted β-keto esters were employed successfully in this reaction sequence, although under a different set of experimental conditions.[53] Alkylation of the keto ester with DBP using sodium hydride in THF produced the isolable intermediate **40**, which in the case of the *tert*-butyl ester can be decarboxylated with acid to give **41**. Subjection of **41** to the basic experimental conditions described above afforded cyclo-



pentenones **33** (69%) and **42** (64%), respectively.



One of the particular strengths of the methodology lies in the convenience with which each of the substituents can be incorporated into the ring. For example, the C_2 substituent in the cyclopentenone ring may be introduced by C_2-alkylation of the initial 1,3-diketone. To demonstrate the applicability of the method to natural product synthesis, we considered *cis*-jasmone to be a particularly amenable target.[54] To carry out the synthesis, a methanolic solution of DBP and the substituted 2,4-pentanedione **43** was treated sequentially with 2 equiv of sodium methoxide to give the sulfonyl substituted cyclopentenone **44**. This vinylogous α-keto sulfone was desulfonylated according to the procedure of Smith[55] to produce *cis*-jasmone (**45**) in 72% overall yield.



The synthetic application of sulfones to the preparation of natural products has increased enormously during the past decade.[56,57] This increased interest stems in part from the recognition that sulfones can stabilize anions,[58,59] may be removed reductively,[60] and, where appropriate, may be

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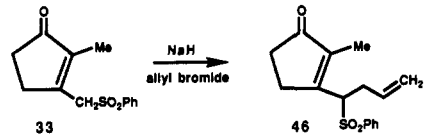
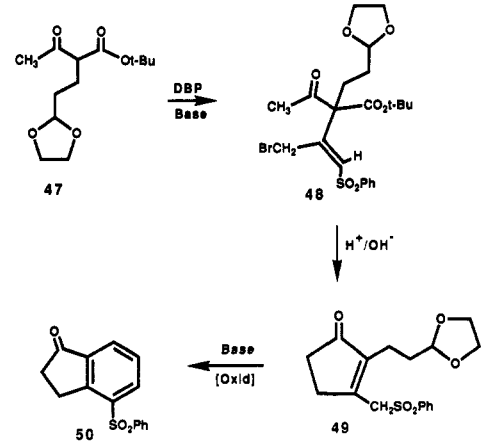
eliminated to form olefins.[61] Monometallated allyl sulfones have played a particularly important role as reactive intermediates in total synthesis.[62] We have studied the chemical behavior of the 3-[(phenylsulfonyl)methyl]-substituted cyclopentenone ring system in order to demonstrate its synthetic versatility. The pendant sulfonyl group at the C_3 position of the cyclopentenone ring offers a versatile site for further elaboration via alkylation[58] or Julia coupling.[61] Indeed, we have found that cyclopentenone **33** is easily metallated with sodium hydride. The resulting carbanion can be alkylated with allyl bromide to give sulfone **46** in good yield.



Another typical reaction of α-sulfonyl carbanions is condensation with aldehydes or ketones, followed by dehydration, to give an olefin.[62] We have carried out this process in an intramolecular fashion to prepare indenone **50**. Acetal keto ester **47** was prepared in the normal fashion and was treated with DBP to give the vinyl substituted adduct **48** in 89% yield. Decarboxylation in refluxing benzene using *p*-toluenesulfonic acid was followed by ring closure to afford acetal cyclopentenone **49**. Treatment of this material with acidic acetone induced hydrolysis of the acetal, and the transient aldehyde so formed was immediately cyclized with base to a putative dihydroindenone intermediate which undergoes an apparently rapid air oxidation to provide indenone **50** in 60% yield.



In conclusion, we have demonstrated that 2,3-dihalo-1-(phenylsulfonyl)-1-propene reacts with simple dicarbonyl enolates to give substituted and annulated furans. The use of 1,3-dicarbonyls substituted at the C_2 position with DBP induces a complete reversal in the mode of ring closure. The reaction of substituted β-diketone and β-keto ester anions with DBP provides a simple and efficient route to functionalized cyclopentenones and should be a valuable reaction in the repertoire of synthetic organic chemists. We are continuing to explore the scope, generality, and synthetic application of this versatile reagent and will report additional findings at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate–hexane mixture as the eluent unless specified otherwise.

2-Methoxy-5-[(phenylsulfonyl)methyl]-3-(phenylsulfonyl)furan (6). To a stirred solution containing 214 mg of methyl (phenylsulfonyl)acetate in 7 mL of THF at 0 °C under N_2 was added 29 mg of NaH. The resulting solution was stirred for 3 h at 0 °C and then transferred dropwise via syringe to an ice-cooled solution containing 500 mg of DIP in 2 mL of THF under N_2. After allowing the reaction to slowly warm to rt over 12 h, a saturated NH_4Cl solution was added. The mixture was concentrated under reduced pressure and partitioned between CH_2Cl_2 and water. The organic layer was washed with water, a 10% $Na_2S_2O_3$ solution, and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give methyl 2,5-bis(phenylsulfonyl)-4-iodo-4-pentenoate (**3**; W = SO_2Ph, R = CH_3O): IR (neat) 1715, 1550, 1300, 1050, and 920 cm^{-1}; ^1H-NMR ($CDCl_3$, 360 MHz) δ 3.56–3.67 (m, 2 H), 3.61 (s, 3 H), 4.38 (dd, 1 H, J = 10.3 and 4.1 Hz), 7.04 (s, 1 H), and 7.48–7.92 (m, 10 H). This material was used in the next step without further purification.

To a stirred solution containing 241 mg of **3** in 4 mL of THF under N_2 was added 67 mg of *t*-BuOK. The resulting solution was stirred for 14 h at rt. Removal of the solvent left a crude residue which was subjected to silica gel chromatography to give 94 mg (52%) of furan **6**: IR ($CHCl_3$) 1600, 1450, 1330, 1160, 795, and 690 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.89 (s, 3 H), (s, 2 H), 6.36 (s, 1 H), and 7.44–7.90 (m, 10 H); HRMS calcd for $C_{12}H_{13}O_4S_2$ ($M^+ - SO_2Ph$): 251.0378, found 251.0376.

Preparation of 2-Methyl-4-[(phenylsulfonyl)methyl]furan (11). To a solution containing 0.20 g of DBP and 0.06 mL of 2,4-pentanedione in 2.5 mL of absolute CH_3OH at 0 °C was added 1.2 mL of 0.5 N methanolic NaOMe. After stirring at 25 °C for 15 min, the reaction was quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated and the residue was extracted with CH_2Cl_2 and washed with water. The organic layer was separated, dried, concentrated, and subjected to silica gel chromatography to give 128 mg (61%) of 3-acetyl-4-(bromomethyl)-5-(phenylsulfonyl)-4-penten-2-one (**8**): IR (neat) 1610, 1400, 1310, 1155, and 1090 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 6 H), 4.20 (s, 1 H0, 4.22 (s, 2 H), 6.65 (s, 1 H), and 7.50–8.05 (m, 5 H).

A solution containing 100 mg of **8** in 1 mL of absolute methanol was cooled to 0 °C and treated with 0.10 mL of 0.5 N methanolic NaOMe. The solution was allowed to stir at 25 °C for 3 h and then was quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded 90 mg (85%) of 4-(bromomethyl)-5-(phenylsulfonyl)-4-penten-2-one (**9**) as a yellow oil: IR (neat) 1710, 1300, 1150, and 1080 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3 H), 3.64 (s, 2 H), 4.17 (s, 2 H), 6.27 (s, 1 H), and 7.50–7.95 (m, 5 H); HRMS calcd for $C_{12}H_{13}BrO_3S$ 315.9769, found 315.9771.

To a solution containing 0.18 g of **9** in 2.5 mL of THF at 0 °C was added a solution of 64 mg of *t*-BuOK in 2.5 mL of dry THF. The dark brown solution was allowed to stir at rt overnight and was then quenched with a saturated NH_4Cl solution. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer yielded a brown oily solid, which was percolated through a short silica gel column with chloroform and crystallized from ether to give 0.12 g (67%) of 2-methyl-4-[(phenylsulfonyl)methyl]furan (**11**) as a pale yellow solid: mp 91–92 °C; IR (KBr) 1450, 1290, 1135, 1095, and 760 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 3 H), 4.10 (s, 2 H), 5.91 (s, 1 H), 7.01 (s, 1 H), and 7.50–7.95 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.9, 53.0, 106.9, 112.5, 127.9, 128.3, 133.1, 137.3, 140.3, and 152.6. Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: C, 60.91, H, 5.12.

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Furan 11 was also prepared in a single step in the following fashion. To a solution containing 200 mg of DBP and 0.06 mL of 2,4-pentanedione in 2.5 mL of absolute methanol at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir for 5 h, cooled to 0 °C, and treated with an additional 1.4 mL of the NaOMe solution. The solution was allowed to stir at rt overnight and was then quenched with a saturated NH_4Cl solution. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded a brown oil which was purified by silica gel chromatography to give furan 11 in 95% yield.

2-Phenyl-4-[(phenylsulfonyl)methyl]furan (12). To a solution containing 200 mg of DBP and 100 mg of benzoylacetone in 2.5 mL of absolute methanol at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stire overnight at rt, cooled to 0 °C, and treated with an additional 1.4 mL of the NaOMe solution. This solution was allowed to stir at rt for 12 h and then quenched with a saturated NH_4Cl solution. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and washed with water. The organic layer was concentrated and subjected to silica gel chromatography to give 2-phenyl-4-[(phenylsulfonyl)methyl]furan (12) (82%): mp 117–118 °C; IR (KBr) 1450, 1310, 760, and 695 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 4.20 (s, 2 H), 6.56 (s, 1 H), 7.20 (s, 1 H), and 7.20–7.95 (m, 10 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 52.9, 105.9, 114.0, 123.2, 127.3, 128.0, 128.1, 128.4, 129.5, 133.2, 137.1, 141.4, and 154.2; HRMS calcd for $C_{17}H_{14}O_3S$ 298.0664, found 298.0679.

To an efficiently stirred suspension containing 50 mg of 12 and 0.40 g of $NaH_2PO_4 \cdot H_2O$ in 3.5 mL of methanol was added 1.5 g of 2% Na/Hg. The mixture was allowed to stir overnight at rt and then filtered. The filtrate was concentrated under reduced pressure to give 4-methyl-2-phenylfuran (13) in quantitative yield, whose spectroscopic data match those reported in the literature.[45]

1,2-Dimethyl-4-[(phenylsulfonyl)methyl]pyrrole (14). To a solution containing 0.20 g of DBP and 0.6 mL of 2,4-pentanedione in 2.5 mL of absolute MeOH at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir overnight at rt and then treated with 0.10 mL of CH_3NH_2 (40% aqueous solution). After stirring at rt for 12 h, the solution was quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated and the residue extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded 100 mg (73%) of pyrrole 14: mp 115–116 °C; IR (KBr) 1420, 1300, 1275, 1165, 1135 and 710 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 3 H), 3.42 (s, 3 H), 4.14 (s, 2 H), 5.66 (s, 1 H), 6.39 (s, 1 H), and 7.4–7.8 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 11.2, 33.0, 55.3, 106.6, 107.9, 121.6, 127.9, 128.1, 128.8, 132.7 and 138.2; HRMS calcd for $C_{13}H_{15}NO_2S$ 249.0824, found 249.0838.

4,5,6,7-Tetrahydro-2-[(phenylsulfonyl)methyl]-4(5*H*)-benzofuranone (18). To a solution containing 200 mg of DBP and 1.0 equiv of 1,3-cyclohexanedione (15) in 2.5 mL of absolute methanol at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir overnight at rt, cooled to 0 °C and treated with an additional 1.4 mL of the NaOMe solution. The resulting solution was stirred at rt for 24 h and then quenched with a saturated NH_4Cl solution. Aqueous workup and isolation using silica gel chromatography afforded tetrahydrobenzofuranone 18 as a pale yellow oil in 85% yield: IR (neat) 1680, 1450, 1250, 1160, 1090 and 740 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.10 (m, 2 H), 2.43 (t, 2 H, J = 6.5 Hz), 2.75 (t, 2 H, J = 6.5 Hz), 4.36 (s, 2 H), 6.40 (s, 1 H), and 7.40–7.85 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.7, 22.6, 36.9, 55.1, 108.0, 121.6, 127.8, 128.6, 133.5, 137.3, 142.2, 167.4, and 193.2; HRMS calcd for $C_{15}H_{14}O_4S$ 290.0613, found 290.0622.

4,5,6,7-Tetrahydro-7-methyl-3-[(phenylsulfonyl)methyl]-benzofuran (21). A solution containing 200 mg of DBP, 1.0 equiv of the preformed sodium salt of 2-formyl-6-methylcyclohexanone (19), and a catalytic amount of NaOMe in 2.5 mL of absolute methanol was allowed to stir overnight at rt. At the end of this time the solution was quenched with a saturated NH_4Cl solution. Aqueous workup and concentration under reduced pressure afforded a yellow oil which was subjected to silica gel chromatography to give 2-[1-(bromomethyl)-2-(phenylsulfonyl)ethenyl]-6-methylcyclohexanone (20) as a clear oil: IR (neat) 1720, 1455, 1330, 1090, and 700 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.02 (d, 3 H, J = 6.4 Hz), 1.30–2.35 (m, 7 H), 2.60 (m, 1 H), 3.82 (bs, 1 H), 3.89 (d, 1 H, J = 14.1 Hz), 4.37 (d, 1 H, J = 14.1 Hz), 6.23 (s, 1 H), and 7.40–7.95 (m, 5 H).

The above material was dissolved in 2.5 mL of dry THF, cooled to 0 °C, and treated with 1.0 equiv of t-BuOK. The solution was allowed to stir at rt for 5 h and was then quenched with a saturated NH_4Cl solution. Aqueous workup and isolation using silica gel chromatography afforded 100 mg (62%) of 4,5,6,7-tetrahydro-7-methyl-3-[(phenylsulfonyl)methyl]benzofuran (21): IR (KBr) 1450, 1310, 1160, 1090, and 710 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.14 (d, 3 H, J = 6.9 Hz), 1.20–2.05 (m, 6 H), 2.72 (m, 1 H), 4.06 (s, 2 H), 7.08 (s, 1 H), and 7.40–7.85 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.1, 19.7, 20.8, 28.3, 31.2, 51.9, 111.2, 116.3, 128.1, 128.3, 133.1, 137.4, 140.3, and 155.0; HRMS calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0978.

Preparation of (*R*)-Menthofuran (25). A solution containing 200 mg of DBP, 1.0 equiv of the preformed sodium salt of (5*R*)-2-formyl-5-methylcyclohexanone (22), and a catalytic amount of NaOMe in 2.5 mL of absolute methanol was allowed to stir overnight at rt and was then quenched with a saturated NH_4Cl solution. Aqueous workup and concentration under reduced pressure afforded a yellow oil which was subjected to silica gel chromatography to give (5*R*)-2-[1-(bromomethyl)-2-(phenylsulfonyl)ethenyl]-5-methylcyclohexanone (23): IR (neat) 2950, 1710, 1450, 1320, 1150, and 750 cm^{-1}; ^1H-NMR (360 MHz, $CDCl_3$) δ 0.96 (d, 3 H, J = 6.3 Hz), 1.40–2.45 (m, 7 H), 3.70 (dd, 1 H, J = 13.1 and 4.0 Hz), 3.84 (d, 1 H, J = 14.2 Hz), 4.29 (d, 1 H, J = 14.2 Hz), 6.15 (s, 1 H), and 7.40–7.55 (m, 5 H).

The above material was dissolved in 2.5 mL of dry THF, cooled to 0 °C, and treated with 1.0 equiv of t-BuOK. The solution was allowed to stir at rt for 5 h and then quenched with a saturated NH_4Cl solution. Aqueous workup and isolation using silica gel chromatography afforded 0.10 g (59%) of (5*R*)-4,5,6,7-tetrahydro-6-methyl-3-[(phenylsulfonyl)methyl]benzofuran (24): mp 115–116 °C; IR (KBr) 2930, 1440, 1400, 1300, 1180, 1140, and 760 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 0.99 (d, 3 H, J = 6.7 Hz), 1.10–2.25 (m, 6 H), 2.59 (dd, 1 H, J = 16.1 and 5.2 Hz), 4.06 (s, 2 H), 7.06 (s, 1 H), and 7.40–7.85 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.6, 20.6, 28.7, 30.3, 30.5, 51.9, 111.2, 116.4, 128.1, 128.3, 133.1, 137.4, 140.4 and 150.9; HRMS calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0973.

To an efficiently stirred suspension containing 38 mg of 24 and 0.31 g of $NaH_2PO_4 \cdot H_2O$ in 2.7 mL of methanol was added 1.5 g of 2% Na/Hg. The mixture was allowed to stir overnight at rt and then filtered in order to remove the inorganic salts. The filtrate was concentrated under reduced pressure to give (*R*)-menthofuran (25) in quantitative yield and whose spectroscopic data matched those reported in the literature.[48]

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]cyclopentanone (27a) was prepared from the silyl enol ether of cyclopentanone (82%): mp 98–99 °C; IR (KBr) 1739, 1592, 1306, 1144, 1082, and 691 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.60–1.90 (m, 2 H), 2.00–2.30 (m, 3 H), 2.30–2.52 (m, 2 H), 3.05 (dd, 1 H, J = 14.4 and 4.2 Hz), 3.46 (dd, 1 H, J = 14.4 and 9.9 Hz), 7.05 (s, 1 H), 7.50–7.70 (m, 3 H), and 7.80–8.00 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.4, 28.0, 37.6, 39.2, 49.4, 123.0, 127.4, 129.5, 133.8, 139.9, 140.3, and 217.9; m/e (relative intensity) 263 (M^+ – I, 8), 249 (28), 121 (49), and 77 (100). Anal. Calcd for $C_{14}H_{15}IO_3S$: C, 43.09; H, 3.87. Found: C, 43.11; H, 3.84.

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]cyclohexanone (27b) was prepared from the silyl enol ether of cyclohexanone (71%): mp 108–109 °C; IR (KBr) 1710, 1592, 1310, 1283, 1146, 837, and 691 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.40–1.60 (m, 1 H), 1.60–1.80 (m, 2 H), 1.90–2.00 (m, 1 H), 2.00–2.20 (m, 2 H), 2.30–2.50 (m, 2 H), 2.60–2.70 (m, 1 H), 3.05 (dd, 1 H, J = 14.7 and 3.8 Hz), 3.44 (dd, 1 H, J = 14.7 and 9.3 Hz), 7.05 (s, 1 H), 7.50–7.70 (m, 3 H), and 7.90–8.00 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.9, 27.3, 32.0, 38.8, 41.8, 50.9, 123.7, 127.4, 129.4, 133.7, 140.3, 140.7, and 209.7; m/e (relative intensity) 277 (M^+ – I, 68), 263 (14), 135 (100), 107 (21), and 77 (90). Anal. Calcd for $C_{15}H_{17}IO_3S$: C, 44.57; H, 4.23. Found: C, 44.64; H, 4.23.

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]cycloheptanone (27c) was prepared from the silyl enol ether of cycloheptanone (88%): mp 85–86 °C; IR (KBr) 1694, 1150, 1310, 1084, 724, and 683 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.30–1.57 (m, 3 H), 1.57–1.95 (m, 5 H), 2.45–2.65 (m, 2 H), 2.80–2.92 (m, 1 H), 3.07 (dd, 1 H, J = 14.7 and 5.7 Hz), 3.37 (dd, 1 H, J = 14.7

and 8.7 Hz), 7.04 (s, 1 H), 7.50–7.67 (m, 3 H), and 7.87–7.95 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.3, 28.5, 29.0, 29.6, 40.2, 42.9, 53.0, 123.6, 127.5, 129.4, 133.7, 140.2, 140.4, and 213.0; *m/e* (relative intensity) 291 (M^+ – I, 51), 149 (98), 128 (25), 107 (22), and 77 (100). Anal. Calcd for $C_{16}H_{19}IO_3S$: S, 45.94; H, 4.58. Found: C, 45.85; H, 4.60.

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]cyclooctanone (27d) was prepared from the silyl enol ether of cyclooctanone (81%): mp 68–69 °C; IR (KBr) 1702, 1596, 1310, 1152, 1084, and 745 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.10–1.30 (m, 1 H), 1.35–1.60 (m, 4 H), 1.60–2.10 (m, 5 H), 2.35–2.60 (m, 2 H), 2.90–3.05 (m, 1 H), 3.17 (dd, 1 H, *J* = 14.7 and 6.0 Hz), 3.34 (dd, 1 H, *J* = 14.7 and 7.5 Hz), 7.03 (s, 1 H), 7.50–7.70 (m, 3 H), and 7.90–8.00 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.6, 25.2, 25.7, 27.1, 30.5, 40.0, 41.8, 51.6, 122.5, 127.5, 129.4, 133.7, 139.9, 140.3, and 216.8; *m/e* (relative intensity) 305 (M^+ – I, 5), 207 (72), 143 (82), 110 (11), and 77 (100). Anal. Calcd for $C_{17}H_{21}IO_3S$: C, 47.23; H, 4.90. Found: C, 47.32; H, 4.94.

General Procedure for the Synthesis of Furans from Cycloalkanone–DIP Adducts. To a solution containing 0.4 mmol of the cycloalkanone adduct in 8 mL of THF was added 2 mL of Et_3N. The mixture was stirred at 25 °C in the dark under a N_2 atmosphere for 48 h. The solvent was removed under reduced pressure, and the residue was diluted with 20 mL of CH_2Cl_2 and then washed with 30 mL of a 5% NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed successively with 1% aqueous sodium bisulfite solution and water and then dried over $MgSO_4$. Removal of the solvent under reduced pressure, followed by silica gel chromatography, gave the pure furan whose structure was assigned on the basis of its spectral properties.

4,5,6,7-Tetrahydro-2-[(phenylsulfonyl)methyl]benzofuran (28b) was prepared from 2-[(*E*)-2-iodo-3-(phenylsulfonyl)-2-propenyl]cyclohexanone (**27b**) in 65% yield: mp 100–101 °C; IR (KBr) 1559, 1447, 1312, 1144, 1084, 971, and 727 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.60–1.70 (m, 2 H), 1.70–1.80 (m, 2 H), 2.34 (t, 2 H, *J* = 5.9 Hz), 2.41 (t, 2 H, *J* = 6.0 Hz), 4.33 (s, 2 H), 6.09 (s, 1 H), 7.45–7.55 (m, 2 H), 7.60–7.67 (m, 1 H), and 7.73–7.80 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.8, 22.7, 22.8, 22.9, 56.2, 113.1, 118.3, 128.4, 128.7, 133.6, 138.5, 139.6, and 152.3; *m/e* (relative intensity) 276 (M^+, 1), 135 (100), 105 (9), and 77 (45). Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.83. Found: C, 65.28; H, 5.89.

5,6,7,8-Tetrahydro-2-[(phenylsulfonyl)methyl]-4*H*-cyclohepta[*b*]furan (28c) was prepared from 2-[(*E*)-2-iodo-3-(phenylsulfonyl)-2-propenyl]cycloheptanone (**27c**) in 76% yield: mp 92–93°C; IR (KBr) 1561, 1447, 1310, 1289, 1148, 1086, 768, and 718 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.53–1.80 (m, 6 H), 2.38 (t, 2 H, *J* = 5.4 Hz), 2.54 (t, 2 H, *J* = 5.9 Hz), 4.29 (s, 2 H), 6.06 (s, 1 H), 7.45–7.55 (m, 2 H), 7.60–7.70 (m, 1 H), and 7.70–7.80 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.8, 26.3, 28.4, 28.6, 30.5, 56.1, 115.6, 122.3, 128.4, 128.7, 133.5, 137.3, 138.5, and 154.9; *m/e* (relative intensity) 290 (M^+, 0.3), 149 (100), 133 (12), 110 (17), 105 (14), 91 (12), and 77 (23). Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.29; H, 6.25.

4,5,6,7,8,9-Hexahydro-2-[(phenylsulfonyl)methyl]cycloocta[*b*]furan (28d) was prepared from 2-[(*E*)-2-iodo-3-(phenylsulfonyl)-2-propenyl]cyclooctanone (**27d**) in 86% yield: mp 64–65 °C; IR (KBr) 1447, 1385, 1293, 1156, 971, and 749 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.35–1.47 (m, 4 H), 1.50–1.65 (m, 4 H), 2.43 (t, 2 H, *J* = 6.3 Hz), 2.54 (t, 2 H, *J* = 6.3 Hz), 4.32 (s, 2 H), 6.04 (s, 1 H), 7.43–7.50 (m, 2 H), 7.55–7.65 (m, 1 H), and 7.67–7.75 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.4, 25.1, 25.5, 25.8, 27.2, 28.8, 56.2, 114.9, 120.0, 128.5, 128.7, 133.5, 138.26, 138.29, and 153.2; *m/e* (relative intensity) 304 (M^+, 0.4), 163 (100), 128 (6), 110 (7), 91 (6), and 77 (11). Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62. Found: C, 67.00; H, 6.64.

Reaction of (*E*)-2,3-Diiodo-1-(phenylsulfonyl)-1-propene with [(6-Methyl-1-cyclohexen-1-yl)oxy]trimethylsilane. A mixture containing 868 mg (2.0 mmol) of DIP, 737 mg (4.0 mmol) of [(6-methyl-1-cyclohexen-1-yl)oxy]trimethylsilane, and 778 mg (4.0 mmol) of $AgBF_4$ in 80 mL of CH_2Cl_2 was stirred at 25 °C for 18 h. The usual work-up gave a 3:1-mixture of *trans*- and *cis*-6-methyl-2-[(*E*)-2-iodo-3-(phenylsulfonyl)-2-propenyl]cyclohexanone (**29a** and **29b**, respectively) together with 2-methyl-2-[(*E*)-2-iodo-3-(phenylsulfonyl)-2-propenyl]cyclohexanone (**30**) (5%). Analytical samples were obtained by chromatography followed by fractional recrystallization.

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]-6-methylcyclohexanone (29a): mp 86–87 °C; IR (KBr) 1708, 1598, 1447, 1310, 1287, 1150, and 726 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.18 (d, 3 H, *J* = 7.2 Hz), 1.55–1.70 (m, 2 H), 1.75–1.85 (m, 2 H), 1.90–2.05 (m, 2 H), 2.60–2.72 (m, 1 H), 2.80–2.90 (m, 1 H), 3.16 (dd, 1 H, *J* = 14.7 and 5.1 Hz), 3.42 (dd, 1 H, *J* = 14.7 and 8.4 Hz), 7.05 (s, 1 H), 7.52–7.70 (m, 3 H), and 7.85–7.95 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 16.3, 20.0, 31.3, 33.5, 39.2, 43.8, 47.9, 123.2, 127.4, 129.4, 133.7, 140.0, 140.3, and 213.6; *m/e* (relative intensity) 291 (M^+ – I, 58), 149 (80), 125 (21), 93 (33), and 77 (100). Anal. Calcd for $C_{16}H_{19}IO_3S$: C, 45.94; H, 4.58. Found: C, 46.08; H, 4.59.

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]-6-methylcyclohexanone (29b): mp 107–108 °C; IR (KBr) 1708, 1596, 1308, 1148, and 754 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.03 (d, 3 H, *J* = 6.3 Hz), 1.30–1.55 (m, 2 H), 1.65–1.95 (m, 2 H), 2.05–2.18 (m, 2 H), 2.37–2.53 (m, 1 H), 2.60–2.73 (m, 1 H), 3.03 (dd, 1 H, *J* = 14.7 and 3.5 Hz), 3.49 (dd, 1 H, *J* = 14.7 and 9.3 Hz), 7.07 (s, 1 H), 7.50–7.70 (m, 3 H), and 7.87–7.97 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.5, 25.1, 33.0, 36.5, 39.0, 45.4, 51.0, 124.0, 127.5, 129.4, 133.7, 140.3, 140.5, and 211.0; *m/e* (relative intensity) 291 (M^+ – 1, 61), 262 (78), 232 (11), 203 (10), 183 (10), 149 (80), 125 (25), 102 (47), and 77 (100). Anal. Calcd for $C_{16}H_{19}IO_3S$: C, 45.94; H, 4.58. Found: C, 45.88; H, 4.58.

2-[(*E*)-2-Iodo-3-(phenylsulfonyl)-2-propenyl]-2-methylcyclohexanone (30): mp 105–106 °C; IR (KBr) 1702, 1592, 1449, 1312, 1152, 1084, and 751 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.24 (s, 3 H), 1.70–1.95 (m, 6 H), 2.40–2.55 (m, 1 H), 2.55–2.65 (m, 1 H), 3.56 (d, 1 H, *J* = 14.4 Hz), 3.85 (d, 1 H, *J* = 14.4 Hz), 7.10 (s, 1 H), 7.50–7.70 (m, 3 H), and 7.85–7.95 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.9, 23.1, 26.9, 38.8, 38.9, 44.7, 49.1, 117.7, 127.4, 129.4, 133.8, 140.4, 141.1, and 213.5; *m/e* (relative intensity) 291 (M^+ – I, 42), 149 (43), 125 (24), 105 (21), 91 (48), and 77 (100). Anal. Calcd for $C_{16}H_{19}IO_3S$: C, 45.94; H, 4.58. Found: C, 46.04; H, 4.59.

2-Methyl-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (33). To a solution containing 0.20 g of DBP and 0.06 mL of 3-methyl-2,4-pentanedione in 2.5 mL of absolute CH_3OH at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir for 5 h and then cooled to 0 °C and treated with an additional 1.4 mL of the NaOMe solution. The solution was allowed to stir 15 h at rt and then quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2, washed with water, and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by silica gel chromatography provided 0.07 g (47%) of 2-methyl-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (**33**) as a white solid: mp 166–167 °C; IR (KBr) 1705, 1450, 1300, 1155, 1090, and 760 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 3 H), 2.45 (m, 2 H), 2.73 (m, 2 H), 4.15 (s, 2 H), and 7.40–7.95 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 7.2, 29.4, 33.7, 57.9, 127.5, 128.9, 133.7, 137.7, 142.4, 155.8, and 207.8. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.14; H, 5.47.

Another method used to prepare furan **33** involved the treatment of *tert*-butyl methylacetoacetate with DBP. A 139-mg (3.31-mmol) sample of NaH (60% dispersion in mineral oil) was rinsed with two 5-mL portions of hexane to remove the mineral oil and was taken up in 10 mL of THF. The suspension was cooled in an ice bath, and a solution containing 608 mg of *tert*-butyl methylacetoacetate in 2 mL of THF was added slowly via syringe. The reaction mixture was allowed to stir at 0 °C for 30 min. To this reaction mixture was added a solution of 929 mg (2.73 mmol) of DBP in 4 mL of THF. The reaction mixture was allowed to stir at 0 °C for 1 h and allowed to warm slowly to rt. After stirring for 16 h, the reaction mixture was diluted with Et_2O and quenched with a saturated NH_4Cl solution. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was chromatographed on silica gel to provide 1.13 g (95%) of adduct **40**: IR (neat) 1735, 1712, 1321, 1256, and 1153 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 9 H), 1.78 (s, 3 H), 2.28 (s, 3 H), 4.35 (d, 2 H, *J* = 1 Hz), 6.50 (s, 1 H), 7.55 (m, 2 H), 7.65 (m, 1 H), and 7.95 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 21.6, 26.8, 27.7, 57.5, 65.6, 83.2, 118.4, 128.6, 129.3, 130.6, 133.9, 139.5, 169.2, and 203.0. Anal. Calcd for $C_{18}H_{23}BrO_5S$: C, 50.12; H, 5.37. Found: C, 50.15; H, 5.40.

A solution containing 255 mg of **40** in 1.5 mL of trifluoroacetic acid was stirred at rt for 1.5 h. A solution of 1.0 g of KOH in 10 mL of CH_3OH was added, and the reaction mixture was stirred for 1 h. The CH_3OH was removed under reduced pressure, and the residue was partitioned between CH_2Cl_2 and pH 7 buffer. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica to give 102 mg (69% yield) of furan **33**.

2-(4-Carbomethoxybutyl)-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (36). To a solution of 0.20 g of DBP and 0.06 mL of 2-acetylcyclohexanone in 2.5 mL of absolute CH_3OH at 0 °C was added 1.2 mL of 0.5 N methanolic NaOMe. After stirring at rt for 3 h, the reaction was quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. The organic layer was separated, concentrated, and subjected to silica gel chromatography to give 80 mg of 2-acetyl-2-[1-(bromomethyl)-2-(phenylsulfonyl)ethenyl]cyclohexanone (**34**): IR (neat) 1730, 1700, 1450, 1320, 1150, and 1080 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.50–2.05 (m, 4 H), 2.21 (s, 3 H), 2.30–2.75 (m, 4 H), 4.21 (d, 1 H, J = 14.4 Hz), 4.39 (d, 1 H, J = 14.4 Hz), 6.30 (s, 1 H), and 7.4–8.0 (m, 5 H).

A solution containing 80 mg of **34** in 1 mL of absolute CH_3OH was cooled to 0 °C and treated with 0.48 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to warm to rt, stirred for 3 h, and then quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded 44 mg of methyl 6-acetyl-7-(bromomethyl)-8-(phenylsulfonyl)-7-octenoate (**35**): IR (neat) 1740, 1720, 1450, 1330, 1160, and 1090 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.20–2.35 (m, 8 H), 2.27 (s, 3 H), 3.62 (s, 3 H), 3.74 (t, 1 H, J = 7.2 Hz), 3.92 (d, 1 H, J = 13.9 Hz), 4.16 (d, 1 H, J = 13.9 Hz), 6.36 (s, 1 H), and 7.50–7.95 (m, 5 H).

A solution containing 44 mg of **35** in 1 mL of absolute CH_3OH was cooled to 0 °C and treated with 0.25 mL of 0.5 N methanolic NaOMe. The solution was allowed to warm to rt, stirred for 15 h, and then quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded 28 mg (79%) of cyclopentenone **36**: mp 91–92 °C; IR (KBr) 1740, 1700, 1450, 1325, 1150, 1090, and 740 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.19 (quint, 2 H, J = 8 Hz), 1.46 (quint, 2 H, J = 8 Hz), 1.81 (t, 2 H, J = 8 Hz), 2.21 (t, 2 H, J = 8 Hz), 2.40 (m, 2 H), 2.75 (m, 2 H), 3.63 (s, 3 H), 4.16 (s, 2 H), and 7.50–7.95 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 22.3, 24.2, 26.5, 29.3, 32.9, 33.8, 50.9, 57.8, 127.5, 128.9, 133.7, 138.0, 145.9, 156.0, 173.2, and 207.6; HRMS calcd for $C_{18}H_{22}O_5S$ 350.1188, found 350.1169.

Cyclopentenone **36** also could be formed in a one-pot procedure as follows. To a solution containing 0.20 g of DBP and 0.06 mL of 2-acetylcyclohexanone in 2.5 mL of absolute CH_3OH at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir for 5 h, cooled to 0 °C, and treated with an additional 1.4 mL of the NaOMe solution. The solution was allowed to stir an additional 24 h at rt and then quenched with a saturated NH_4Cl solution. Workup and isolation as previously described gave a 52% yield of **36** which was spectroscopically identical to that prepared by the method outline above.

5-(2-Carbomethoxyethyl)-2-methyl-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (39). To a suspension containing 15 mg of NaH in 1.5 mL of DMF at 0 °C was added a solution of 0.08 g of 2-methyl-1,3-cyclohexanedione in 1.5 mL of DMF. The ice bath was removed, and the mixture was allowed to stir 15 min at rt, cooled again to 0 °C, and treated with a solution of 0.20 g of DBP in 1 mL of DMF. The brown solution was allowed to warm to rt and stirred overnight. The reaction mixture was poured into 10% HCl and extracted with CH_2Cl_2. The organic layer was washed first with 10% HCl and then with water to neutrality and finally dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was subjected to silica gel chromatography to give 0.08 g of 2-[1-(bromomethyl)-2-(phenylsulfonyl)ethenyl]-2-methyl-1,3-cyclohexanedione (**37**): IR (neat) 1725, 1690, 1450, 1310, 1145, 910, and 740 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 3 H), 2.02 (m, 1 H), 2.31 (m, 1 H), 2.73 (ddd, 2 H, J = 17.4, 8.5, 5.3 Hz), 2.93 (ddd, 2 H, J = 17.4, 8.5, 5.3 Hz), 4.28 (s, 2 H), 6.54 (s, 1 H), and 7.40–7.85 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 16.5, 24.9, 37.4, 56.6, 67.4, 117.9, 128.1, 128.5, 129.6, 133.4, 138.0, and 207.0.

A solution containing 65 mg of **37** in 1 mL of absolute CH_3OH was cooled to 0 °C and treated with 0.41 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to warm to rt, stirred for 3 h, and then quenched with saturated NH_4Cl. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded 39 mg of methyl 5-oxa-7-(bromomethyl)-6-methyl-8-(phenylsulfonyl)-7-octenoate (**38**): IR (neat) 1742, 1719, 1303, and 1145 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.25 (d, 3 H, J = 7.1 Hz), 1.90 (m, 2 H), 2.40 (m, 2 H), 2.72 (m, 2 H), 3.85 (q, 1 H, J = 7.1 Hz), 4.00 (d, 1 H, J = 14 Hz), 4.09 (d, 1 H, J = 14 Hz), 6.31 (s, 1 H), and 7.40–7.95 (m, 5 H).

A solution containing 39 mg of **38** in 1 mL of absolute CH_3OH was cooled to 0 °C and treated with 0.22 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to warm to rt, stirred for 15 h, and then quenched with saturated NH_4Cl. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer afforded 20 mg (67%) of 5-(2-carbomethoxyethyl)-2-methyl-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (**39**) as a clear oil: IR (neat) 1730, 1700, 1440, 1310, 1150, 1080, and 750 cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 1.15 (s, 3 H), 1.56 (m, 1 H), 1.92 (m, 1 H), 2.20–2.45 (m, 4 H), 2.78 (m, 1 H), 3.56 (s, 3 H), 4.05 (s, 2 H), and 7.40–7.85 (m, 5 H); HRMS calcd for $C_{17}H_{21}O_5S$ (M + H) 337.1109, found 337.1089.

Cyclopentenone **39** also could be prepared without isolation of intermediates as follows. To a suspension containing 15 mg of NaH in 1.5 mL of DMF at 0 °C was added a solution of 0.08 g of 2-methyl-1,3-cyclohexanedione in 1.5 mL of DMF. The ice bath was removed, and the mixture was allowed to stir 15 min at rt, after which it was again cooled to 0 °C and treated with a solution of 0.20 g of DBP in 1 mL of DMF. The brown solution was allowed to warm to rt and to stir overnight. The reaction mixture was poured into 10% HCl and extracted with CH_2Cl_2. The organic layer was worked up in the normal fashion, treated with 1.4 mL of a 0.5 N methanolic NaOMe solution, allowed to warm to rt, and stirred overnight. The excess methoxide was quenched using a saturated NH_4Cl solution and then subjected to aqueous workup as previously described. In this fashion 5-(2-carbomethoxyethyl)-2-methyl-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (**39**) was prepared in 65% yield.

2-Allyl-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (42). Using a procedure identical to that outlined for the synthesis of cyclopentenone **33**, the reaction of 2.03 g of *tert*-butyl methylacetoacetate with 2.9 g of DBP gave 3.5 g (93%) of adduct **41** (R = allyl): IR (neat) 2936, 1735, 1710, 1640 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 9 H), 2.37 (s, 3 H), 2.75 (d, 2 H, J = 7 Hz), 4.30 (d, 1 H, J = 14 Hz), 4.73 (d, 1 H, J = 14 Hz), 5.07 (m, 2 H), 5.70 (m, 1 H), 6.48 (s, 1 H), 7.55 (m, 2 H), 7.63 (m, 1 H), and 7.92 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) 27.9, 28.2, 41.9, 56.9, 68.5, 84.0, 118.5, 119.6, 128.3, 129.3, 130.5, 132.6, 133.9, 140.2, 168.1, and 202.2. Anal. Calcd for $C_{20}H_{25}BrO_5S$: C, 52.52; H, 5.51. Found: C, 52.61; H, 5.53.

A 336-mg sample of **41** was converted into 135 mg (64% yield) of cyclopentenone **42**: IR (neat) 1701, 1641, 1446, 1312, and 1144 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 2.44 (m, 2 H), 2.60 (d, 2 H, J = 6 Hz), 2.76 (m, 2 H), 4.22 (s, 2 H), 4.9 (m, 2 H), 5.52 (m, 1 H), 7.59 (m, 2 H), 7.59 (m, 2 H), 7.70 (m, 1 H), and 7.87 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 26.8, 30.0, 34.2, 58.2, 116.4, 128.0, 129.5, 133.2, 134.3, 138.5, 144.1, 157.9, and 207.6; HRMS calcd for $C_{15}H_{16}SO_3$ 276.0821, found 276.0820.

Preparation of *cis*-Jasmone (45). A mixture containing 1.0 g of 2,4-pentanedione, 1.5 g of *cis*-1-bromo-2-pentene, and 1.3 g of anhydrous potassium carbonate in 5 mL of acetone was heated at reflux for 2 h and then allowed to stir at rt an additional 12 h. Distillation of the residue gave 1.1 g of *cis*-3-acetyl-5-octen-2-one (**43**) as a clear oil: IR (neat) 1698, 1424, 1354, and 1151 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3 H, J = 7.5 Hz), 2.00–2.15 (m, 2 H), 2.57 (br t, 2 H, J = 7.3 Hz), 3.64 (t, 1 H, J = 7.3 Hz), and 5.10–5.55 (m, 2 H).

To a solution containing 0.20 g of DBP and 0.12 g of **43** in 2.5 mL of absolute CH_3OH at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir for 5 h, cooled to 0 °C, and treated with an additional 1.4 mL of

the NaOMe solution. The solution was allowed to stir 15 h at rt and then quenched with a saturated NH_4Cl solution. The CH_3OH was evaporated, and the residue was extracted with CH_2Cl_2, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica gel chromatography provided 0.14 g (76%) of 2-(*cis*-2-pentenyl)-3-[(phenylsulfonyl)methyl]-2-cyclopenten-1-one (**44**): IR (neat) 1705, 1645, 1450, 1325, 1155, 1090, and 745 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3 H, J = 7.5 Hz), 1.98 (m, 2 H), 2.39 (m, 2 H), 2.58 (d, 2 H, J = 7.0 Hz), 2.68 (m, 2 H), 4.18 (s, 2 H), 4.80–5.05 (m, 1 H), 5.20–5.45 (m, 1 H), and 7.50–7.95 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.4, 20.0, 20.3, 29.4, 33.7, 57.8, 123.0, 127.5, 128.9, 132.8, 133.7, 138.1, 145.0, 156.4, and 207.0.

A solution containing 0.17 g of **44** and 0.62 g of tri-*n*-butyltin hydride in 6.2 mL of refluxing benzene was treated with a solution containing 62 mg of AIBN in 1 mL of benzene. The resulting solution was allowed to reflux for 3 min and then treated with an additional 40 mg of AIBN in 1 mL of benzene. Heating was continued for another hour, after which time the solution was allowed to cool and was concentrated under reduced pressure. The oily residue was subjected to silica gel chromatography to give 79 mg (71%) of *cis*-jasmone (**45**), whose spectral data matches that reported in the literature.[54]

2-Methyl-3-[1-(phenylsulfonyl)-3-butenyl]-2-cyclopenten-1-one (46). To a 34-mg sample of NaH (60% dispersion in mineral oil) was added 5 mL of THF, and the suspension was cooled to 0 °C. To this mixture was added 76 mg (0.3 mmol) of cyclopentenone **33** in 2 mL of dry DMSO, and the solution was allowed to stir at 0 °C for 30 min. Allyl bromide (0.1 mL) was added, and the reaction mixture allowed to stir for 12 h, slowly warming to rt. The reaction mixture was quenched with pH 7 buffer and extracted with several portions of CH_2Cl_2. The combined organic fractions were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel to give 57 mg (65%) of cyclopentenone **46**: IR (neat) 1703, 1642, 1447, 1308, 1148, and 1084 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 3 H), 2.31 (t, 2 H, J = 5 Hz), 2.50 (m, 1 H), 2.85 (m, 2 H), 3.05 (m, 1 H), 4.2 (dd, 1 H, J = 11 and 3 Hz), 5.05 (m, 2 H), 5.50 (m, 1 H), 7.50 (m, 2 H), 7.65 (m, 1 H), and 7.85 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 7.9, 26.0, 29.4, 33.9, 65.9, 118.7, 128.5, 129.4, 131.9, 134.3, 137.4, 143.7, 160.2, and 208.5; HRMS calcd for $C_{16}H_{18}SO_3$ 290.0976, found 290.0975.

Preparation of 4-(Phenylsulfonyl)indenone (50). Using a procedure similar to that used for the preparation of cyclopentenone **33**, acetal **48**[63] was prepared from 165 mg (3.93 mmol) of NaH (60% dispersion in mineral oil) and 1.07 g (3.16 mmol) of DBP in 30 mL of THF. After stirring for 18 h, the reaction was worked up as described for **33**, and the residue was subjected to silica gel chromatography to provide 1.46 g (89%) of **48**: IR (neat) 1733, 1711, 1450, 1369, 1252, 1151, and 1086 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 9 H), 1.70 (m, 2 H), 2.15 (m, 2 H), 2.45 (s, 3 H), 3.95 (m, 4 H), 4.36 (d, 1 H, J = 14 Hz), 4.75 (d, 1 H, J = 14 Hz), 4.88 (d, 1 H, J = 4.3 Hz), 6.57 (s, 1 H), 7.57 (m, 2 H), 7.64 (m, 1 H), and 7.94 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 27.8, 28.0, 28.9, 30.8, 56.7, 64.9, 68.1, 103.6, 118.2, 128.2, 129.4, 130.4, 138.8, 140.1, 168.4, and 202.2.

A solution containing 518 mg (1.0 mmol) of **48** and 94 mg of *p*-toluenesulfonic acid in 20 mL of benzene was heated at reflux for 45 min. The solvent was removed under reduced pressure, and the residue was dissolved in 5 mL of CH_3OH. To this mixture was added 130 mg of LiOH monohydrate, and the reaction mixture was stirred at rt for 4 h. At the end of this time, 5 mL of pH 7 buffer was added and the mixture was extracted with several portions of CH_2Cl_2. The combined organic fractions were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel to provide 140 mg (42%) of acetal cyclopentenone **49**: IR (neat) 1701, 1645, 1447, 1321, 1151, and 1086 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.60 (m, 2 H), 1.93 (t, 2 H, J = 8 Hz), 2.24 (m, 2 H), 2.70 (m, 2 H), 3.80–4.05 (m, 4 H), 4.23 (s, 2 H), 4.69 (t, 1 H, J = 4 Hz), 7.59 (m, 2 H), 7.65 (m, 1 H), and 7.90 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.3, 29.8, 30.9, 34.3, 58.1, 64.7, 103.3, 127.9, 129.3, 134.2, 138.4, 145.9, 156.8, and 208.0; HRMS calcd for $C_{17}H_{20}O_5S$ 336.1032, found 336.1031.

A solution containing 107 mg (0.32 mmol) of **49** and 10 mg of *p*-toluenesulfonic acid in 10 mL of acetone and 0.1 mL of water was heated at reflux for 3 h. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in 10 mL of CH_2Cl_2. To this solution was added 1 drop of triethylamine and 100 mg of K_2CO_3, and the solution was allowed to stir at rt for 12 h. The solution was diluted with CH_2Cl_2, washed with pH 7 buffer, dried over $MgSO_4$, and concentrated under reduced pressure. After chromatography on silica gel, 51 mg (60%) of indenone **50** was isolated: IR (neat) 1721, 1447, 1321, 1264, and 1130 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.65 (m, 2 H), 3.22 (m, 2 H), 7.50–8.05 (m, 7 H), and 8.32 (d, 1 H, J = 8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 25.3, 35.6, 127.8, 128.4, 128.9, 129.4, 133.7, 134.2, 138.9, 139.1, 140.5, 150.2, and 204.8. Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.45. Found: C, 65.94, H, 4.36.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (CA-26750). Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Supplementary Material Available: ^1H-NMR and ^{13}C-NMR spectra (75 MHz) for all compounds with high-resolution mass spectra (10 pages). Ordering information is given on any current masthead page.

(63) Acetal **47** was prepared according to the procedure of Stotter and Hill[64] from *tert*-butyl acetoacetate and 2-(2-iodoethyl)-1,3-dioxolane.[65]

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