JOC Article

Phenylsulfonyl Ene−Allenes as Efficient Precursors to Bicyclic Systems via Intramolecular [2 + 2]-Cycloaddition Reactions

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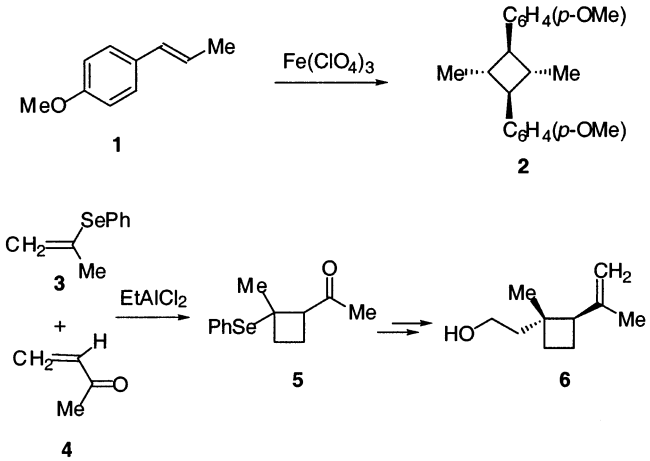
Various phenylsulfonyl allene derivatives were prepared with double bonds tethered either to the α-position or the γ-position of the allene. These substrates underwent a highly regio- and stereospecific thermal [2 + 2]-cycloaddition across the nonactivated cumulene double bond, forming distal cycloadducts (i.e., **57**) in the case of α-tethered allenes and proximal adducts (i.e., **25**) in the case of γ-tethered allenes. The mechanistic rationale for the observed stereospecificity involves initial diradical formation, followed by a rapid ring closure to the more stable cis-fused ring system. The tether may be equipped with heteroatoms, allowing for the formation of fused heterocycles (e.g., **61**), and the cycloaddition can be facilitated by the introduction of sterically bulky groups and/or by conformational rigidity to the tether. Other modes of cyclization were observed in the presence of sodium benzenesulfinate or Lewis acids, in which cases polar mechanisms prevail. The chemoselectivity is reversed for [4 + 2]-cycloadditions, which prefer instead to engage the vinyl sulfone moiety, independent of whether the tether is attached to the α- or γ-position of the allene.

Introduction

The [2 + 2]-cycloaddition of alkenes is a synthetically useful reaction as it provides a rapid and efficient method for accessing strained cyclobutane rings from simple precursors.[1] A recent example of this process involves the iron(III)-catalyzed cyclodimerization of *trans*-anethole (**1**) to form the tetrasubstituted cyclobutane **2** (Scheme 1).[2] Natural products of synthetic interest that contain a four-membered carbocyclic ring represent attractive targets to showcase such methodology. For example, Yamazaki and co-workers[3] utilized a selenium-directed [2 + 2]-cycloaddition as the key step in their concise synthesis of the cyclobutane natural product fragranol (**6**). An alternative approach to this same target involved a [2 + 2]-cycloaddition of allyl-*tert*-butyldiphenylsilane and methyl methacrylate, and this was catalyzed by titanium tetrachloride.[4]

[2 + 2]-Cycloaddition chemistry is often carried out in an intramolecular fashion.[5] This modification brings many benefits, including better defined regioselectivity,[6] rate enhancement, as well as the ability to construct polycyclic structures in one step. A particularly intriguing application of this technology can be seen in the intramolecular [2 + 2]-cycloaddition−fragmentation approach used to prepare the 5−8−5 ring system found in the fusicoccanes and ophiobolanes[7] (Scheme 2). A photochemical dioxenone/alkene [2 + 2]-cycloaddition protocol was also employed to access the bicyclo[2.1.1]hexane system encountered in solanoeclepin A (**12**), a hatching

SCHEME 1



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(1) . (a) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1990**, *8*, 1295. (b) Sekretar, S.; Kopecky, J.; Cerny, M. *Collect. Czech. Chem. Commun.* **1986**, *51*, 899. (c) Aben, R. W. M.; Scheeren, H. W. *Tetrahedron Lett.* **1985**, *26*, 1889.

(2) Ohara, H.; Itoh, T.; Nakamura, M.; Nakamura, E. *Chem. Lett.* **2001**, *7*, 624.

(3) Yamazaki, S.; Fujitsuka, H.; Takara, F.; Inoue, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, *6*, 695.

(4) Knoelker, H.-J.; Baum, G.; Schmitt, O.; Wanzl, G. *J. Chem. Soc., Chem. Commun.* **1999**, *17*, 1737.

(5) For recent examples, see: (a) Joseph, B. K.; Verghese, B.; Sudarsanakumar, C.; Deepa, S.; Viswam, D.; Chandran, P.; Asokan, C. V. *J. Chem. Soc., Chem. Commun.* **2002**, *7*, 736. (b) Dotz, K. H.; Mittenzwey, S. *Eur. J. Org. Chem.* **2002**, *1*, 39. (c) Shim, P.-J.; Kim, H.-D. *Tetrahedron Lett.* **1998**, *39*, 9517.

(6) (a) Baldwin, S. W. *Org. Photochem.* 1981, *5*, 123. (b) Crimmins, M. T.; Reinhold: T. L. *Org. React.* **1993**, *44*, 297.

(7) (a) Lo, P. C.-K.; Snapper, M. L. *Org. Lett.* **2001**, *3*, 2819. (b) Randall, M. L.; Lo, P. C.-K.; Bonitatebus, P. J., Jr.; Snapper, M. L. *J. Am. Chem. Soc.* **1999**, *121*, 4534.

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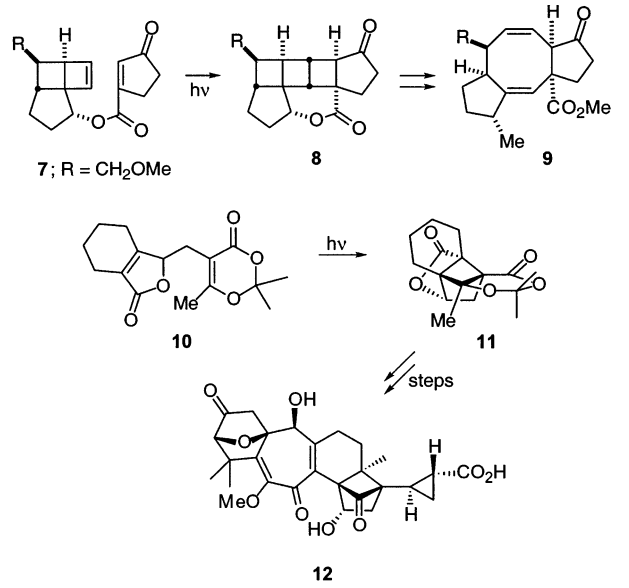
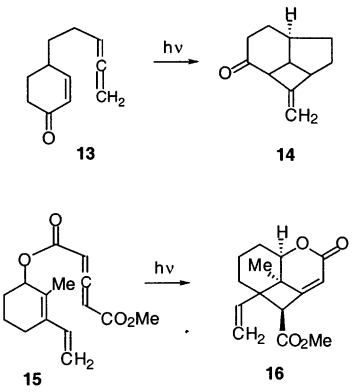
SCHEME 2



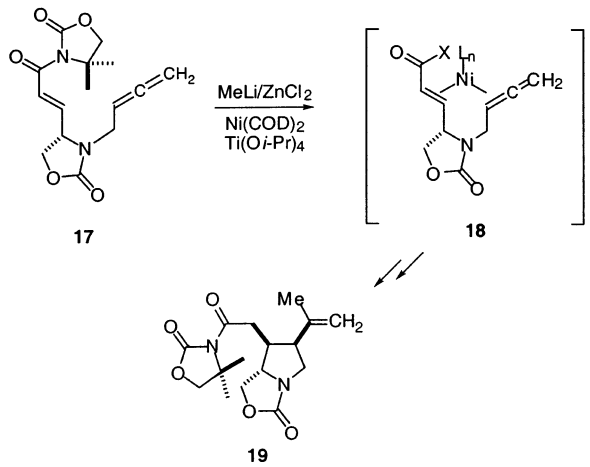
agent of the potato cyst nematode.[8] In the former case, a temporary tether was constructed between the two π-bonds in order to overcome the natural preference for the alternate regiochemical pathway in the [2 + 2]-cycloaddition reaction. In the latter case, the rings formed in the cycloaddition reaction remain an integral part of the final target architecture.

Allenes represent interesting partners for [2 + 2]-cycloadditions because they are inherently strained species[9] and, therefore, more willing participants in a variety of reactions.[10] In addition, the extra double bond functionality can be leveraged to prepare methylenecyclobutanes,[11] which readily undergo a variety of synthetically useful transformations in their own right.[12] The course of the intramolecular allene/alkene–cycloaddition reaction has been found to depend on the nature of the allenyl π-bond and the length of the tether separating the two π-bonds.[13] For example, allenyl cyclohexenone **13** has been reported to undergo intramolecular [2 + 2]-cycloaddition across the proximal allenyl π-bond (Scheme 3),[14] whereas the cyclohexenyl ester **15** engages the distal π-system.[15]

SCHEME 3



SCHEME 4



The adjacent π-bonds present in the allene moiety are orthogonal, a circumstance which provides for orientational differentiation in some regioselective reactions. For example, Montgomery and Chevliakov have argued that the observed regiochemistry in their nickel-catalyzed allene/alkene cyclization (Scheme 4) is dictated by unfavorable nonbonded interactions of the chelated complex involving the distal π-system of the allene. Thus, the reaction proceeds exclusively via the chelate **18**.[16] Facial selectivity can also be controlled by directing substituents on the allene, as demonstrated by Brummond and coworkers in their metal-assisted Pauson–Khand-type allene/alkyne cycloaddition protocol for the construction of variously functionalized cyclopentenones.[17]

Our own interest in allenyl cycloaddition chemistry arose from our ongoing investigations into the reactivity of acetylenic and dienyl sulfones,[18] substrates which continue to provide innovative methodologies in organic

(8) (a) Briere, J.-F.; Blaauw, R. H.; Benningshof, J. C. J.; van Ginkel, A. E.; van Maarseveen, J. H.; Hiemstra, H. *Eur. J. Org. Chem.* **2001**, *12*, 2371. (b) Blaauw, R. H.; Benningshof, J. C. J.; van Ginkel, A. E.; van Maarseveen, J. H.; Hiemstra, H. *J. Chem. Soc., Perkin Trans. 1* **2001**, *18*, 2250. (c) Blaauw, R. H.; Briere, J.-F.; deJong, R.; Benningshof, J. C. J.; van Ginkel, A. E.; Fraanje, J.; Goubitz, K.; Schenk, H.; Rutjes, F. P. J. T.; Hiemstra, H. *J. Org. Chem.* **2001**, *66*, 233.

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(12) (a) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453. (b) Pasto, D. J.; Brophy, J. *J. Phys. Org. Chem.* **1993**, *6*, 95.

(13) (a) Hayakawa, K.; Ohsuki, S.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 4205. (b) Hayakawa, K.; Aso, K.; Shiro, M.; Kanematsu, K. *J. Am. Chem. Soc.* **1989**, *111*, 5312. (c) Yoshida, M.; Hiromatsu, M.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1168. (d) Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1989**, *30*, 6559. (e) Hayakawa, K.; Takewaki, M.; Fujimoto, T.; Kanematsu, K. *J. Org. Chem.* **1986**, *51*, 5100. (f) Kanematsu, K.; Kinoyama, I. *J. Chem. Soc., Chem. Commun.* **1992**, 735. (g) Yeo, S. K.; Shiro, M.; Kanematsu, K. *J. Org. Chem.* **1994**, *59*, 1621.

(14) Dauben, W. G.; Shapiro, G.; Luders, L. *Tetrahedron Lett.* **1985**, *26*, 1429.

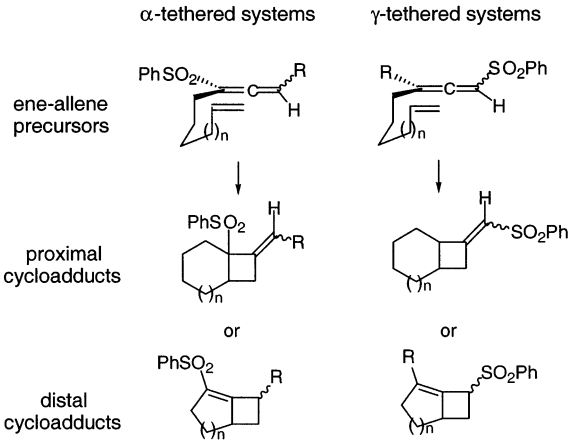
(15) Yoshida, M.; Hidaka, Y.; Nawata, Y.; Rudzinski, J. M.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1988**, *110*, 1232.

(16) Chevliakov, M. V.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 11139.

(17) (a) Brummond, K. M.; Kerekes, A. D.; Wan, H. *J. Org. Chem.* **2002**, *67*, 5156. (b) Brummond, K. M.; Wan, H.; Kent, J. L. *J. Org. Chem.* **1998**, *63*, 6535. (c) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087. (d) Kent, J. L.; Wan, H.; Brummond, K. M. *Tetrahedron Lett.* **1995**, *36*, 2407.

(18) (a) Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. N. *Tetrahedron Lett.* **1986**, *27*, 2683. (b) Padwa, A.; Kline, D. N.; Perumattam, J. *Tetrahedron Lett.* **1987**, *28*, 913. (c) Padwa, A.; Yeske, P. E. *J. Org. Chem.* **1991**, *56*, 6386. (d) Padwa, A.; Austin, D. J.; Ishida, M.; Muller, C. L.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.* **1992**, *57*, 1161.

SCHEME 5



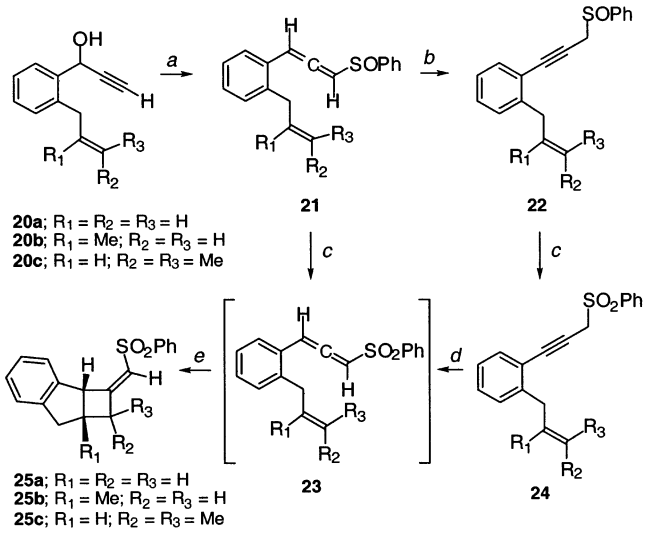
synthesis.[19] In earlier publications, we had reported a highly chemo- and stereospecific intramolecular [2 + 2]-cycloaddition reaction involving sulfonyl allenes with tethered olefins.[20] In this paper, we describe the scope and mechanistic details of further studies with related allenyl sulfones.

Results and Discussion

In considering the intramolecular [2 + 2]-cycloaddition between sulfonyl allenes and olefins, there are two possible points of attachment for the tethered olefin. These structural variations can be described as α-tethered and γ-tethered (Scheme 5). Within each of these alternatives, there is also the added dimension of undergoing cycloaddition with either the proximal or distal cumulene π-bond. As part of our continuing studies in this area, we became interested in probing the effects on the reaction of several structural and electronic features, including point of attachment, allene and olefin substitution, and the nature and length of the tether on the course of the cycloaddition reaction.

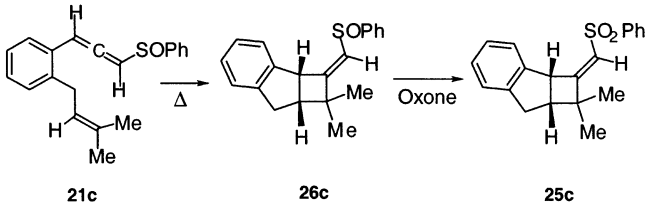
γ-Tethered Systems. Our initial investigation began with the γ-tethered ene−allene systems shown in Scheme 6. Formation of the desired substrates relied upon propargyl alcohols **20**, which are accessible in good to excellent yields via the addition of alkynyl Grignards onto suitably substituted aldehydes.[21] These alcohols were then converted to the corresponding propargyl sulfenates that are known to undergo a spontaneous 2,3-sigmatropic shift[22] to furnish allenyl sulfoxides (i.e., **21**). Indeed, treatment of propargyl alcohols **20a**−**c** with phenylsulfenyl chloride led to the formation of allenes **21a**−**c**,

SCHEME 6[a]



[a] Reagents: (a) PhSCl, Et_3N, THF, −78 °C; (b) THF, warm −78 to +25 °C; (c) Oxone, MeOH, 0 °C; (d) Et_3N, benzene 80 °C; (e) benzene, 60 °C.

SCHEME 7[a]



[a] Reagents: (a) (i) *n*-BuLi, *t*-BuOH, THF, −45 °C, (ii) Br-$(CH_2)_3CH{=}CH_2$, THF; (b) TBAF, THF, 0 °C; (b) TBAF, THF, 0 °C; (c) PhSCl, Et_3N, THF, 25 °C; (d) Oxone, MeOH, 0 °C; (e) *o*-DCB, 250 °C.

which could be isolated as pure compounds when the reaction was carried out at low temperatures (−78 °C). However, if the reaction mixture was allowed to warm to room temperature before quenching, propargylic sulfoxides **22a**−**c** were obtained instead, presumably arising from the base catalyzed isomerization of the initially formed allene **21**, a phenomenon which has been observed previously with related γ-phenylsulfonyl allenes.[23]

Conversion of the allenic sulfoxide system **21** to the corresponding sulfones **23** with Oxone[24] proceeded in good to excellent yields. The sulfonyl allenes so formed underwent rapid [2 + 2]-cycloaddition at room temperature to form the γ-proximal cycloadducts **25a**−**c** (Scheme 6). As a matter of practical convenience, the more stable propargyl sulfoxides **22a**−**c** could be oxidized to the propargyl sulfones **24a**−**c**. Exposing these substrates to catalytic amounts of triethylamine under thermal conditions allowed for equilibrium concentrations of allene **23** to be formed, which then underwent rapid cycloaddition to give the methylenecyclobutanes **25a**−**c**.

The [2 + 2]-cycloaddition can also be induced to occur at the sulfoxide stage (Scheme 7). Thus, warming a sample of **21c** in chloroform at 40 °C for 10 min provided

(19) For example, see: (a) Back, T. G.; Nakajima, K. *J. Org. Chem.* **2000**, *65*, 4543. (b) Garrido, J. L.; Alonso, I.; Carretero, J. C. *J. Org. Chem.* **1998**, *63*, 9406. (c) Padwa, A.; Murphree, S. S.; Ni, Z.; Watterson, S. H. *J. Org. Chem.* **1996**, *61*, 3829. (d) Bäckvall, J.-E.; Chinchilla, R.; Nájera, C.; Yus, M. *Chem. Rev.* **1998**, *98*, 2291. (e) Back, T. G. *Tetrahedron* **2001**, *57*, 5263.

(20) (a) Padwa, A.; Filipkowski, M. A.; Meske, M.; Watterson, S. H.; Ni, Z. J. *J. Am. Chem. Soc.* **1993**, *115*, 3776. (b) Padwa, A.; Lipka, H.; Watterson, S. H. *Tetrahedron Lett.* **1995**, *36*, 4521.

(21) (a) Midland, M. M.; McLoughlin, J. I.; Werley, R. T. *Org. Synth.* **1990**, *68*, 14. (b) Umeno, M.; Suzuki, A. *Chem. Ind.* **1996**, *64* (Handbook of Grignard Reagents), pp 645−666.

(22) (a) Miller, E. G.; Raynor, D. R.; Mislow, K. *J. Am. Chem. Soc.* **1966**, *88*, 3139. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (c) Braverman, S.; Stabinsky, Y. *J. Chem. Soc., Chem. Commun.* **1967**, 270.

(23) Braverman, S.; Mechoulam, H. *Tetrahedron* **1974**, *30*, 3883.

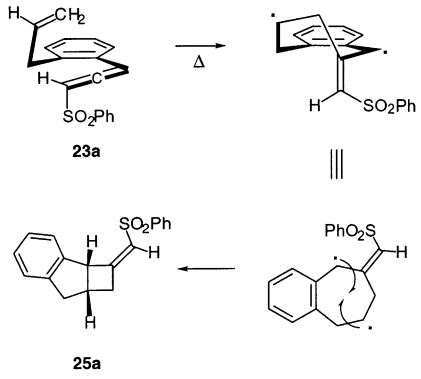
(24) Leonard, J.; Hague, A. B.; Jones, M. F.; Ward, R. A. *Synthesis* **2000**, 507 and references therein.

cycloadduct **26c** in high yield after evaporation of the solvent. A subsequent oxidation with Oxone gave **25c**, which was spectroscopically identical to the product obtained by the alternative route.

The above cycloadditions are somewhat unique in that they occur under strictly thermal conditions. Photochemical [2 + 2]-cycloadditions are much more common than thermal ones.[25] Nevertheless, thermal variants are known, usually facilitated by Lewis acid catalysts, and typically occur in a stepwise fashion either through the intervention of diradical or dipolar intermediates.[26,27] An interesting feature of the above reaction is the formation of only a single stereoisomer of cycloadduct **25**. The overall [2 + 2]-cycloaddition exhibits double stereospecificity: the *exo*-methylene geometry (i.e., *E*-sulfone) and the cis-ring juncture were consistently observed. This stereochemical relationship was unequivocally established by X-ray crystallography of cycloadduct **25b**. While this high degree of selectivity is consistent with a concerted *supra-antara* mechanism, MO calculation studies have called into question whether such pathways are energetically relevant for thermal [2 + 2]-cycloadditions.[28] We therefore propose an alternative mechanism proceeding through a diradical intermediate arising from initial attack of the terminal olefinic carbon onto the central allene carbon atom (Scheme 8). The resulting diradical intermediate would be expected to close rapidly (i.e., before bond rotation can occur) to the more stable cis-fused 4,5 ring system.[29]

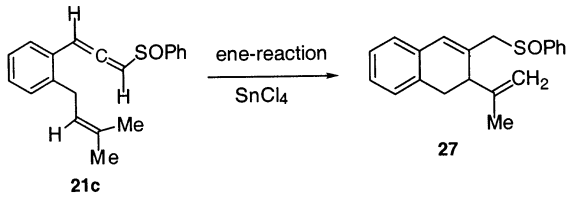
To further probe the features of this novel [2 + 2]-cycloaddition, we carried out the reaction of **21c** in the presence of an added Lewis acid. Sulfonyl allene **21c** was

SCHEME 8[a]



[a] Reagents: (a) NaH, CH_2=C(CH_3)CH_2Br, THF, 0 °C; (b) TBAF, THF, 0 °C; (c) MsCl, Et_3N; (d) NaH, PhSH; (e) Oxone, MeOH, 0 °C; (f) Et_3N, benzene 80 °C.

SCHEME 9



treated with tin tetrachloride in CH_2Cl_2 at 25 °C for 24 h. To our surprise, these conditions led to another mode of reactivity, namely an intramolecular ene reaction, which produced the dihydronaphthalene derivative **27** in 81% yield (Scheme 9). A related Lewis-acid-promoted cyclization of an allenyl sulfoxide has been reported by Parsons.[30] While this result is equivocal with respect to the proposed mechanism for the [2 + 2]-cycloaddition, the fact that a Lewis acid introduces such a dramatic perturbation in the outcome is consistent with a catalyst-induced changeover from a radical to a polar pathway.

We next investigated the sensitivity of the [2 + 2]-cycloaddition to changes in the configuration of the tether. Toward this end, allenyl sulfones **29** and **34** were studied. With these systems, the two reacting moieties are connected by an aliphatic chain and an ether linkage, respectively. To prepare the former, the silyl-protected propargyl alcohol was deprotonated with *n*-butyllithium, and the resulting dianion underwent reaction with 5-bromo-1-pentene at the more nucleophilic carbanion to give alcohol **28** in moderate yield. Sulfenylation, rearrangement, and oxidation to sulfonyl allene **29** occurred without event (Scheme 10). However, the thermal [2 + 2]-cycloaddition of this substrate to give **30** was considerably more sluggish than that previously encountered, requiring 24 h reflux in *o*-dichlorobenzene (250 °C) for reasonable conversion to take place. We attribute this sluggish behavior to the greater conformational flexibility of the tether in **29** relative to the orientationally constrained environment about the *o*-dialkylbenzene ring in allenes **23**. Similar dependency upon the flexibility of the tether has been documented in other intramolecular cycloadditions.[31]

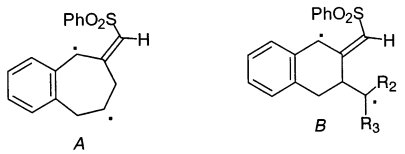
(25) For recent examples of photocycloadditions with various mechanistic subtleties, see: (a) Booker-Milburn, K. I.; Wood, P. M.; Dainty, R. F.; Urquhart, M. W.; White, A. J.; Lyon, H. J.; Charmant, J. P. H. *Org. Lett.* **2002**, *4*, 1487. (b) Mehta, G.; Sreenivas, K. *Tetrahedron Lett.* **2002**, *43*, 703. (c) Galoppini, E.; Chebolu, R.; Gilardi, R.; Zhang, W. *J. Org. Chem.* **2001**, *66*, 162. (d) Piers, E.; Orellana, A. *Synthesis* **2001**, 2138. (e) Doepp, D.; Mohamed, S. K.; El-Khawaga, A. *Helv. Chim. Acta* **2001**, *84*, 3673.

(26) (a) Snider, B. B.; Spindell, D. K. *J. Org. Chem.* **1980**, *45*, 5017. (b) Snider, B. B.; Ron, E. *J. Org. Chem.* **1986**, *51*, 3643. (c) Hoffmann, H. M. R.; Ismail, Z. M.; Weber, A. *Tetrahedron Lett.* **1981**, *22*, 1953. (d) Lukas, J. H.; Kouwenhoven, A. P.; Baardman, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 709. (e) Komiya, Z.; Nishida, S. J. *J. Org. Chem.* **1983**, *48*, 1500.

(27) (a) Dolbier, W. R.; Weaver, S. L. *J. Org. Chem.* **1990**, *55*, 711. (b) Dolbier, W. R.; Burkholder, C. R.; Wicks, G. E.; Palenik, G. J.; Gawron, M. *J. Am. Chem. Soc.* **1985**, *107*, 7183. (c) Cripps, H. N.; Williams, J. K.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 2723. (d) Baldwin, J. E.; Roy, U. V. *Chem. Commun.* **1969**, 1225. (e) Kiefer, E. F.; Okamura, M. Y. *J. Am. Chem. Soc.* **1968**, *90*, 4187. (f) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1988**, *53*, 4807.

(28) Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106. (b) Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1988**, *110*, 5993. (c) Bernardi, F.; Bottoni, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260.

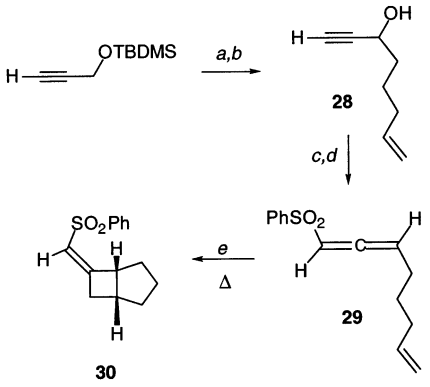
(29) One of the reviewers has pointed out that the mechanism proposed in Scheme 8 only seems valid for the highly loaded allene structure **23a**, where the aromatic ring makes the benzylic/allylic radical most favored and $R_2 = R_3 = H$ makes the secondary radical A favored over the alternate diradical *B*. This reviewer notes that a competing mechanism, where diradical B is also formed, may explain why the yield of **25a** (89%) is greater than the yield of **25c** (82%), since diradical *B* is more favored when $R_2 = R_3 =$ Me.



(30) For a related cyclization of an allenyl sulfoxide, see: Parsons, P. J.; Parkes, K. E. G.; Penkett, C. S. *Synlett* **1995**, *7*, 709.

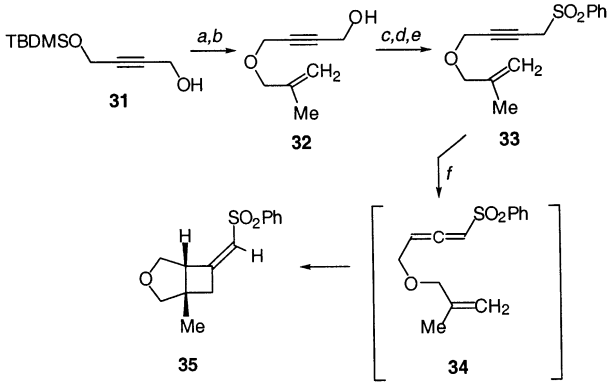
(31) Broggini, G.; Bruche, L.; Garanti, L.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1994**, 4, 433.

SCHEME 10[a]



[a] Reagents: (a) (i) *n*-BuLi, *t*-BuOH, THF, −45 °C, (ii) $Br(CH_2)_3$-$CH{=}CH_2$, THF; (b) TBAF, THF, 0 °C (b) TBAF, THF, 0 °C; (c) PhSCl, Et_3N, THF, 25 °C; (d) Oxone, MeOH, 0 °C; (e) *o*-DCB, 250 °C.

SCHEME 11[a]

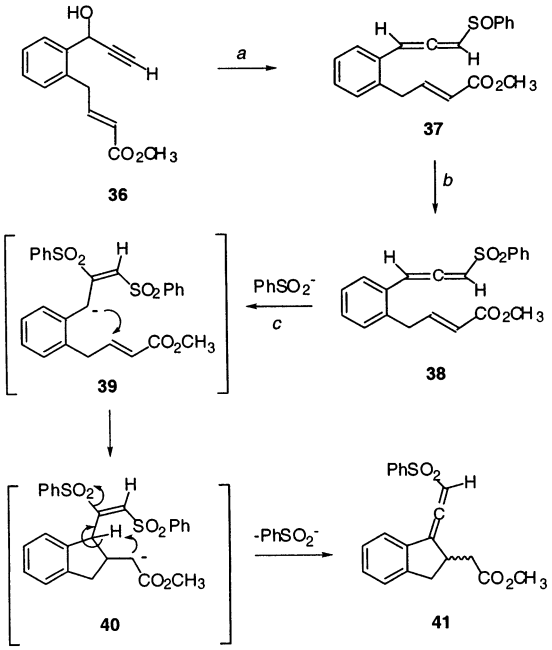


[a] Reagents: (a) NaH, $CH_2{=}C(CH_3)CH_2Br$, THF, 0 °C; (b) TBAF, THF, 0 °C; (c) MsCl, Et_3N; (d) NaH, PhSH; (e) Oxone, MeOH, 0 °C; (f) Et_3N, benzene 80 °C.

The oxygen-containing tethered allene **34** was accessed starting from the monoprotected ynediol **31**, and the alkenyl side chain was attached by O-alkylation. The silyl protecting group was removed, the resultant alcohol mesylated, and the mesylate leaving group was displaced with thiophenolate to give an intermediate sulfide. Subsequent oxidation to propargyl sulfone **33** was accomplished using Oxone. Exposure of **33** to catalytic quantities of triethylamine promoted the isomerization to allene **34**, which underwent thermal cycloaddition to **35** at 80 °C in 94% yield (Scheme 11). This last cycloaddition reaction was somewhat more reticent than its benzenoid counterpart (i.e., **23**) but, on the other hand, far more facile than the systems connected by a strictly aliphatic chain (i.e., **29**). We have observed similar behavior in another series of cycloaddition precursors (vide infra), and the inclusion of heteroatoms in the tethers of intramolecular furan Diels−Alder (IMDAF) precursors is also known to play a critical role in facilitating the course of those reactions as well.[32]

In exploring the scope of these cycloaddition reactions, we considered a reasonable next step in the overall evaluation to be an electronic modification of the alkenyl

SCHEME 12[a]



[a] Reagents: (a) PhSCl, Et_3N, THF, −78 °C; (b) Oxone, MeOH, 0 °C; (c) $NaSO_2Ph$, K_2CO_3, THF.

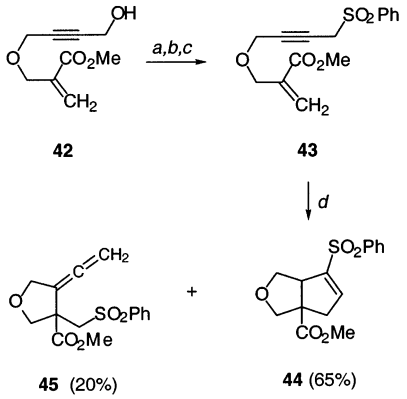
π-bond. With this in mind, we prepared allene **38** bearing an α,β-unsaturated ester residue. We found that this substrate exhibited an entirely different mode of reactivity which, as it turned out, was catalyzed by a trace amount of benzenesulfinate anion and gave rise to the formation of exocyclic sulfonyl allene **41** in high yield (Scheme 12). This product most likely originates by the initial attack of benzenesulfinate onto the central allene carbon of **38** to give the sulfonyl-stabilized allylic anion **39**, which then engages in an intramolecular Michael addition onto the unsaturated ester producing enolate **40**. Elimination of benzenesulfinate anion then propagates the catalytic cycle and furnishes the observed product **41**. Changing the position of the electron-withdrawing group on the olefin redirects the course of this reaction. Thus, the major product derived from the allene precursor **43** is the oxabicyclo[3.3.0]octene derivative **44**, which was also accompanied by a smaller amount of exocyclic allene **45** (Scheme 13).

Compounds **44** and **45** represent unusual products, and the mechanism for their formation deserves some discussion. It seems reasonable to assume that benzenesulfinate anion will add to the central carbon of the allene moiety of **46** to form an intermediate bis(phenylsulfonyl)-propene derivative **47** (Scheme 14). Conjugate addition of this anion onto the remaining electron-deficient double bond would give the intermediate enolate **48**. This anion could undergo a rapid 5-*exo*-*trig* cyclization, followed by subsequent ejection of benzenesulfinate to give the tetrahydrofuran anion intermediate **49**. We had observed analogous addition−elimination ring closures in earlier studies in our laboratory using 2,3-bis(phenylsulfonyl)-1-propene.[33a] Once formed, **49** could react further by a

(32) Wright, D. L.; Robotham, C. V.; Aboud, K. *Tetrahedron Lett.* **2002**, *43*, 943.

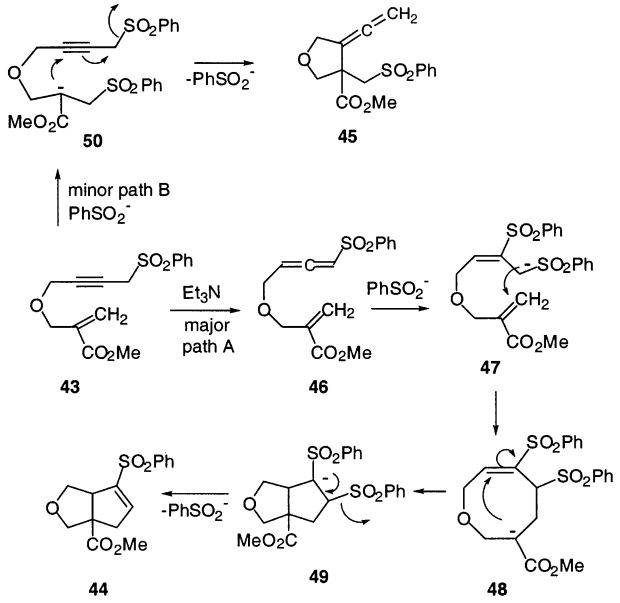
(33) (a) Padwa, A.; Kline, D. N.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.* **1992**, *57*, 298. (b) Padwa, A.; Meske, M.; Murphree, S. S.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1995**, *117*, 7071.

SCHEME 13[a]

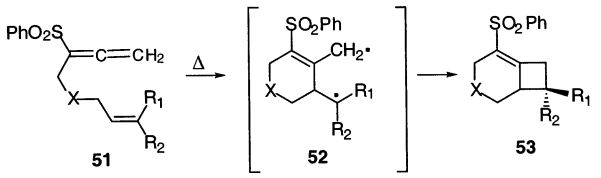


[a] Reagents: (a) MsCl, Et_3N, THF; (b) PhSH, NaH; (c) Oxone, MeOH, 0 °C; (d) $NaSO_2Ph$, Et_3N, THF.

SCHEME 14



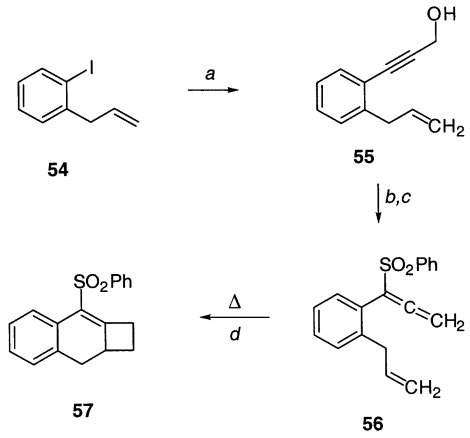
SCHEME 15



base-catalyzed elimination to provide cyclopentene **44** (Scheme 14, path A). The minor product **45** is probably derived from a competing alternative path which involves addition of benzenesulfinate onto the acrylate activated π-bond followed by conjugate addition to the acetylenic group and subsequent elimination of benzenesulfinate.

α-Tethered Systems. We had previously reported on the [2 + 2]-cycloaddition reaction of several α-tethered allenyl sulfones, which we found tended to form distal cycloadducts of type **53** (Scheme 15).[33b] Thus, 3-sulfonyl-substituted allenes such as **51** undergo smooth transformation to the bicyclo[4.2.0]octene system **53** under

SCHEME 16[a]



[a] Reagents: (a) proparagyl alcohol, Pd(II), CuI, Ph_3P, NEt_3; (b) PhSCl, Et_3N, THF; (c) Oxone, MeOH, 0 °C; (d) benzene, 80 °C.

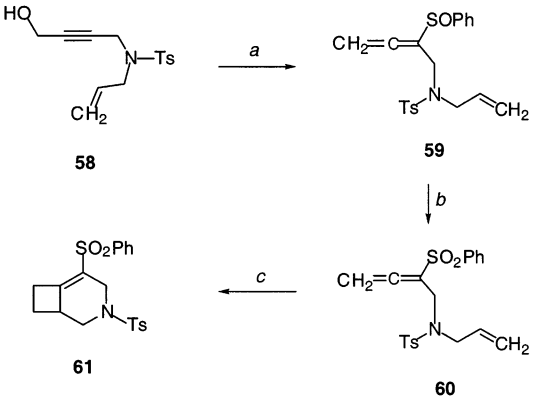
generally mild conditions. The results of these earlier studies showed that the introduction of an oxygen atom into the tether allowed for the formation of heterocyclic adducts without significantly hindering the cycloaddition reaction. Furthermore, the rate of the [2 + 2]-cycloaddition was enhanced by substituents on the tether, an observation which is in keeping with the conventional wisdom of the Thorpe−Ingold effect,[34] although the origin of this acceleration is still a matter of some debate.[35] We had attributed the cycloaddition to be occurring via a diradical intermediate **52**, which rapidly closes to produce the cyclobutane ring.

At this point in time, we decided to examine the cycloaddition behavior of several additional α-tethered allenes in light of the more recent results encountered with the systems described above. Toward this end, allene **56** which is equipped with an *o*-dialkylbenzene tether and is analogous to the γ-tethered allenyl system **23** was prepared starting from commercially available *o*-iodobenzyl alcohol. Castro-Stevens coupling of *o*-iodoallyl benzene (**54**) with propargyl alcohol gave enyne **55**. Subsequent phenylsulfenylation/rearrangement and oxidation provided **56** in good overall yield (Scheme 16). This substrate underwent smooth [2 + 2]-cycloaddition to provide the α-distal cycloadduct **57** in 94% yield. The α-tethered system was also found to be quite tolerant of heteroatoms in the tether, as illustrated by the thermolysis of allenyl tosylamide **60**. This allene was easily converted to the azabicyclo[4.2.0]octene **61** in refluxing benzene in 98% yield (Scheme 17). The relative facility of this cycloaddition compared to the oxa analogue (i.e., **51**, $R_1 = R_2 = H$; X = O) which required higher temperatures and gave a lower yield of cycloadduct is yet another example of the accelerating effect of steric bulk on the tether, which in this case is provided by the tosyl residue. The preference to cycloadd across the nonactivated double bond of the cumulene group appears to be general among [2 + 2]-cycloadditions of these sulfonyl allenes, except in cases of large ring size or when steric

(34) (a) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305. (b) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080.

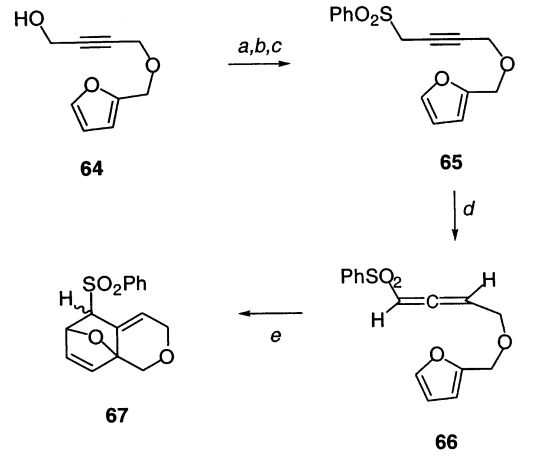
(35) (a) Jung, M. E.; Gervay, J. *Tetrahedron Lett.* **1988**, *29*, 2429. (b) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224. (c) Parrill, A. L.; Dolata, D. P. *Tetrahedron Lett.* **1994**, *35*, 7319.

SCHEME 17[a]



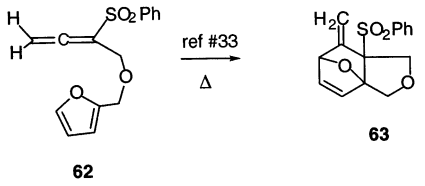
[a] Reagents: (a) PhSCl, Et_3N, THF; (b) Oxone, MeOH, 0 °C; (c) benzene, 80 °C.

SCHEME 18[a]



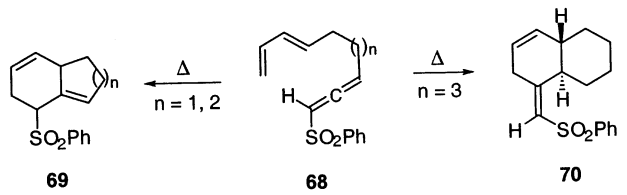
[a] Reagents: (a) MsCl, Et_3N; (b) NaH, PhSH; (c) Oxone, MeOH, 0 °C; (d) Et_3N, benzene, 80 °C; (e) benzene, 80 °C.

hindrance is an important factor. It should be noted that this behavior is contrary to the chemoselectivity we had observed in earlier studies of intramolecular [4 + 2]-cycloadditions of ene−allenes, as illustrated with the α-tethered allenyl furan **62** (Scheme 18). We were curious



to ascertain whether this result is general for all such Diels−Alder reactions and if so, whether it would carry over into the γ-substituted allenyl system. To test this hypothesis, alkynyl sulfone **65** was prepared by mesylation of alkynol **64**, and this was followed by S_N2 displacement with sodium thiophenolate and subsequent oxidation with Oxone. Heating **65** in benzene with catalytic triethylamine isomerized the alkyne to the allene **66** which subsequently furnished the Diels−Alder adduct **67** in quantitative yield. This result substantiates our initial assumption regarding a general trend for the electron-deficient double bond of the allene to serve as the 2π-component in [4 + 2]-cycloaddition reactions.

SCHEME 19



The origin of this curious and remarkable difference in chemoselectivity is more likely attributable to geometric rather than electronic factors. In fact, Bull and co-workers have studied the intramolecular Diels−Alder reaction of the γ-tethered phenylsulfonyl allenyl system **68** in some detail.[36] They found that the tether length was of defining importance, such that shorter aliphatic tethers preferred the formation of distal cycloadducts **69**, whereas longer chains allowed for the generation of proximal adducts **70** (Scheme 19).

In summary, easily prepared phenylsulfonyl allene derivatives equipped with tethered alkenyl groups were found to undergo a highly regio- and stereospecific [2 + 2]-cycloaddition reaction across the more electron-rich allene π-bond. α-Tethered systems cycloadd to form distal cycloadducts, while γ-tethered systems provide proximal cycloadducts, a result which is distinct from the analogous intramolecular [4 + 2]-cycloadditions which tend to involve the more electron-deficient allenic double bond. The resultant bicyclic adducts not only have inherently useful architecture that can be transformed into other ring systems of interest,[37−40] but they also contain a vinyl sulfone functionality which provides a handy leverage point for further chemical transformations.[41] We are continuing to examine the synthetic utility of these fascinating substrates and will report additional findings at a later date.

Experimental Section

1-Prop-2-enyl-2-[3-(benzenesulfinyl)propa-1,2-dienyl]-benzene (21a). To a 2.3 g (15 mmol) sample of 2-allylbenzaldehyde[42] in 30 mL of dry THF at 0 °C was added 40 mL (20 mmol) of a 0.5 M solution of ethynylmagnesium bromide in THF. The reaction was stirred for 10 min at 0 °C and was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The organic layer was collected, washed with water, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification afforded 2.1 g (78%) of 1-(2-allylphenyl)prop-2-yn-1-ol (**20a**): IR (neat) 3100−3600, 2116, 1626, 1018 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.64 (d, 1H, J = 2.1 Hz), 2.77 (brs, 1H), 3.54 (m, 2H), 5.03 (dd, 1H, J = 16.8, 1.5 Hz), 5.10 (dd, 1H, J = 10.2, 1.5 Hz), 5.63 (d, 1H, J = 2.1 Hz), 6.01 (m, 1H), 7.20 (m, 1H), 7.28 (m,

(36) Bull, J. R.; Gordon, R.; Hunter, R. *J. Chem. Soc., Perkin Trans. 1* **2000**, *18*, 3129.
(37) (a) Kelly, R. B.; Zamecnik, J.; Beckett, B. A. *Can. J. Chem.* **1972**, *50*, 3455. (b) Kelly, R. B.; Eber, J.; Hung, H. K. *Can. J. Chem.* **1973**, *51*, 2534.
(38) (a) Guthrie, R. W.; Valenta, Z.; Wiesner, K. *Tetrahedron Lett.* **1966**, 4645. (b) Wiesner, K. *Pure Appl. Chem.* **1975**, *41*, 93. (c) Wiesner, K.; Uyeo, S.; Philipp, A.; Valenta, Z. *Tetrahedron Lett.* **1968**, 6279.
(39) Duc, D. K. M.; Fetizon, M.; Lazare, S. *J. Chem. Soc., Chem. Commun.* **1975**, 282.
(40) (a) Ziegler, F. E.; Kloek, J. A. *Tetrahedron Lett.* **1974**, 315. (b) Ziegler, F. E.; Kloek, J. A. *Tetrahedron* **1977**, *33*, 373.
(41) For a recent review of vinyl sulfones in asymmetric synthesis, see: Carretero, J. C.; Arrayas, R. G.; Buezo, N. D.; Garrido, J. L.; Alonso, I.; Adrio, J. *Phosphorus, Sulfur Silicon* **1999**, *153−154*, 259.

2H), 7.71 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.4, 61.5, 74.7, 83.4, 116.1, 126.7, 126.9, 128.7, 130.1, 137.0, 137.3, 137.7.

To a solution containing 0.6 g (3.5 mmol) of the above alcohol and 1 mL (7 mmol) of triethylamine in 10 mL of dry THF at −78 °C was slowly added 0.55 g (3.8 mmol) of benzenesulfenyl chloride. The reaction was stirred for 45 min at −78 °C. The cooling bath was removed, and the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The organic layer was collected, washed with a 5% HCl solution, washed with water, and dried over Na_2SO_4. Concentration under reduced pressure followed by purification afforded allene **21a** in 80% yield: IR (neat) 1928, 1630, 1438, 1035 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.20−2.38 (m, 2H), 2.70−2.81 (m, 2H), 4.90−5.05 (m, 1H), 6.40 (d, 1H, J = 6.0 Hz), 6.88 (d, 1H, J = 6 Hz), 7.25 (m, 4H), 7.44−7.55 (m, 3H), 7.62−7.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.7, 34.9, 98.8, 105.6, 115.2, 124.1, 126.6, 128.1, 128.6, 129.3, 130.0, 131.1, 137.4, 139.6, 144.5, 205.3. Anal. Calcd for $C_{18}H_{16}SO$: C, 77.12; H, 5.76. Found: C, 77.09; H, 5.83.

1-Prop-2-enyl-2-(3-phenylsulfinylprop-1-ynyl)benzene (22a). The above reaction was also carried out at −78 °C, warmed to room temperature over 12 h, quenched with a saturated aqueous solution of NH_4Cl, and extracted with CH_2Cl_2. The organic layer was collected, washed with a 5% HCl solution and water, and dried over Na_2SO_4. Concentration under reduced pressure followed by purification afforded alkyne **22a**: IR (neat) 1630, 1481, 1439, 1082, 1047 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (s, 1H), 3.38 (s, 1H), 3.88 (d, 1H, J = 15.5 Hz), 4.00 (d, 1H, J = 15.5 Hz), 4.95−5.05 (m, 2H), 5.79−5.93 (m, 1H), 7.12−7.18 (m, 2H), 7.23−7.32 (m, 2H), 7.52−7.57 (m, 3H), 7.74−7.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.4, 49.1, 81.6, 86.7, 116.1, 121.6, 124.6, 126.0, 128.8, 129.0, 129.1, 131.7, 132.6, 136.3, 142.3, 143.2. Anal. Calcd for $C_{18}H_{16}SO$: C, 77.12; H, 5.76. Found: C, 76.92; H, 5.61.

2-(Phenylsulfonylethylidene)-1,1,2,2a,7,7a-tetrahydro-1*H*-cyclobutane[*a*]indene (25a). To a 0.3 g (1.0 mmol) sample of **21a** in 12 mL of MeOH at 0 °C was added 0.7 g (1.1 mmol) of Oxone in 6 mL of water. The reaction was stirred for 4 h at room temperature, diluted with water, and extracted several times with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification on silica gel afforded 0.24 g (81%) of 1-prop-2-enyl-2-[3-(benzenesulfonyl)propa-1,2-dienyl]benzene (**23a**) as a transient species. The [2 + 2]-cycloaddition of **23a** proceeded so rapidly at 25 °C that a pure sample could not be isolated. However, examination of the crude NMR allowed for its partial characterization: NMR (300 MHz, $CDCl_3$) δ 3.40 (m, 2H), 4.90 (dd, 1H, J = 17, 1.5 Hz), 5.05 (dd, 1H, J = 10, 1.5 Hz), 5.78−5.91 (m, 1H), 6.57 (d, 1H, J = 6.0 Hz), 6.96 (d, 1H, J = 6.0 Hz), 7.10−8.00 (m 9H).

When a 0.06 g sample of **23a** in 5 mL of benzene was allowed to stand at room temperature for 30 min, it afforded cycloadduct **25a** in 92% yield: mp 137−138 °C; IR (KBr) 3032, 1645, 1310, 1140, 1083 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.55−2.65 (m, 1H), 2.85−3.02 (m, 2H), 3.13−3.30 (m, 2H), 5.14 (brs, 1H), 5.92 (s, 1H), 7.26 (m, 3H), 7.55 (m, 3H), 7.93 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.4, 37.9, 39.4, 56.2, 119.6, 125.5, 127.1, 127.2, 127.4, 127.7, 129.1, 133.0, 141.9, 142.0, 142.8, 163.1. Anal. Calcd for $C_{18}H_{16}SO_2$: C, 72.95; H, 5.45. Found: C, 72.87; H, 5.39.

1-(3-Phenylsulfonylprop-1-ynyl)-2-(2-methylallyl)benzene (24a). An alternate method that was used to prepare cycloadduct **25a** involved the oxidation of sulfoxide **22a** followed by base-catalyzed isomerization of alkyne **24a**. To a 0.5 g (1.7 mmol) sample of **22a** in 12 mL of MeOH at 0 °C was added 1.2 g (1.9 mmol) of Oxone in 6 mL of water. The reaction was stirred for 4 h at room temperature, diluted with water, and extracted several times with $CHCl_3$. The organic layer was washed with water and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification by silica gel chromatography afforded 0.19 g (92%) of **24a** as a clear oil: IR (neat) 2904, 1638, 1446, 1325, 1140 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (s, 1H), 3.37 (s, 1H), 4.23 (s, 2H), 4.93−5.03 (m, 2H), 5.78−5.91 (m, 1H), 7.10−7.17 (m, 2H), 7.23−7.30 (m, 2H), 7.55 (t, 2H, J = 7.5 Hz), 7.66 (t, 1H, J = 7.5 Hz), 8.00 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.4, 49.6, 80.3, 86.3, 116.2, 121.7, 126.1, 128.8, 129.1, 129.2, 132.6, 134.2, 136.2, 137.9, 142.5. Anal. Calcd for $C_{18}H_{16}SO_2$: C, 72.95; H, 5.45. Found: C, 72.71; H, 5.24.

A 0.1 g sample of alkyne **24a** in 8 mL of benzene was heated at reflux for 5 h with a catalytic amount of triethylamine. Concentration under reduced pressure followed by purification by silica gel chromatography afforded cycloadduct **25a** in 89% yield.

1-(3-Phenylsulfinylprop-1-ynyl)-2-(2-methylallyl)benzene (22b). A 5.0 g (22 mmol) sample of the acetal of 2-bromobenzaldehyde[42] was alkylated with 2.2 mL (22 mmol) of 3-bromo-2-methylpropene. Deacetalization with HCl afforded 2.9 g (83%) of 2-(2-methylallyl)benzaldehyde as a pale yellow liquid: IR (neat) 3070, 2752, 1695, 1594, 1449 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 3H), 3.72 (s, 2H), 4.45 (s, 1H), 4.83 (s, 1H), 7.27 (d, 1H, J = 7.6 Hz), 7.38 (t, 1H, J = 7.6 Hz), 7.52 (td, 1H, J = 7.6, 1.2 Hz), 7.86 (dd, 1H, J = 7.6, 1.2 Hz), 10.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 40.2, 112.5, 126.9, 130.6, 131.6, 133.8, 134.3, 142.0, 145.2, 192.

A 0.7 g (4.6 mmol) sample of the above aldehyde was treated with 9.2 mL (4.6 mmol) of a 0.5 M solution of ethynylmagnesium bromide in THF to afford 0.8 g (97%) of 1-[2-(2-methylallyl)phenyl]prop-2-yn-1-ol (**20b**) as a pale yellow oil: IR (neat) 3387, 1645, 1449 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 3H), 2.27 (brs, 1H), 2.62 (d, 1H, J = 2.4 Hz), 3.43 (d, 1H, J = 16.1 Hz), 3.54 (d, 1H, J = 16.1 Hz), 4.53 (s, 1H), 4.84 (s, 1H), 5.64 (s, 1H), 7.15−7.19 (m, 1H), 7.24−7.31 (m, 2H), 7.69−7.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8, 40.8, 61.8, 74.6, 83.5, 112.2, 127.0, 127.1, 128.7, 130.8, 137.0, 138.4, 145.3.

A 0.3 g (1.4 mmol) sample of **20b** was treated with 0.2 g (1.5 mmol) of benzenesulfenyl chloride at −78 °C, and the mixture was stirred at room temperature for 12 h to give 0.3 g (76%) of **22b**: IR (neat) 2358, 1645, 1442, 1085, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 3.31 (s, 2H), 3.85 (d, 1H, J = 15.6 Hz), 3.97 (d, 1H, J = 15.6 Hz), 4.54 (s, 1H), 4.76 (s, 1H), 7.09−7.16 (m, 2H), 7.21−7.30 (m, 2H), 7.49−7.53 (m, 3H), 7.72−7.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 42.3, 49.1, 81.4, 86.9, 112.2, 122.0, 124.6, 126, 128.8, 129.0, 129.2, 131.7, 132.6, 142.0, 143.2, 144.2. Anal. Calcd for $C_{19}H_{18}SO$: C, 77.52; H, 6.17. Found: C, 77.44; H, 6.08.

1-(3-Phenylsulfinyl-propa-1,2-dienyl)-2-(2-methylallyl)benzene (21b). When the above reaction was carried out at −78 °C for 45 min, allene **21b** was isolated as a 3:2 mixture of diastereomers in 74% yield as evidenced by NMR analysis: IR (neat) 1928, 1650, 1445, 1081, 1042 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (s, 3H), 3.34 (s, 2H), 4.47 (s, 1H), 4.82 (s, 1H), 6.40 (d, 1H, J = 6.2 Hz), 6.87 (d, 1H, J = 6.2 Hz), 7.13−7.24 (m, 4H), 7.47−7.52 (m, 3H), 7.65−7.68 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 41.7, 98.9, 99.0, 105.6, 112.5, 124.2, 126.9, 128.0, 128.5, 129.3, 131.0, 131.2, 137.2, 143.9, 144.7, 205.2. Anal. Calcd for $C_{19}H_{18}SO$: C, 77.52; H, 6.17. Found: C, 77.39; H, 6.11.

1-(3-Phenylsulfonylprop-1-ynyl)-2-(2-methylallyl)benzene (24b). A 0.3 g (1.0 mmol) sample of **22b** was oxidized with 0.7 g (1.1 mmol) of Oxone to give 0.19 g (59%) of **24b** as a clear oil: IR (neat) 3066, 2224, 1649, 1445, 1319, 1137 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 3.33 (s, 2H), 4.21 (s, 2H), 4.53 (s, 1H), 4.76 (s, 1H), 7.10−7.17 (m, 2H), 7.23−7.30 (m, 2H), 7.55 (t, 2H, J = 7.5 Hz), 7.66 (t, 1H, J = 7.5 Hz), 8.00 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 42.2, 49.6, 80.0, 86.5, 112.1, 121.7, 126.1, 127.1, 128.8, 129, 129.1, 129.2, 132.5, 134.2, 137.9, 142.2, 144.3. Anal. Calcd for $C_{19}H_{18}SO_2$: C, 73.52; H, 5.84. Found: C, 73.40; H, 5.72.

2-Phenylsulfonylmethylene-7a-methyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene (25b). A 0.13 g (0.4 mmol)

(42) Ashby, E. C.; Coleman, D.; Gamasa, M. *J. Org. Chem.* **1987**, *52*, 4079.

sample of **24b** in 10 mL of dry benzene was heated at reflux for 24 h with a catalytic amount of triethylamine. Concentration under reduced pressure afforded **25b** as a colorless solid: mp 140−141 °C; IR (KBr) 2919, 1645, 1439, 1304, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3H), 2.52 (ddd, 1H, J = 16.4, 4.2, 1.2 Hz), 2.81 (dt, 1H, J = 16.4, 2.7 Hz), 3.01 (s, 2H), 4.71 (s, 1H), 6.00 (d, 1H, J = 1.2 Hz), 7.23−7.25 (m, 3H), 7.50−7.62 (m, 3H), 7.83−7.94 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 42.9, 43.6, 46.5, 61.0, 121.2, 125.3, 127.1, 127.2, 127.5, 127.7, 129.2, 133.0, 142.1, 142.6, 143.3, 162.2. Anal. Calcd for $C_{19}H_{18}SO_2$: C, 73.52; H, 5.84. Found: C, 73.55; H, 5.83.

1-(3-Phenylsulfinylpropa-1,2-dienyl)-2-(3-methylbut-2-enyl)benzene (21c). A 5.0 g (22 mmol) sample of the acetal of 2-bromobenzaldehyde[42] was alkylated with 2.5 mL (22 mmol) of 4-bromo-2-methyl-2-butene to give 2.9 g (75%) of 2-(3-methylbut-2-enyl)benzaldehyde as a pale yellow liquid: IR (neat) 1695, 1595, 1446, 1197, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 6H), 3.73 (d, 2H, J = 6.9 Hz), 5.22−5.27 (m, 1H), 7.23−7.35 (m, 2H), 7.45−7.51 (m, 1H), 7.79−7.82 (m, 1H), 10.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0, 25.7, 31.2, 122.6, 126.5, 130.5, 131.2, 133.1, 133.9, 192.4.

A 1.0 g (6 mmol) sample of the above aldehyde was treated with 12 mL (6 mmol) of a 0.5 M solution of ethynylmagnesium bromide to give 1.15 g (96%) of 1-[2-(2-methylbut-2-enyl)-phenyl]prop-2-yn-1-ol (**20c**) as a pale yellow oil: IR (neat) 3391, 3299, 1446, 1014, 950 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 6H), 2.44 (brs, 1H), 2.64 (d, 1H, J = 2.3 Hz), 3.50 (t, 2H, J = 6.3 Hz), 5.24−5.29 (m, 1H), 5.65 (d, 1H, J = 2.3 Hz), 7.19−7.28 (m, 3H), 7.68−7.71 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0, 25.7, 31.3, 61.8, 74.7, 83.6, 122.8, 126.5, 126.8, 128.8, 129.7, 133.1, 137.8, 139.4.

Treatment of a 0.4 g (2 mmol) sample of **20c** with 0.3 g (2.2 mmol) of benzenesulfenyl chloride at −78 °C for 45 min gave **21c** as a 3:2 mixture of diastereomers in 65% yield as evidenced by NMR analysis: IR (neat) 1928, 1475, 1086, 1043, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 3H), 1.72 (s, 3H), 3.35 (d, 2H, J = 6.9 Hz), 5.15−5.19 (m, 1H), 6.40 (t, 1H, J = 6.0 Hz), 6.90 (d, 1H, J = 6.0 Hz), 7.13−7.24 (m, 4H), 7.49−7.51 (m, 3H), 7.66−7.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0, 25.7, 32.3, 98.9, 99.1, 105.5, 122.2, 122.3, 124.2, 126.6, 128.1, 128.7, 129.3, 129.8, 131.1, 133.1, 139.6, 144.7, 205.3. Anal. Calcd for $C_{20}H_{20}SO$: C, 77.89; H, 6.54. Found: C, 77.75; H, 6.46.

1-(3-Phenylsulfinylprop-1-ynyl)-2-(3-methylbut-2-enyl)benzene (22c). A 0.4 g (2 mmol) sample of **20c** was treated with 0.3 g (2.2 mmol) of benzenesulfenyl chloride at −78 °C and then stirred at room temperature for 12 h to give 0.47 g (76%) of **22c** as a clear oil: IR (neat) 1474, 1445, 1083, 1047, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H), 1.71 (s, 3H), 3.31 (d, 2H, J = 7.2 Hz), 3.85 (d, 1H, J = 15.5 Hz), 4.00 (d, 1H, J = 15.5 Hz), 5.16−5.22 (m, 1H), 7.06−7.15 (m, 2H), 7.20−7.29 (m, 2H), 7.49−7.53 (m, 3H), 7.73−7.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 25.7, 32.8, 49.2, 81.5, 87.0, 121.4, 122.1, 124.6, 125.6, 128.9, 129.0, 131.7, 132.5, 132.9, 143.2, 144.1. Anal. Calcd for $C_{20}H_{20}SO$: C, 77.89; H, 6.54. Found: C, 77.61; H, 6.33.

1-(3-Phenylsulfonylprop-1-ynyl)-2-(3-methylbut-2-enyl)-benzene (24c). A 0.3 g (1 mmol) sample of **22c** was oxidized with 0.7 g (1.1 mmol) of Oxone to give 0.17 g (50%) of **24c** as a clear oil: IR (neat) 2224, 1446, 1325, 1133, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 3H), 1.71 (s, 3H), 3.31 (d, 2H, J = 7.2 Hz), 4.23 (s, 2H), 5.20 (t, 1H, J = 7.2 Hz), 7.07−7.15 (m, 2H), 7.22−7.29 (m, 2H), 7.55 (t, 2H, J = 7.4 Hz), 7.67 (t, 1H, J = 7.4 Hz), 8.01 (d, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 25.7, 32.7, 49.6, 80.3, 86.6, 121.0, 122.0, 125.7, 128.4, 128.9, 129.1, 129.2, 132.5, 133, 134.1, 139.1, 144.2. Anal. Calcd for $C_{20}H_{20}SO_2$: C, 74.05; H, 6.22. Found: C, 73.89; H, 6.17.

2-(1-Phenylsulfonylethylidene)-1,1-dimethyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene (25c). A 0.1 g (0.4 mmol) of alkyne **24c** in 10 mL of dry benzene was heated at reflux for 24 h with a catalytic amount of triethylamine. Concentration under reduced pressure followed by purification afforded 0.06 g (82%) of cycloadduct **25c** as a colorless solid: mp 136−137 °C; IR (KBr) 1666, 1446, 1310, 1140, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 3H), 1.27 (s, 3H), 2.78 (dt, 1H, J = 6.9, 3.2 Hz), 2.78 (dt, 1H, J = 16.6, 3.2 Hz), 3.21 (dd, 1H, J = 16.6, 3.2 Hz), 4.18 (d, 1H, J = 6.9 Hz), 6.07 (s, 1H), 7.01−7.06 (m, 1H), 7.08−7.17 (m, 3H), 7.33 (t, 2H, J = 7.5 Hz), 7.47 (t, 1H, J = 7.5 Hz), 7.59 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 26.8, 35.1, 52.0, 57.2, 88.8, 116.4, 118.9, 126.4, 126.9, 127.3, 128.9, 129.1, 129.3, 132.8, 133.5, 141.7, 142.2, 148.6, 166.5. Anal. Calcd for $C_{20}H_{20}SO_2$: C, 74.05; H, 6.22. Found: C, 73.95; H, 6.19.

2-(1-Phenylsulfinylethylidene)-1,1-dimethyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene (26c). A 0.8 g (2.7 mmol) sample of **21c** in 35 mL of dry benzene was heated at reflux for 3.5 h. Concentration under reduced pressure followed purification affored 0.7 g (86%) of a 3:2 mixture of the diastereomers of **26c**. The major diastereomer was a colorless solid: mp 119−120 °C; IR (KBr) 1474, 1446, 1083, 1033, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.33 (s, 3H), 2.56 (dd, 1H, J = 13.5, 6.6 Hz), 2.87 (dt, 1H, J = 6.6, 1.6 Hz), 2.93 (d, 1H, J = 13.5 Hz), 4.03 (d, 1H, J = 1.6 Hz), 6.64 (t, 1H, J = 2.4 Hz), 6.99−7.12 (m, 4H), 7.52−7.56 (m, 3H), 7.74−7.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 27.4, 29.7, 40.9, 45.1, 73.8, 119.1, 125.0, 126.6, 126.7, 126.8, 128.4, 129.4, 131.5, 134.2, 134.3, 135.8, 144.3. Anal. Calcd for $C_{20}H_{20}SO$: C, 77.89; H, 6.54. Found: C, 77.68; H, 6.61.

The minor diastereomer was obtained as a yellow oil: IR (neat) 1474, 1446, 1083, 1033, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 3H), 1.57 (s, 3H), 2.58 (dd, 1H, J = 12.5, 5.9 Hz), 2.87 (d, 1H, J = 12.5 Hz), 2.81−2.84 (m, 1H), 4.17 (s, 1H), 5.52 (t, 1H), 5.52 (t, 1H, J = 2.3 Hz), 6.74−6.71 (m, 1H), 7.02−7.05 (m, 3H), 7.54−7.58 (m, 3H), 7.83−7.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 27.5, 31.3, 41.8, 44.8, 74.1, 118.7, 126.2, 126.4, 126.6, 126.9, 128.6, 129.5, 132.1, 133.7, 134.5, 134.7, 143.9. Anal. Calcd for $C_{20}H_{20}SO$: C, 77.89; H, 6.54. Found: C, 77.66; H, 6.23.

Oxidation of a 0.2 g (0.7 mmol) sample of the major diastereomer of **26c** with 0.78 g (1.3 mmol) of Oxone gave 0.19 g (82%) of **25c**.

3-Phenylsulfinylmethyl-2-isopropenyl-1,2-dihydronaphthalene (27). A 0.16 g (0.53 mmol) sample of allenyl sulfoxide **21c** in 10 mL of dry CH_2Cl_2 was stirred at 25 °C with a catalytic amount of $SnCl_4$ for 24 h. The mixture was diluted with CH_2Cl_2, washed with water and brine, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification affored 0.13 g (81%) of **27** as an inseparable 1:1 mixture of diastereomers: IR (neat) 1638, 1481, 1083, 1040, 891 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 3H), 2.74−2.83 (m, 3H), 2.91−3.09 (m, 2H), 3.52−3.68 (m, 2H), 4.67 (d, 2H, J = 15.0 Hz), 6.39 (s, 1H), 6.90−7.11 (m, 4H), 7.46−7.64 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 32.8, 45.2, 64.6, 112.8, 119.1, 124.4, 126.5, 127.8, 129.1, 131.1, 133.5, 143.9, 144.3. Anal. Calcd for $C_{20}H_{20}SO$: C, 77.89; H, 6.54. Found: C, 77.74; H, 6.39.

(Octa-1,2,7-triene-1-sulfonyl)benzene (29). To a solution of 0.11 mol of *n*-BuLi in 70 mL of hexane at −90 °C was added 35 mL of THF followed by a solution of 0.11 mol of *t*-BuOK in 45 mL of THF at −90 °C.[43] To this solution was added 8.5 g (0.05 mol) of 3-*tert*-butyldimethylsilylpropargyl ether[44] over a 10 min period at −80 °C. The temperature was allowed to rise to −45 °C, and the mixture was stirred for 2.5 h at this temperature. A 6.0 g (0.04 mol) sample of 5-bromopent-1-ene was added dropwise over a 10 min period. After the mixture was stirred for 15 min, the temperature was allowed to warm to 10 °C, and 150 mL of ice−water was added. The mixture was extracted with ether, and the organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Distil-

(43) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 73.

(44) Wender, P. A.; Sieburth, S.; Petraitis, J. J.; Singh, S. K. *Tetrahedron* **1981**, *37*, 3967.

lation of the residue afforded 6.0 g (63%) of 6-*tert*-butyldimethylsiloxyoct-1-en-7-yne (bp 90 °C/5 mm): IR (neat) 2113, 1640, 1264 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 1.52 (m, 2H), 1.65 (m, 2H), 2.05 (m, 2H), 2.35 (d, 1H, J = 2.1 Hz), 4.32 (m, 1H), 4.96 (m, 2H), 5.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$), δ −5.1, −4.6, 18.2, 24.3, 25.8, 33.3, 37.9, 62.6, 72.0, 85.6, 114.6, 138.5.

A sample containing 0.48 g (2 mmol) of the above compound in 2 mL of THF was added dropwise to a solution of 3.0 mmol of TBAF in 3 mL of THF at O°C. The mixture was warmed to room temperature, stirred for 5 h, and quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with ether, and the combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified to provide 0.2 g (81%) of oct-7-en-1-yn-3-ol (**28**): IR (neat) 3100−3600, 2113, 1633 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.50−1.58 (m, 2H), 1.65−1.74 (m, 2H), 2.02−2.10 (m, 2H), 2.38 (brs, 1H), 2.43 (d, 1H, J = 2.1 Hz), 4.34 (dt, 1 H, J = 6.6, 2.1 Hz), 4.90−5.01 (m, 2H), 5.72−5.81 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2, 33.2, 37.0, 62.1, 72.9, 84.9, 114.8, 138.3.

A 1.2 g (10 mmol) of the above alcohol **28** was treated with 1.6 g (11 mmol) of benzenesulfenyl chloride to give 1.8 g (79%) of (octa-1,2,7-triene-1-sulfinyl)benzene as a 3:2 mixture of diastereomers: IR (neat) 1948, 1633, 1446, 1045, 902 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.41−1.53 (m, 2H), 1.98−2.15 (m, 4H), 4.91−4.99 (m, 2H), 5.66−5.77 (m, 2H), 5.98−6.01 (m, 1H), 7.47 (m, 3H), 7.60 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 27.6, 32.7, 98.9, 102.7, 115.0, 124.1, 129.0, 130.8, 137.7, 144.7, 203.6.

A 0.46 g (2.0 mmol) sample of the above sulfoxide was oxidized with 3.7 g (6 mmol) of Oxone to give 0.4 g (85%) of **29**: IR (neat) 1948, 1633, 1446, 1138, 1074 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.42 (q, 2H, J = 7.5 Hz), 1.95−2.09 (m, 4H), 4.90−4.96 (m, 2H), 5.60−5.75 (m, 1H), 5.79 (q, 1H, J = 6.6 Hz), 6.14 (m, 1H), 7.47 (t, 2H, J = 7.5 Hz), 7.56 (t, 1H, J = 7.5 Hz), 7.84 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 27.4, 32.8, 100.9, 101.2, 115.2, 127.5, 129.1, 133.4, 137.7, 141.3, 205.7. Anal. Calcd for $C_{14}H_{16}SO_2$: C, 67.72; H, 6.50. Found: C, 67.60; H, 6.41.

6-Phenylsulfonylmethylenebicyclo[3.2.0]heptane (30). A 0.1 g (0.4 mmol) of **29** in 3 mL of *o*-dichlorobenzene was heated at reflux for 24 h. The solvent was removed under reduced pressure and the residue was purified to give 0.06 g (62%) of cycloadduct **30**: IR (neat) 1637, 1445, 1300, 1148, 1088 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.49−1.85 (m, 5H), 2.10−2.35 (m, 2H), 2.75−2.95 (m, 2H), 3.81 (brs, 1H), 5.95 (brs, 1H), 7.50 (tt, 2H, J = 7.5, 1.5 Hz), 7.57 (tt, 1H, J = 7.5, 1.5 Hz), 7.86 (dt, 2H, J = 7.5, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 33.1, 33.4, 35.4, 49.1, 121.6, 127.1, 129.1, 133.0, 142.2, 166.9. Anal. Calcd for $C_{14}H_{16}SO_2$: C, 67.72; H, 6.50. Found: C, 67.57; H, 6.33.

1-Phenylsulfonyl-4-(2-allyloxy)but-2-yne (33). A 2.2 g (56 mmol) sample of NaH (60%) was washed with hexane and suspended in 85 mL of THF. To this mixture was added 4.8 g (56 mmol) of 2-butyne-1,4-diol in 75 mL of THF at room temperature. The mixture was stirred for 3.5 h, and then 8.4 g (56 mmol) of *tert*-butyldimethylsilyl chloride was added. The mixture was vigorously stirred for another 2.5 h, poured into ether, washed with 10% aqueous K_2CO_3 and brine, and dried over Na_2SO_4. Concentration under reduced pressure followed by purification affored 3.3 g (30%) of 4-(*tert*-butyldimethylsilyloxy)-2-butyn-1-ol (**31**): IR (neat) 3368, 1469, 1350, 1245, 1006, 826 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 6H), 0.90 (s, 9H), 1.78 (s, 1H), 4.29 (d, 2H, J = 1.2 Hz), 4.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 5.2, 18.3, 25.8, 51.1, 51.7, 83.0, 84.3.

To a solution of 1.4 g (7 mmol) of the above compound in 50 mL of THF at 0 °C was added 0.04 g (9.2 mmol) of 60% NaH in one portion. The mixture was stirred at 0 °C for 30 min, and then 1 mL (9.2 mmol) of 3-bromo-2-methyl-1-propene was added. The mixture was stirred at room temperature for 3 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl solution, and the solvent was removed under reduced pressure. The residue was extracted with ether, and the organic layer was washed with water and brine and dried over Na_2SO_4. After concentration under reduced pressure, the residue was dissolved in 80 mL of THF and cooled to 0 °C. To this solution was added 8 mL (8.4 mmol) of TBAF, and the mixture was stirred at room temperature for 1.25 h. The reaction was quenched with a saturated aqueous NH_4Cl solution, and the solvent was removed under reduced pressure. The residue was extracted with ether, and the organic layer was washed with water, brine, and dried over Na_2SO_4. Concentration under reduced pressure followed by silica gel chromatography afforded 0.8 g (77%) of 4-(2-methylallyloxy)-but-2-yn-1-ol (**32**) as a clear oil: IR (neat) 3402, 2357, 1709, 1652, 1446 cm^{-1}; ^1H NMR (MHz,) δ 1.73 (s, 3H), 1.82 (brs, 1H), 3.94 (s, 2H), 4.14 (s, 2H), 4.30 (s, 2H), 4.91 (s, 1H), 4.96 (s, 1H); ^{13}C NMR (75 MHz,) δ 19.5, 51.2, 57.2, 73.7, 81.9, 84.4, 113.0, 141.3.

To a solution of 0.5 g (3.3 mmol) of **32** and 0.7 mL (4.9 mmol) of triethylamine in 25 mL of dry CH_2Cl_2 at 0 °C was slowly added 0.3 mL (3.3 mmol) of methanesulfonyl chloride. The mixture was warmed to room temperature and was stirred for an additional 2 h. The reaction was quenched with water, and the organic layer was collected, washed with brine, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure afforded the crude mesylate which was used in the next step without further purification.

To a suspension of 0.14 g (3.6 mmol) of 60% NaH in 15 mL of dry THF at 0 °C was slowly added 0.3 mL (3.3 mmol) of thiophenol. The reaction was stirred for 20 min at 0 °C and was then cannulated into a solution of the above mesylate in 20 mL of dry THF at 0 °C. The mixture was stirred at 0 °C for 30 min and was quenched with a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The organic layer was collected, washed with water, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification afforded 0.46 g (61%) of 1-(2-methylallyloxy)-4-phenylsulfanyl-but-2-yne as a pale yellow oil: IR (neat) 2357, 1581, 1474, 1438, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.69 (s, 3H), 3.65 (t, 2H, J = 2.1 Hz), 3.85 (s, 2H), 4.09 (t, 2H, J = 2.1 Hz), 4.87 (s, 1H), 4.91 (s, 1H), 7.18−7.32 (m, 3H), 7.39−7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 22.9, 57.3, 73.4, 79.4, 82.1, 112.8, 126.8, 128.9, 130.0, 135.2, 141.4.

To a 0.3 g (1.5 mmol) sample of the above compound in 25 mL of MeOH at 0 °C was added 2.0 g (3.2 mmol) of Oxone in 15 mL of water. Standard workup followed by purification afforded 0.24 g (61%) of alkyne **33** as a clear oil: IR (neat) 2912, 1446, 1318, 1140, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.67 (s, 3H), 3.81 (s, 2H), 3.99 (t, 2H, J = 2.0 Hz), 4.07 (t, 2H, J = 2.0 Hz), 4.88 (s, 1H), 4.90 (s, 1H), 7.55 (t, 2H, J = 7.6 Hz), 7.66 (t, 1H, J = 7.6 Hz), 7.95 (d, 2H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 48.7, 57.0, 73.6, 73.8, 84.2, 113.0, 128.8, 129.1, 134.2, 137.7, 141.1. Anal. Calcd for $C_{14}H_{16}SO_3$: C, 63.62; H, 6.11. Found: C, 63.49; H, 6.04.

6-Phenylsulfonylmethylene-1-methyl-3-oxabicyclo[3.2.0]heptane (35). A 0.16 g (0.6 mmol) of **33** in 10 mL of toluene was heated at reflux for 36 h with a catalytic amount of triethylamine. Concentration under reduced pressure followed by purification afforded 0.15 g (94%) of cycloadduct **35** as a colorless solid: mp 110−111 °C; IR (KBr) 2954, 1645, 1446, 1304, 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 3H), 2.54 (dt, 1H, J = 17.7, 2.2 Hz), 2.74 (dt, 1H, J = 17.7, 2.8 Hz), 3.29 (d, 1H, J = 9.3 Hz), 3.61 (t, 1H, J = 2.8 Hz), 3.83 (d, 1H, J = 9.3 Hz), 3.84 (d, 1H, J = 9.8 Hz), 4.27 (d, 1H, J = 9.8 Hz), 6.07 (d, 1H, J = 2.2 Hz), 7.51 (t, 2H, J = 7.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.85 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 41.2, 44.3, 54.8, 74.1, 79.2, 122.8, 127.1, 129.2, 133.2, 141.8, 161.0. Anal. Calcd for $C_{14}H_{16}SO_3$: C, 63.62; H, 6.11. Found: C, 63.60; H, 6.09.

4-[2-(3-Phenylsulfinylpropa-1,2-dienyl)phenyl]but-2-enoic Acid Methyl Ester (37). A 1.2 g (5.9 mmol) sample of

methyl[4-(2-formyl)phenyl]-2-butenoate[45] was treated with 12 mL (5.9 mmol) of a 0.5 M solution of ethynylmagnesium bromide in THF to give 0.6 g (47%) of 4-[2-(1-hydroxyprop-2-ynyl)phenyl]but-2-enoic acid methyl ester (**36**) as a pale yellow oil: IR (neat) 3431, 3289, 1709, 1652, 1275 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.63 (d, 1H, J = 2.1 Hz), 2.73 (brs, 1H), 3.67 (s, 3H), 3.65−3.71 (m, 2H), 5.53 (d, 1H, J = 2.1 Hz), 5.73 (dt, 1H, J = 15.9, 1.7 Hz), 7.06−7.15 (m, 2H), 7.24−7.30 (m, 2H), 7.65−7.68 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 51.5, 62.0, 75.2, 83.2, 122.1, 127.2, 127.3, 129.0, 130.5, 135.6, 137.9, 147.4, 166.9.

A 0.6 g (2.7 mmol) of **36** was treated with 0.44 g (3.0 mmol) of benzenesulfenyl chloride to give 0.7 g (80%) of a 3:2 diastereomeric mixture of allene **37** as a pale yellow oil: IR (neat) 1930, 1716, 1439, 1275, 1040 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.53−3.57 (m, 2H), 3.68 (s, 3H), 5.64 (d, 1H, J = 15.6 Hz), 6.40 and 6.41 (d, 1H, J = 6.0 Hz), 6.71 and 6.75 (d, 1H, J = 6.0 Hz), 6.99−7.25 (m, 5H), 7.47−7.52 (m, 3H), 7.63−7.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 51.5, 98.8, 105.8, 122.5, 124.2, 127.5, 128.5, 128.8, 128.9, 129.3, 130.6, 131.3, 135.3, 144.5, 146.4, 166.6, 204.9. Anal. Calcd for $C_{20}H_{18}SO_3$: C, 70.99; H, 5.37. Found: C, 70.84; H, 5.22.

4-[2-(3-Phenylsulfonylpropa-1,2-dienyl)phenyl]but-2-enoic Acid Methyl Ester (38). A 0.5 g (1.6 mmol) sample of **37** was oxidized with 1.0 g (1.7 mmol) of Oxone to give 0.5 g (87%) of **38**, which was obtained as a clear oil after purification by silica gel chromatography: IR (neat) 1937, 1716, 1439, 1311, 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.52 (d, 1H, J = 1.1 Hz), 3.54 (d, 1H, J = 1.1 Hz), 3.69 (s, 3H), 5.62 (dt, 1H, J = 15.6, 1.7 Hz), 6.58 (d, 1H, J = 6.0 Hz), 6.84 (d, 1H, J = 6.0 Hz), 7.01 (dt, 1H, J = 15.6, 6.0 Hz), 6.83−7.27 (m, 4H), 7.51 (t, 2H, J = 7.5 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.92 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.9, 51.5, 100.3, 104.1, 122.5, 127.6, 127.7, 128.9, 129.2, 129.4, 130.6, 133.7, 135.6, 141.1, 146.2, 166.6, 208.1. Anal. Calcd for $C_{20}H_{18}SO_4$: C, 67.78; H, 5.12. Found: C, 67.61; H, 5.01.

(3-Phenylsulfonylvinylideneindan-2-yl)acetic Acid Methyl Ester (41). A 0.35 g (1.0 mmol) sample of **38** was stirred in 12 mL of dry THF with 0.16 g (1.0 mmol) of the sodium salt of bezenesulfinic acid and 0.14 g (1.0 mmol) of K_2CO_3 for 10 h at room temperature. The mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. The filtrate was washed with water and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification afforded 0.3 g (88%) of a 1:1 mixture of the diastereomers of **41** which were separated by silica gel chromatography. Diastereomer **41a** showed the following spectrqal properties: IR (neat) 1944, 1730, 1439, 1318, 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.50 (dd, 1H, J = 16.7, 9.5 Hz), 2.65 (dd, 1H, J = 16.7, 5.4 Hz), 2.79 (dd, 1H, J = 16.7, 5.4 Hz), 3.34 (dd, 1H, J = 16.7, 8.4 Hz), 3.64−3.75 (m, 1H), 3.69 (s, 3H), 6.61 (d, 1H, J = 4.2 Hz), 7.07−7.30 (m, 4H), 7.49 (t, 2H, J = 7.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.90 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9, 38.9, 39, 51.8, 106.6, 121.3, 123.6, 125.3, 127.5, 127.8, 129.2, 129.9, 133.5, 141.4, 143.9, 172.3, 201.8. Anal. Calcd for $C_{20}H_{18}SO_4$: C, 67.78; H, 5.12. Found: C, 67.70; H, 4.98.

Diastereomer **41b**: IR (neat) 1944, 1730, 1439, 1310, 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.51 (dd, 1H, J = 16.3, 8.7 Hz), 2.59 (dd, 1H, J = 16.3, 6.0 Hz), 2.77 (dd, 1H, J = 16.3, 5.3 Hz), 3.32 (dd, 1H, J = 16.3, 8.4 Hz), 3.61−3.69 (m, 1H), 3.64 (s, 3H), 6.64 (d, 1H, J = 2.1 Hz), 7.07−7.28 (m, 4H), 7.50 (t, 2H, J = 7.4 Hz), 7.59 (t, 1H, J = 7.4 Hz), 7.92 (d, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.8, 38.8, 39.0, 51.7, 106.7, 121.1, 123.6, 125.2, 127.5, 127.7, 129.2, 129.9, 133.5, 135.0, 141.2, 143.8, 171.8, 201.6. Anal. Calcd for $C_{20}H_{18}SO_4$: C, 67.78; H, 5.12. Found: C, 67.55; H, 4.92.

2-(4-Phenylsulfonylbut-2-ynyloxymethyl)acrylic Acid Methyl Ester (43). A 0.85 g (4.2 mmol) sample of the sodium salt of *(tert*-butyldimethylsilyloxy)-2-butyn-1-ol was treated with 0.5 mL (4.2 mmol) of methyl 2-(bromomethyl)acrylate. Standard workup afforded a residue which was treated with 5 mL (5.1 mmol) of TBAF to give 0.5 g (69%) of 2-(4-hydroxybut-2-ynyloxymethyl)acrylic acid methyl ester (**42**) as a pale yellow oil: IR (neat) 3431, 2954, 1716, 1439, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.84 (brs, 1H), 3.75 (s, 3H), 4.21−4.29 (m, 6H), 5.87 (s, 1H), 6.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.9, 51.9, 58.1, 68.0, 81.3, 85.0, 126.7, 136.5, 166.3.

A 2.4 mmol sample of the mesylate of **42** was treated with freshly prepared NaSPh (2.4 mmol) to give 0.5 g (76%) of 2-(4-phenylsulfanylbut-2-ynyloxymethyl)acrylic acid methyl ester as a pale yellow oil: IR (neat) 2947, 1723, 1439, 1090, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.64 (t, 2H, J = 2.0 Hz), 3.74 (s, 3H), 4.16−4.17 (m, 4H), 5.80 (d, 1H, J = 1.2 Hz), 6.27 (d, 1H, J = 1.2 Hz), 7.18−7.31 (m, 3H), 7.40−7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 51.9, 58.1, 67.7, 79.0, 82.6, 124.4, 126.6, 126.9, 128.9, 130.1, 130.7, 135.1, 136.5, 166.1.

A 0.3 g (1.02 mmol) sample of the above compound was oxidized with 1.4 g (2.2 mmol) of Oxone to give 0.3 g (88%) of **43** as a clear oil: IR (neat) 1717, 1439, 1318, 1140, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.99 (t, 2H, J = 2.1 Hz), 4.13 (t, 2H, J = 1.2 Hz), 4.15 (t, 2H, J = 2.1 Hz), 5.81 (d, 1H, J = 1.4 Hz), 6.29 (d, 1H, J = 1.4 Hz), 7.56 (t, 2H, J = 7.5 Hz), 7.67 (t, 1H, J = 7.5 Hz), 7.96 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.7, 51.9, 57.9, 68, 74.3, 83.7, 126.6, 128.8, 129.2, 134.2, 136.3, 137.7, 166.0. Anal. Calcd for $C_{15}H_{16}SO_5$: C, 58.43; H, 5.23. Found: C, 58.51; H, 5.37.

6-Phenylsulfonyl-4,6a-dihydro-1*H*-cyclopenta[*c*]furan-3a-carboxylic Acid Methyl Ester (44). To a 0.2 g (0.7 mmol) sample of **43** and 0.1 mL (0.7 mmol) of triethylamine in 10 mL of dry THF was added 0.1 g (0.7 mmol) of the sodium salt of benzenesulfinic acid. The mixture was stirred for 10 h at room temperature, diluted with CH_2Cl_2, and filtered through a pad of Celite. The filtrated was washed with water and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by silica gel column chromatography afforded 0.15 g (65%) of **44**. Cycloadduct **44** showed the following spectroscopic properties: IR (neat) 1730, 1446, 1304, 1211, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.65 (dt, 1H, J = 19.3, 2.5 Hz), 3.17 (dd, 1H, J = 19.3, 2.1 Hz), 3.64−3.73 (m, 2H), 3.66 (s, 3H), 3.82 (dd, 1H, J = 9.3, 7.2 Hz), 3.91 (dd, 1H, J = 9.3, 3.3 Hz), 4.00 (d, 1H, J = 9.3 Hz), 6.59 (d, 1H, J = 0.9 Hz), 7.54 (t, 2H, J = 7.5 Hz), 7.64 (t, 1H, J = 7.5 Hz), 7.87 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.8, 52.7, 55.2, 61.2, 72.1, 78.0, 128.0, 129.4, 133.8, 139.4, 141.9, 143.5, 173.9. Anal. Calcd for $C_{15}H_{16}SO_5$: C, 58.43; H, 5.23. Found: C, 58.36; H, 5.05.

3-Phenylsulfonylmethyl-4-vinylidenetetrahydrofuran-3-carboxylic Acid Methyl Ester (45). In addition to cycloadduct **44**, 0.04 g (20%) of allene **45** was also isolated from the silica gel column and exhibited the following spectroscopic properties: IR (neat) 1958, 1730, 1446, 1311, 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.41 (d, 1H, J = 14.3 Hz), 3.64 (s, 3H), 3.97 (d, 1H, J = 14.3 Hz), 4.07 (d, 1H, J = 9.8 Hz), 4.32 (dt, 1H, J = 12.0, 4.3 Hz), 4.42 (dt, 1H, J = 12.0, 4.3 Hz), 4.68 (d, 1H, J = 9.8 Hz), 5.03 (t, 2H, J = 4.3 Hz), 7.55 (t, 2H, J = 7.4 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.88 (d, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.9, 53.4, 61.2, 68, 73.7, 82.9, 104.6, 128.0, 129.3, 133.9, 140.2, 170.3, 199.6. Anal. Calcd for $C_{15}H_{16}SO_5$: C, 58.43; H, 5.23. Found: C, 58.40; H, 5.16.

1-Allyl-2-(1-phenylsulfonylpropa-1,2-dienyl)benzene (56). A 3.1 g (11 mmol) of 2-iodobenzyl bromide[46] was used for the preparation of 1.6 g (61%) of 1-allyl-2-iodobenzene:[47] IR (neat) 1461, 1427, 1006, 910, 738 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.48 (d, 2H, J = 6.6 Hz), 5.04−5.14 (m, 2H), 5.87−6.01 (m, 1H), 6.86−6.91 (m, 1H), 7.19−7.30 (m, 2H), 7.80−

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7.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.9, 100.8, 116.7, 127.9, 128.4, 129.6, 135.7, 139.4, 142.7.

A mixture containing 1.4 g (5.7 mmol) of the above compound, 0.1 g of bis(triphenylphosphine)-1-palladium(II) chloride, 0.2 g of copper(I) iodide, and 0.02 g of triphenylphosphine in 25 mL of dry triethylamine was stirred at room temperature for 1 h. To the mixture was added 0.7 mL (11 mmol) of propargyl alcohol. The reaction was stirred for 12 h and was then filtered through a pad of Celite topped with a pad of Florisil. The resulting solution was washed with a saturated aqueous solution of NH_4Cl and then water and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification by silica gel chromatography afforded 0.9 g (94%) of 3-(2-allylphenyl)prop-2-yn-1-ol (**55**) as a pale yellow oil: IR (neat) 3346, 2228, 1631, 1481, 1019 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 1H), 3.54 (d, 2H, J = 6.6 Hz), 4.51 (s, 2H), 5.04 (t, 1H, J = 1.7 Hz), 5.09 (t, 1H, J = 1.7 Hz), 5.90−6.03 (m, 1H), 7.12−1.28 (m, 3H), 7.40−7.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.6, 51.7, 84.3, 91.1, 116.1, 122.0, 126.1, 128.7, 128.8, 132.4, 136.5, 142.0.

A 0.3 g (1.7 mmol) sample of **55** was treated with 0.3 g (1.9 mmol) of benzenesulfenyl chloride for 1 h at −78 °C to give 0.3 g (69%) of 1-allyl-2-(1-phenylsulfinylpropa-1,2-dienyl)-benzene as a yellow oil: IR (neat) 1937, 1439, 1083, 1040, 749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.00 (d, 2H, J = 6.6 Hz), 4.83−4.94 (m, 2H), 5.37 (d, 2H), 5.52−5.65 (m, 1H), 7.03−7.42 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.0, 83.0, 113.5, 116.0, 124.6, 126, 128.7, 129.1, 129.5, 130.4, 131.2, 132.4, 136.6, 139.8, 143.0, 203.8.

A 0.3 g (1 mmol) sample of the above compound was oxidized with 1.2 g (2 mmol) of Oxone to give 0.2 g (73%) of allene **56** as a yellow oil: IR (neat) 1970, 1449, 1303, 1150 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (d, 2H, J = 6.6 Hz), 4.90 (d, 1H, J = 17.1 Hz), 4.97 (d, 1H, J = 7.5 Hz), 5.52 (s, 2H), 5.59−5.72 (m, 1H), 7.13−7.21 (m, 2H), 7.24−7.36 (m, 2H), 7.45 (t, 2H, J = 7.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.69 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.2, 82.8, 112.3, 116.2, 126.1, 127.6, 128.6, 128.8, 129.5, 129.6, 131.0, 133.5, 136.4, 139.6, 140.1, 208.2. Anal. Calcd for $C_{18}H_{16}SO_2$: C, 72.95; H, 5.45. Found: C, 72.83; H, 5.36.

8-Phenylsulfonyl-1,2,2a,3-tetrahydrocyclobuta[*b*]naphthalene (57). A 0.07 g (0.2 mmol) sample of **56** in 10 mL of benzene was heated at reflux for 24 h. Concentration under reduced pressure followed by purification on silica gel affored 0.07 g (94%) of **57**: IR (neat) 2940, 1645, 1446, 1304, 1147 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86 (m, 2H), 2.41 (ddd, 1H, J = 20.0, 10.3, 4.0 Hz), 2.57 (t, 1H, J = 14.7 Hz), 2.78 (dd, 1H, J = 14.7, 7.8 Hz), 3.18−3.31 (m, 1H), 3.32−3.48 (m, 1H), 3.49−3.59 (m, 1H), 7.02−7.16 (m, 4H), 7.44 (t, 2H, J = 7.3 Hz), 7.51 (t, 1H, J = 7.3 Hz), 7.90 (d, 2H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 32.4, 34.3, 39.2, 124.6, 127.0, 127.1, 127.4, 127.8, 128.3, 128.7, 129, 133, 135.5, 141.7, 162.3. Anal. Calcd for $C_{18}H_{16}SO_2$: C, 72.95; H, 5.45. Found: C, 72.74; H, 5.40.

***N*-Allyl-*N*-(4-hydroxybut-2-ynyl)-4-methylbenzenesulfonamide (58).** To a solution of 1.2 g (5.9 mmol) of (*tert*-butyldimethylsilyloxy)-2-butyn-1-ol and 1.2 mL (8.9 mmol) of triethylamine in 30 mL of dry CH_2Cl_2 at 0 °C was slowly added 0.5 mL (5.9 mmol) of methanesulfonyl chloride. The reaction was warmed to room temperature and was quenched with a saturated aqueous solution of NH_4Cl. The organic layer was collected, washed with brine, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure affored the mesylate as a clear oil which was used in the next step without any further purification.

To a solution of 1.25 g (5.9 mmol) of *N*-allyl-4-methylbenzenesulfonamide[45] in 60 mL of dry THF at 0 °C was added 0.28 g (7 mmol) of 60% NaH in two portions. The mixture was stirred for 10 min at 0 °C, and the above mesylate in 15 mL of dry THF was slowly added. The ice bath was removed, and the mixture was heated to reflux for 5 min. The reaction was then allowed to cool to room temperature, stirred overnight, and quenched with a saturated aqueous solution of NH_4Cl, and the solvent was removed under reduced pressure. The residue was extracted with ether, and the organic layer was collected, washed with water, and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the residue was dissolved in 50 mL of dry THF, and 5.9 mL (5.9 mmol) of TBAF was added at 0 °C. The mixture was stirred for 5 min and quenched with a saturated aqueous solution of NH_4Cl, and the solvent was removed under reduced pressure. The residue was extracted, and the organic layer was collected, washed with water, brine, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure followed by purification afforded 0.85 g (54%) of *N*-allyl-*N*-(4-hydroxybut-2-ynyl)-4-methylbenzenesulfonamide (**58**) as a yellow oil: IR (neat) 3509, 2919, 1424, 1339, 1154 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (brs, 1H), 2.40 (s, 3H), 3.78 (s, 1H), 3.80 (s, 1H), 3.94 (s, 1H), 3.96 (s, 1H), 4.08 (t, 2H, J = 1.8 Hz), 5.19−5.28 (m, 2H), 5.63−5.77 (m, 1H), 7.28 (d, 2H, J = 8.3 Hz), 7.71 (d, 2H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 36.0, 49.2, 50.7, 78.5, 83.7, 119.9, 127.9, 129.4, 131.9, 136.1, 143.6. This compound was used in the next step without further purification.

5-Phenylsulfonyl-3-(toluene-4-sulfonyl)-3-azabicyclo-[4.2.0]oct-5-ene (59). A 0.4 g (1.3 mmol) sample of **58** was treated with 0.2 g (1.3 mmol) of benzenesulfenyl chloride to give 0.4 g (74%) of 1-(6-phenylsulfinylocta-1,6,7-triene-4-sulfonyl)-4-methylbenzene (**59**) as a pale yellow oil: IR (neat) 1944, 1339, 1154, 1083, 1040 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.62−3.78 (m, 2H), 3.91−3.96 (m, 2H), 4.92−5.02 (m, 2H), 5.19 (d, 2H, J = 2.4 Hz), 5.38−5.51 (m, 1H), 7.22 (d, 2H, J = 8.7 Hz), 7.49−7.61 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 41.3, 50.2, 84.1, 104.9, 109.4, 119.6, 124.6, 127.2, 129.2, 129.6, 131.2, 131.9, 137.1, 143.4, 205.6. Anal. Calcd for $C_{20}H_{21}NS_2O_3$: C, 62.00; H, 5.47. Found: C, 61.88; H, 5.25.

1-(6-Phenylsulfonylocta-1,6,7-triene-4-sulfonyl)-4-methylbenzene (60). A 0.34 g (0.9 mmol) sample of **59** was oxidized with 0.6 g (0.9 mmol) of Oxone to give 0.3 g (88%) of **60** as a colorless solid: mp 96−97 °C; IR (KBr) 1965, 1339, 1318, 1154, 1090 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.67 (s, 1H), 3.69 (s, 1H), 4.05 (t, 2H, J = 3.3 Hz), 4.90−5.01 (m, 2H), 5.27 (t, 2H, J = 3.3 Hz), 5.36−5.50 (m, 1H), 7.22 (d, 2H, J = 7.8 Hz), 7.54 (t, 4H, J = 7.5 Hz), 7.64 (t, 1H, J = 7.5 Hz), 7.85 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 43.6, 50.4, 85.8, 109.8, 119.8, 127.2, 128.1, 129.2, 129.7, 131.7, 133.8, 137.1, 140.1, 143.5, 208.6. Anal. Calcd for $C_{20}H_{21}NS_2O_4$: C, 59.53; H, 5.25. Found: C, 59.37; H, 5.30.

5-Phenylsulfonyl-3-(toluene-4-sulfonyl)-3-azabicyclo-[4.2.0]oct-5-ene (61). A 0.15 g sample of **60** was heated at reflux in toluene for 36 h. The solvent was removed under reduced pressure to give 0.15 g (98%) of **61** as a colorless solid: mp 140−141 °C; IR (KBr) 1681, 1446, 1346, 1317, 1154 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65−1.77 (m, 1H), 2.11−2.25 (m, 2H), 2.41 (s, 3H), 3.04−3.24 (m, 2H), 3.31−3.49 (m, 2H), 3.98 (dd, 1H, J = 11.6, 6.8 Hz), 4.08 (d, 1H, J = 15.9 Hz), 7.27 (d, 2H, J = 8.1 Hz), 7.51−7.65 (m, 5H), 7.81 (d, 2H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 23.4, 33.1, 42.5, 43.0, 46.3, 123.3, 127.2, 127.3, 129.4, 129.9, 133.6, 133.9, 140.3, 144.0, 155.6. Anal. Calcd for $C_{20}H_{21}NS_2O_4$: C, 59.53; H, 5.25. Found: C, 59.46; H, 5.23.

2-(4-Phenylsulfonylbut-2-ynyloxymethyl)furan (65). A 1.4 g (7 mmol) sample of the sodium salt of *(tert*-butyldimethylsilyloxy)-2-butyn-1-ol was reacted with 1.5 g (9.2 mmol) of furfuryl bromide.[48] Standard workup afforded a residue which was treated with 8 mL (8 mmol) of TBAF to give 1 g (86%) of 4-(furan-2-ylmethoxy)but-2-yn-1-ol (**64**) as a clear oil: IR (neat) 3388, 1346, 1069, 1005, 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83 (brs, 1H), 4.17 (t, 2H, J = 1.7 Hz), 4.29 (t, 2H, J = 1.7 Hz), 4.52 (s, 2H), 6.31−6.35 (m, 2H), 7.39 (d, 1H, J = 1.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.1, 57.1, 63.3, 81.4, 85.0, 110.0, 110.3, 143.1, 150.8.

(48) Zanetti, J. *J. Am. Chem. Soc.* **1927**, *49*, 1065.

Alcohol **64** was converted into the corresponding mesylate (4.9 mmol) which was treated with freshly prepared NaSPh (4.9 mmol) to give 0.8 g (67%) of 2-(4-phenylsulfanylbut-2-ynyloxymethyl)furan as a pale yellow oil: IR (neat) 2855, 1439, 1147, 1062, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.66 (t, 2H, J = 2.0 Hz), 4.12 (t, 2H, J = 2.0 Hz), 4.42 (s, 2H), 6.27 (d, 1H, J = 3.1 Hz), 6.31 (dd, 1H, J = 3.1, 2.0 Hz), 7.19−7.32 (m, 3H), 7.38−7.45 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 57.1, 62.8, 78.9, 82.7, 109.9, 110.3, 126.9, 129.0, 130.1, 135.1, 143.0, 150.9.

A 0.5 g (1.9 mmol) sample of the above compound was oxidized with 2.6 g (4.3 mmol) of Oxone to give 0.5 g (85%) of 2-(4-phenylsulfonylbut-2-ynyloxymethyl)furan (**65**) as a clear oil: IR (neat) 1446, 1318, 1140, 1062, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.00 (t, 2H, J = 2.0 Hz), 4.10 (t, 2H, J = 2.0 Hz), 4.40 (s, 2H), 6.30−6.33 (m, 2H), 7.39 (s, 1H), 7.55 (t, 2H, J = 7.4 Hz), 7.66 (t, 1H, J = 7.4 Hz), 7.97 (d, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.7, 56.8, 63.1, 74.4, 83.7, 110.1, 110.3, 128.8, 129.2, 134.2, 137.7, 143.1, 150.6. Anal. Calcd for $C_{15}H_{14}SO_4$: C, 62.05; H, 4.86. Found: C, 62.01; H, 4.73.

7-Phenylsulfonyl-3,11-dioxatricyclo[6.2.1.0^{1,6}]undeca-5,9-diene (67). A 0.3 g (0.9 mmol) sample of **65** with a trace of NEt_3 was heated at reflux in benzene for 12 h. Concentration under reduced pressure afforded 0.3 g (100%) of a 2:3 mixture of diastereomers of **67** as a colorless solid. The major diastereomer **67a**, mp 127−130 °C, showed the following spectral properties: IR (KBr) 2855, 1446, 1303, 1147, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.63 (d, 1H, J = 11.0 Hz), 4.08 (dd, 1H, J = 16.5, 2.2 Hz), 4.22 (dd, 1H, J = 16.8, 2.6 Hz), 4.37 (t, 1H, J = 2.2 Hz), 4.37 (d, 1H, J = 11.0 Hz), 5.03 (dd, 1H, J = 4.2, 1.7 Hz), 5.78 (dd, 1H, J = 4.2, 1.7 Hz), 6.39 (d, 1H, J = 5.4 Hz), 6.53 (d, 1H, J = 5.4 Hz), 7.57 (t, 2H, J = 7.4 Hz), 7.67 (t, 1H, J = 7.4 Hz), 7.86 (d, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.5, 66.0, 67.0, 78.2, 83.8, 121.9, 128.4, 129.3, 133.3, 134.1, 136.5, 139.1, 148.6. Anal. Calcd for $C_{15}H_{14}SO_4$: C, 62.05; H, 4.86. Found: C, 62.03; H, 4.93.

The minor diastereomer **67b** was a pale yellow oil: IR (neat) 2855, 1446, 1303, 1147, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.17 (d, 1H, J = 10.8 Hz), 3.72 (d, 1H, J = 1.2 Hz), 4.01−4.11 (m, 1H), 4.18−4.26 (m, 1H), 4.22 (d, 1H, J = 10.8 Hz), 5.27 (d, 1H, J = 1.2 Hz), 6.21 (brs, 1H), 6.35 (d, 1H, J = 5.6 Hz), 6.53 (d, 1H, J = 5.6 Hz), 7.51 (t, 2H, J = 7.5 Hz), 7.65 (t, 1H, J = 7.5 Hz), 7.83 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.5, 65.9, 67.5, 79.6, 81.7, 123.0, 128.6, 129.7, 133.9, 134.2, 136.5, 139.3, 148.6. Anal. Calcd for $C_{15}H_{14}SO_4$: C, 62.05; H, 4.86. Found: C, 62.11; H, 4.80.

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Supporting Information Available: ORTEP drawing and X-ray table data for structure **25b**.The authors have deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. This material is available free of charge via the Internet at http://pubs.acs.org.

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