Addition of γ-Methoxy Allylsulfonyl Anions to Cyclopentenyl Phenyl Sulfones. A Facile Synthesis of β-Cyclopentenyl-Substituted Dienones and Trienones[1]

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Abstract: γ-Methoxy allylsulfonyl anions undergo smooth conjugate addition to mono- and bicyclic cyclopentyl sulfones. Hydrolysis of the intermediate adducts affords δ-sulfonyl-substituted enones which may be eliminated to dienyl ketones. The mechanism of this reaction is shown to involve the intermediacy of spiro-fused cyclopropyl sulfones conjugated to an enol ether moiety. Exploration of the scope and limitations of this procedure demonstrates the potential for triply-convergent synthesis of tricyclic dienones via cyclization of a trienyl ketone.

Recently we reported that six- and seven-membered γ-methoxy vinyl sulfones **1b,c** were smoothly converted to γ-methoxy allylsulfonyl anions **2b,c** upon reaction with *t*-BuLi. Regiospecific trapping of these intermediates by a series of electrophiles provided enol ethers **3b,c** which underwent hydrolysis to β-substituted enones **4b,c** upon workup with aqueous bicarbonate. The average overall yield for 13 cases was 94% (Scheme 1).[2a]

Unfortunately, attempts to extend this chemistry to the cyclopentenyl series were compromised by the propensity of γ-methoxycyclopentenyl sulfone **1a** to intercept intermediate allylsulfonyl anion **2a** via conjugate addition. This ultimately led to the formation of δ-sulfonyl-substituted enone **6a** which was further treated with DBU to complete the elimination process. The final yield of **7a** was 88%, which suggested the potential for unsymmetrical cross-coupling reactions (Scheme 2).

The ability of five-membered-ring vinyl sulfones to serve as Michael acceptors in unsymmetrical condensations was initially tested by adding a slight excess of cyclopentenyl phenyl sulfone **8** to a solution of γ-methoxy allylsulfonyl anion **2b** which was prepared in the standard fashion by metalation of γ-methoxycyclohexenyl phenyl sulfone **1b** with *t*-BuLi in THF at −78 °C.[2] The conjugate addition of anion **2b** was essentially instantaneous at this temperature as indicated by thin-layer chromatography (TLC). The TLC profile of these reactions was complicated by the fact that several reaction products had the same R_f value; moreover, the proton quenched product (not shown) of **9b** was shown to be unstable to silica gel by two-dimensional TLC. Nevertheless, enone **10b** was obtained in 80% yield after an aqueous bicarbonate workup although the yield was not as high as was expected (Scheme 3).

Reaction of vinyl sulfone **8** with cycloheptyl γ-methoxy allylsulfonyl anion **2c** in the presence of 1 equiv of HMPA provided an intermediate which was far easier to analyze (Scheme 4). Careful workup and chromatography on deactivated silica gel afforded tricyclic cyclopropyl sulfone **11c** in 94% yield. Cyclopropane annulations which occur via intramolecular displacement of the sulfinate anion have been previously observed in alkylations of ketone-, ester-, nitrile-, and sulfone-stabilized anions.[3] The diminished yield of **10b** obtained in the initial experiment (Scheme 3) suggested that the reaction of **8** with γ-methoxy allylsulfonyl anion **2b** was competitively forming tricyclic cyclopropyl sulfone **11b**, a fact which was not recognized until the structure of **11c** had been ascertained. Repeating the reaction of **8** with **2b** in the presence of 1 equiv of HMPA, followed by warming to room temperature, indeed afforded the analogous six-membered sulfone **11b** in 98% yield (Scheme 4). Compounds **11b** and **11c** are stable both to TLC and to bicarbonate solution. They are tricyclic cyclopropyl sulfones bearing a methyl enol ether moiety as judged from carbon and proton NMR data. These materials are single diastereomers which have been tentatively assigned as having the cyclopropyl methine H_b anti to the enol ether H_a based upon nOe experiments on **11b**.[4] Compound **11b** was converted to enone **10b** after being heated at reflux for 24 h in THF and H_2O solution in the presence of silica gel, while conversion of **11c** to **10c** was slower under the same conditions.

Reactions utilizing cyclohexenyl sulfone donor **2b** directly afforded δ-sulfonyl enone **10b** at −98 °C in high overall yield simply by adding aqueous bicarbonate to the one-pot reaction mixture (Scheme 5). This implies that the formation of the spiro-fused cyclopropyl sulfone **11b** is minimized at −98 °C. The preparation of dienyl ketone **13b** was completed by elimination of sulfinic acid using DBU in acetonitrile at reflux. The concept of synthesis of dienyl ketones via the sequential bis elimination of β,δ-disulfonyl ketones can be found in the total synthesis of coriolin by Trost and Curran.[5]

By comparison, the reaction utilizing cycloheptyl sulfone donor **2c** did not directly afford δ-sulfonyl enone **10c** because

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) Syntheses Via Vinyl Sulfones. 56.

(2) (a) Jin, Z.; Fuchs, P. L. *J. Am. Chem. Soc.* **1994**, *116*, 5995. (b) See also: Craig, D.; Etheridge, C. J.; Smith, A. M. *Tetrahedron Lett.* **1992**, *33*, 7445. Craig, D.; Etheridge, C. J. *Tetrahedron Lett.* **1993**, *34*, 7487. Craig has shown that acyclic γ-benzyloxy allylsulfones undergo smooth metalation to afford acyclic γ-benzyloxy allylsulfonyl anions which were shown to efficiently react at the α-sulfonyl position with aldehydes and alkyl halides. The resulting intermediates were converted to butenolides and furans.

(3) (a) Parker, W. L.; Woodward, R. B. *J. Org. Chem.* **1969**, *34*, 3085. (b) Cory, R. M.; Renneboog, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1081. (c) Britten-Kelly, M. R.; Willis, B. J.; Barton, D. H. R. *J. Org. Chem.* **1981**, *46*, 5027. (d) Krief, A.; DeVos, M. J. *Tetrahedron Lett.* **1985**, *26*, 6115. (e) Agawa, T.; Yoshida, Y.; Komatsu, M.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, *81*, 751. (f) Hutchinson, D. K.; Hardinger, S. A.; Fuchs, P. L. *Tetrahedron Lett.* **1986**, *27*, 1425.

(4) Less than 1% of an nOe enhancement was observed when either H_a or H_b of compound **11b** were irradiated. Based upon this (negative) evidence, structures of **11b** and **11c** were tentatively assigned as having the cyclopropyl methine H_b anti to the enol ether H_a.

(5) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380.

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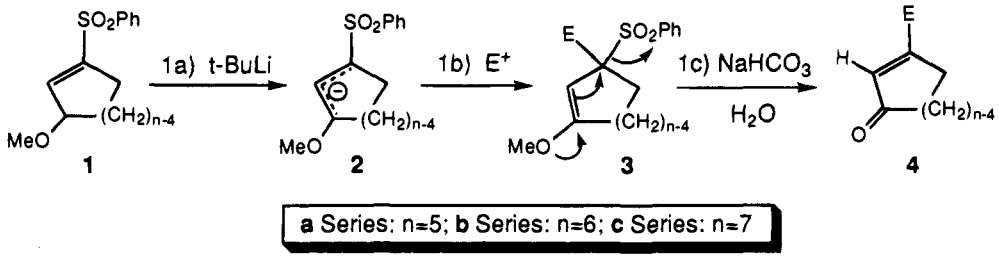
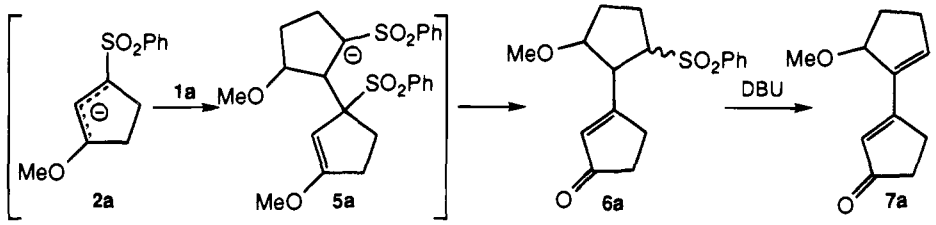
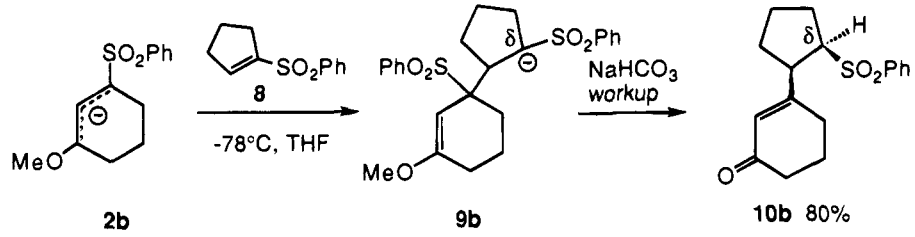
Scheme 1



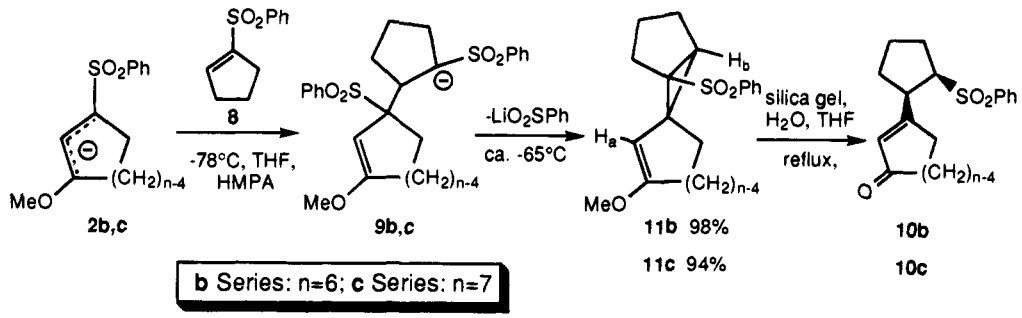
Scheme 2



Scheme 3



Scheme 4



the rate of cyclopropane formation was appreciable even at −98 °C. Therefore, additional processing via intermediate **12c** was required to convert **11c** to **13c**. Mild acid hydrolysis of enol ether **11c** smoothly afforded tricyclic keto-sulfone **12c** without any apparent rupture of the activated cyclopropyl sulfone moiety. Treatment of **12c** with DBU effected cleavage of the cyclopropane, generating δ-sulfonyl enone intermediate **10c** which was not isolated but further processed to dienone **13c** under basic conditions.[6]

The chemistry described in Scheme 5 appears to be general for other *five-membered-ring* vinyl sulfone acceptors. Table 1 describes the synthesis of several additional dienyl ketones by this procedure. In these examples, no effort was made to extensively characterize the probable cyclopropyl sulfone intermediates. The reaction of the seven-membered ring substrate **2c** with the strained bridged bicyclic sulfone **19** yielded an intermediate which was easily transformed to δ-sulfonyl enone **22** (entry 4). The δ-sulfonyl enones were subsequently subjected to the DBU-mediated elimination reaction to smoothly afford dienones except in the case of compound **22** which was especially slow to produce dienone **23**. Simple six- and seven-membered-ring phenyl vinyl sulfones do not serve as Michael acceptors in the conjugate-addition reaction.

The finding of high reactivity for the five-membered vinyl sulfones is consistent with our previous experience in anionic conjugate addition, S_N2', and intramolecular Heck reactions.[3e,7] This increased reactivity likely results from destabilization of the ground state of the cyclopentenyl species[8] relative to cyclohexenyl and heptenyl sulfones.

Encouraged by our success with norbornenyl sulfone **19**, we next elected to examine the conjugate addition of γ-methoxy allylsulfonyl anion **2b** to azabicyclic vinyl sulfone **24**[9] (Scheme 6). Although a rapid reaction occurred, we were surprised to

(6) Treatment of **12b** with 5% HCl at 25 °C for 2 h affords the spiro-fused cyclohexyl ketone **13b** (not shown) in 96% yield. As expected, **13b** is smoothly converted to δ-sulfonylenone **10b** in 92% yield upon reaction with saturated bicarbonate at 25 °C for 24 h.

(7) (a) Saddler, J. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2112. (b) Donaldson, R. E.; Saddler, J. C.; McKenzie, A. T.; Byrn, S.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 2167. (c) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1985**, *107*, 6137. (d) Pan, Y.; Hutchinson, D. K.; Nantz, M. H.; Fuchs, P. L. *Tetrahedron* **1989**, *45*, 467. (e) Pan, Y.; Hardinger, S. A.; Fuchs, P. L. *Synth. Commun.* **1989**, *19*, 403. (f) Jin, Z.; Fuchs, P. L. *Tetrahedron Lett.* **1993**, *34*, 5205.

(8) Wiberg, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

Scheme 5

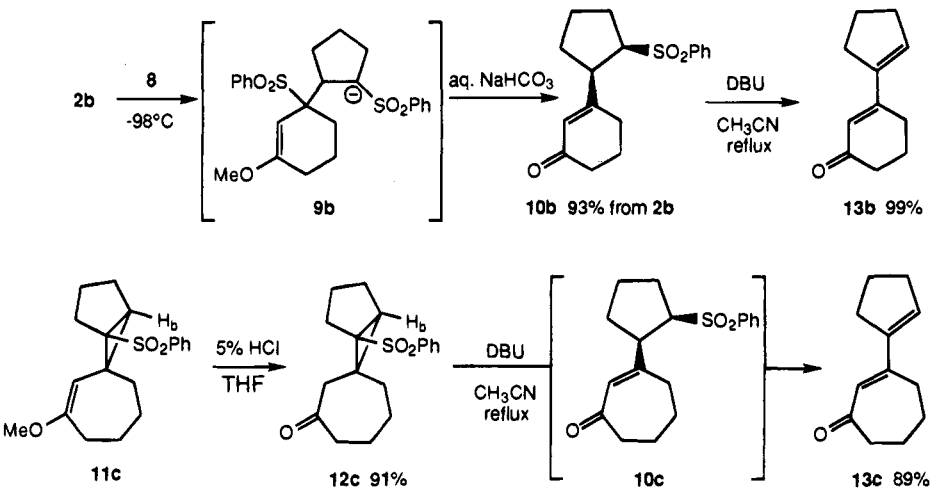
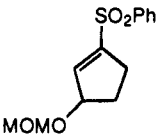
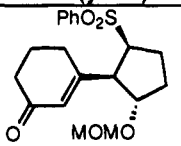
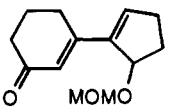
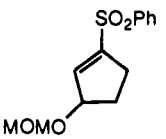
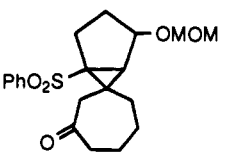
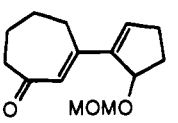
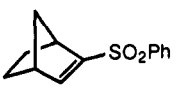
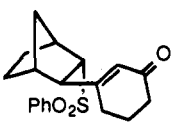
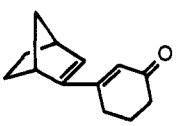
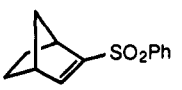
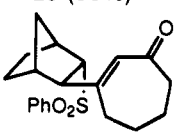
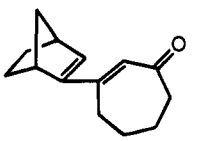


Table 1

Entry	Donor Anion	Acceptor sulfone	δ-sulfonyl enone (yield)	Dienyl ketone (yield)
1	2b	 14	 15 (98%)	 16 (96%)
2	2c	 14	 2 diast'rs 17*	 18 (86%)†
3	2b	 19	 20 (99%)	 21 (90%)
4	2c	 19	 22 (88%)	 23 (42%)§

*Compound 17 is a mixture of two (unassigned) diastereomers which arose from HCl (aq) hydrolysis of a pair of diastereomeric enol ether derivatives using the same protocol employed for conversion of **11c** to **12c**.

†Neither **17** nor the enol ether precursors were purified, and the yield for **18** is the overall yield from **2c**.

§The yield is 59% based upon recovered starting material after 5.5 d reaction.

observe that the products from sulfone **24** consisted of an approximate 1:1 mixture of δ-sulfonylenone **26** and pyrrole **27**.[10] The formation of compounds **26** and **27** suggested that the conjugate addition of **2b** to azabicyclic vinyl sulfone **24** had occurred to generate intermediate **25** which, after quenching by bicarbonate solution, was instantaneously converted to compounds **26** and **27** via retro-Diels–Alder reaction at room temperature. The facility of the retro-Diels–Alder reaction under the mild reaction conditions is likely due to the simultaneous formation of pyrrole as well as the conjugated δ-sulfonylenone **26**.[11]

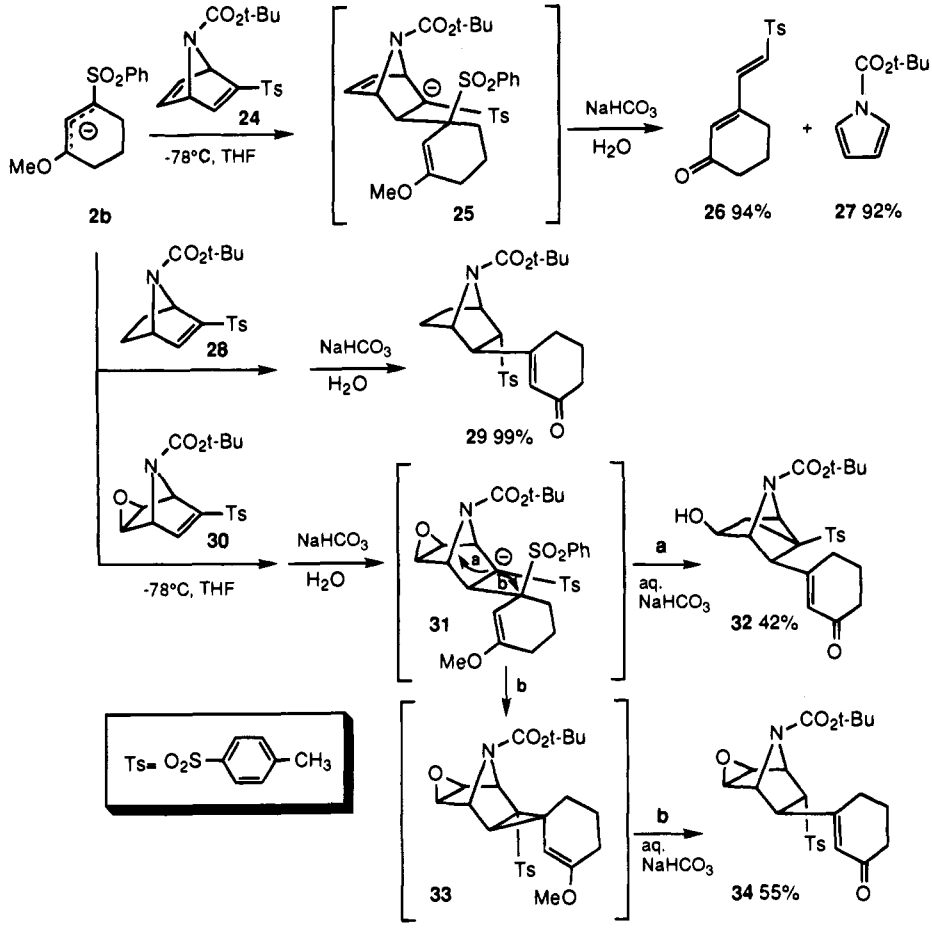
Consistent with the retro-Diels–Alder hypothesis, reaction of **2b** with the dihydroazabicyclic vinyl sulfone **28** (prepared in 98% yield from **24** via hydrogenation over Pd/C in CH_3CN for 4 h at 25 °C) afforded an essentially quantitative yield of enone **29**. In contrast, treatment of epoxide **30** (prepared in 82% yield from **26** via reaction with mCPBA in CH_2Cl_2 for 18 h at 40 °C) with anion **2b** afforded a mixture of the expected enone **34** and azatricyclic alcohol **32**. Apparently the intermedi-

(9) (a) Leung-Toung, R.; Liu, Y.; Muchowski, J. M.; Wu, Y-L. *Tetrahedron Lett.* **1994**, *35*, 1639. (b) Altenbach, H-J.; Blech, B.; Marco, J. A.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 778.

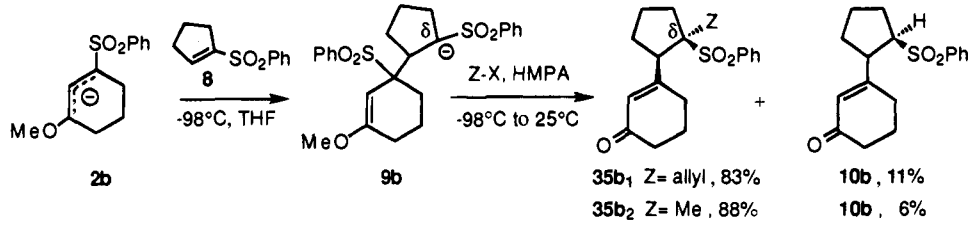
(10) Grehn, L.; Ragnarsson, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 296.

(11) For other references on retro-Diels–Alder reactions under mild conditions see: Reinhoudt, D. N.; Kouwenhoven, C. G. *Tetrahedron Lett.* **1974**, *16*, 2163.

Scheme 6



Scheme 7



ate α-tolylsulfonyl anion **31** was kinetically partitioned between two modes of intramolecular cyclopropanation. Allowing the reaction mixture additional time and warming to room temperature prior to quenching did not change the ratio of **32/34**. This finding either requires the intermediate α-tolylsulfonyl anion to be in equilibrium with the alkoxide of **32** or calls for the presence of a competitive irreversible step such as the formation of non-isolable spirocyclic species **33**, a hypothesis we believe is more consistent with the observations of Scheme 4 and Table 1.

Having demonstrated that cyclopropane formation was slower at lower temperatures, we returned to investigate the possibility of intermolecular alkylation of the intermediate **9b** with electrophiles at −98 °C (Scheme 7). Conjugate addition of γ-methoxy allylsulfonyl anion **2b** to vinyl sulfone **8** occurred instantaneously at −98 °C as judged by TLC assay. Immediate addition of excess alkylating agent and HMPA followed by a slow warmup period, mild bicarbonate workup, and heating the crude mixture at reflux in aqueous THF in the presence of silica gel provided the desired δ-functionalized enones **35b$_1$**−**35b$_2$** in addition to small amounts of "quenched" enone **10b**, probably by way of cyclopropyl sulfone **11b**.

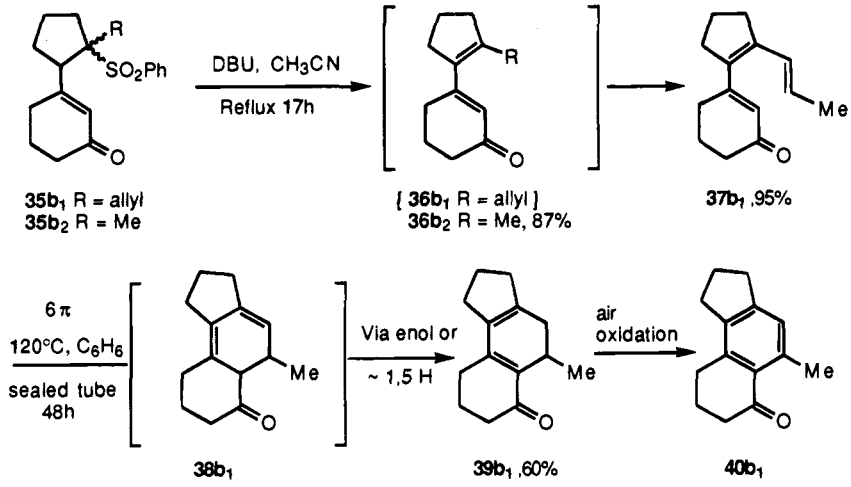
Application of the DBU-mediated sulfinic acid elimination reaction to enones **35b$_2$** and **35b$_1$** produced δ-functionalized dienone **36b$_2$** as well as trienyl ketone **37b$_1$**, which was produced via further isomerization of **36b$_1$** (Scheme 8). Electrocyclization of trienyl ketone **37b$_1$** provided tricyclic dienyl ketone **39b$_1$** in 60% yield after heating in degassed benzene in a sealed tube at 120 °C for 48 h (unoptimized). Compound **39b$_1$** was easily oxidized to the aromatized product **40b$_1$**. It should be noted that this example demonstrates a new triply convergent, three-step procedure which could evolve into a broadly applicable protocol for the synthesis of functionalized polycyclic ketones. Research directed toward this goal is underway.

Experimental Section

General Methods. Melting points were determined on a Meltemp apparatus and are uncorrected. Unless otherwise stated, reactions were performed under argon in flame-dried glassware. Tetrahydrofuran (THF) was distilled from sodium−benzophenone ketyl. Acetonitrile, dichloromethane, and benzene were distilled from calcium hydride. All other reagents were used as purchased. Flash column chromatography

(12) Conrad, P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346.

Scheme 8



was carried out using 230−400 mesh silica gel from Whatman. ^{1}H spectra were obtained using either a GE QE-300 NMR spectrometer at 300 MHz or a Gemini-200 NMR spectrometer at 200 MHz; and ^{13}C NMR were obtained using either a GE QE-300 NMR spectrometer at 75 MHz or a Gemini-200 NMR spectrometer at 50 MHz. The nOe experiment was carried out on a VNMR-500 at 500 MHz. ^{1}H NMR chemical shifts are reported in ppm relative to residual protonated solvent resonance: $CHCl_3$, δ 7.26; C_6D_5H, δ 7.15. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; ap, apparent; q, quartet; m, multiplet; br, broadened; ABq, AB quartet. Coupling constants (J) are reported in Hz. ^{13}C NMR chemical shifts are reported in ppm relative to solvent resonance: $CDCl_3$, d 77.00; C_6D_6, d 128.00. Peaks in ^{13}C NMR spectra are denoted as "e" for carbons with zero or two attached protons or "o" for carbons with one or three attached protons as determined from APT pulse sequence. Mass spectral data were obtained from Purdue University Campus-wide Mass Spectral Facility.

General Procedure for Formation of γ-Methoxy Allylsulfonyl Anions. To a 0.1 M solution of γ-methoxy vinyl sulfone **1b** or **1c** in THF at −78 °C was added 1.05 equiv of *t*-BuLi. A bright red-orange solution of γ-methoxy allylsulfonyl anion was formed instantaneously.

General Procedure for Conjugate Addition of γ-Methoxy Allylsulfonyl Anions to Cyclopentyl Sulfones. To a 0.1 M solution of γ-methoxy allylsulfonyl anions **2b** or **2c** at −78 °C was added dropwise a THF solution of mono- or bicyclic cyclopentyl sulfone (1.2 equiv). TLC (30% ethyl acetate in hexane) of the −78 °C reaction mixture, 10−15 min after the addition was complete, demonstrated the consumption of the γ-methoxy allylsulfone.

General Procedure for Alkylation at the δ-Carbon. To a 0.1 M solution of γ-methoxy allylsulfonyl anion **2b** at −98 °C was slowly added a THF solution of vinyl sulfone **8** (1.5 equiv). After addition, the reaction was stirred 10−15 min at −98 °C; TLC (30% ethyl acetate in hexane) showed disappearance of the γ-methoxy allylsulfone. Five to six equivalents of MeI or allyl bromide was added dropwise slowly at −98 °C, followed by 2 equiv of HMPA. The reaction was stirred 45−60 min at −98 °C, followed by slow warming to 25 °C. The reaction was quenched with saturated aqueous sodium bicarbonate solution and stirred at 25 °C for 2 h. The reaction was extracted with dichloromethane three times; the combined organic phases were concentrated in vacuo; then to the crude mixture was added THF, H_2O, and silica gel; the mixture was then heated at reflux until hydrolysis of the enol ether intermediate was complete. The silica gel was filtered and the resultant dichoromethane solution was concentrated in vacuo and purified by flash column chromatography on silica gel.

General Procedure for DBU-Mediated Sulfinic Acid Elimination. To an acetonitrile solution of δ-sulfonyl-substituted enones was added 1−2 equiv of DBU. The reaction mixture was heated at reflux until disappearance of the starting material. Acetonitrile was evaporated and the crude product was purified by flash column chromatography on silica gel to afford pure dienones or trienone.

Preparation of Compound 10b. The general procedure for δ-alkylation was followed with omission of the alkylating agents. The general workup and purification procedure afforded compound **10b** in 94% yield. Compound **10b:** white solid; mp 82.5−83.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85−7.26 (5H, m), 5.65 (1H, s), 3.56−3.48 (1H, ddd, J = 9.1, 8.0, 6.4 Hz), 3.12-3.02 (1H, q, J = 8.0 Hz), 2.30−1.50 (12H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2 (e), 165.0 (e), 138.5 (e), 134.0 (o), 129.4 (o), 128.7 (o), 125.9 (o), 67.0 (o), 48.3 (o), 37.3 (e), 33.7 (e), 28.0 (e), 27.9 (e), 25.2 (e), 22.7 (e); HRMS (EI) calcd for $C_{17}H_{20}O_3S$ 304.1133 $(M)^+$, found 304.1130.

Preparation of Compound 11b. The general procedure for the conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones was followed. In addition, 1 equiv of HMPA was added at −78 °C. The reaction mixture was gradually warmed to 25 °C over the period of 1 h and stirred at 25 °C for 3 h. After rapid filtration through fluorisil, the crude product was concentrated in vacuo and purified by flash column chromatography on silica gel to give compound **11b** in 98% yield. Compound **11b**: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86−7.49 (5H, m), 4.12 (1H, s), 3.48 (3H, s), 2.60−2.39 (1H, m), 2.40−2.38 (1H, d, J = 6.1 Hz), 2.20−1.55 (11H, m); ^{13}C NMR (50 MHz, C_6D_6) δ 160.9 (e), 142.9 (e), 132.8 (o), 129.3 (o), 128.0 (o), 91.1 (o), 60.7 (e), 53.7 (o), 41.0 (o), 38.6 (e), 29.7 (e), 29.6 (e), 29.3 (e), 28.5 (e), 25.9 (e), 22.9 (e); HRMS (CI) calcd for $C_{18}H_{22}O_3S$ 319.1368 $(M + 1)^+$, found 319.1362.

Preparation of Compound 11c. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones was followed. In addition, 1 equiv of HMPA was added at −78 °C. After 20 min at −78 °C the TLC (30% ethyl acetate in hexane) showed disappearance of the γ-methoxy allylsulfone. Standard workup and purification procedure afforded compound **11c** in 94% yield. Compound **11c**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89−7.53 (5H, m), 4.25 (1H, s), 3.41 (3H, s), 2.40−1.30 (15H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.8 (e), 142.2 (e), 133.3 (o), 129.5 (o), 128.1 (o), 94.7 (o), 60.0 (e), 54.9 (o), 41.0 (o), 38.0 (e), 33.2 (e), 32.9 (e), 30.3 (e), 29.5 (e), 27.3 (e), 26.3 (e), 25.1(e); HRMS (CI) calcd for $C_{19}H_{24}O_3S$ 333.1524 $(M + H)^+$, found 333.1527.

Preparation of Compound 12c. To a 2 mL THF solution of compound **11c** (0.048 mmol, 16 mg) was added 1 mL of 5% HCl aqueous solution. The reaction was stirred at 25 °C for 2 h, the enol ether being completely converted to ketone. Standard workup and purification afforded 14 mg of compound **12c** (91% yield). Compound **12c**: white solid; mp 145.5−146.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88−7.52 (5H, m), 2.76−1.50 (17H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 212.9 (e), 141.5 (e), 133.8 (o), 129.7 (o), 128.1 (o), 60.2 (e), 46.1 (e), 44.0 (e), 40.9 (o), 37.4 (e), 36.8 (e), 29.7 (e), 29.4 (e), 28.4 (e), 26.0 (e), 24.5 (e); HRMS (CI) calcd for $C_{18}H_{22}O_3S$ 319.1368 $(M + H)^+$, found 319.1359.

Preparation of Compound 13b. The general procedure for DBU-mediated sulfinic acid elimination was followed using 1.5 equiv of DBU. Reaction time was 3 h and the yield was 99%. Compound **13b**: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.31 (1H, s), 5.90 (1H, s), 5.90−2.38 (8H, m), 2.10−1.90 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9 (e), 155.3 (e), 143.5 (e), 136.4 (o), 124.5 (o), 37.7 (e),

34.0 (e), 31.9 (e), 26.6 (e), 23.0 (e), 22.7 (e); HRMS (EI) calcd for $C_{11}H_{14}O$ 162.1045 $(M)^+$, found 162.1043.

Preparation of Compound 13c. The general procedure for DBU-mediated sulfinic acid elimination was followed using 2.0 equiv of DBU. Reaction time was 48 h and the yield was 91%. Compound **13c**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 6.29 (1H, s), 5.95 (1H, s), 2.80−2.45 (8H, m), 2.10−1.78 (6H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.8 (e), 152.8 (e), 145.2 (e), 135.5 (o), 128.7 (o), 42.3 (e), 34.4 (e), 33.1 (e), 29.1 (e), 25.3 (e), 23.7 (e), 21.5 (e); HRMS (EI) calcd for $C_{12}H_{16}O$ 176.1201 $(M)^+$, found 176.1203.

Preparation of Compound 14. 3-Hydroxycyclopent-1-enyl phenyl sulfone[12] (3.35 mmol, 750 mg, 1.0 equiv) was dissolved in 12 mL of dichoromethane. Tetrabutylammonium bromide (0.335 mmol, 108 mg, 0.1 equiv), was added, followed by MOMCl (26.78 mmol, 2.156 g, 8.0 equiv). To the vigorously stirred solution was added 8 mL of 50% aqueous KOH solution. The reaction mixture was stirred at 25 °C until the disappearance of the γ-hydroxy vinyl sulfone was evident by TLC (40% ethyl acetate in hexane). Standard workup and purification afforded 850 mg of compound **14** (95%). Compound **14:** colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90−7.50 (5H, m), 6.67−6.66 (1H, d, J = 1.3 Hz), 4.77−4.71 (1H, m), 4.65−4.63 (1H, AB, J = 6.9 Hz), 4.61−4.59 (1H, AB, J = 6.9 Hz), 3.3 (3H, s), 2.65−2.30 (3H, m), 2.00−1.80 (1H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.1 (e), 141.5 (o), 139.3 (e), 134.2 (o), 129.7 (o), 128.4 (o), 96.5 (e), 82.2 (o), 55.7 (o), 32.1 (e), 29.4 (e); HRMS (CI) calcd for $C_{13}H_{16}O_4S$ 269.0848 $(M + H)^+$, found 269.0845.

Preparation of Compound 15. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones was used. Standard workup and purification afforded compound **15** in 98% yield. Compound **15**: pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85−7.49 (5H, m), 5.68 (1H, s), 4.57−4.55 (1H, AB, J = 8.1 Hz), 4.51−4.47 (1H, AB, J = 8.1 Hz), 3.95−3.88 (1H, ap q, J = 6.7 Hz), 3.54−3.46 (1H, ap q, J = 8.8 Hz), 3.25 (3H, d, J = 1.2 Hz), 3.03−2.97 (1H, dd, J = 8.8, 6.7 Hz), 2.45−1.75 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9 (e), 162.9 (e), 138.1 (e), 134.2 (o), 129.4 (o), 128.9 (o), 127.5 (o), 95.8 (e), 82.2 (o), 65.0 (o), 55.6 (o), 54.3 (o), 37.3 (e), 31.4 (e), 28.0 (e), 24.0 (e), 22.6 (e); HRMS (CI) calcd for $C_{19}H_{24}O_5S$ 365.1423 $(M + H)^+$, found 365.1420.

Preparation of Compound 16. The general procedure for DBU-mediated sulfinic acid elimination was followed using 1.5 equiv of DBU. Reaction time was 5 h and the yield was 94%. Compound **16**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 6.54−6.52 (1H, m), 6.14 (1H, s), 4.96−4.92 (1H, m), 4.76 (1H, AB, J = 7.1 Hz), 4.68 (1H, AB, J = 7.1 Hz), 3.42 (3H, s), 2.80−2.60 (1H, m), 2.60−2.52 (2H, m), 2.52−2.40 (3H, m), 2.20−2.00 (4H, m); ^{13}C NMR (50 Hz, $CDCl_3$) δ 201.1 (e), 153.5 (e), 143.6 (e), 140.8 (o), 125.5 (o), 96.5 (e), 81.6 (o), 56.7 (o), 38.0 (e), 31.9 (e), 31.3 (e), 27.2 (e), 22.9 (e); HRMS (CI) calcd for $C_{13}H_{18}O_3$ 223.1334 $(M + H)^+$, found 223.1329.

Preparation of Compound 18. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones was modified by the addition of 1.0 equiv of HMPA. The reaction mixture was warmed to 25 °C and worked up using the standard procedure. Without further purification, the crude mixture was dissolved in THF and treated with 5% aqueous hydrochloric acid at 25 °C for 1 h. Workup and purification afforded a mixture of the two diastereomers of ketone **17** (The ^1H NMR showed two $-OCH_3$ groups at 3.31 ppm and 3.32 ppm). The diastereomeric mixture was treated using the general procedure for DBU-mediated sulfinic acid elimination using 1.5 equiv of DBU, and the reaction mixture was heated at reflux for 18 h. The yield for three steps was 86%. Compound **18**: pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 6.48−6.46 (1H, t, J = 2.8 Hz), 6.20 (1H, s), 4.93−4.90 (1H, m), 4.77−4.74 (1H, AB, J = 7.0 Hz), 4.67−4.65 (1H, AB, J = 7.0 HZ), 3.41 (3H, s), 2.74−1.75 (12H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.0 (e), 150.2 (e), 144.6 (e), 138.7 (o), 128.9 (o), 95.9 (e), 81.4 (o), 56.2 (o), 42.0 (e), 31.1 (e), 31.0 (e), 29.3 (e), 24.9 (e), 21.1 (e); HRMS (CI) calcd for $C_{14}H_{20}O_3$ $(M + H)^+$ 237.1491, found 237.1482.

Preparation of Compound 20. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones followed by standard workup and purification afforded compound **20** in 99% yield. Compound **20**: colorless oil; ^1H NMR (300 MHz, C_6D_6) δ 7.62−7.59 (2H, m), 6.91−6.81 (3H, m), 5.46 (1H, s), 3.11−3.07 (1H, m), 2.58−2.49 (2H, m), 2.27 (1H, s), 1.92−1.86 (2H, m), 1.78−1.77 (1H, s), 1.61−1.43 (2H, m), 1.41−1.10 (5H, m), 0.89−0.85 (1H, AB, J = 10.4 Hz), 0.76−0.73 (1H, AB, J = 10.4 Hz); ^{13}C NMR (75 MHz, CDCl3) δ 199.2 (e), 165.0 (e), 140.0 (e), 133.8 (o), 129.4 (o), 128.0 (o), 124.3 (o), 68.7 (o), 50.8 (o), 43.7 (o), 40.0 (o), 38.3 (e), 37.3 (e), 30.5 (e), 29.8 (e), 23.0 (e), 22.7 (e); HRMS (EI) calcd for $C_{19}H_{22}O_3S$ 330.1290 $(M)^+$, found 330.1293.

Preparation of Compound 21. The general procedure for DBU-mediated sulfinic acid elimination was followed using 2.0 equiv of DBU. Reaction time was 36 h and the yield was 90%. Compound **21**: colorless oil; ^1H NMR (300 MHz, C_6D_6) δ 6.14 (1H, s), 5.93−5.92 (1H, d, J = 3.2 Hz), 2.79 (1H, s), 2.61 (1H, s), 2.20−2.00 (2H, m), 1.90−1.70 (2H, m), 1.50−1.00 (5H, m), 0.90−0.70 (3H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 201.2 (e), 154.4 (e), 149.0 (e), 140.2 (o), 123.3 (o), 48.0 (e), 44.2 (o), 42.4 (o), 38.2 (e), 27.2 (e), 26.3 (e), 25.1 (e), 23.0 (e); HRMS (EI) calcd for $C_{13}H_{16}O$ 188.1201 $(M)^+$, found 188.1195.

Preparation of Compound 22. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones was modified by the addition of 1.0 equiv of HMPA. The reaction mixture was gradually warmed to −25 °C and was quenched by saturated aqueous sodium bicarbonate solution and stirred at 25 °C for 2 h. The THF was evaporated and the crude residue was extracted with dichoromethane three times. To the dichoromethane solution was added 1 g of silica gel and the mixture was heated at reflux for 18 h to complete hydrolysis. The silica gel was filtered and the crude product was concentrated in vacuo and purified by flash chromatography on silica gel to afford compound **22** in 88%. Compound **22**: colorless oil; ^1H NMR (300 MHz, C_6D_6) δ 7.64−7.60 (2H, m), 6.90−6.84 (3H, m), 5.42 (1H, s), 3.14−3.11 (1H, dd, J = 4.5, 4.4 Hz), 2.62−2.54 (2H, m), 2.39 (1H, s), 2.23−2.08 (2H, m), 1.84−1.74 (3H, m), 1.48−1.00 (7H, m), 0.97−0.93 (1H, AB, J = 10.4 Hz), 0.77−0.74 (1H, AB, J = 10.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 204.2 (e), 160.5 (e), 140.7 (e), 134.1 (o), 129.7 (o), 128.5 (o), 127.9 (o), 69.0 (o), 53.4 (o), 44.1 (o), 42.0 (e), 40.6 (o), 38.1 (e), 33.8 (e), 30.4 (e), 25.2 (e), 23.6 (e), 21.0 (e); HRMS (EI) calcd for $C_{20}H_{24}O_3S$ 344.1446 $(M)^+$, found 344.1439.

Preparation of Compound 23. The general procedure for DBU-mediated sulfinic acid elimination was followed using 2.0 equiv of DBU. Reaction time was 5.5 days and the yield was 42% (59% based on recovered starting material). Compound **23**: colorless oil; ^1H NMR (300 MHz, C_6D_6) δ 6.26 (1H, s), 5.94−5.93 (1H, d, J = 3.2 Hz), 2.82 (1H, s), 2.62 (1H, s), 2.39−2.34 (2H, t), 2.18−1.96 (2H, m), 1.50−1.20 (7H, m), 0.90−0.88 (3H, m); ^{13}C NMR (50 MHz, C_6D_6) δ 202.9 (e), 151.0 (e), 149.6 (e), 137.7 (o), 127.3 (o), 48.1 (e), 44.4 (o), 43.5 (o), 42.4 (e), 28.2 (e), 27.8 (e), 25.4 (e), 25.3 (e), 21.6 (e); HRMS (EI) calcd for $C_{14}H_{18}O$ 202.1358 $(M)^+$, found 202.1361.

Preparation of Compounds 26 and 27. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones followed by standard workup and purification afforded compound **26** in 94% yield and compound **27**[13] in 92% yield. Compound **26**: white solid; mp 121−122 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80−7.77 (2H, d, J = 8.2 Hz), 7.38−7.35 (2H, d, J = 8.2 Hz), 7.33−7.28 (1H, d, J = 15.0 Hz), 6.73−6.68 (1H, d, J = 15.0 Hz), 6.20 (1H, s), 2.45 (3H, s), 2.43−2.36 (4H, m), 2.09−2.00 (2H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.6 (e), 152.2 (e), 145.6 (e), 141.8 (o), 137.1 (e), 134.4 (o), 134.0 (o), 130.7 (o), 128.5 (o), 38.0 (e), 25.4 (e), 22.4 (e), 22.2 (o); HRMS (EI) calcd for $C_{15}H_{16}O_3S$ 276.0820 $(M)^+$, found 276.0814.

Preparation of Compound 28. Azanorbornene **24** (0.16 mmol, 56 mg) was dissolved in 2 mL of acetonitrile. Palladium on carbon (6 mg) was added to the solution. The reaction was stirred under 1 atm of hydrogen. After 4 h, the hydrogenation was complete, palladium catalyst was filtered, and the crude product was concentrated in vacuo and purified by flash chromatography on silica gel to give 55 mg (98%). Compound **28**: white solid; mp 149−150 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80−7.78 (2H, d, J = 8.1 Hz), 7.35−7.33 (2H, d, J = 8.1 Hz), 7.04 (1H, d, J = 1.9 Hz), 4.81 (1H, br s), 4.76−4.74 (1H, d, J = 3.3 Hz), 2.43 (3H, s), 2.08−1.90 (2H, br), 1.42−1.10 (11H, br); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.3, 149.3, 145.3, 144.4, 137.2, 130.5, 128.4, 81.2, 62.2, 61.3, 28.3, 25.7, 24.7, 22.1; HRFAB (NBA) calcd for $C_{18}H_{23}NO_4S$ $(M + 1)^+$ 350.1426, found 350.1419.

Preparation of Compound 29. The general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones followed by quenching with saturated sodium bicarbonate solution at −78 °C and stirring at 25 °C for 2 h afforded a crude product which was extracted with dichoromethane three times. To the dichoromethane solution was added 0.5 g of silica gel and the resulting mixture was heated at reflux for 12 h to complete hydrolysis. The silica gel was filtered, and the crude product was concentrated in vacuo and purified by flash chromatography on silica gel to afford compound **29** in 99% yield. Compound **29**: white solid; mp 134−135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.67 (2H, d, J = 8.2 Hz), 7.32−7.29 (2H, d, J = 8.2 Hz), 5.55 (1H, br), 4.45 (1H, br), 4.21−4.19 (1H, d, J = 4.2 Hz), 3.61−3.57 (1H, ap t), 2.90−2.80 (1H, br), 2.60−2.50 (1H, m), 2.39 (3H, s), 2.30−2.10 (4H, br), 2.00−1.65 (5H, m), 1.36 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.2, 162.9, 154.3, 145.9, 136.8, 130.6, 128.5, 126.3, 81.4, 69.0, 62.6, 58.5, 52.9, 37.7, 30.4, 29.2, 28.6, 24.5, 23.0, 22.1; HRFAB (NBA) calcd for $C_{24}H_{31}NO_5S$ $(M + 1)^+$ 446.2001, found 446.2016.

Preparation of Compound 30. To the dichoromethane solution of azanorbornene **24** (0.081 mmol, 28 mg, 1.0 equiv) at 25 °C was added mCPBA (0.097 mmol, 24 mg (70%), 1.2 equiv), and the mixture was heated at reflux for 18 h. The reaction was quenched by 10% aqueous $NaHSO_3$ solution, extracted with dichoromethane, washed with saturated aqueous sodium bicarbonate solution, water, and brine, and dried over anhydrous sodium sulfate. The crude product was concentrated in vacuo and purified by flash column chromatography on silica gel to afford 24 mg of compound **30** (82%). Compound **30**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.79 (1H, d, J = 8.2 Hz), 7.80−7.77 (1H, d, J = 8.2 Hz), 7.41−7.38 (1H, d, J = 8.2 Hz), 7.38−7.35 (1H, d, J = 8.2 Hz), 7.25−7.24 (0.5H, dd, J = 2.7, 0.7 Hz), 7.12−7.11 (0.5H, dd, J = 2.7, 0.7Hz), 4.85−4.84 (0.5H, d, J = 2.7 Hz), 4.79 (0.5H, s), 4.75 (0.5H, s), 4.73−4.72 (0.5H, d, J = 2.7 Hz), 3.65−3.63 (0.5H, d, J = 3.5 Hz), 3.60−3.59 (0.5H, d, 3.6 Hz), 3.58−3.57 (0.5H, d, J = 3.6 Hz), 3.48−3.46 (0.5H, d, J = 3.5 Hz), 2.47 (1.5H, s), 2.45 (1.5H, s), 1.43 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.8, 155.6, 155.1, 146.0, 145.5, 145.2, 136.2, 136.0, 130.8, 130.7, 128.6, 128.5, 81.7, 81.6, 63.2, 62.7, 62.5, 62.2, 57.4, 57.1, 57.0, 56.6, 28.5, 22.2; HRMS (CI) calcd for $C_{18}H_{21}NO_5S$ $(M + 1)^+$ 364.1219, found 364.1200.

Preparation of Compounds 32 and 34. Following the general procedure for conjugate addition of γ-methoxy allylsulfonyl anions to cyclopentyl sulfones yielded a mixture of two products as assayed by TLC (60% ethyl acetate in hexane). Standard workup and purification procedure provided compound **32** (42%) and compound **34** (55%). Compound **32**: colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.64 (2H, d, J = 8.2 Hz), 7.36−7.33 (2H, d, J = 8.2 Hz), 5.72 (1H, br s), 4.70−4.68 (1H, d, J = 4.7 Hz), 4.05 (1H, br s), 3.92 (1H, br s), 2.45 (3H, s), 2.42−1.90 (9H, m), 1.46 (9H, br s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.5, 158.7, 154.8, 146.0, 136.4, 130.6, 129.6, 128.5, 82.4, 73.7, 53.9, 49.6, 47.0, 39.0, 37.9, 28.7, 28.0, 27.1, 23.2, 22.2; HRFAB (DTT/DTE) calcd for $C_{24}H_{29}NO_6S$ $(M + 1)^+$ 460.1794, found 460.1799. Compound **34**: white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75−7.72 (1H, d, J = 8.6 Hz), 7.72−7.69 (1H, d, J = 8.6 Hz), 7.40−7.37 (1H, d, J = 8.6 Hz), 7.37−7.34 (1H, d, J = 8.6 Hz), 5.84 (0.5H, s), 5.55 (0.5H, s), 4.65−4.64 (0.5H, d, J = 4.0 Hz), 4.47−4.46 (0.5H, d, J = 4.0 Hz),4.34 (0.5H, s), 4.24 (0.5H, s), 4.02−4.01 (0.5H, d, J = 3.3 Hz), 3.98−3.97 (0.5H, d, J = 3.3 Hz), 3.75−3.71 (0.5H, dd, J = 5.9, 4.0 Hz), 3.64−3.60 (0.5H, dd, J = 5.9, 4.0 Hz), 3.57−3.56 (0.5H, d, J = 3.3 Hz), 3.56−3.55 (0.5H, d, J = 3.3 Hz), 2.88−2.86 (0.5H, d, J = 5.9 Hz), 2.74−2.72 (0.5H, d, J = 5.9 Hz), 2.45 (1.5H, s), 2.43 (1.5H, s), 2.40−1.75 (6H, m), 1.44 (4.5H, s), 1.41 (4.5H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.4, 199.0, 162.1, 161.0, 156.9, 156.8, 146.5, 136.1, 136.0, 130.9, 130.8, 128.5, 128.4, 128.0, 127.9, 82.0, 77.7, 71.8, 71.4, 63.3, 62.8, 60.0, 59.2, 50.2, 50.0, 49.1, 48.7, 48.1, 47.6, 37.7, 37.6, 34.4, 28.8, 28.6, 28.5, 28.1, 25.4, 23.0, 22.9, 22.2; HRFAB (NBA) calcd for $C_{24}H_{29}NO_6S$ $(M + 1)^+$ 460.1794, found 460.1803.

Preparation of Compound 35b$_1$. Using the general procedure for alkylation at the δ-carbon provided compound **35b$_1$** in 83% yield accompanied by 11% **10b**. Compound **35b$_1$**: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93−7.53 (5H, m), 5.99 (1H, s), 5.68−5.59 (1H, m), 5.03−4.95 (2H, m), 3.47−3.41 (1H, dd, J = 10.0, 7.8 Hz), 2.86−2.75 (1H, dt, J = 11.6, 5.8 Hz), 2.59−2.51 (1H, dd, J = 15.3, 6.7 Hz), 2.45−2.25 (5H, m), 2.10−1.50 (7H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.1 (e), 164.3 (e), 137.3 (e), 134.4 (o), 132.9 (o), 131.1 (o), 130.0 (o), 129.3 (o), 120.0 (e), 75.8 (e), 50.7 (o), 38.0 (e), 37.6 (e), 34.9 (e), 32.2 (e), 31.9 (e), 24.0 (e), 23.3 (e); HRMS (CI) calcd for $C_{20}H_{24}O_3S$ $(M + H)^+$ 345.1524, found 345.1518.

Preparation of Compound 35b$_2$. Using the general procedure for alkylation at the δ-carbon provided compound **35b$_2$** in 88% yield accompanied by 6% **10b**. Compound **35b$_2$**: white solid; mp 79.5−80.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92−7.54 (5H, m), 5.96 (1H, s), 3.51−3.45 (1H, t, J = 8.6 Hz), 2.86−2.76 (1H, dt, J = 18.4, 5.5 Hz), 2.86−1.25 (11H, m), 1.21 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.3 (e), 165.3 (e), 136.8 (e), 134.3 (o), 130.8 (o), 129.4 (o), 128.7 (o), 72.7 (e), 49.1 (o), 38.6 (e), 38.0 (e), 32.2 (e), 32.1 (e), 23.9 (e), 23.2 (e), 20.5 (o); HRMS (EI) calcd for $C_{18}H_{22}O_3S$ 318.1290 $(M)^+$, found 318.1287.

Preparation of Compound 36b$_2$. The general procedure for DBU-mediated sulfinic acid elimination was followed using 2.0 equiv of DBU. The reaction time was 32 h and the yield was 88%. Compound **36b$_2$**: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (1H, s), 2.60−2.43 (6H, m), 2.42−2.37 (2H, t), 2.06−1.97 (2H, m), 1.89 (3H, s), 1.87−1.77 (2H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.8 (e), 159.6 (e), 144.3 (e), 135.3 (e), 126.1 (o), 41.8 (e), 37.9 (e), 36.1 (e), 29.5 (e), 23.6 (e), 22.1 (e), 17.3(o); HRMS (EI) calcd for $C_{12}H_{16}O$ 176.1201 $(M)^+$, found 176.1196.

Preparation of Compound 37b$_1$. The general procedure for DBU-mediated sulfinic acid elimination was followed using 1.5 equiv of DBU. The reaction time was 18 h, and the yield was 96%. Compound **36b$_1$**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.55−6.50 (1H, dd, J = 15.3, 1.3 Hz), 5.99 (1H, s), 5.87−5.79 (1H, m), 2.66−2.58 (4H, t), 2.54−2.51 (2H, t), 2.50−2.40 (2H, t), 2.10−2.00 (2H, m), 1.90−1.80 (5H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.5 (e), 159.4 (e), 142.8 (e), 137.1 (e), 131.0 (o), 127.3 (o), 127.2 (o), 38.0 (e), 36.6 (e), 35.3 (e), 29.8 (e), 23.6 (e), 22.1 (e), 19.4 (o); HRMS (EI) calcd for $C_{14}H_{18}O$ $(M)^+$ 202.1358, found 202.1352.

Preparation of Compound 39b$_1$. Compound **37b$_1$** (0.0891 mmol, 18 mg) was dissolved in 3 mL of benzene in a sealed tube. The solution was frozen, thawed, and purged under vacuum three times to exclude oxygen. The sealed tube was heated at 120 °C for 2 days. After evaporation of benzene, the crude product was purified by flash column chromatography on silica gel to afford compound **39b$_1$** 10 mg (56%). Compound **39b$_1$**: white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12−3.00 (1H, m), 2.50−2.30 (9H, m), 2.06−1.90 (5H, m), 0.88 −0.85 (3H, d, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.5 (e), 149.7 (e), 147.2 (e), 134.3 (e), 133.3 (e), 38.3 (e), 37.3 (e), 32.4 (e), 31.3 (e), 27.5 (e), 25.0 (o), 23.0 (e), 22.9 (e), 19.5 (o).

Preparation of Compound 40b$_1$. This compound was prepared in a manner similar to that of compound **39b$_1$** except the sealed tube was filled with air. This provided 42% yield of the aromatized derivative **40b$_1$**. Compound **40b$_1$**: white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (1H, s), 2.95−2.90 (2H, t), 2.86−2.81 (4H, m), 2.65−2.60 (2H, m), 2.62 (3H, s), 2.20−2.00 (4H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.7, 149.5, 141.6, 140.7, 140.6, 129.9, 126.7, 41.4, 33.9, 31.6, 28.5, 25.2, 24.1, 23.2; HRMS (EI) calcd for $C_{14}H_{16}O$ 200.1201 $(M)^+$, found 200.1196.

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Supplementary Material Available: Proton and carbon spectra for all new compounds (53 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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