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Intermolecular [4 + 2] Cycloaddition of *o*-Quinodimethanes Derived from Ene−Bis(sulfinylallenes)

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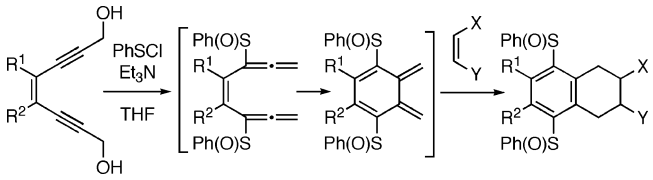

Intermolecular [4 + 2] cycloaddition of *o*-quinodimethanes, prepared in situ from ene−bis(propargyl alcohols) and benzenesulfenyl chloride via ene−bis(sulfinylallene) formation, was investigated. Benzene-bridged bis(propargyl alcohols) reacted with both electron-deficient and electron-rich olefins to give the corresponding [4 + 2] cycloadducts. Ethylene-bridged bis(propargyl alcohols) underwent similar cycloaddition with electron-deficient olefins. Construction of some heterocycles based on the newly developed sequential reaction is also described.

Introduction

Inter- and intramolecular [4 + 2] cycloaddition reactions are extremely useful processes for rapid assembly of complex polycyclic systems.[1] The *o*-quinodimethane intermediates have been widely utilized as a powerful diene counterpart in the cascade-based synthesis of polycyclic aromatic compounds.[2] The hitherto known methods for the generation of the *o*-quinodimethane species include thermolysis of benzocyclobutenes, thermal cheletropic extrusion of small-sized molecules, and 1,4-elimination of α,α′-substituted *o*-xylenes. These conventional procedures generally require a considerably high reaction temperature and/or a multiple-step route for the preparation of the precursors for the *o*-quinodimethanes.

On the other hand, ene−diallenes had been shown to be rapidly transformed into the *o*-quinodimethanes via the 6π-electrocyclic reaction under much milder conditions (at room temperature or below)[3] compared to the other reported procedures. Nevertheless, little attention has so far been paid to the chemistry of the ene−diallenes. Recent efforts in this laboratory disclosed a novel one-pot synthesis of the polycyclic aromatic compounds based on the sequential pericyclic reaction of the ene-bis(sulfinylallene) intermediates **3**, derived from the ene−bis(propargyl alcohol) **1** and benzenesulfenyl chloride (PhSCl) via the ene−bis(propargyl sulfenate) **2**.[4] Thus, the consecutive sequences, which entirely involve the sulfenic ester formation (first step), dual [2,3]-sigmatropic rearrangement of **2** (second step),[5,6] 6π-electrocyclic reaction of ene−diallenes **3** (third step), and finally intramolecular [4 + 2] cycloaddition of *o*-quinodimethanes **4** (fourth step), enabled the one-pot construction of the polycyclic compounds **5** from the acyclic substrates **1**

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(1) (a) Takao, K.; Munakata, R.; Tadano, K. *Chem. Rev.* **2005**, *105*, 4779−4807. (b) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668−1698. (c) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650−1667. (d) Fringuelli, F.; Taticchi, A. *The Diels−Alder Reaction: Selected Practical Methods*; John Wiley & Sons: Chichester, West Sussex, 2002.

(2) (a) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199−3246. (b) Martin, N.; Seoane, C.; Hanack, M. *Org. Prep. Proc. Int.* **1991**, *23*, 237−272. (c) Charlton, J. L. Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873−2889. (d) Oppolzer, W. *Synthesis* **1978**, 793−802.

(3) (a) Tanaka, K.; Takamoto, N.; Tezuka, Y.; Kato, M.; Toda, F. *Tetrahedron* **2001**, *57*, 3761−3767. (b) Toda, F.; Tanaka, K.; Sano, I.; Isozaki, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1757−1758. (c) Sugimoto, Y.; Hanamoto, T.; Inanaga, J. *Appl. Organomet. Chem.* **1995**, *9*, 369−375. (d) Inanaga, J.; Sugimoto, Y.; Hanamoto, T. *Tetrahedron Lett.* **1992**, *33*, 7035−7038. (e) Ezcurra, J. E.; Moore, H. W. *Tetrahedron Lett.* **1993**, *34*, 6177−6180. (f) Braverman, S.; Duar, Y. *J. Am. Chem. Soc.* **1990**, *112*, 5830−5837. (g) Höhn, J.; Weyerstahl, P. *Chem. Ber.* **1983**, *116*, 808−814. (h) Staab, H. A.; Draeger, B. *Chem. Ber.* **1972**, *105*, 2320−2333. (i) Bowes, C. M.; Montecalvo, D. F.; Sondheimer, F. *Tetrahedron Lett.* **1973**, 3181−3184. (j) Ben-Efraim, D. A.; Sondheimer, F. *Tetrahedron Lett.* **1963**, 313−315.

(4) Kitagaki, S.; Ohdachi, K.; Katoh, K.; Mukai, C. *Org. Lett.* **2006**, *8*, 95−98.

(5) Horner, L.; Binder, V. *Liebigs Ann. Chem.* **1972**, *757*, 33−68.

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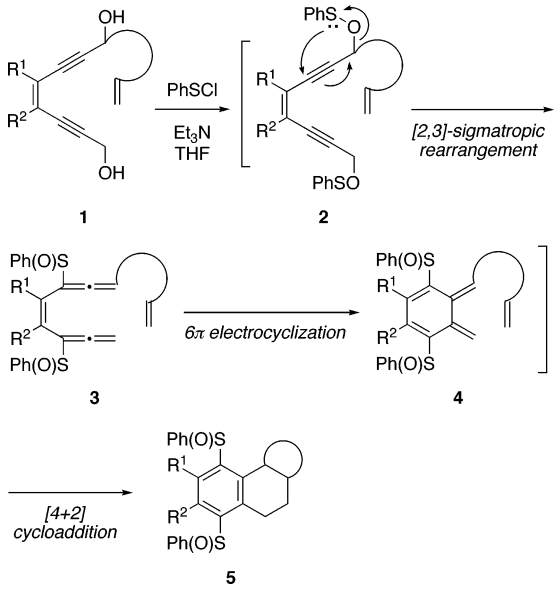
SCHEME 1

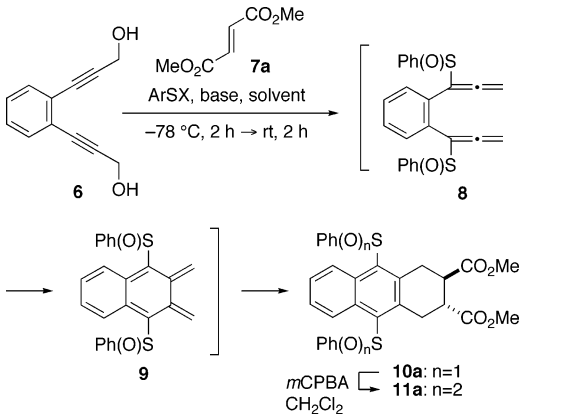


(Scheme 1). The efficiency of the newly developed method has been verified by a convenient synthesis of the estra-1,3,5(10)-trien-17-one.[4] We have now investigated the intermolecular [4 + 2] cycloaddition between the *o*-quinodimethanes, generated from ene−bis(sulfinylallene) species, and several dienophiles. In this paper, the details of the successful application of this methodology to the intermolecular version is described.[7]

Results and Discussion

We first examined a tandem ene−diallene/*o*-quinodimethane formation from benzene-bridged bis(propargyl alcohol) **6**[8] and subsequent [4 + 2] cycloaddition with dimethyl fumarate (**7a**). The reaction was performed as follows. PhSCl was added to a solution of **6** and **7a** in the presence of a base at −78 °C and then warmed to room temperature for 2 h. After the usual workup and a subsequent short column chromatography, the crude products were treated with *m*-CPBA in CH_2Cl_2 to simplify structure determination of the cycloadduct. The results are summarized in Table 1. Reaction using Et_3N as a base in THF provided the desired cycloadduct **11a** in 84% yield (entry 1).[4] While a similar result was obtained using Hunig's base (entry 2), pyridine provided a rather low yield (entry 3). Of the solvents surveyed using Et_3N as a base, THF was found to be the optimal solvent for this transformation (entries 1, 4, and 5). Reaction with 4-nitrobenzenesulfenyl chloride gave a complex mixture of products (entry 6), and no reaction occurred when *S*-phenyl benzenethiosulfate was used (entry 7).

TABLE 1. Reaction of Benzene-Bridged Bis(propargyl alcohol) 6 with 7a[a]



entry	ArSX	base	solvent	yield of **11** (%)
1	PhSCl	Et_3N	THF	84
2	PhSCl	$^iPr_2NEt$	THF	84
3	PhSCl	pyridine	THF	33
4	PhSCl	Et_3N	toluene	76
5	PhSCl	Et_3N	CH_2Cl_2	44
6	4-$NO_2C_6H_4SCl$	Et_3N	THF	0
7	$PhSSO_2Ph$	Et_3N	THF	0

[a] All reactions were performed on a 0.2 mmol scale (0.08 M) with 6 equiv of ArSX, 7 equiv of base, and 2 equiv of **7a**.

By using the optimized conditions described above (Et_3N, THF), the sequential reaction of benzene-bridged bis(propargyl alcohols) **6** and **12** with various dienophiles were investigated (Table 2). Cycloaddition of **6** with dimethyl maleate (**7b**) gave the cis-adduct **11b** in 24% yield along with a trace amount of trans-adduct **11a** (entry 2).[9,10] Neither dimethyl maleate or product **11b** isomerized to the corresponding trans-isomers under the reaction conditions.[11] These results strongly suggest that the [4 + 2]-type cycloaddition between the *o*-quinodimethane **9** and maleate **7b** must have proceeded at least in part in a nonconcerted fashion. On the other hand, other electron-deficient olefins **7c**−**e** and styrene (**7f**) provided the corresponding cycloadducts in good yields (entries 3−6). Interestingly, the electron-rich olefin **7g** also took part in the cycloaddition reaction to afford **11g**, although a prolonged reaction time and a large excess of **7g** were required (entry 7). In addition, a slightly lower yield (72%) of **13**, compared to that of **11a**, was observed when the bis(propargyl alcohol) derivative, having a methyl group at the C-3 position on the benzene ring, was exposed to the standard conditions (entry 8 vs 1). To summarize the results obtained in Table 2, the *o*-quinodimethane intermediate **9** reacts with a variety of dienophiles irrespective of the property of the olefinic counterpart, although it is obvious that the electron-deficient olefin has a much higher reactivity than the electron-rich ones.

(6) The tandem formation and intramolecular [4 + 2] cycloaddition of 1-sulfinyl-1-vinylallenes, triggered by [2,3]-sigmatropic rearrangement of the corresponding propargyl sulfenates, have been reported: (a) Okamura, W. H.; Curtin, M. L. *Synlett* **1990**, 1−9. (b) Curtin, M. L.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 5278−5287. (c) Gibbs, R. A.; Bartels, K.; Lee, R. W. K.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 3717−3725. (d) Gibbs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062−4063.

(7) The intermolecular cycloaddition reaction of the *o*-quinodimethane derived from *cis*-4-octene-2,6-diyne-1,8-diol and PhSCl was described in the review article by Grissom (Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453−6518). However, no original manuscript dealing with the details of this reaction is available.

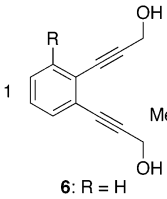
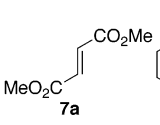
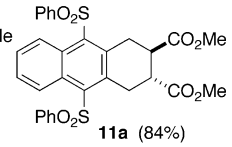
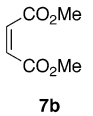
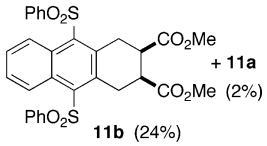
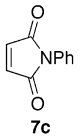
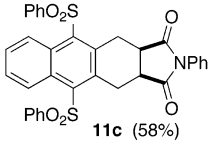
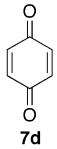
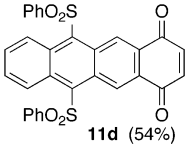
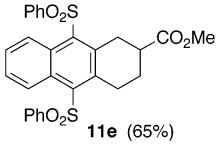
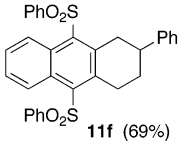
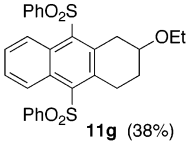
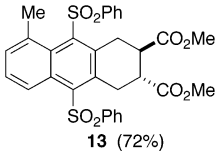
(8) Basak, A.; Shain, J. C.; Khamrai, U. K.; Rudra, K. R.; Basak, A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1955−1964.

(9) Stereochemistry of cycloadduct **11b** was determined to be cis by the chemical correlation with the sole cyclized product, which was obtained from **6** and maleic anhydride by the following successive reaction: (1) **6**, PhSCl, Et_3N, maleic anhydride, THF, −78 °C to rt, then 10% HCl; (2) $TMSCHN_2$, MeOH; (3) *m*-CPBA, CH_2Cl_2.

(10) For the low reactivity of maleate esters for dienes, see: Lenihan, B. D.; Shechter, H. *J. Org. Chem.* **1998**, *63*, 2072−2085 and references therein.

(11) There are some examples where cycloadditions of *o*-quinodimethanes with maleate esters give mixtures of cis- and trans-cycloadducts due to the isomerization of maleates prior to the cycloaddition process occurring: (a) Reference 10. (b) Inaba, S.; Wehmeyer, R. M.; Forkner, M. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 339−344. See also ref 3c.

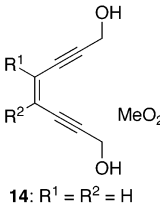
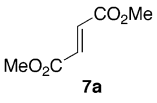
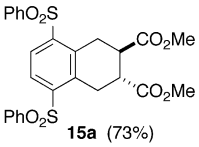
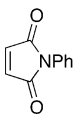
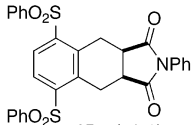
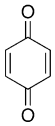
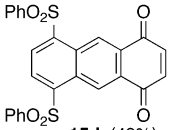
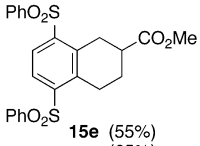
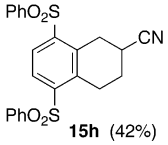
TABLE 2. Reaction of Benzene-Bridged Bis(propargyl alcohols) with Various Dienophiles[a]

entry	substrate	dienophile **7**	products (yield)
1	 **6**: R = H	 **7a**	 **11a** (84%)
2	**6**	 **7b**	 **11b** (24%) + **11a** (2%)
3	**6**	 **7c**	 **11c** (58%)
4[b]	**6**	 **7d**	 **11d** (54%)
5	**6**	 **7e**	 **11e** (65%)
6[c,d]	**6**	 **7f**	 **11f** (69%)
7[d,e]	**6**	 **7g**	 **11g** (38%)
8	**12**: R = Me	**7a**	 **13** (72%)

[a] Reactions were performed according to the procedure described in footnote a of Table 1, unless otherwise stated. [b] Reaction was performed with 5 equiv of **7d**. [c] Reaction was performed with 6 equiv of **7f**. [d] Reaction mixture was stirred at −78 °C for 1.5 h and then at room temperature for 17 h after addition of PhSCl. [e] Reaction was performed with 10 equiv of **7g**.

Reaction of the ethylene-bridged bis(propargyl alcohol) **14**[12] with various dienophiles was the next subject to examine (Table 3). The reaction of **14** with the electron-deficient olefins **7a**, **7c**−**e**, and **7h** resulted in the formation of the polycyclic products in slightly decreased yields compared to those for **6** (entries1−9). Interestingly, it was found that the addition of BHT or TEMPO in the reaction mixture led to an increase in

TABLE 3. Reaction of Ethylene-Bridged Bis(propargyl alcohols) 14 with Various Dienophiles[a]

entry	substrate	dienophile **7**	product
1	 **14**: $R^1 = R^2$ = H	 **7a**	 **15a** (73%)
2[b]	**14**	**7a**	**15a** (56%)
3[c]	**14**	**7a**	**15a** (8%)
4	**14**	 **7c**	 **15c** (56%)
5	**14**	 **7d**	 **15d** (49%)
6	**14**	 **7e**	 **15e** (55%)
7[d]	**14**	**7e**	(65%)
8[e]	**14**	**7e**	(69%)
9	**14**	 **7h**	 **15h** (42%)

[a] All reactions were performed on a 0.2 mmol scale (0.08 M) with 4−6 equiv of PhSCl, 5−7 equiv of Et_3N, and 2−5 equiv of dienophile. [b] After a solution of **14**, Et_3N, and PhSCl was stirred at −78 °C for 1 h, **7a** was added to the mixture, which was stirred at −78 °C for 1 h and at room temperature for 2 h. [c] After a solution of **14**, Et_3N, and PhSCl was stirred at −78 °C for 1 h and at 0 °C for 1 h, **7a** was added to the mixture, which was stirred at room temperature for 2 h. [d] Reaction was performed in the presence of BHT (2 equiv). [e] Reaction was performed in the presence of TEMPO (2 equiv).

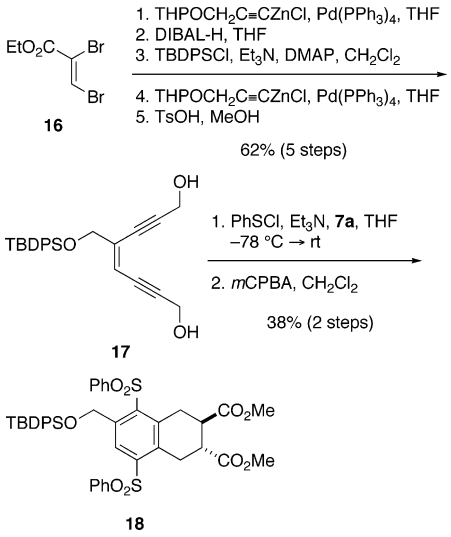
yield in the reaction of **14** with **7e** (entries 7 and 8). The fact that the effect of a radical scavenger was remarkable when the long-stored PhSCl[13] was used indicates that the radical scavenger might partially inhibit the side reactions due to the thiyl radical, derived from sulfenyl chloride.[14] Unfortunately, cycloaddition of **14** with electron-rich olefins did not occur, which might be predictable on the basis of the results in Table 2. As mentioned in the reaction of **6** with **7g**, the electron-rich olefin has less reactivity for [4 + 2] cycloaddition and needs a prolonged reaction time. Therefore, the reaction of the electron-rich olefin with the *o*-quinodimethane, derived from **14**, would be considered to require a rather long reaction time that must have caused the decomposition of the quinodimethane intermediate. Experiments with entries 2 and 3 may indirectly support the above considerations. Namely, addition of PhSCl to the mixture of

(12) Mladenova, M.; Alami, M.; Linstrumelle, G. *Synth. Commun.* **1996**, *26*, 2831−2842.

(13) PhSCl was prepared by a literature procedure and stored in the freezer: Barrett, A. G. M.; Dhanak, D.; Graboski, G. G.; Taylor, S. J. *Org. Synth.* **1990**, *68*, 8−12.

(14) Davies, M. J.; Hawkins, C. L. *Free Radic. Res.* **2000**, *33*, 719−729.

SCHEME 2

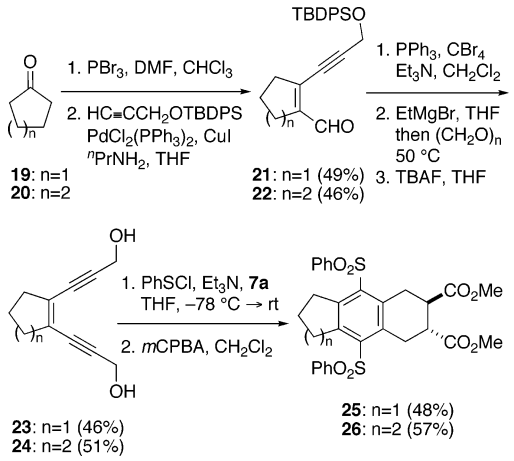


16 **17** **18**

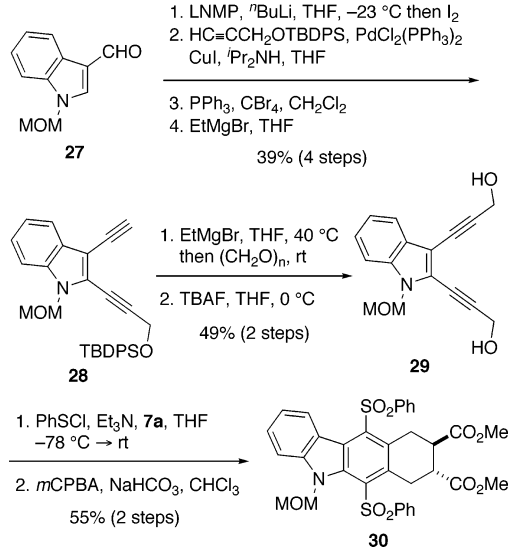
14, Et_3N, and dienophile **7a** at −78 °C and then raising the reaction temperature to 0 °C (standard conditions) afforded **15a** in 73% yield (entry 1). When a solution of **14**, Et_3N, and PhSCl was stirred at −78 °C for 1 h, followed by addition of **7a**, **15a** was obtained in 56% yield (entry 2), while addition of **7a** to the reaction mixture at 0 °C instead of −78 °C gave **15a** in only 8% yield (entry 3). This is not the case in the reaction of benzene-bridged bis(propargyl alcohol) **6** with **7a**.

Thus, it turns out that the reactivity of the *o*-quinodimethane derived from the olefinic compound **14** toward the dienophiles was generally lower than that of the *o*-quinodimethane **9** having a benzene ring. We next became interested in the effects of substituents on the ethylene moiety of **14** in the [4 + 2] cycloaddition reaction. Thus, bis(propargyl alcohol) **17**, bearing siloxymethyl-substituted ethylene, was prepared in a five-step procedure including stepwise Negishi coupling[15] from the known ethyl (*Z*)-dibromopropenoate (**16**)[16] as depicted in Scheme 2. The sequential reaction of **17** with **7a** under the standard conditions gave the expected cycloadduct **18**, but the chemical yield was rather low (38%). Alternatively, bis(propargyl alcohols) **23** and **24** containing five- and six-membered carbocycles, respectively, were synthesized from cycloalkanones **19** and **20** via 2-(3-siloxypropynyl)-1-cycloalkenecarbaldehydes **21** and **22**[17] by taking advantage of the consecutive Vilsmeier reaction, Sonogashira coupling,[18] and Corey−Fuchs alkynylation[19] (Scheme 3). With the two additional bis(propargyl alcohols) **23** and **24** in hand, we examined the sequential pericyclic reaction of **23** and **24** with **7a** under the standard conditions to provide the cycloadducts **25** and **26** in 48 and 57% yields, respectively. In comparison with the result in Table 3, entry 1, these three examples show a decrease in the chemical yields of the desired products, which may be attributable to the nonbonding interaction between a phenylsulfonyl group and a substituent such as

SCHEME 3



SCHEME 4



27 **28** **29** **30**

the $TBDPSOCH_2$ group in **18** and the methylene side chain in **25** and **26**. This would not be the case with **15a** where no similar nonbonding interaction could be predicted.

Next, three types of heterocycle-containing ene−diallenes were examined. Indole-containing substrate **29** was synthesized starting from iodination at the C-2 position of *N*-methoxymethylindole-3-carbaldehyde (**27**)[20] (Scheme 4). According to the aforementioned procedure in Scheme 3, introduction of the bis(propargyl alcohol) unit to the 2-iodo derivative of **27** was realized via **28** to furnish the desired **29**.

Treatment of **29** with **7a** gave the cycloadduct **30** in 55% yield after *m*-CPBA oxidation in the presence of $NaHCO_3$. Furan-containing substrate **33** was prepared by a procedure similar to that described in Scheme 4, except for the protection of the formyl group (Scheme 5).[21] Cycloaddition of **33** with **7a** under the standard conditions gave **34** in a low yield.

Pyrazine-containing substrate **36** was also prepared by dual Sonogashira coupling of readily available diiodopyrazine **35**[22] and 3-siloxypropyne (Scheme 6). Treatment of **36** with PhSCl

(15) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358−360.

(16) (a) Myers, A. G.; Alauddin, M. M.; Fuhry, M. A. M.; Dragovich, P. S.; Finney, N. S.; Harrington, P. M. *Tetrahedron Lett.* **1989**, *30*, 6997−7000. (b) Hall, R. G.; Trippett, S. *Tetrahedron Lett.* **1982**, *23*, 2603−2604.

(17) (a) Herndon, J. W.; Wang, H. *J. Org. Chem.* **1998**, *63*, 4562−4563. (b) Arnold, Z.; Holy, A. *Collect. Czech. Chem. Commun.* **1961**, *26*, 3059−3073.

(18) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

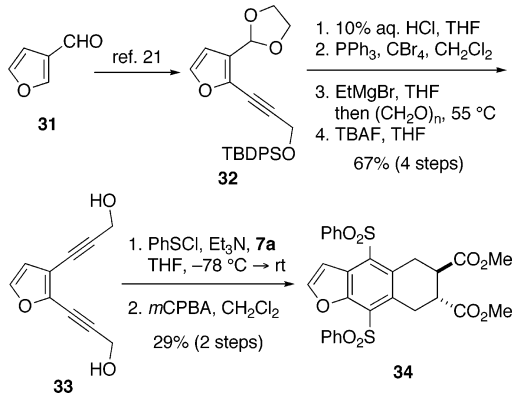
(19) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769−3772.

(20) Comins, D. L.; Killpack, M. O. *J. Org. Chem.* **1987**, *52*, 104−109.

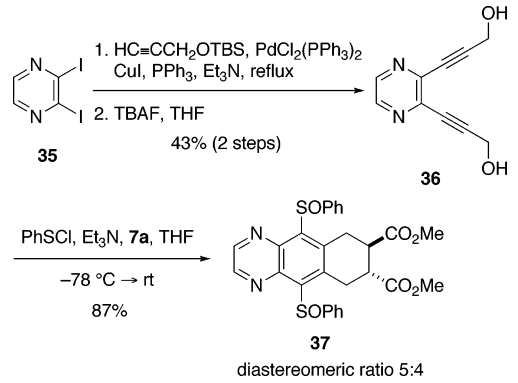
(21) Mukai, C.; Hirose, T.; Teramoto, S.; Kitagaki, S. *Tetrahedron* **2005**, *61*, 10983−10994.

(22) Plé, N.; Turck, A.; Heynderickx, A.; Quéguiner, G. *Tetrahedron* **1998**, *54*, 9701−9710.

SCHEME 5



SCHEME 6

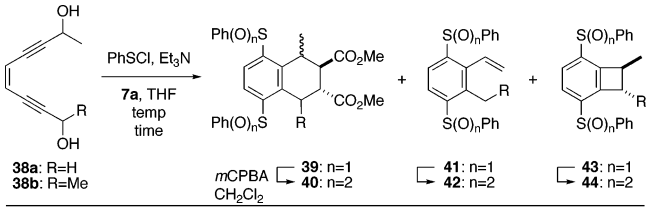


in the presence of **7a** provided **37** in high yield as a separable mixture of two diastereomers in a ratio of 5:4, due to the chirality of the sulfinyl group. Simple oxidation of **37** with *m*-CPBA to the corresponding sulfonyl derivative was unsuccessful and gave a complex mixture of several products, presumably due to undesired oxidation of the amine functionalities. Thus, the pyrazine derivative **36** afforded the cyclized product **37** in a satisfactory yield, while the indole derivative **29** resulted in the formation of **30** in a moderate yield. On the other hand, the furan derivative **33** led to the low yield of **34**. We do not yet have a reasonable clue to understanding the difference in chemical yield observed between these three compounds in combination with the benzene derivative **11a**.

Finally, the effect of substituents at the propargylic position of ene−bis(propargyl alcohols) was studied. Monomethyl-substituted bis(propargyl alcohol) **38a** was exposed to PhSCl in the presence of **7a** to afford cycloadduct **40a** in 38% yield (Table 4, entry 1). Higher reaction temperature (reflux in THF) led to a slight improvement in the yield of **40a** along with an increase in the [1,5] hydrogen-shift product **42a** (entry 2).[23] Dimethyl-substituted derivative **38b**[12] no longer gave the [4 + 2] product **40b** but rather the benzocyclobutene derivative **44b** (38−42% yield), which should have arisen from the intramolecular [2 + 2] cycloaddition reaction, along with **42b** (15% yield) (entries 3 and 4). Upon treatment with PhSCl under the standard conditions, the benzene-bridged bis(propargyl alcohol) **45**, possessing a methyl group at the propargyl position, gave the [2 + 2] cycloadduct **46** (43%) as well as the [1,5] hydrogen-shift product **47** (14%), but not the [4 + 2] cycloadduct (Scheme 7). This result is in contrast to those observed in the reaction of **6** with **7a** where the corresponding tetrahydroanthracene derivatives ([4 + 2] products) could be obtained as a major product.

(23) In the study of intramolecular [4 + 2] cycloaddition on the basis of this methodology, improvement in the cycloadduct yield was observed when a reaction mixture was heated under reflux. See ref 4.

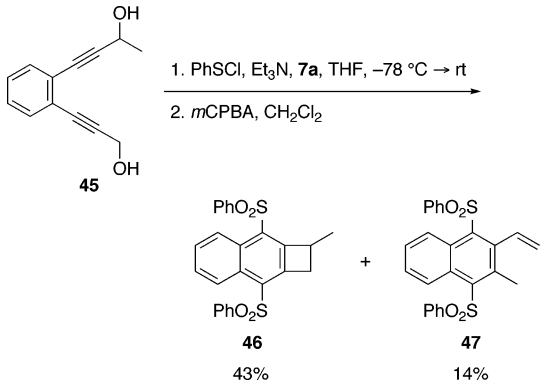
TABLE 4. Reaction of Methyl-Substituted Bis(propargyl alcohols) 38 with 7a



				yield (%)		
entry	substrate	R	*T* (°C)/time (h)	**40**	**42**	**44**
1	**38a**	H	−78/2 → rt/2	38[a]	trace	0
2	**38a**	H	rt/0.5 → reflux/15	42[b]	9	0
3	**38b**	Me	−78/2 → rt/2	0	15	38
4	**38b**	Me	rt/0.5 → reflux/15	0	15	42

[a] Product was obtained as a mixture of diastereomers (ratio not determined). [b] Product was obtained as a mixture of diastereomers in a ratio of 2:1.

SCHEME 7



In summary, we have demonstrated that benzene-bridged bis(sulfinylallenes), derived from the ene-bis(propargyl alcohols), underwent an intermolecular [4 + 2] cycloaddition with various dienophiles to give polycyclic aromatic compounds. Application of this method to the ethylene-bridged bis(sulfinylallenes) was realized. In addition, ene−bis(sulfinylallenes) having one or two methyl group at the allenic termini were shown to collapse to form the cyclobutene derivatives and/or the [1,5] hydrogen-shift products. The present reaction system allows considerable structural variations in the "ene" part of the ene−diallene such as benzene, ethylene, and heterocycles.

Experimental Section

Sequential Pericyclic Reaction of Ene−Bis(propargyl alcohols): General Procedure. To a solution of bis(propargyl alcohol) (0.200 mmol) in THF (3.0 mL) were successively added dienophile (0.400 mmol), Et_3N (0.20 mL, 1.4 mmol), and a solution of PhSCl (175 mg, 1.20 mmol) in THF (0.5 mL) at −78 °C. After being stirred for 2 h, the reaction mixture was allowed to warm to room temperature. After 2 h, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH_2Cl_2 (2 mL) was added *m*-CPBA (82.8 mg, 0.480 mmol) at 0 °C, and the reaction mixture was allowed to warm to room temperature.

After 12 h, the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue gave **11**.

Dimethyl *cis*-9,10-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene-2,3-dicarboxylate (11b): pale yellow oil; IR 1734, 1308, 1150 cm^{-1}; ^1H NMR δ 9.10−9.03 (2H, m), 7.96−7.82 (4H, m), 7.62−7.46 (8H, m), 4.14 (2H, dd, J = 17.2, 5.3 Hz), 3.62 (6H, s), 3.51 (2H, dd, J = 17.2, 8.9 Hz), 3.02−2.93 (2H, m); ^{13}C NMR δ 172.7, 143.0, 139.9, 138.9, 133.4, 130.0, 129.4, 127.6, 126.1, 125.3, 52.1, 39.9, 29.1; MS m/z 578 (M^+, 6.1); HRMS calcd for $C_{30}H_{26}O_8S_2$ 578.1069, found 578.1064.

***N*-Phenyl-9,10-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene-2,3-dicarboximide (11c):** pale yellow oil; IR 1717, 1327, 1308, 1150 cm^{-1}; ^1H NMR δ 9.06−9.00 (2H, m), 7.94 (4H, d, J = 7.3 Hz), 7.60−7.29 (11H, m), 6.99 (2H, dd, J = 7.3, 1.3 Hz), 4.02−3.80 (4H, m), 3.23−3.13 (2H, m); ^{13}C NMR δ 176.4, 142.6, 139.8, 139.2, 133.6, 131.3, 130.1, 129.5, 129.0, 128.5, 128.0, 126.2, 126.0, 125.5, 39.0, 27.3; MS m/z 607 (M^+, 35); HRMS calcd for $C_{34}H_{25}NO_6S_2$ 607.1123, found 607.1125.

6,11-Bis(phenylsulfonyl)-1,4-naphthacenequinone (11d): pale yellow oil; IR 1682, 1296, 1153 cm^{-1}; ^1H NMR δ 9.99 (2H, s), 9.57−9.51 (2H, m), 8.01−7.97 (4H, m), 7.79−7.73 (2H, m), 7.60−7.47 (6H, m), 7.10 (2H, s); ^{13}C NMR δ 183.1, 143.0, 140.8, 140.5, 133.8, 132.4, 130.0, 129.6, 129.5, 127.9, 126.8, 126.5, 125.4; MS m/z 538 (M^+, 10); HRMS calcd for $C_{30}H_{18}O_6S_2$ 538.0545, found 538.0543.

Methyl 9,10-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene-2-carboxylate (11e): pale yellow oil; IR 1734, 1325, 1304, 1148 cm^{-1}; ^1H NMR δ 9.13−9.00 (2H, m), 7.87 (2H, dd, J = 7.3, 1.6 Hz), 7.82 (2H, dd, J = 7.3, 1.6 Hz), 7.61−7.47 (8H, m), 3.90 (1H, dd, J = 15.5, 5.9 Hz), 3.65 (3H, s), 3.65−3.56 (1H, m), 3.42 (1H, dd, J = 15.5, 8.9 Hz), 3.28−3.17 (1H, m), 2.69−2.57 (1H, m), 2.01−1.88 (1H, m), 1.82−1.68 (1H, m); ^{13}C NMR δ 175.2, 143.44, 143.38, 143.26, 141.5, 138.6, 137.7, 133.3, 133.2, 129.8, 129.7, 129.31, 129.29, 127.5, 127.4, 126.0, 125.9, 125.31, 125.27, 52.0, 36.9, 28.8, 25.9, 23.2; MS m/z 520 (M^+, 19); HRMS calcd for $C_{28}H_{24}O_6S_2$ 520.1015, found 520.1013.

2-Phenyl-9,10-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene (11f): pale yellow oil; IR 1323, 1304, 1148 cm^{-1}; ^1H NMR δ 9.18−9.07 (2H, m), 7.85 (2H, d, J = 8.3 Hz), 7.72 (2H, d, J = 8.3 Hz), 7.59−7.40 (8H, m), 7.29−7.20 (3H, m), 7.03 (2H, d, J = 7.6 Hz), 4.02 (1H, dd, J = 15.8, 5.0 Hz), 3.82 (1H, dt, J = 15.8, 5.9 Hz), 3.35−3.16 (2H, m), 2.78−2.67 (1H, m), 1.98−1.89 (2H, m); ^{13}C NMR δ 145.9, 143.5, 143.2, 138.3, 138.0, 133.3, 133.2, 129.9, 129.8, 129.3, 128.6, 127.4, 126.8, 126.5, 125.9, 125.3, 125.2, 38.0, 35.0, 28.2, 27.3; MS m/z 538 (M^+, 36); HRMS calcd for $C_{32}H_{26}O_4S_2$ 538.1273, found 538.1274.

2-Ethoxy-9,10-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene (11g): pale yellow oil; IR 1325, 1304, 1148 cm^{-1}; ^1H NMR δ 9.10−9.05 (1H, m), 8.96−8.91 (1H, m), 7.95 (2H, dd, J = 7.3, 1.7 Hz), 7.82 (2H, dd, J = 7.3, 1.7 Hz), 7.57−7.46 (8H, m), 3.86−3.73 (2H, m), 3.62−3.49 (2H, m), 3.44−3.33 (2H, m), 3.25−3.14 (1H, m), 2.04−1.92 (1H, m), 1.60−1.47 (1H, m), 1.09 (3H, t, J = 6.9 Hz); ^{13}C NMR δ 144.2, 143.5, 143.3, 141.3, 138.7, 137.4, 133.2, 129.8, 129.3, 127.3, 127.2, 126.0, 125.9, 125.4, 125.2, 72.4, 63.7, 32.3, 27.9, 25.5, 15.4; MS m/z 506 (M^+, 12); HRMS calcd for $C_{28}H_{26}O_5S_2$ 506.1221, found 506.1221.

Dimethyl *trans*-5-methyl-9,10-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene-2,3-dicarboxylate (13): pale yellow oil; IR 1734, 1317, 1310, 1159, 1150 cm^{-1}; ^1H NMR δ 8.75−8.71 (1H, m), 7.88 (2H, d, J = 7.6 Hz), 7.58−7.38 (10H, m), 4.04−3.97 (1H, m), 3.71 (3H, s), 3.71−3.04 (4H, m), 3.60 (3H, s), 2.97 (3H, s), 2.52−2.44 (1H, m); ^{13}C NMR δ 173.8, 173.4, 144.6, 142.9, 139.6, 139.3, 139.1, 137.8, 136.4, 133.3, 132.9, 130.8, 130.5, 130.0, 129.2, 128.9, 127.8, 126.8, 126.2, 121.8, 52.4, 39.9, 39.0, 28.6, 27.8, 26.0; MS m/z 592 (M^+, 9.8); HRMS calcd for $C_{31}H_{28}O_8S_2$ 592.1226, found 592.1227.

Dimethyl *trans*-5,8-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (15a): colorless powder; mp 198−200 °C (acetone-hexane); IR 1736, 1319, 1138 cm^{-1}; ^1H NMR δ 8.23 (2H, s), 7.87−7.48 (10H, m), 3.62 (6H, s), 3.48−3.40 (2H, m), 3.06−2.87 (4H, m); ^{13}C NMR δ 173.2, 143.6, 139.7, 136.8, 133.9, 129.4, 128.0, 127.7, 52.3, 39.7, 27.8; MS m/z 528 (M^+, 7.2). Anal. Calcd for $C_{26}H_{24}O_8S_2$: C, 59.08; H, 4.58. Found: C, 58.96; H, 4.60.

***N*-Phenyl-5,8-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene-2,3-dicarboximide (15c):** colorless powder; mp 280.5−282.5 °C (CH_2Cl_2−AcOEt-hexane); IR 1717, 1321, 1140 cm^{-1}; ^1H NMR δ 8.30 (2H, s), 7.90−7.89 (4H, m), 7.61−7.58 (2H, m), 7.53−7.50 (4H, m), 7.37−7.32 (3H, m), 6.97−6.96 (2H, m), 3.61−3.57 (2H, m), 3.19−3.15 (2H, m), 2.95−2.93 (2H, m); ^{13}C NMR δ 175.9, 143.8, 140.2, 138.6, 133.9, 131.3, 129.6, 128.9, 128.5, 128.1, 127.8, 126.0, 38.7, 25.9; MS m/z 557 (M^+, 7.3). Anal. Calcd for $C_{30}H_{23}NO_6S_2$: C, 64.62; H, 4.16; N, 2.51. Found: C, 64.46; H, 4.16; N, 2.50.

5,8-Bis(phenylsulfonyl)-1,4-anthraquinone (15d): yellow powder; mp 289−291 °C dec ($CHCl_3$−hexane); IR 1680, 1614, 1317, 1150 cm^{-1}; ^1H NMR δ 9.48 (2H, s), 8.82 (2H, s), 8.09−8.05 (4H, m), 7.60−7.51 (6H, m), 7.09 (2H, s); ^{13}C NMR δ 183.1, 144.2, 139.9, 134.2, 130.9, 130.6, 129.7, 128.1, 125.6; FABMS m/z 489 ($M^+ + 1$, 5.6); FABHRMS calcd for $C_{26}H_{17}O_6S_2$ 489.0467, found 489.0493.

Methyl 5,8-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (15e): colorless powder; mp 166−167 °C (CH_2Cl_2−AcOEt); IR 1732, 1310, 1138 cm^{-1}; ^1H NMR δ 8.26−8.21 (2H, m), 7.88−7.82 (4H, m), 7.65−7.52 (6H, m), 3.61 (3H, s), 3.45 (1H, dd, J = 17.6, 5.3 Hz), 3.15 (1H, dt, J = 16.1, 5.4 Hz), 2.85 (1H, dd, J = 17.6, 9.3 Hz), 2.82−2.76 (1H, m), 2.53−2.47 (1H, m), 2.00−1.95 (1H, m), 1.69−1.61 (1H, m); ^{13}C NMR δ 174.3, 143.9, 143.6, 139.9, 139.8, 138.4, 137.6, 133.81, 133.76, 129.33, 129.30, 128.1, 127.9, 127.33, 127.31, 51.9, 37.7, 28.6, 25.6, 23.8; MS m/z 470 (M^+, 23). Anal. Calcd for $C_{24}H_{22}O_6S_2$: C, 61.26; H, 4.71. Found: C, 60.93; H, 4.75.

2-Cyano-5,8-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene (15h): colorless oil; IR 2245, 1321, 1140 cm^{-1}; ^1H NMR δ 8.23 (1H, d, J = 8.8 Hz), 8.21 (1H, d, J = 8.8 Hz), 7.86−7.83 (4H, m), 7.68−7.63 (2H, m), 7.59−7.54 (4H, m), 3.46 (2H, dd, J = 7.6, 5.4 Hz), 3.18−3.08 (2H, m), 3.03−2.96 (1H, m), 2.84−2.80 (1H, m), 2.03−2.00 (1H, m), 1.89−1.84 (1H, m); ^{13}C NMR δ 144.0, 143.9, 139.44, 139.36, 137.2, 134.7, 134.1, 134.0, 129.6, 129.4, 128.1, 127.90, 127.88, 127.75, 120.5, 29.3, 24.4, 24.2, 23.9; MS m/z 437 (M^+, 34); HRMS calcd for $C_{23}H_{19}O_4NS_2$ 437.0756, found 437.0759.

Dimethyl *trans*-6-(*tert*-butyldiphenylsiloxy)methyl-5,8-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (18): colorless oil; IR 1736, 1317, 1138 cm^{-1}; ^1H NMR δ 8.96 (1H, s), 7.88−7.83 (2H, m), 7.66−7.33 (18H, m), 5.34 (2H, s), 3.64 (3H, s), 3.60 (3H, s), 3.45−2.79 (6H, m), 1.15 (9H, s); ^{13}C NMR δ 173.5, 173.4, 143.2, 142.6, 141.6, 140.2, 139.5, 139.1, 135.6, 135.5, 135.4, 133.7, 133.5, 132.9, 129.9, 129.4, 129.2, 128.0, 127.8, 127.1, 126.3, 63.3, 52.3, 52.2, 40.3, 39.7, 28.7, 27.7, 26.9, 19.3; FABMS m/z 796 ($M^+ + 1$, 17). Anal. Calcd for $C_{43}H_{44}O_9S_2Si$: C, 64.80; H, 5.56. Found: C, 64.41; H, 5.69.

Dimethyl *trans*-4,9-bis(phenylsulfonyl)-2,3,5,6,7,8-hexahydro-1*H*-cyclopenta[*b*]naphthalene-6,7-dicarboxylate (25): colorless oil; IR 1734, 1308, 1144 cm^{-1}; ^1H NMR δ 7.83−7.50 (10H, m), 3.62 (6H, s), 3.67−3.15 (8H, m), 2.88−2.84 (2H, m), 2.11−2.03 (2H, m); ^{13}C NMR δ 173.7, 146.9, 142.1, 139.2, 136.9, 133.5, 129.2, 126.6, 52.2, 40.1, 34.3, 28.2, 24.9; MS m/z 568 (M^+, 14); HRMS calcd for $C_{29}H_{28}O_8S_2$ 568.1226, found 568.1202.

Dimethyl *trans*-9,10-bis(phenylsulfonyl)-1,2,3,4,5,6,7,8-octahydroanthracene-2,3-dicarboxylate (26): colorless oil; IR 1734, 1308, 1146 cm^{-1}; ^1H NMR δ 7.80−7.50 (10H, m), 3.66 (6H, s), 3.71−3.53 (4H, m), 3.04−3.00 (6H, m), 1.46−1.41 (4H, m); ^{13}C NMR δ 174.1, 143.3, 141.7, 140.7, 138.0, 133.1, 129.3, 126.0, 52.3,

40.4, 28.4, 27.1, 20.0; MS *m*/*z* 582 (M^+, 11); HRMS calcd for $C_{30}H_{30}O_8S_2$ 582.1382, found 582.1410.

Dimethyl *trans*-5-(methoxymethyl)-6,11-bis(phenylsulfonyl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-8,9-dicarboxylate (30): colorless oil; ^{1}H NMR δ 8.81 (1H, d, J = 8.4 Hz), 7.88−7.22 (13H, m), 5.99 (2H, s), 3.66 (3H, s), 3.66−3.59 (1H, m), 3.51 (3H, s), 3.27−3.17 (2H, m), 3.04−2.99 (1H, m), 2.84−2.69 (2H, m), 2.77 (3H, s); ^{13}C NMR δ 173.8, 173.7, 143.3, 142.9, 142.5, 140.7, 136.9, 135.6, 133.3, 132.4, 129.3, 129.1, 128.2, 127.1, 126.8, 126.4, 125.6, 125.5, 121.7, 120.8, 112.8, 81.9, 56.3, 52.3, 52.2, 40.4, 39.8, 28.8, 27.8. Because of its instability, compound **30** spontaneously collapsed to the *N*-demethoxymethyl derivative **30′**. Thus, full characterization data of compound **30′** is shown as follows: colorless oil; IR 3416, 1734, 1315, 1144 cm^{-1}; ^{1}H NMR δ 10.97 (1H, s), 8.83 (1H, d, J = 8.3 Hz), 7.91−7.47 (12H, m), 7.21 (1H, t, J = 7.6 Hz), 3.65 (3H, s), 3.61 (1H, dd, J = 16.1, 7.3 Hz), 3.54−3.50 (1H, m), 3.50 (3H, s), 3.40 (1H, dd, J = 16.1, 5.9 Hz), 3.18 (1H, dd, J = 15.9, 8.5 Hz), 3.01−2.97 (1H, m), 2.92−2.88 (1H, m); ^{13}C NMR δ 173.72, 173.66, 142.4, 141.7, 140.6, 137.9, 136.4, 135.5, 134.0, 133.3, 130.8, 129.4, 129.3, 128.4, 127.4, 126.6, 125.6, 123.7, 123.6, 120.7, 119.2, 111.2, 52.3, 52.2, 40.5, 40.0, 28.6, 27.9; MS *m*/*z* 617 (M^+, 100); HRMS calcd for $C_{32}H_{27}O_8NS_2$ 617.1178, found 617.1173.

Dimethyl *trans*-4,9-bis(phenylsulfonyl)-5,6,7,8-tetrahydronaphtho[2,3-*b*]furan-6,7-dicarboxylate (34): colorless oil; IR 1734, 1151 cm^{-1}; ^{1}H NMR δ 8.09 (2H, d, J = 7.4 Hz), 7.87−7.49 (10H, m), 3.83−3.56 (3H, m), 3.67 (6H, s), 3.21−3.12 (2H, m), 2.95−2.90 (1H, m); ^{13}C NMR δ 173.7, 173.6, 150.6, 147.7, 141.4, 141.3, 135.1, 134.7, 134.0, 133.7, 133.6, 129.3, 129.1, 128.2, 128.1, 127.7, 126.9, 107.5, 52.33, 52.32, 40.2, 40.1, 27.8, 27.2; MS *m*/*z* 568 (M^+, 23); HRMS calcd for $C_{28}H_{24}O_9S_2$ 568.0862, found 568.0866.

Dimethyl *trans*-5,10-bis(phenylsulfinyl)-6,7,8,9-tetrahydronaphtho[2,3-*b*]pyrazine-7,8-dicarboxylate (37): the diastereoisomers were separated by chromatography with hexane-AcOEt (1:1). Less polar **37**: yellow oil; IR 1734 cm^{-1}; ^{1}H NMR δ 8.99 (2H, s), 7.67−7.65 (4H, m), 7.45−7.39 (6H, m), 3.82 (2H, dd, J = 16.5, 8.5 Hz), 3.70 (6H, s), 3.47 (2H, dd, J = 16.5, 5.5 Hz), 2.95−2.93 (2H, m); ^{13}C NMR δ 173.8, 144.8, 144.1, 144.0, 142.2, 139.2, 130.4, 129.1, 124.4, 52.4, 39.8, 25.5; MS *m*/*z* 548 (M^+, 79); HRMS calcd for $C_{28}H_{24}O_6N_2S_2$ 548.1076, found 548.1079. More polar **37**: yellow oil; IR 1736 cm^{-1}; ^{1}H NMR δ 8.92 (2H, s), 7.70−7.68 (4H, m), 7.44−7.39 (6H, m), 4.30 (1H, dd, J = 16.5, 6.1 Hz), 3.94 (1H, dd, J = 17.1, 7.9 Hz), 3.74 (3H, s), 3.57 (3H, s), 3.53−3.48 (1H, m), 3.31 (1H, dd, J = 14.0, 7.9 Hz), 3.18−3.13 (1H, m), 2.99 (1H, dd, J = 14.0, 8.5 Hz); ^{13}C NMR δ 173.8, 173.6, 144.8, 144.7, 144.0, 143.9, 143.2, 143.1, 142.0, 141.8, 139.3, 139.1, 130.3, 130.2, 129.04, 129.01, 124.6, 124.5, 52.5, 52.4, 40.1, 39.8, 26.0, 25.1; MS *m*/*z* 548 (M^+, 85); HRMS calcd for $C_{28}H_{24}O_6N_2S_2$ 548.1076, found 548.1082.

Dimethyl 1-methyl-5,8-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (40a): colorless oil; IR 1736, 1319, 1153 cm^{-1}; ^{1}H NMR δ 8.24−8.16 (2H, m), 7.88−7.82 (4H, m), 7.67−7.52 (6H, m), 4.25−4.86 (1H, m) 3.70, 3.68, 3.61, 3.47 (total 6H, each s), 3.36−3.09 (2H, m), 2.66−2.55 (2H, m), 0.97, 0.96 (total 3H, each d, J = 7.3 Hz); ^{13}C NMR δ 174.4, 173.6, 173.5, 172.4, 143.9, 143,6, 143.34, 143.31, 143.2, 142.9, 140.39, 140.36, 140.2, 139.5, 139.0, 136.2, 133.9, 133.82, 133.77, 133.74, 129.40, 129.37, 129.35, 128.0, 127.93, 127.90, 127.83, 127.77, 127.67, 127.58, 127.3, 52.35, 52.25, 52.23, 52.16, 46.7, 43.8, 40.4, 35.3, 33.2, 32.1, 26.7, 25.9, 22.1, 16.3; MS *m*/*z* 542 (M^+, 25); HRMS calcd for $C_{27}H_{26}O_8S_2$ 542.1069, found 542.1065.

2-Ethenyl-3-methyl-1,4-bis(phenylsulfonyl)benzene (42a): colorless oil; IR 1319, 1138 cm^{-1}; ^{1}H NMR δ 8.34 (1H, d, J = 8.6 Hz), 8.30 (1H, d, J = 8.6 Hz), 7.87−7.77 (4H, m), 7.67−7.39 (6H, m), 6.68 (1H, dd, J = 18.2, 11.6 Hz), 5.44 (1H, dd, J = 11.6, 1.3 Hz), 4.77 (1H, dd, J = 18.2, 1.3 Hz), 2.35 (3H, s); ^{13}C NMR δ 144.4, 143.9, 141.3, 140.6, 140.1, 138.4, 133.7, 133.5, 131.2, 129.3, 128.8, 128.4, 128.2, 128.0, 126.7, 123,5, 17.5; FABMS *m*/*z* 399 (M^+ + 1, 100); FABHRMS calcd for $C_{21}H_{19}O_4S_2$ 399.0725, found 399.0713.

2-Ethenyl-3-ethyl-1,4-bis(phenylsulfonyl)benzene (42b): colorless oil; IR 1319, 1153, cm^{-1}; ^{1}H NMR δ 8.32 (1H, d, J = 8.6 Hz), 8.28 (1H, d, J = 8.6 Hz), 7.90−7.77 (4H, m), 7.67−7.44 (6H, m), 6.64 (1H, dd, J = 18.2, 11.9 Hz), 5.38 (1H, dd, J = 11.9, 1.3 Hz), 4.76 (1H, dd, J = 18.2, 1.3 Hz), 2.89, (2H, q, J = 7.3 Hz), 0.71 (3H, t, J = 7.3 Hz); ^{13}C NMR δ 144.7, 144.3, 144.1, 141.7, 140.81, 140.78, 133.7, 133.5, 130.3, 129.4, 128.8, 128.7, 128.4, 127.9, 126.8, 122.7, 22.9, 13.6; FABMS *m*/*z* 413 (M^++1, 100); FABHRMS calcd for $C_{22}H_{21}O_4S_2$ 413.0881, found 413.0892.

***trans*-7,8-Dimethyl-2,5-bis(phenylsulfonyl)bicyclo[4.2.0]octa-1,3,5-triene (44b):** colorless powder; mp 150.5−152 °C (CH_2Cl_2); IR 1323, 1157 cm^{-1}; ^{1}H NMR δ 7.92−7.90 (4H, m), 7.73 (2H, s), 7.63−7.60 (2H, m), 7.55−7.52 (4H, m), 3.23 (2H, q, J = 6.9 Hz), 1.49 (6H, d, J = 6.9 Hz); ^{13}C NMR δ 149.8, 140.8, 140.1, 133.8, 129.4, 127.8, 127.4, 48.2, 17.5; MS *m*/*z* 412 (M^+, 0.5). Anal. Calcd for $C_{22}H_{20}O_4S_2$: C, 64.05; H, 4.89. Found: C, 64.13; H, 4.87.

1-Methyl-3,8-bis(phenylsulfonyl)-1,2-dihydrocyclobuta[*b*]naphthalene (46): colorless oil; IR 1321, 1145 cm^{-1}; ^{1}H NMR δ 8.67 (1H, dd, J = 8.3, 1.4 Hz), 8.52 (1H, dd, J = 8.3, 1.4 Hz), 8.06−7.92 (2H, m), 7.60−7.24 (10H, m), 4.21−4.17 (1H, m), 3.89 (1H, dd, J = 16.8, 6.3 Hz), 3.28 (1H, dd, J = 16.8, 3.6 Hz), 1.76 (3H, d, J = 7.1 Hz); ^{13}C NMR δ 153.0, 146.7, 141.5, 141.3, 134.90, 134.89, 129.4, 129.3, 129.2, 129.1, 127.4, 127.3, 127.2, 127.1, 126.92, 126.90, 124.8, 124.6, 40.6, 39.7, 19.6; MS *m*/*z* 448 (M^+, 100); HRMS calcd for $C_{25}H_{20}O_4S_2$ 448.0803, found 448.0800.

2-Ethenyl-3-methyl-1,4-bis(phenylsulfonyl)naphthalene (47): colorless oil; IR 1321, 1307, 1145 cm^{-1}; ^{1}H NMR δ 9.07−8.98 (2H, m), 7.86−7.79 (2H, m), 7.60−7.24 (10H, m), 6.97 (1H, dd, J = 17.8, 11.4 Hz), 5.45 (1H, dd, J = 11.4, 1.2 Hz), 4.94 (1H, dd, J = 17.8, 1.2 Hz), 2.71 (3H, s); ^{13}C NMR δ 153.0, 146.7, 143.0, 142.7, 138.9, 134.2, 134.1, 129.5, 129.3, 129.2, 129.1, 127.4, 127.3, 127.2, 127.1, 126.92, 126.91, 125.4, 125.2, 120.9, 19.7; MS *m*/*z* 448 (M^+, 59); HRMS calcd for $C_{25}H_{20}O_4S_2$ 448.0803, found 448.0807.

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Supporting Information Available: Experimental procedure for the preparation of substrates **12**, **17**, **23**, **24**, **29**, **33**, **36**, **38a**, and **45** and characterization data for compounds **11b**−**g**, **12**, **13**, **15d**,**h**, **17**, **21**, **22**, **25**, **26**, **28**−**30**, **34**, **36**, **37**, **38a**, **40a**, **42a**,**b**, and **45**−**47**. This material is available free of charge via the Internet at http://pubs.acs.org.

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