Thiacyclophane Cages and Related Bi- and Tripodal Molecules via Transient Polysulfenic Acids

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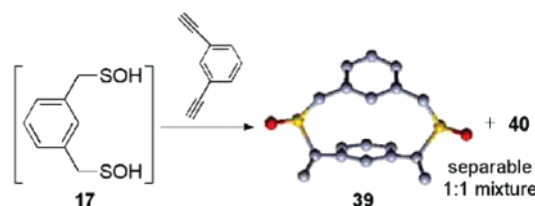
A series of bis- and tris-bridged thiacyclophane S-oxides, as racemates or *meso* products, have been synthesized with a new procedure. Starting from the corresponding thiols, in three steps, transient polyarene- and polyarylmethane-sulfenic acids were generated in the presence of di- and triethynylbenzenes. The thermal *syn*-addition of these sulfenic acids onto the triple bonds of the unsaturated acceptors was conducted in CH_2Cl_2 at 40 °C. The concentration of sulfoxide precursors of sulfenic acid and the sulfoxide/acceptor molar ratio addressed the *syn*-addition toward open-chain benzene sulfoxides or thiacyclophane S-oxides. Complete stereochemical control was observed in some reactions between polysulfenic acids and ethynylbenzenes, where the *meso* dithiacyclophane S,S′-dioxides were obtained exclusively, whereas 1:1 mixtures of *meso*/*rac* dithiacyclophanes S,S′-dioxides were isolated as products of other reactions. In almost all the cases, the obtained compounds were separated by column chromatography. The structure assignment of the new heterophanes was done on the basis of their diagnostic NMR spectra and X-ray crystallographic analysis of some of them. Open-chain polysulfinyl and polysulfinylmethyl benzenes, obtained as *meso*/*rac* mixtures, were separated and the products were fully characterized. Both synthesized cages, including trithia[3₃](1,3,5)cyclophane S,S′,S″-trioxides, and bi- and tripodal benzene sulfoxides, appear promising in the field of coordination and material chemistry.

Introduction

Bridged aromatic compounds, such as cyclophanes (CPs), are potential building blocks in the design of molecules for catalytic processes or electronic devices. The restricted conformational mobility of these compounds, their intrinsic symmetry, and their structural features, some of which are very exotic, addressed the attention on the development of a number of synthetic pathways.[1] ThiaCPs[2] represent significant components of the CP family because the presence of sulfur atoms into the skeleton of the cage allows a number of possible transformations of the hetero function[3] and some interesting conformational changes.[4] Nevertheless, the methodologies developed for obtaining thiaCPs suffer some limitations, such as long reaction times and yields dependent on the structural features of the starting products, which required slow addition of the reactants.[5]
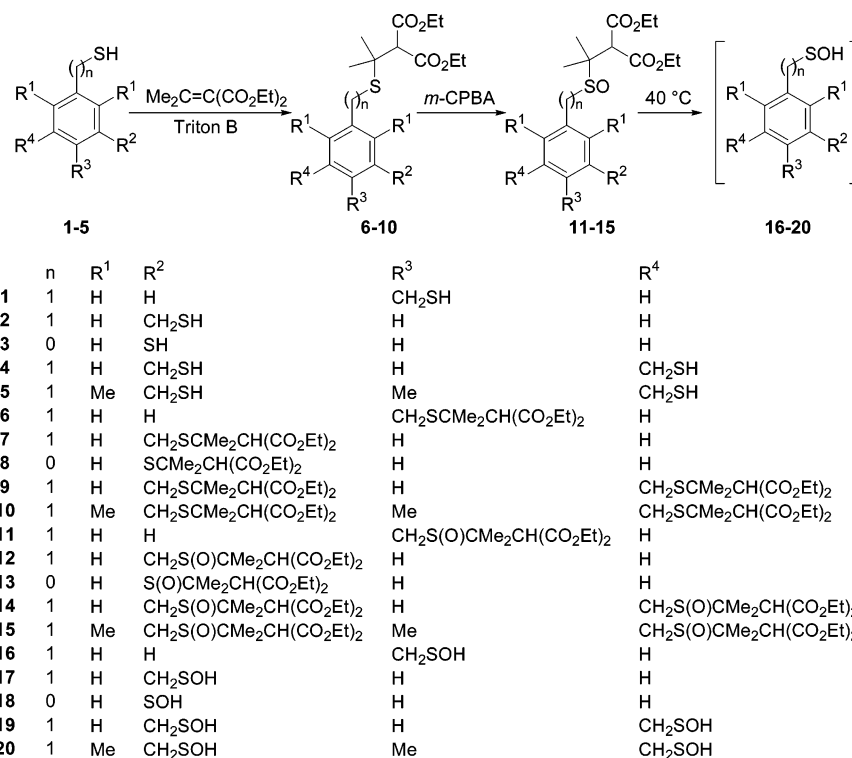
Very recently, we envisaged that the *syn*-addition of poly-arene- and poly-arylmethane-sulfenic acids onto the triple bonds

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SCHEME 1

	n	R^1	R^2	R^3	R^4
1	1	H	H	CH_2SH	H
2	1	H	CH_2SH	H	H
3	0	H	SH	H	H
4	1	H	CH_2SH	H	CH_2SH
5	1	Me	CH_2SH	Me	CH_2SH
6	1	H	H	$CH_2SCMe_2CH(CO_2Et)_2$	H
7	1	H	$CH_2SCMe_2CH(CO_2Et)_2$	H	H
8	0	H	$SCMe_2CH(CO_2Et)_2$	H	H
9	1	H	$CH_2SCMe_2CH(CO_2Et)_2$	H	$CH_2SCMe_2CH(CO_2Et)_2$
10	1	Me	$CH_2SCMe_2CH(CO_2Et)_2$	Me	$CH_2SCMe_2CH(CO_2Et)_2$
11	1	H	H	$CH_2S(O)CMe_2CH(CO_2Et)_2$	H
12	1	H	$CH_2S(O)CMe_2CH(CO_2Et)_2$	H	H
13	0	H	$S(O)CMe_2CH(CO_2Et)_2$	H	H
14	1	H	$CH_2S(O)CMe_2CH(CO_2Et)_2$	H	$CH_2S(O)CMe_2CH(CO_2Et)_2$
15	1	Me	$CH_2S(O)CMe_2CH(CO_2Et)_2$	Me	$CH_2S(O)CMe_2CH(CO_2Et)_2$
16	1	H	H	CH_2SOH	H
17	1	H	CH_2SOH	H	H
18	0	H	SOH	H	H
19	1	H	CH_2SOH	H	CH_2SOH
20	1	Me	CH_2SOH	Me	CH_2SOH

of polyethynyl benzenes could represent an original and efficient methodology for the construction of thiaCP S-oxides.

Sulfenic acids are implicated in a wide variety of relevant chemical and biochemical reactions and, although the vast majority of them are too unstable to be isolated, they cannot be considered just casual intermediates in organic and biological processes. For instance, the *syn*-addition of sulfenic acids onto carbon−carbon triple bonds gives a reliable, easy way to obtain vinyl sulfoxides in mild conditions without the need for acidic or basic catalysis and with some stereo- and regio-selectivities in the formation of the S-epimeric mixtures of sulfoxides, induced by the structural features of the sulfenic acid and the electronic ones of its unsaturated acceptor. This reaction and its applications in organic synthesis have been widely studied by us, showing that (i) it is possible to generate sulfenic acids in three steps starting from the suitable thiols; in the thermolysis, that represents the last step, with the sulfenic acid generated in the presence of the unsaturated acceptor leading to sulfoxide

formation;[6] (ii) it is possible to generate enantiopure sulfenic acids by synthesizing their precursors with an enantiopure alkyl or aryl residue;[7] and (iii) the generation of sulfenic acids carrying an aminoacidic or a glycosidic residue corresponds to a direct strategy for the stereocontrolled preparation of sulfinyl molecules possessing biological active residues.[8]

In this paper we describe the three-step generation of transient diarenesulfenic acids and di- and triarylmethanesulfenic acids,[9] starting from the corresponding thiols, and the results of their additions onto the triple bonds of di- and triethynyl benzenes. The presence of elements of symmetry, such as C_2 and C_3 axes, in some of the aromatic polysulfenic acids and acceptors, the formation of stereogenic sulfoxide sulfur atoms, the partner choice in the addition sulfenic acid/triple bond, and the nature and conditions of the *syn*-addition allowed the preparation of π-electron-rich molecules, such as the predicted thiaCP S-oxides, together with open-chain polysulfinyl and polysulfinylmethyl benzenes, quite promising in the field of organic materials.

Results and Discussion

Synthesis of the Precursors of Polysulfenic Acids 16−20. Thiols **1−3** (Scheme 1) are commercially available, while thiols

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TABLE 1. Generation of Sulfenic Acids and Their *syn*-Addition to Alkyne Acceptors in Dichloromethane at Reflux

entry	sulfoxide precursor (sulfenic acid)	acceptor of sulfenic acid	sulfox concn (mM)	sulfox/acceptor molar ratio	adducts[a] (yield %)	chromatographic eluant (EtOAc/petrol)
1	**11 (16)**	$p(HC\equiv C)_2C_6H_4$	60	1:4	**21** (20) + **22** (20)	5:5
2	**11 (16)**	$m(HC\equiv C)_2C_6H_4$	60	1:4	**23** (20) + **24** (20)	5:5
3	**11 (16)**	$p(HC\equiv C)_2C_6H_4$	10	1:1	**25** (30)	9:1
4	**11 (16)**	$m(HC\equiv C)_2C_6H_4$	10	1:1	**27** (15) + **26** (15)	9:1
5	**12 (17)**	$p(HC\equiv C)_2C_6H_4$	60	1:4	**34** (20) + **35** (20)	5:5
6	**12 (17)**	$m(HC\equiv C)_2C_6H_4$	60	1:4	**36** (10) + **37** (10) + **40** (10) + **39** (10)	5:5 up to 8:2
7	**12 (17)**	$p(HC\equiv C)_2C_6H_4$	10	1:1	**38** (30)	8:2
8	**12 (17)**	$m(HC\equiv C)_2C_6H_4$	10	1:1	**40** (15) + **39** (15)	8:2
9	**13 (18)**	$p(HC\equiv C)_2C_6H_4$	10	1:1	**30** (15) + **31** (15)	2.5:7.5
10	**13 (18)**	$p(HC\equiv C)_2C_6H_4$	60	1:4	**30** (35) + **31** (35)	2.5:7.5
11	**13 (18)**	$m(HC\equiv C)_2C_6H_4$	10	1:1	**32** (15) + **33** (15)	3:7
12	**13 (18)**	$m(HC\equiv C)_2C_6H_4$	60	1:4	**32** (30) + **33** (30)	3:7
13	**14 (19)**	$HC\equiv CC_6H_5$	60	1:9	**42** (5) + **43** (15)	8:2
14	**14 (19)**	$sym(HC\equiv C)_3C_6H_3$	60	1:9	**44** (5) + **45** (12) + **48/49** (15)	6:4 up to 10:0
15	**14 (19)**	$p(HC\equiv C)_2C_6H_4$	60	1:9	**46** (8) + **47** (20)	8:2
16	**14 (19)**	$sym(HC\equiv C)_3C_6H_3$	10	1:1	**48/49** (20)	10:0
17	**15 (20)**	$sym(HC\equiv C)_3C_6H_3$	10	1:1	**51** (10) + **52** (10)	10:0

[a] If more then one adduct is obtained, the products are reported in order of increasing retention times. Several products of sulfenic acid self-condensation are always detected in the crudes by ^{1}H NMR analysis.

4 and **5** were prepared following literature procedures.[10] The reaction of each of these compounds with diethyl isopropylidenemalonate in the presence of benzyltrimethylammonium hydroxide (Triton B), at −78 °C, led to the corresponding sulfides **6−10** in good yields. Oxidation of these sulfides to sulfoxides **11−15**, respectively, was conducted in dichloromethane, using *m*-CPBA as the oxidizing agent at −78 °C. Sulfoxides **11−15**, which represent the direct precursors of the corresponding transient polysulfenic acids **16−20**, were obtained in almost quantitative yield, not needing further purification before undergoing the thermolysis toward sulfenic acids.

The choice of such sulfinyl precursors **11−15** was done taking into account previously disappointing experiments. At the beginning of this investigation, we decided to thermolyze 2-cyanoethyl sulfoxides coming from the nucleophilic addition of thiols **1−5** to acrylonitrile,[11] followed by the oxidation to sulfoxides. On the basis of our experience,[8c] 2-cyanoethyl sulfoxides can be easier handled than (1,1-diethoxycarbonyl-2-methyl)-2-propyl sulfoxides: 2-cyanoethyl sulfoxides can be purified by column chromatography and left on the bench for quite a long time. On the contrary, sulfoxides **11−15** must be prepared and immediately used to avoid the spontaneous formation of products coming from self-condensation of the corresponding sulfenic acids. However, in the present case, the crude mixtures of 2-cyanoethyl sulfoxides were found difficult to treat for the high insolubility of the sulfoxide products, which were detected by proton magnetic resonance, but could not be easily separated and fully characterized. For these reasons, they were discarded.

Synthesis of thiaCP S-Oxides 25−27, 38−40, 48, 49, 51, 52, and Open-Chain Bis and Tris Sulfinyl and Sulfinylmethyl Benzenes 21−24, 30−37, 42−47. The reaction conditions adopted for the generation of sulfenic acids **16−20** and their *syn*-addition to alkyne acceptors are reported in Table 1.

When 1,4-benzenedimethanesulfenic acid (**16**) was generated from sulfoxide **11** in the presence of *p*- or *m*-diethynylbenzene

in 1:4 sulfoxide/acceptor molar ratio, 1,4-bis(sulfinylmethyl)-benzenes **21−24** were obtained, each pair in 40% yield (Scheme 2). Compounds **21/22** and **23/24** were 1:1 mixtures of *meso* compound and racemate that could be easily separated by column chromatography (Table 1, entries 1 and 2). A 1:1 molar ratio of sulfoxide **11** with each of the two diethynylbenzenes and a reduced concentration of sulfenic acid precursor in dichloromethane allowed the formation of dithiaCP S-oxides **25−27**. The *syn*-addition of transient 1,4-benzenedimethanesulfenic acid (**16**) onto the triple bonds of *p*-diethynylbenzene led to the obtainment, in 30% yield, of adduct **25** as the unique product of the reaction (Table 1, entry 3) to which the *meso* structure was unambiguously attributed by NMR (see section below). ThiaCPs **26** and **27** were obtained, in a 1:1 ratio of *meso* compound and racemate, respectively, from the reaction of sulfenic acid **16** with *m*-diethynylbenzene (Table 1, entry 4). Subsequent oxidation of the 1:1 mixture of **26** and **27** gave bis-sulfone **29** as a proof that the two diastereoisomers **26** and **27** differ only in the configuration at one sulfinyl sulfur atom, while bissulfone **28** was the expected product of the *m*-CPBA oxidation of paraCP **25**.

The stereochemical outcome of the reactions between sulfenic acid **16** and the two diethynylbenzenes for the preparation of thiaCP S-oxides was quite unexpected; when *p*-diethynylbenzene was the acceptor, a complete stereoselection was observed, whereas in the addition of transient compound **16** to *m*-diethynylbenzene, no stereoselection at all was pointed out. To further explore these results, the generation of 1,3-benzenedimethanesulfenic acid (**17**) from the sulfinyl precursor **12** and its addition onto the triple bonds of *p*- and *m*-diethynylbenzenes were performed in the same conditions we have used for sulfenic acid **16** (Scheme 3).

Sulfoxide concentration and the sulfoxide/acceptor molar ratio addressed the *syn*-addition toward the open-chain benzene derivatives **34−37** (Table 1, entries 5 and 6) or the thiaCP S-oxides **38−40** (Table 1, entries 7 and 8). Complete stereochemical control was again observed in the reaction of sulfenic acid **17** with the *p*-diethynylbenzene, where the *meso* thiaCP S-oxide **38** was obtained in 30% yield. A 1:1 mixture of the *meso* macrocycle **39** and the racemate **40** was obtained in 30% total yield by the addition of the transient **17** to
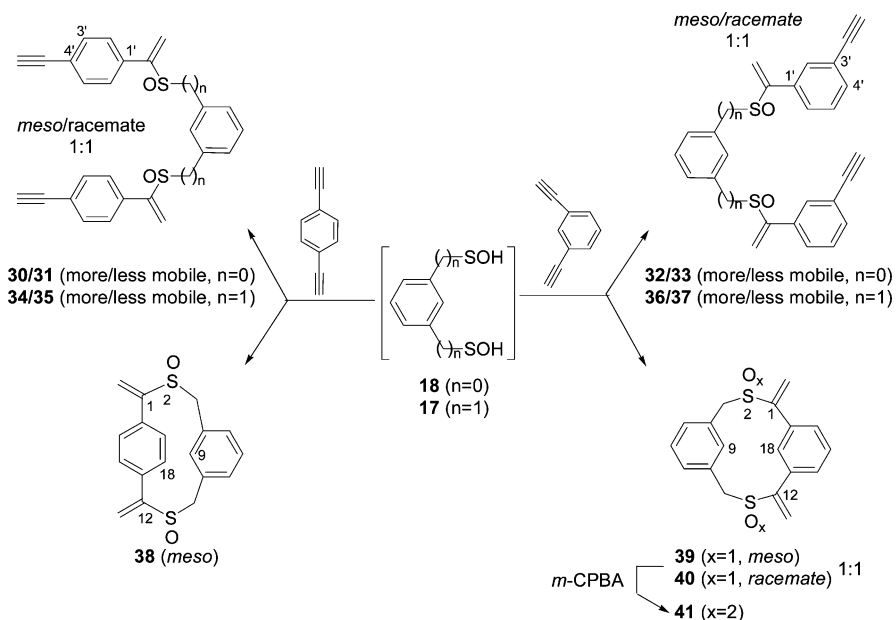
(10) Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825−6836.

(11) For 3,3′-(*m*-phenylenedithio)dipropionitrile, see: Kuliev, A. M.; Aliev, S. M. *Zh. Org. Khim.* **1967**, *3*, 1045−1047; *Chem. Abstr.* **1967**, *67*, 108360.

SCHEME 2
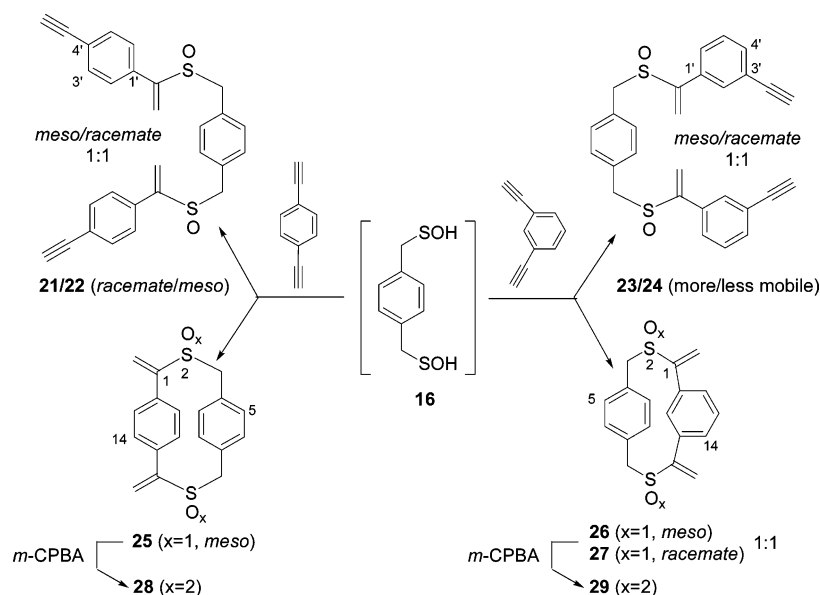
SCHEME 3

m-diethynylbenzene, the two products were easily separated by column chromatography and their mixture oxidized to sulfone **41**.
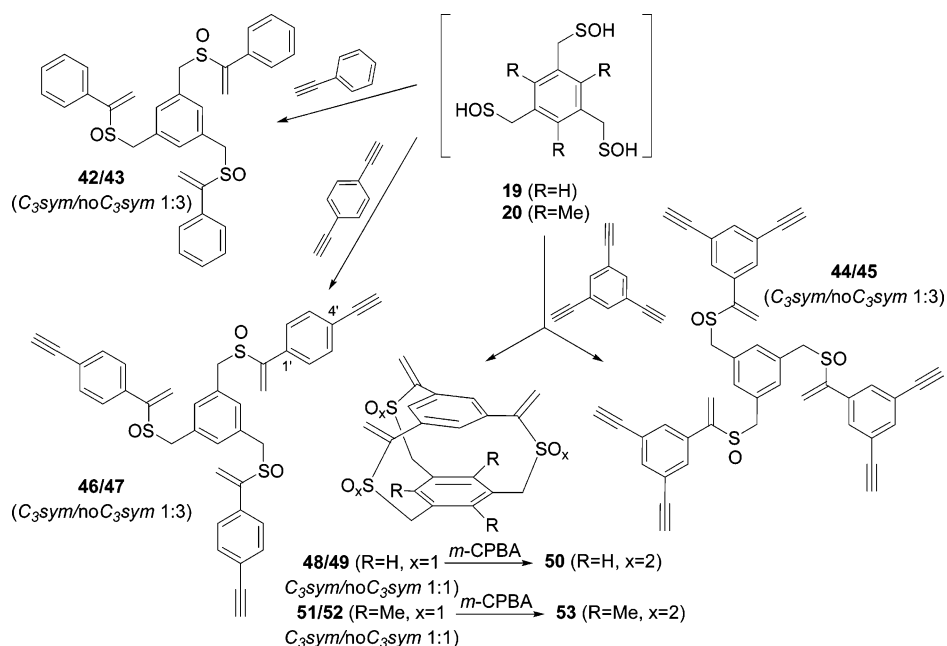
These results, identical from a stereochemical point of view to the ones observed for sulfenic acid **16**, suggest a different attack pathway for compounds **16** and **17** onto the electronically different triple bonds of the two diethynylbenzenes. At the actual level of our knowledge, indeed, the only difference we can surely envisage is the widespread π-conjugation characterizing *p*-diethynylbenzene, against the more localized triple bonds of the *m*-diethynylbenzene. Noteworthy are the results shown in Table 1 as entry 6 compared to the analogous results in entry 8; when the two partners of the double *syn*-addition are both *m*-substituted, a relevant amount of CPs is obtained even if the concentration of the sulfoxide precursor is the one identified as more suitable to the formation of open-chain benzene derivatives. We suggest that the attack of the one sulfenic function of **17** onto one triple bond in *m*-diethynylbenzene is preferably

followed by the intramolecular cyclization affording metaCPs **39/40** instead of the expected sole formation of open-chain benzene derivatives **36/37**. This can be ascribed to the favorable geometrical contiguity of the reactive moieties in the second step of the intramolecular cyclization toward CPs.

We have also prepared the precursors of 1,3-benzenedisulfenic acid (**18**; Scheme 3) that was generated in the presence of the two diethynylbenzene acceptors and gave in good yields the open-chain sulfoxides **30**−**33** as 1:1 *meso/rac* mixtures, separable by column chromatography (Table 1, entries 10 and 12). The same reactions were performed in diluted solutions and sulfoxide/acceptor 1:1 molar ratio (Table 1, entries 9 and 11); again, sulfoxides **30**−**33** were obtained, but in reduced yields.

Later we turned our attention to the synthesis of thiaCPs with a "cylindrical" structure, because they appear as attractive cages, able to participate in metal ion complexation.[3] For this purpose, we began with a model reaction and synthesized 1,3,5-tris-

SCHEME 4

42/43
(C_3sym/noC_3sym 1:3)

19 (R=H)
20 (R=Me)

44/45
(C_3sym/noC_3sym 1:3)

46/47
(C_3sym/noC_3sym 1:3)

48/49 (R=H, x=1) $\xrightarrow{m\text{-CPBA}}$ 50 (R=H, x=2)
C_3sym/noC_3sym 1:1)
51/52 (R=Me, x=1) $\xrightarrow{m\text{-CPBA}}$ 53 (R=Me, x=2)
C_3sym/noC_3sym 1:1)

(sulfinylmethyl)benzene **14** (Scheme 1) as the precursor of the "three-branched" sulfenic acid **19**, which was thermolyzed in dichloromethane in the presence of phenylacetylene, with the idea of trapping the three sulfenic functions and proving the existence of the transient intermediate **19**. Actually, a 1:3 mixture of tripodal sulfoxides **42** and **43** was obtained in 20% total yield, as shown in Scheme 4 (Table 1, entry 13). The *syn*-addition of sulfenic acid **19** to an equimolecular quantity of 1,3,5-triethynylbenzene in the reaction conditions reported in Table 1 (entry 16) led to the formation of the thiaCP S-oxides **48** and **49**, as two diastereomeric mixtures of racemates in about 1:1 ratio, respectively, that were converted into one sulfonyl derivative **50** by oxidation with *m*-CPBA. The structural differences between the cage **48**, possessing a C_3 axis of symmetry, and the cage **49**, where only two of the three sulfinyl sulfur atoms show the same configuration, were clear once we obtained the "thiacylindrophanes" **51** and **52** as an approximate 1:1 mixture. Compounds **48** and **49** were not completely separable by column chromatography, while if the **48**/**49** mixture was incompletely dissolved in ethyl acetate, the mother liquors were enriched in **48** up to 90%. CPs **51** and **52**, possessing three methyl substituents in one of the two benzene rings, could be separated and their spectra completely interpreted (see section below). Cages **51** and **52** were the products of the *syn*-addition of sulfenic acid **20** to 1,3,5-triethynylbenzene in the same conditions of reaction adopted for the preparation of **48** and **49** (Table 1, entry 17). The mixture **51**/**52** was quantitatively converted in sulfone **53**.

Finally, we directed our interest toward the synthesis of other tripodal molecules such as **44** and **45** and **46** and **47**, shown in Scheme 4. Similar compounds have demonstrated a certain encapsulating tendency or stimulating coordination capabilities due to the presence of the sulfinyl functions.[12] Furthermore, they possess carbon–carbon triple bonds that can be used for subsequent *syn*-additions of arenesulfenic acids, thereby building dendrimeric structures. Sulfoxides **46** and **47** were obtained in

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the reaction of sulfenic acid **19** with *p*-diethynylbenzene (Table 1, entry 15), while compounds **44** and **45** were the products of the reaction between the transient **19** and the symmetrical triethynylbenzene in the reaction conditions shown in Table 1, entry 14. In this last reaction, an almost equal quantity of the cages **48** and **49** was also obtained, analogously to the results in entry 6.

Structure Assignments. The presence of two stereogenic sulfinyl sulfur atoms into the thiaCP cage of compounds **25**–**27** and **38**–**40**, and in the open-chain benzene derivatives **21**–**24** and **30**–**37**, led to the formation of racemates and/or *meso* products.

The structure assignment of dithiaCP S,S′-oxides, with at least a *p*-substituted aromatic ring (**25**–**27**, **38**), was easily done on the basis of their diagnostic ¹H NMR spectra. The *meso* CPs **25**, **26**, and **38** were unequivocally identified because their spectra showed no *ortho* spin–spin couplings, owing to the symmetry plane perpendicularly cutting the *p*-disubstituted aromatic ring and bisecting its two HC/CH carbon–carbon bonds. The corresponding $J_{ortho} = 7.9$ Hz was instead measured for *rac*-1,12-dimethylene-2,11-dithia[3.3]parametacyclophane 2,11-dioxide (**27**).

The attribution of the structure to metaCP **39** was done by means of X-ray crystallographic analysis (Figure 1). *meso*-1,-12-Dimethylene-2,11-dithia[3.3]metametacyclophane 2,11-di-oxide (**39**), with the two sulfinyl oxygen atoms pointing away from the methylene moieties, shows a *syn*-chair-chair (Scc) conformation, in line with the conformational studies already conducted on this kind of molecule.[4] In the solid state, the two aromatic rings of **39** are not coplanar and their planes form an angle of 28.74 (0.16)°, with the distance between the corresponding two centroids being 3.677 Å.

The ¹H NMR parameters are very similar for the open-chain benzene derivatives **21**–**24** and **30**–**37**, aside from their stereochemistry of *meso* or racemate compounds. Again, the configurational nature of *rac*-1,4-bis{[1-(4-ethynylphenyl)-ethenylsulfinyl]methyl}benzene (**21**) was assigned on the basis of the X-ray investigation. Figure 2 shows the asymmetric unit
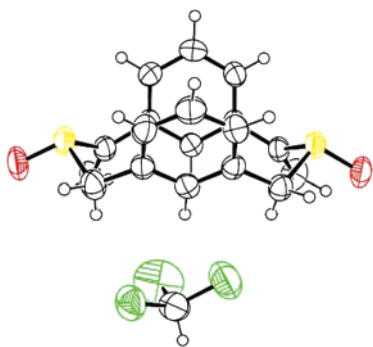
FIGURE 1. Molecular structure of **39**; ellipsoids are drawn with 50% probability; a chloroform molecule is cocrystallized.
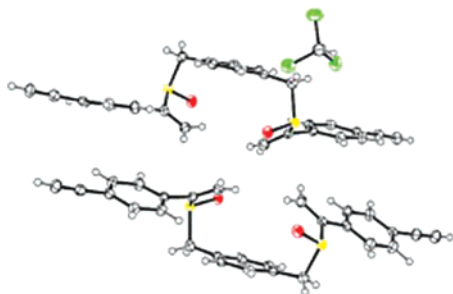

FIGURE 2. Molecular structure of racemate **21**; ellipsoids are drawn with 50% probability; a chloroform molecule is cocrystallized.

of **21**, where two independent enantiomeric molecules, unequivalent from a crystallographic point of view, cocrystallize with a chloroform molecule. Noteworthy is the different reciprocal orientations of the benzene rings in the two molecules, both showing the oxygen atoms pointing one toward the other. This last steric feature allows the foresight of effective coordination capabilities to electron-deficient species.[13]

All synthesized trisulfoxides **42−49**, **51**, and **52** show typically different NMR spectra in dependence of their C_3 symmetry or not. As an example, apart from aromatic (m, 7.6−7.5 ppm) and alkyne (s, 3.18 ppm) absorptions, the ^{1}H NMR spectrum of C_3sym-1,3,5-tris{[1-(3,5-diethynylphenyl)ethenylsulfinyl]methyl}benzene (**44**) shows a simple pattern of signals [δ 6.70 (s, 3H, H-2,4,6), 5.98, and 5.73 (two d, 6H, 3 × =CH₂), 3.95 and 3.54 (AB system, 6H, 3 × SCH₂)], which divide into two 2:1 parts for noC_3sym-1,3,5-tris{[1-(3,5-diethynylphenyl)ethenylsulfinyl]methyl}benzene (**45**) [δ 6.78 (s, 2H) and 6.75 (s, 1H) (H-2,4,6), 6.00 and 5.90 (two d, 2H, =CH₂), 5.99 and 5.83 (two d, 4H, 2 × =CH₂), 3.91 and 3.59 (AB system, 4H, 2 × SCH₂), 3.87 and 3.61 (AB system, 2H, SCH₂)]. Even the ^{13}C NMR spectrum of **45** shows signal doubling for almost all the resonances (see Experimental Section).

Finally, the nearly quantitave *m*-CPBA formation of sulfones **28**, **29**, **41**, **50**, and **53** confirmed the structures assigned to their sulfoxide precursors **25**, **26/27**, **39/40**, **48/49**, and **51/52**, respectively.

Conclusions

We have described an original synthetic pathway for the preparation of new members of the class of thiaCP S-oxides.[2a,c,d]

(13) Khiar, N.; Araújo, C. S.; Alcudia, F.; Fernández, I. *J. Org. Chem.* **2002**, *67*, 345−356.

The proposed strategy allowed the obtainment of these cages in mild reaction conditions. The key step of the synthetic process is the thermal *syn*-addition sulfenic acid/carbon−carbon triple bond. Because no acidic or basic conditions are required during this reaction, a broad range of substituents can be present in the structural skeleton of reactants. The easy access to the starting materials, the precursors of polysulfenic acids on one hand and the alkyne acceptors on the other, guarantees a wide range of possible modulations for the synthesis. The presence of stereogenic sulfinyl sulfur atoms into the thiaCP scaffold of the products caused the formation of *meso* and racemic cages but enabled in general the easy separation and characterization of the diastereomeric mixtures of such molecules. The thiaCP core holds methylene moieties in a favorable position for further transformations. Thus, these CPs can be useful for investigating new properties of this kind of cage and can also represent versatile starting materials for building new polycyclic structures. Finally, the significant structural features of tripodal molecules, such as **42−47**, forward investigations on their coordinating properties as they are and/or after modifications of their skeleton.

Experimental Section

All reactions were monitored by TLC on commercially available aluminum supported silica gel plates (F 254), and the products were visualized with acidic vanillin solution. The NMR assignments are fully supported by attached proton test (APT) and homodecoupling experiments.

2,4,6-Trimethyl-1,3,5-benzenetrimethanethiol (5). Trithiol **5**[14] was prepared according to Whitesides protocol.[9] To commercially available 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (5.0 g, 12.53 mmol) suspended in EtOH (55 mL), thiourea (2.8 g, 36.78 mmol) was added, and the reaction mixture was maintained under stirring at rt overnight. The solvent was then removed under vacuum, a NaOH solution (3.0 g, 75 mmol in 50 mL H₂O) was added, and the mixture was refluxed for 4 h. HCl (6 N) was added to the mixture, which was cooled in an ice bath, up to pH 2. Finally, the water phase was extracted with CHCl₃ (4 × 30 mL), dried over Na₂SO₄, and concd under vacuum to give trithiol **5** as a white solid (2.9 g, 11.22 mmol, 90%). TLC R_f (petrol/EtOAc 8:2) 0.75; mp 143 °C; ^{1}H NMR (300 MHz, CDCl₃) δ 3.79 (d, $^3J_{vic}$ = 6.5 Hz, 6H, 3 × CH₂), 2.44 (s, 9H, 3 × Me), 1.59 (t, $^3J_{vic}$ = 6.5 Hz, 3H, 3 × SH); ^{13}C NMR (75 MHz, CDCl₃) δ 136.2 (C-1,3,5), 133.2 (C-2,4,6), 24.1 (3 × CH₂), 15.6 (3 × Me); Elem anal. Calcd (%) for C₁₂H₁₈S₃ (258.47): C, 55.76; H, 7.02. Found: C, 55.96; H, 6.88.

General Procedure A. To a stirred solution of the thiol in anhyd THF at −78 °C, Triton B (40 wt.% solution in MeOH) and, after 5 min, diethyl isopropylidenemalonate were added. The molar ratio of thiol/Triton B/malonate was 1:0.3:6 for the synthesis of disulfides **6−8**, and 1:0.45:9 for the synthesis of trisulfides **9** and **10**. The THF volume was related to the malonate amount as 0.5 mL THF/malonate mmol. The mixture was allowed to reach rt spontaneously, and when the reaction appeared complete by TLC (petrol/EtOAc 8:2), it was quenched by water addition. The crude product was extracted three times with Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. After filtration of the inorganic solid, the solvent was removed under reduced pressure,

(14) Ciba-Geigy A.-G., Switzerland, Jpn. Kokai Tokkyo Koho, JP 54058751, 1979; *Chem. Abstr.* **1979**, *91*, 141655. Ohwa, M.; Yamoto, H.; Birbaum, J.-L.; Nakashima, H.; Matsumoto, A.; Oka, H., Ciba Speciality Chemicals Holding Inc., Switzerland, Ger. Offen., DE 19753655, 1998; *Chem. Abstr.* **1998**, *129*, 68148. Hirai, O.; Uchida, T.; Watanabe, I.; Fujinawa, M.; Tsukagoshi, I.; Fukushima, N.; Kobayashi, K.; Muramatsu, Y., Hitachi Chemical Co., Ltd., Japan, Jpn. Kokai Tokkyo Koho, JP 11130841, 1999; *Chem. Abstr.* **1999**, *131*, 6316.

and the oily residue containing the sulfide product was purified by flash column chromatography on silica gel.

1,4-Bis{[(1,1-diethoxycarbonyl-2-methyl)-2-propylthio]methyl}-benzene (6). Commercial dithiol **1** (1.0 g, 5.87 mmol) was subjected to general procedure A. The reaction was completed after 0.5 h stirring at rt. Chromatographic purification (petrol/EtOAc 9.5:0.5) gave disulfide **6** (2.8 g, 4.91 mmol, 84%) as a white solid. TLC R_f 0.32; mp 70 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.24 (s, 4H, ArH), 4.21 (q, $^3J_{vic}$ = 7.1 Hz, 8H, 4 × OCH$_2$), 3.79 (s, 4H, 2 × SCH$_2$), 3.72 [s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 1.58 (s, 12H, 2 × C*Me$_2$*), 1.29 (t, $^3J_{vic}$ = 7.1 Hz, 12H, 4 × OCH$_2$C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.1 (4 × CO), 136.1 (C-1,4), 129.3 (C-2,3,5,6), 61.3 (4 × OCH$_2$), 60.3 [2 × C*H*(CO$_2$Et)$_2$], 46.2 (2 × C*Me$_2$*), 33.0 (2 × SCH$_2$), 26.6 (2 × C*Me$_2$*), 14.1 (4 × OCH$_2$CH$_3$); IR (CHCl$_3$) 1753 and 1727 cm^{-1} (CO); Elem anal. Calcd (%) for C$_{28}$H$_{42}$O$_8$S$_2$ (570.76): C, 58.92; H, 7.42. Found: C, 58.66; H, 7.39.

1,3-Bis{[(1,1-diethoxycarbonyl-2-methyl)-2-propylthio]methyl}-benzene (7). Commercial dithiol **2** (1.0 g, 5.87 mmol) was subjected to general procedure A. The reaction was completed after 1 h of stirring at rt. Chromatographic purification (petrol/EtOAc 9.5:0.5) gave disulfide **7** (2.6 g, 4.56 mmol, 78%) as a white solid. TLC R_f 0.35; mp 55 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.3−7.2 (m, 4H, ArH), 4.22 (q, $^3J_{vic}$ = 7.1 Hz, 8H, 4 × OCH$_2$), 3.80 (s, 4H, 2 × SCH$_2$), 3.72 [s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 1.58 (s, 12H, 2 × C*Me$_2$*), 1.29 (t, $^3J_{vic}$ = 7.1 Hz, 12H, 4 × OCH$_2$C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.1 (4 × CO), 137.5 (C-1,3), 129.8 (C-2), 128.7 (C-5), 127.9 (C-4,6), 61.3 (4 × OCH$_2$), 60.2 [2 × C*H*(CO$_2$Et)$_2$], 46.2 (2 × C*Me$_2$*), 33.2 (2 × SCH$_2$), 26.6 (2 × C*Me$_2$*), 14.1 (4 × OCH$_2$CH$_3$); MS (70 eV, EI) *m/z* (%) 570 (2) [M$^+$], 336 (47), 209 (53), 201 (36), 155 (47), 105 (41), 99 (65), 44 (35), 28 (100); Elem anal. Calcd (%) for C$_{28}$H$_{42}$O$_8$S$_2$ (570.76): C, 58.92; H, 7.42. Found: C, 58.90; H, 7.35.

1,3-Bis[(1,1-diethoxycarbonyl-2-methyl)-2-propylthio]benzene (8). Commercial 1,3-benzenedithiol (**3**; 1.0 g, 7.03 mmol) was subjected to general procedure A. The reaction was completed after 24 h stirring at rt. Chromatographic purification (petrol/EtOAc 9:1) gave disulfide **8** (2.9 g, 5.34 mmol, 76%) as a pale yellow oil. TLC R_f 0.34; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.86 (t, $^4J_{meta}$ = 1.7 Hz, 1H, H-2), 7.66 (dd, $^3J_{ortho}$ = 7.6 Hz, $^4J_{meta}$ = 1.7 Hz, 2H, H-4,6), 7.36 (t, $^3J_{ortho}$ = 7.6 Hz, 1H, H-5), 4.21 (q, $^3J_{vic}$ = 7.1 Hz, 8H, 4 × OCH$_2$), 3.53 [s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 1.49 (s, 12H, 2 × C*Me$_2$*), 1.29 (t, $^3J_{vic}$ = 7.1 Hz, 12H, 4 × OCH$_2$C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$) δ = 167.0 (4 × CO), 146.9 (C-2), 138.5 (C-4,6), 131.6 (C-1,3), 129.0 (C-5), 61.3 (4 × OCH$_2$), 60.2 [2 × C*H*(CO$_2$Et)$_2$], 49.2 (2 × C*Me$_2$*), 26.7 (2 × C*Me$_2$*), 14.0 (4 × OCH$_2$CH$_3$); Elem anal. Calcd (%) for C$_{26}$H$_{38}$O$_8$S$_2$ (542.71): C, 57.54; H, 7.06. Found: C, 57.65; H, 7.35.

1,3,5-Tris{[(1,1-diethoxycarbonyl-2-methyl)-2-propylthio]methyl}benzene (9). Trithiol **4** (0.6 g, 2.77 mmol) was subjected to general procedure A. The reaction was completed after 0.5 h stirring at rt. Chromatographic purification (petrol/EtOAc 8.5:1.5) gave trisulfide **9** (1.3 g, 1.59 mmol, 57%) as a white solid. TLC R_f 0.12; mp 46 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.13 (s, 3H, ArH), 4.21 (split q, $^3J_{vic}$ = 7.1 Hz, 12H, 6 × OCH$_2$), 3.77 (s, 6H, 3 × SCH$_2$), 3.71 [s, 3H, 3 × C*H*(CO$_2$Et)$_2$], 1.57 (s, 18H, 3 × C*Me$_2$*), 1.29 (t, $^3J_{vic}$ = 7.1 Hz, 18H, 6 × OCH$_2$C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.1 (6 × CO), 137.8 (C-1,3,5), 128.6 (C-2,4,6), 61.3 (6 × OCH$_2$), 60.3 [3 × C*H*(CO$_2$Et)$_2$], 46.2 (3 × C*Me$_2$*), 33.1 (3 × SCH$_2$), 26.6 (3 × C*Me$_2$*), 14.1 (6 × OCH$_2$CH$_3$); IR (CHCl$_3$) 1753 and 1728 cm^{-1} (CO); Elem anal. Calcd (%) for C$_{39}$H$_{60}$O$_{12}$S$_3$ (817.08): C, 57.33; H, 7.40. Found: C, 57.02; H, 7.44.

1,3,5-Tris{[(1,1-diethoxycarbonyl-2-methyl)-2-propylthio]methyl}-2,4,6-trimethylbenzene (10). Trithiol **5** (3.2 g, 12.38 mmol) was subjected to general procedure A. The reaction was completed after 18 h of stirring at rt. Chromatographic purification (petrol/EtOAc 9:1) gave trisulfide **10** (5.5 g, 6.40 mmol, 52%) as a white solid. TLC R_f 0.13; mp 73 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.23 (m, 12H, 6 × OCH$_2$), 3.81 (s, 6H, 3 × SCH$_2$), 3.75 [s, 3H, 3 × C*H*(CO$_2$Et)$_2$], 2.43 (s, 9H, 3 × Ar*Me*), 1.64 (s, 18H, 3 ×

CMe$_2$), 1.30 (t, $^3J_{vic}$ = 7.2 Hz, 18H, 6 × OCH$_2$C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.2 (6 × CO), 136.1 (C-1,3,5), 130.9 (C-2,4,6), 61.4 (6 × OCH$_2$), 60.4 [3 × C*H*(CO$_2$Et)$_2$], 45.9 (3 × C*Me$_2$*), 28.9 (3 × SCH$_2$), 26.3 (3 × C*Me$_2$*), 15.4 (3 × Ar*Me*), 14.1 (6 × OCH$_2$CH$_3$); Elem anal. Calcd (%) for C$_{42}$H$_{66}$O$_{12}$S$_3$ (859.16): C, 58.71; H, 7.74. Found: C, 58.69; H, 7.44.

General Procedure B. *m*-CPBA (80%) was dissolved in CH$_2$Cl$_2$ (10 mL/*m*-CPBA mmol) and added dropwise to a solution of the sulfide or sulfoxide in the same volume of CH$_2$Cl$_2$ at −78 °C (1 mol of *m*-CPBA for every molar site to be oxidized in the substrate). When the reaction appeared complete by TLC (EtOAc/petrol 7.5:2.5), a 10% solution of Na$_2$S$_2$O$_3$ was added. Almost all experiments performed were concluded just after finishing the addition of the oxidant. The separated organic layer was washed twice with a saturated solution of NaHCO$_3$ and then twice with brine. Evaporation of the solvent gave the expected sulfoxide or sulfone.

1,4-Bis{[(1,1-diethoxycarbonyl-2-methyl)-2-propylsulfinyl]-methyl}benzene 11. Disulfide **6** (1.1 g, 1.93 mmol) was oxidized following the general procedure B. Disulfoxide **11** (*meso*/racemate 1:1) was obtained as an oil (1.1 g, 1.82 mmol, 94%) not needing any purification before its involvement in the next reaction steps. TLC R_f 0.19; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35 (s, 4H, ArH), 4.23 (m, 8H, 4 × OCH$_2$), 3.92 and 3.66 (AB system, $^2J_{gem}$ = 12.4 Hz, 4H, 2 × SCH$_2$), 3.85 [s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 1.55 (s, 12H, 2 × CMe$_2$), 1.30 and 1.28 (two t, $^3J_{vic}$ = 7.1 Hz, 12H, 4 × OCH$_2$C*H$_3$*); ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 7.25 (s, 4H, ArH), 4.01 and 4.00 [two s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 4.0−3.8 (m, 8H, 4 × OCH$_2$), 3.43 and 3.38, 3.42 and 3.37 (two AB systems, $^2J_{gem}$ = 12.4 Hz, 4H, 2 × SCH$_2$), 1.53 (s, 6H, CMe$_2$ of *meso*-compound), 1.523 and 1.517 (two s, 6H, CMe$_2$ of racemate), 0.87 and 0.86 (two t, $^3J_{vic}$ = 7.1 Hz, 12H, 4 × OCH$_2$CH$_3$).

1,3-Bis{[(1,1-diethoxycarbonyl-2-methyl)-2-propylsulfinyl]-methyl}benzene 12. Disulfide **7** (0.8 g, 1.40 mmol) was oxidized following the general procedure B. Disulfoxide **12** (*meso*/racemate 1:1) was obtained as an oil (0.8 g, 1.33 mmol, 95%), not needing any purification before its involvement in the next reaction steps. TLC R_f 0.20; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.4−7.3 (m, 4H, ArH), 4.24 (m, 8H, 4 × OCH$_2$), 3.92 and 3.68 (or 3.66), 3.90 and 3.66 (or 3.68) (two AB systems, $^2J_{gem}$ = 12.6 Hz, 4H, 2 × SCH$_2$), 3.85 [s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 1.56, 1.55, and 1.54 (three s, 12H, 2 × CMe$_2$), 1.30 and 1.27 (two t, $^3J_{vic}$ = 7.2 Hz, 12H, 4 × OCH$_2$C*H$_3$*).

1,3-Bis[(1,1-diethoxycarbonyl-2-methyl)-2-propylsulfinyl]benzene 13. Disulfide **8** (1.0 g, 1.84 mmol) was oxidized following the general procedure B. Disulfoxide **13** (*meso*/racemate 1:1) was obtained as an oil (1.0 g, 1.74 mmol, 95%), not needing any purification before its involvement in the next reaction steps. TLC R_f 0.22; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.93 (t, $^4J_{meta}$ = 1.5 Hz, 1H, H-2), 7.85 (dd, $^3J_{ortho}$ = 7.7 Hz, $^4J_{meta}$ = 1.5 Hz, 2H, H-4,6), 7.70 (t, $^3J_{ortho}$ = 7.7 Hz, 1H, H-5), 4.3−4.2 (m, 8H, 4 × OCH$_2$), 3.73 and 3.72 [two s, 2H, 2 × C*H*(CO$_2$Et)$_2$], 1.31 (m, 24H, 2 x CMe$_2$, 4 × OCH$_2$C*H$_3$*).

1,3,5-Tris{[(1,1-diethoxycarbonyl-2-methyl)-2-propylsulfinyl]-methyl}benzene 14. Trisulfide **9** (0.8 g, 0.98 mmol) was oxidized following the general procedure B. Trisulfoxide **14** (diastereomeric mixture) was obtained as an oil (0.8 g, 0.92 mmol, 94%), not needing any purification before its involvement in the next reaction steps. TLC R_f 0.15; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.33 (m, 3H, ArH), 4.3−4.2 (m, 12H, 6 × OCH$_2$), 3.9−3.6 (m, 6H, 3 × SCH$_2$), 3.85 [s, 3H, 3 × C*H*(CO$_2$Et)$_2$], 1.56, 1.55, and 1.53 (three s, 18H, 3 × CMe$_2$), 1.30 (t, $^3J_{vic}$ = 7.2 Hz) and 1.28 (t, $^3J_{vic}$ = 7.0 Hz) (18H, 6 × OCH$_2$C*H$_3$*); ^{13}C NMR (75 MHz, CDCl$_3$) δ 166.8 and 166.3 (6 × CO), 132.8 (C-1,3,5), 132.2 (C-2,4,6), 62.0 and 61.9 (6 × OCH$_2$), 58.6 (3 × C*Me$_2$*), 55.4 [3 × C*H*(CO$_2$Et)$_2$], 51.8 (3 × SCH$_2$), 18.2 (3 × C*Me$_2$*), 14.0 (6 × OCH$_2$CH$_3$).

1,3,5-Tris{[(1,1-diethoxycarbonyl-2-methyl)-2-propylsulfinyl]-methyl}-2,4,6-trimethylbenzene 15. Trisulfide **10** (0.8 g, 0.93 mmol) was oxidized following the general procedure B. Trisulfoxide **15** (diastereomeric mixture) was obtained as an oil

(0.8 g, 0.88 mmol, 95%), not needing any purification before its involvement in the next reaction steps. TLC R_f 0.16; ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.3−3.8 [m, 21H, 6 × OCH$_2$,3 × SCH$_2$,3 × C*H*(CO$_2$Et)$_2$], 2.40 (m, 9H, 3 × Ar*Me*), 1.63 and 1.60 (two s, 18H, 3 × CMe$_2$), 1.29 (m, 18H, 6 × OCH$_2$C*H*$_3$).

General Procedure C. A solution of the sulfoxide and commercial ethynyl acceptor in CH$_2$Cl$_2$ was maintained at reflux temp. When the reaction appeared complete by TLC (disappearance of starting sulfoxide required about one night), the solvent was removed under reduced pressure and the reaction crude was purified by flash column chromatography on silica gel (see Table 1).

***rac*-1,4-Bis{[1-(4-ethynylphenyl)ethenylsulfinyl]methyl}-benzene (21).** Compound **21** was prepared, together with its diastereoisomer **22**, from 1,4-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] following procedure C (entry 1 in Table 1). The more mobile adduct **21** was isolated after chromatographic separation as a white solid melting at 145 °C. Single crystals suitable for X-ray structure were obtained by recrystallization from petrol/CHCl$_3$ 5:5. TLC R_f (EtOAc/petrol 7.5:2.5) 0.47; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.56 and 7.37 (AA′BB′system, $^3J_{ortho}$ = 8.3 Hz, 8H, 2 x H-2′,3′,5′,6′), 7.01 (s, 4H, H-2,3,5,6), 5.92 and 5.70 (two s, 4H, 2 × = CH$_2$), 3.97 and 3.56 (AB system, $^2J_{gem}$ = 13.2 Hz, 4H, 2 × SCH$_2$), 3.19 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ = 150.4 (2 × *C*=CH$_2$), 134.1 (C-1,4), 132.9 (2 × C-3′,5′), 130.2 (C-2,3,5,6), 129.1 (2 × C-1′), 126.4 (2 × C-2′,6′), 123.4 (2 × C-4′), 119.0 (2 × =CH$_2$), 82.7 (2 × *C*≡CH), 79.1 (2 × ≡CH), 56.9 (2 × SCH$_2$); IR (CHCl$_3$) 1502, 1054, 929, 844 cm^{-1}; Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 73.65; H, 5.11.

***meso*-1,4-Bis{[1-(4-ethynylphenyl)ethenylsulfinyl]methyl}-benzene (22).** Compound **22** was prepared, together with its diastereoisomer **21**, from 1,4-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] following procedure C (entry 1 in Table 1). The less mobile adduct **22** was isolated after chromatographic separation as a white solid melting at 170 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.45; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.56 and 7.37 (AA′BB′system, $^3J_{ortho}$ = 8.5 Hz, 8H, 2 × H-2′,3′,5′,6′), 7.04 (s, 4H, H-2,3,5,6), 5.94 and 5.77 (two s, 4H, 2 × =CH$_2$), 3.95 and 3.57 (AB system, $^2J_{gem}$ = 13.2 Hz, 4H, 2 × SCH$_2$), 3.19 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.6 (2 × *C*=CH$_2$), 134.2 (C-1,4), 132.9 (2 × C-3′,5′), 130.2 (C-2,3,5,6), 129.4 (2 × C-1′), 126.4 (C-2′,6′), 123.3 (2 × C-4′), 118.9 (2 × =CH$_2$), 82.7 (2 × *C*≡CH), 79.1 (2 × ≡CH), 57.4 (2 × SCH$_2$); IR (CHCl$_3$) 1503, 1053, 928, 844 cm^{-1}; Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 73.94; H, 4.94.

More Mobile 1,4-Bis{[1-(3-ethynylphenyl)ethenylsulfinyl]-methyl}benzene 23. Compound **23** was prepared, together with its diastereoisomer **24**, from 1,3-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] following procedure C (entry 2 in Table 1). The more mobile adduct **23** was isolated after chromatographic separation as a white solid melting at 100 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.46; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−7.4 (m, 8H, 2 × H-2′,4′,5′,6′), 7.04 (s, 4H, H-2,3,5,6), 5.93 and 5.73 (two s, 4H, 2 × =CH$_2$), 3.97 and 3.58 (AB system, $^2J_{gem}$ = 13.3 Hz, 4H, 2 × SCH$_2$), 3.17 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.4 (2 × *C*=CH$_2$), 134.2 (2 × C-1,4), 133.0 (2 × C-4′), 130.3 (C-2,3,5,6), 130.0 (2 × C-2′), 129.3 (2 × C-5′), 129.2 (2 × C-1′), 126.9 (2 × C-6′), 123.3 (2 × C-3′), 119.1 (2 × =CH$_2$), 82.6 (2 × *C*≡CH), 78.5 (2 × ≡CH), 57.1 (2 × SCH$_2$); Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 73.86; H, 4.68.

Less Mobile 1,4-Bis{[1-(3-ethynylphenyl)ethenylsulfinyl]-methyl}benzene 24. Compound **24** was prepared, together with its diastereoisomer **23**, from 1,3-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] following procedure C (entry 2 in Table 1). The less mobile adduct **24** was isolated after chromatographic separation as a white solid melting at 105 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.44; ^{1}H NMR (300 MHz,

CDCl$_3$) δ 7.6−7.4 (m, 8H, 2 × H-2′,4′,5′,6′), 7.05 (s, 4H, H-2,3,5,6), 5.94 and 5.76 (two s, 4H, 2 × =CH$_2$), 3.96 and 3.58 (AB system, $^2J_{gem}$ = 13.3 Hz, 4H, 2 × SCH$_2$), 3.17 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.4 (2 × *C*=CH$_2$), 134.2 (2 × C-1,4), 133.0 (2 × C-4′), 130.3 (C-2,3,5,6), 130.1 (2 × C-2′), 129.4 (2 × C-1′), 129.3 (2 × C-5′), 126.9 (2 × C-6′), 123.3 (2 × C-3′), 119.1 (2 × =CH$_2$), 82.6 (2 × *C*≡CH), 78.5 (2 × ≡CH), 57.3 (2 × SCH$_2$); Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 73.68; H, 4.75.

***meso*-1,12-Dimethylene-2,11-dithia[3.3]paraparacyclophane 2,11-Dioxide (25).** Following procedure C (entry 3 in Table 1), compound **25** was prepared from 1,4-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] and isolated after chromatographic purification as a white solid decomposing at 135 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.12; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.29 and 6.79 (two split d, $^4J_{meta}$ = 2.3 Hz, 4H, H-14,-15,17,18), 7.14 and 6.46 (two split d, $^4J_{meta}$ = 2.2 Hz, 4H, H-5,6,8,9), 6.17 and 6.16 (two d, $^2J_{gem}$ = 1.0 Hz, 4H, 2 × =CH$_2$), 4.60 and 3.76 (AB system, $^2J_{gem}$ = 11.6 Hz, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 152.6 (C-1,12), 136.1 and 129.8 (C-4,7,13,16), 133.3, 128.8, 127.2, and 127.1 (C-5,6,8,9,14,15,17,18), 115.3 (2 × = CH$_2$), 65.0 (C-3,10); MS (70 eV, EI) *m/z* (%) 328 (1) [M$^+$], 104 (4), 44 (3), 32 (20), 28 (100); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_2$S$_2$ (328.45): C, 65.82; H, 4.91. Found: C, 65.99; H, 5.02.

***rac*-1,12-Dimethylene-2,11-dithia[3.3]parametacyclophane 2,-11-Dioxide (27).** Racemate **27** was prepared, together with its *meso*-isomer **26**, from 1,3-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] following procedure C (entry 4 in Table 1). The more mobile **27** was isolated after chromatographic purification as a white solid decomposing at 110 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.13; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.22 (t, $^3J_{ortho}$ = 9.2 Hz, 1H, H-15), 7.21 (AB dd, $^3J_{ortho}$ = 9.2 Hz, $^4J_{meta}$ = 0.5 Hz, 1H) and 7.16 (AB dd, $^3J_{ortho}$ = 9.2 Hz, $^4J_{meta}$ = 1.7 Hz, 1H) (H-14,16), 6.80 and 6.68 (two AB dd, $^3J_{ortho}$ = 7.9 Hz, $^4J_{meta}$ = 1.7 Hz, 4H, H-5,6,8,9) 5.98 (dd, $^4J_{meta}$ = 1.7 and 0.5 Hz, 1H, H-18), 6.12 and 5.96 (two s, 4H, 2 × = CH$_2$), 4.74 and 3.70 (AB system, $^2J_{gem}$ = 12.2 Hz, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 152.4 (C-1,12), 135.5 and 130.3 (C-4,7,13,17), 129.9, 129.3, and 127.4 (C-5,6,8,9,14,16), 127.9 (C-15), 123.8 (C-18), 118.0 (2 × =CH$_2$), 64.4 (C-3,10); MS (70 eV, EI) *m/z* (%) 328 (53) [M$^+$], 310 (17), 279 (31), 262 (16), 261 (20), 229 (21), 128 (16), 127 (16), 104 (100), 103 (19); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_2$S$_2$ (328.45): C, 65.82; H, 4.91. Found: C, 65.54; H, 4.96.

***meso*-1,12-Dimethylene-2,11-dithia [3.3]parametacyclophane 2,11-Dioxide (26).** *meso*-Compound **26** was prepared, together with its racemate isomer **27**, from 1,3-diethynylbenzene and disulfoxide **11** [(via 1,4-benzenedimethanesulfenic acid (**16**)] following procedure C (entry 4 in Table 1). The less mobile CP **26** was isolated after chromatographic purification as a white solid decomposing at 100 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.12; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.18 (t, $^3J_{ortho}$ = 7.8 Hz, 1H, H-15), 7.03 and 6.43 (two split s, 4H, H-5,6,8,9) 6.99 (dd, $^3J_{ortho}$ = 7.8 Hz, $^4J_{meta}$ = 1.5 Hz, 2H, H-14,16), 6.21 and 5.95 (two s, 4H, 2 × =CH$_2$), 6.02 (t, $^4J_{meta}$ = 1.5 Hz, 1H, H-18), 4.92 and 3.42 (AB system, $^2J_{gem}$ = 11.8 Hz, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.5 (C-1,12), 136.3 and 130.8 (C-4,7,13,17), 130.1, 128.5 and 128.1 (C-5,6,8,9,14,-16), 128.2 (C-15), 127.5 (C-18), 117.7 (2 × =CH$_2$), 66.3 (C-3,-10); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_2$S$_2$ (328.45): C, 65.82; H, 4.91. Found: C, 65.84; H, 4.89.

1,12-Dimethylene-2,11-dithia[3.3]paraparacyclophane 2,2,11,-11-Tetraoxide (28). Disulfoxide **25** (0.2 g, 0.61 mmol) was oxidized following the general procedure B. Disulfone **28** was obtained as a white solid (0.2 g, 0.58 mmol, 95%) decomposing at 190 °C. TLC R_f 0.82; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 (s, 4H, H-14,15,17,18), 7.10 (s, 4H, H-5,6,8,9), 6.61 and 6.17 (two s, 4H, 2 × =CH$_2$), 4.30 (s, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 148.9 (C-1,12), 131.5 (C-5,6,8,9), 129.8 (C-4,7,13,16), 129.6 (C-

14,15,17,18), 126.8 (2 × =CH$_2$), 63.6 (C-3,10); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_4$S$_2$ (360.45): C, 59.98; H, 4.47. Found: C, 59.92; H, 4.49.

1,12-Dimethylene-2,11-dithia[3.3]parametacyclophane 2,2,11,-11-Tetraoxide (29). A 1:1 mixture of disulfoxides **26** and **27** (0.2 g, 0.61 mmol) was oxidized following the general procedure B. Disulfone **29** was obtained as a white solid (0.2 g, 0.58 mmol, 95%) decomposing at 190 °C. TLC R_f 0.80; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.54 (dd, $^3J_{ortho}$ = 7.9 Hz, $^4J_{meta}$ = 1.8 Hz, 2H, H-14,16), 7.23 (t, $^3J_{ortho}$ = 7.9 Hz, 1H, H-15), 7.00 (s, 4H, H-5,6,8,9), 6.56 and 5.99 (two s, 4H, 2 × =CH$_2$), 5.90 (t, $^4J_{meta}$ = 1.8 Hz, 1H, H-18), 4.42 (s, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 149.0 (C-1,12), 133.2 and 128.9 (C-4,7,13,17), 140.4, 140.0, 129.1, 129.0, and 127.2 (C-5,6,8,9,14−16,18), 121.0 (2 × =CH$_2$), 64.5 (C-3,10); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_4$S$_2$ (360.45): C, 59.98; H, 4.47. Found: C, 60.25; H, 4.53.

More Mobile 1,3-Bis{[1-(4-ethynylphenyl)ethenylsulfinyl]-methyl}benzene 34. Compound **34** was prepared, together with its stereoisomer **35**, from 1,4-diethynylbenzene and disulfoxide **12** [(via 1,3-benzenedimethanesulfenic acid (**17**)] following procedure C (entry 5 in Table 1). The more mobile adduct **34** was isolated after chromatographic separation as a white solid. TLC R_f (EtOAc/petrol 7.5:2.5) 0.52; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.56 (AA′BB′ d, $^3J_{ortho}$ = 8.5 Hz, 4H, 2 × H-3′,5′), 7.42 (AA′BB′ d, $^3J_{ortho}$ = 8.5 Hz, 4H, 2 × H-2′,6′), 7.4−7.0 (m, 3H, H-4−6), 6.76 (br s, 1H, H-2), 5.97 and 5.74 (two s, 4H, 2 × =CH$_2$), 3.95 and 3.54 (AB system, $^2J_{gem}$ = 13.4 Hz, 4H, 2 × SCH$_2$), 3.20 (s, 2H, 2 × ≡CH); Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 74.00; H, 4.68.

Less Mobile 1,3-Bis{[1-(4-ethynylphenyl)ethenylsulfinyl]-methyl}benzene 35. Compound **35** was prepared, together with its stereoisomer **34**, from 1,4-diethynylbenzene and disulfoxide **12** [(via 1,3-benzenedimethanesulfenic acid (**17**)] following procedure C (entry 5 in Table 1). The less mobile adduct **35** was isolated after chromatographic separation as a white solid. TLC R_f (EtOAc/petrol 7.5:2.5) 0.51; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.55 (AA′BB′ d, $^3J_{ortho}$ = 8.6 Hz, 4H, 2 × H-3′,5′), 7.40 (AA′BB′ d, $^3J_{ortho}$ = 8.6 Hz, 4H, 2 × H-2′,6′), 7.3−7.0 (m, 3H, H-4−6), 6.82 (br s, 1H, H-2), 5.98 and 5.82 (two s, 4H, 2 × =CH$_2$), 3.92 and 3.56 (AB system, $^2J_{gem}$ = 13.3 Hz, 4H, 2 × SCH$_2$), 3.20 (s, 2H, 2 × ≡CH); Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 73.67; H, 4.94.

More Mobile 1,3-Bis{[1-(3-ethynylphenyl)ethenylsulfinyl]-methyl}benzene 36. Compound **36** was obtained, together with its diastereoisomer **37** and phanes **39/40**, from 1,3-diethynylbenzene and disulfoxide **12** [(via 1,3-benzenedimethanesulfenic acid (**17**)] following procedure C (entry 6 in Table 1). The more mobile adduct **36** was isolated after chromatographic separation as an oil. TLC R_f (EtOAc/petrol 7.5:2.5) 0.51; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−6.8 (m, 12H, ArH), 5.96 and 5.82 (two s, 4H, 2 × =CH$_2$), 3.92 and 3.59 (AB system, $^2J_{gem}$ = 13.2 Hz, 4H, 2 × SCH$_2$), 3.15 (s, 2H, 2 × ≡CH); Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 74.01; H, 4.95.

Less Mobile 1,3-Bis{[1-(3-ethynylphenyl)ethenylsulfinyl]-methyl}benzene 37. Compound **37** was obtained, together with its diastereoisomer **36** and phanes **39/40**, from 1,3-diethy-nylbenzene and disulfoxide **12** [(via 1,3-benzenedimethane-sulfenic acid (**17**)] following procedure C (entry 8 in Table 1). The less mobile 1,3-bis{[1-(3-ethynylphenyl)ethenylsulfinyl]methyl}-benzene adduct **37** was isolated after chromatographic separation as an oil. TLC R_f (EtOAc/petrol 7.5:2.5) 0.50; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−6.7 (m, 12H, ArH), 5.95 and 5.75 (two s, 4H, 2 × =CH$_2$), 3.95 and 3.56 (AB system, $^2J_{gem}$ = 13.0 Hz, 4H, 2 × SCH$_2$), 3.16 (s, 2H, 2 × ≡CH); Elem anal. Calcd (%) for C$_{28}$H$_{22}$O$_2$S$_2$ (454.61): C, 73.98; H, 4.88. Found: C, 74.03; H, 4.90.

***meso*-1,12-Dimethylene-2,11-dithia[3.3]metaparacyclophane 2,11-Dioxide (38).** Following procedure C (entry 7 in Table 1), compound **38** was prepared from 1,4-diethynylbenzene and disul-foxide **12** [(via 1,3-benzenedimethanesulfenic acid (**17**)] and isolated

after chromatographic purification as a white solid decomposing at 110 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.09; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.53 and 6.48 (two split d, $^4J_{meta}$ = 2.3 Hz, 4H, H-14,15, 17,18), 7.31 (m, 3H, H-5−7), 6.11 and 6.00 (two d, $^2J_{gem}$ = 0.7 Hz, 4H, 2 × =CH$_2$), 5.42 (br s, 1H, H-9), 4.06 and 3.90 (AB system, $^2J_{gem}$ = 12.6 Hz, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 154.3 (C-1,12), 135.0 and 132.1 (C-4,8,13,16), 129.4, 129.3, and 126.6 (C-5,7,14,15,17,18), 129.2 and 128.7 (C-6,9), 115.8 (2 × =CH$_2$), 63.7 (C-3,10); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_2$S$_2$ (328.45): C, 65.82; H, 4.91. Found: C, 65.90; H, 4.95.

***rac*-1,12-Dimethylene-2,11-dithia[3.3]metametacyclophane 2,-11-Dioxide (40).** Racemate **40** was prepared, together with its *meso*-isomer **39**, from 1,3-diethynylbenzene and disulfoxide **12** [(via 1,3-benzenedimethanesulfenic acid (**17**)] following procedure C (entry 8 in Table 1). The more mobile **40** was isolated after chromato-graphic purification as a white solid decomposing at 60 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.12; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.2−7.0 (m, 6H, H-5−7,14−16), 6.80 (s, 1H, H-18), 6.20 (br s, 1H, H-9), 6.10 and 6.01 (two s, 4H, 2 × =CH$_2$), 4.28 and 3.92 (AB system, $^2J_{gem}$ = 13.1 Hz, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 152.6 (C-1,12), 135.0 and 130.4 (C-4,8,13,17), 132.8, 129.6, 129.2, 129.0 and 127.1 (C-5−7,9,14−16,18), 117.4 (2 × =CH$_2$), 63.2 (C-3,10); MS (70 eV, EI) m/z 328 (1) [M$^+$], 105 (6), 104 (4), 84 (3), 77 (5), 49 (3), 44 (7), 40 (6), 32 (100), 29 (6); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_2$S$_2$ (328.45): C, 65.82; H, 4.91. Found: C, 65.72; H, 4.85.

***meso*-1,12-Dimethylene-2,11-dithia[3.3]metametacyclophane 2,11-Dioxide (39).** *meso*-Compound **39** was prepared, together with its racemate isomer **40**, from 1,3-diethynylbenzene and disulfoxide **12** [(via 1,3-benzenedimethanesulfenic acid (**17**)] following pro-cedure C (entry 8 in Table 1). The less mobile CP **39** was isolated after chromatographic purification as a white solid decomposing at 115 °C. Single crystals suitable for X-ray structure were obtained by recrystallization from CHCl$_3$. TLC R_f (EtOAc/petrol 7.5:2.5) 0.10; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.1−6.9 (m, 8H, H-5−7,9,-14−16,18), 6.21 and 6.06 (two d, $^2J_{gem}$ = 0.5 Hz, 4H, 2 × =CH$_2$), 4.54 and 3.83 (AB system, $^2J_{gem}$ = 12.3 Hz, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.4 (C-1,12), 135.6 and 130.2 (C-4,8,13,17), 129.7, 129.5, 128.8, and 127.2 (C-5−7,9,14−16,-18), 117.1 (2 × =CH$_2$), 64.4 (C-3,10); IR (CHCl$_3$) 3031, 1047 (SO), 908 cm^{-1}; MS (70 eV, EI) m/z (%) 328 (2) [M$^+$], 263 (3), 229 (3), 105 (3), 104 (10), 103 (4), 78 (4), 32 (18), 28 (100); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_2$S$_2$ (328.45): C, 65.82; H, 4.91. Found: C, 65.75; H, 4.89.

1,12-Dimethylene-2,11-dithia[3.3]metametacyclophane 2,2,-11,11-Tetraoxide (41). A 1:1 mixture of disulfoxides **39** and **40** (0.1 g, 0.30 mmol) was oxidized following the general procedure B. Disulfone **41** was obtained as a white solid (0.1 g, 0.28 mmol, 93%) decomposing at 185 °C. TLC R_f 0.80; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.53 (dd, $^3J_{ortho}$ = 7.9 Hz, $^4J_{meta}$ = 1.8 Hz, 2H, H-14,16), 7.44 (t, $^4J_{meta}$ = 1.7 Hz, 1H, H-18), 7.3−7.1 (m, 4H, H-5−7,15), 6.57 and 6.07 (two s, 4H, 2 × =CH$_2$), 6.50 (br s, 1H, H-9), 4.28 (s, 4H, H$_2$-3,10); ^{13}C NMR (75 MHz, CDCl$_3$) δ 149.0 (C-1,12), 133.3 and 128.4 (C-4,8,13,17), 134.0, 132.9, 131.5, 129.8, 129.1 and 128.5 (C-5−7,9,14−16,18), 127.2 (2 × =CH$_2$), 62.2 (C-3,-10); MS (70 eV, EI) m/z (%) 360 (14) [M$^+$], 231 (33), 217 (86), 216 (70), 202 (73), 192 (33), 191 (33), 127 (55), 28 (100); Elem anal. Calcd (%) for C$_{18}$H$_{16}$O$_4$S$_2$ (360.45): C, 59.98; H, 4.47. Found: C, 59.67; H, 4.16.

More Mobile 1,3-Bis[1-(4-ethynylphenyl)ethenylsulfinyl]-benzene 30. Compound **30** was prepared, together with its stereoisomer **31**, from 1,4-diethynylbenzene and disulfoxide **13** [(via 1,3-benzenedisulfenic acid (**18**)] following procedure C (entries 9 and 10 in Table 1). The more mobile adduct **30** was isolated after chromatographic separation as a light yellow solid melting at 164 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.72; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.52 (t, $^4J_{meta}$ = 1.7 Hz, 1H, H-2), 7.41 (AA′ m, $^3J_{ortho}$ = 8.5 Hz, 4H, 2 × H-3′,5′), 7.34 (m, $^3J_{ortho}$ = 8.5 Hz, $^4J_{meta}$ = 1.7 Hz, 1H) and 7.33 (m, $^3J_{ortho}$ = 6.5 Hz, $^4J_{meta}$ = 1.7 Hz, 1H,

H-4,6), 7.25 (dd, $^3J_{ortho}$ = 8.5 and 6.5 Hz, 1H, H-5), 7.05 (BB′ m, $^3J_{ortho}$ = 8.5 Hz, 4H, 2 × H-2′,6′), 6.16 and 5.86 (two d, $^2J_{gem}$ = 0.9 Hz, 4H, 2 × =CH$_2$), 3.17 (s, 2H, 2 × ≡CH); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.62 (t, $^4J_{meta}$ = 1.6 Hz, 1H, H-2), 7.12 (AA′ m, $^3J_{ortho}$ = 8.4 Hz, 4H, 2 x H-3′,5′), 6.95 (dd, $^3J_{ortho}$ = 7.7 Hz, $^4J_{meta}$ = 1.6 Hz, 2H, H-4,6), 6.58 (BB′ m, $^3J_{ortho}$ = 8.4 Hz, 4H, 2 × H-2′,6′), 6.39 (t, $^3J_{ortho}$ = 7.7 Hz, 1H, H-5), 6.12 and 5.36 (two s, 4H, 2 × =CH$_2$), 2.68 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.3 (2 × *C*=CH$_2$), 144.3 (C-1,3), 133.4 (2 × C-1′), 132.3 (2 × C-3′,5′), 129.3 (C-5), 127.3 and 127.2 (C-4,6, 2 × C-2′,6′), 123.1 (2 × C-4′), 120.8 (C-2), 117.1 (2 × =CH$_2$), 82.6 (2 × *C*≡CH), 79.1 (2 × ≡CH); MS (70 eV, EI) *m/z* (%) 426 (0.1) [M$^+$], 300 (10), 129 (12), 128 (12), 127 (100), 126 (16), 101 (10), 77 (16), 51 (10); Elem anal. Calcd (%) for C$_{26}$H$_{18}$O$_2$S$_2$ (426.55): C, 73.21; H, 4.25. Found: C, 73.58; H, 4.58.

Less Mobile 1,3-Bis[1-(4-ethynylphenyl)ethenylsulfinyl]benzene 31. Compound **31** was prepared, together with its stereoisomer **30**, from 1,4-diethynylbenzene and disulfoxide **13** [(via 1,3-benzene-disulfenic acid (**18**)] following procedure C (entries 9 and 10 in Table 1). The less mobile adduct **31** was isolated after chromatographic separation as a light yellow solid melting at 125 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.69; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.60 (t, $^4J_{meta}$ = 1.6 Hz, 1H, H-2), 7.38 (AA′ m, $^3J_{ortho}$ = 8.5 Hz, 4H, 2 × H-3′,5′), 7.4−7.3 (m, 2H, H-4,6), 7.27 (dd, $^3J_{ortho}$ = 8.7 and 6.4 Hz, 1H, H-5), 7.07 (BB′ m, $^3J_{ortho}$ = 8.5 Hz, 4H, 2 × H-2′,6′), 6.21 and 5.93 (two d, $^2J_{gem}$ = 0.8 Hz, 4H, 2 × =CH$_2$), 3.15 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.0 (2 × *C*=CH$_2$), 144.2 (C-1,3), 133.2 (2 × C-1′), 132.3 (2 × C-3′,5′), 129.5 (C-5), 127.5 and 127.3 (C-4,6, 2 × C-2′,6′), 123.1 (2 × C-4′), 121.6 (C-2), 118.6 (2 × =CH$_2$), 82.6 (2 × *C*≡CH), 79.0 (2 × ≡CH); Elem anal. Calcd (%) for C$_{26}$H$_{18}$O$_2$S$_2$ (426.55): C, 73.21; H, 4.25. Found: C, 73.18; H, 4.50.

More Mobile 1,3-Bis[1-(3-ethynylphenyl)ethenylsulfinyl]benzene 32. Compound **32** was prepared, together with its stereoisomer **33**, from 1,3-diethynylbenzene and disulfoxide **13** [(via 1,3-benzenedisulfenic acid (**18**)] following procedure C (entries 11 and 12 in Table 1). The more mobile adduct **32** was isolated after chromatographic separation as a light yellow solid melting at 78 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.72; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.52 (t, $^4J_{meta}$ = 1.5 Hz, 1H, H-2), 7.45 (dt, $^3J_{ortho}$ = 7.7, $^4J_{meta}$ = 1.4 Hz, 2H, 2 × H-4′ or H-6′), 7.3−7.2 (m, 3H, H-4−6), 7.27 (t, $^3J_{ortho}$ = 7.7 Hz, 2H, 2 × H-5′), 7.22 (t, $^4J_{meta}$ = 1.4 Hz, 2H, 2 × H-2′), 7.07 (dt, $^3J_{ortho}$ = 7.7, $^4J_{meta}$ = 1.4 Hz, 2H, 2 × H-4′ or H-6′), 6.14 and 5.83 (two d, $^2J_{gem}$ = 0.8 Hz, 4H, 2 × =CH$_2$), 3.13 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.3 (2 × *C*=CH$_2$), 144.3 (C-1,3), 133.5 (2 × C-1′), 132.8 (2 × C-4′), 130.9 (2 × C-2′), 129.3 (C-5), 128.8, 127.8, and 127.2 (C-4,6, 2 × C-5′,6′), 122.9 (2 × C-3′), 120.7 (C-2), 117.4 (2 × =CH$_2$), 82.5 (2 × *C*≡CH), 78.5 (2 × ≡CH); Elem anal. Calcd (%) for C$_{26}$H$_{18}$O$_2$S$_2$ (426.55): C, 73.21; H, 4.25. Found: C, 73.34; H, 4.16.

Less Mobile 1,3-Bis[1-(4-ethynylphenyl)ethenylsulfinyl]benzene 33. Compound **33** was prepared, together with its stereoisomer **32**, from 1,3-diethynylbenzene and disulfoxide **13** [(via 1,3-benzenedisulfenic acid (**18**)] following procedure C (entries 11 and 12 in Table 1). The less mobile adduct **33** was isolated after chromatographic separation as a light yellow solid melting at 130 °C. TLC R_f (EtOAc/petrol 7.5:2.5) 0.69; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.62 (t, $^4J_{meta}$ = 1.8 Hz, 1H, H-2), 7.42 (dt, $^3J_{ortho}$ = 7.6, $^4J_{meta}$ = 1.5 Hz, 2H, 2 × H-4′ or H-6′), 7.35 (m, 2H, H-4,6), 7.27 (dd, $^3J_{ortho}$ = 8.7 and 6.4, 1H, H-5), 7.24 (t, $^4J_{meta}$ = 1.5 Hz, 2H, 2 × H-2′), 7.23 (t, $^3J_{ortho}$ = 7.6 Hz, 2H, 2 × H-5′), 7.06 (dt, $^3J_{ortho}$ = 7.6, $^4J_{meta}$ = 1.5 Hz, 2H, 2 × H-4′ or H-6′), 6.21 and 5.92 (two d, $^2J_{gem}$ = 0.8 Hz, 4H, 2 × =CH$_2$), 3.10 (s, 2H, 2 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.0 (2 × *C*=CH$_2$), 144.2 (C-1,3), 133.3 (2 × C-1′), 132.9 (2 × C-4′), 131.0 (2 × C-2′), 129.4 (C-5), 128.7, 127.9, and 127.7 (C-4,6, 2 × C-5′,6′), 122.8 (2 × C-3′), 121.6 (C-2), 118.6 (2 × =CH$_2$), 82.6 (2 × *C*≡CH), 78.4 (2 × ≡CH); Elem anal. Calcd (%) for C$_{26}$H$_{18}$O$_2$S$_2$ (426.55): C, 73.21; H, 4.25. Found: C, 73.19; H, 4.60.

***C$_3$sym*-1,3,5-Tris{[1-(phenyl)ethenylsulfinyl]methyl}-benzene (42).** Compound **42** was prepared, together with its diastereoisomer **43**, from phenylacetylene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 13 in Table 1). The more mobile adduct **42** was isolated after chromatographic separation as a light yellow low-melting solid. TLC R_f (EtOAc/petrol 9:1) 0.46; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.5−7.4 (m, 15H, 3 × H-2′-6′), 6.79 (s, 3H, H-2,4,6), 5.97 and 5.70 (two s, 6H, 3 × =CH$_2$), 3.95 and 3.48 (AB system, $^2J_{gem}$ = 13.3 Hz, 6H, 3 × SCH$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.9 (3 × *C*=CH$_2$), 133.9 (C-1,3,5), 132.6 (C-2,4,6), 129.5 (3 × C-4′), 129.4 (3 × C-1′), 129.3 (3 × C-3′,5′), 126.6 (3 × C-2′,6′), 118.4 (3 × =CH$_2$), 56.8 (3 × SCH$_2$); Elem anal. Calcd (%) for C$_{33}$H$_{30}$O$_3$S$_3$ (570.78): C, 69.44; H, 5.30. Found: C, 69.52; H, 5.68.

no*C$_3$sym*-1,3,5-Tris{[1-(phenyl)ethenylsulfinyl]methyl}-benzene (43). Compound **43** was prepared, together with its diastereoisomer **42**, from phenylacetylene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 13 in Table 1). The less mobile adduct **43** was isolated after chromatographic separation as a light yellow low-melting solid. TLC R_f (EtOAc/petrol 9:1) 0.45; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.5−7.4 (m, 15H, 3 × H-2′-6′), 6.84 (s, 2H) and 6.78 (s, 1H) (H-2,4,6), 5.98 and 5.82 (two s, 2H, =CH$_2$), 5.97 and 5.74 (two s, 4H, 2 × CH$_2$), 3.91 and 3.51 (AB system, $^2J_{gem}$ = 13.2 Hz, 4H, 2 × SCH$_2$), 3.89 and 3.55 (AB system, $^2J_{gem}$ = 12.8 Hz, 2H, SCH$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 151.7 and 151.2 (3 × *C*=CH$_2$), 133.9 (C-1,3,5), 132.2 and 132.1 (C-2,4,6), 130.3 and 130.0 (3 × C-1′), 129.5 (3 × C-4′), 129.3 (3 × C-3′,5′), 126.6 (3 × C-2′,6′), 118.3 and 118.1 (3 × =CH$_2$), 58.1 and 57.3 (3 × SCH$_2$); Elem anal. Calcd (%) for C$_{33}$H$_{30}$O$_3$S$_3$ (570.78): C, 69.44; H, 5.30. Found: C, 69.38; H, 5.45.

(*R*,*R*,*R*)- and (*R*,*R*,*S*)-1,12,19-Trimethylene-2,11,20-trithia[3$_3$](1,3,5)cyclophane 2,11,20-Trioxides (48) and (49). *C$_3$*-Symmetrical **48** was prepared, together with its stereoisomer **49**, from 1,3,5-triethynylbenzene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 16 in Table 1). After chromatographic purification, various mixtures of the cage compounds **48/49** as white solids were obtained; TLC R_f (EtOAc/petrol 9:1) 0.03; Elem anal. Calcd (%) for C$_{21}$H$_{18}$O$_3$S$_3$ (414.56): C, 60.84; H, 4.38. Found: C, 60.72; H, 4.30. The following NMR data come from suitably enriched mixtures: ^{1}H NMR of (*R*,*R*,*R*)-1,12,19-trimethylene-2,11,20-trithia[3$_3$](1,3,5)-cyclophane 2,11,20-trioxide (**48**; 300 MHz, CDCl$_3$) δ 7.11 and 6.92 (two br s, 6H, ArH), 6.21 and 6.04 (two d, $^2J_{gem}$ = 0.6 Hz, 6H, 3 × =CH$_2$), 4.62 and 3.77 (AB system, $^2J_{gem}$ = 12.1 Hz, 6H, H$_2$-3,10,21). ^{1}H NMR of (*R*,*R*,*S*)-1,12,19-trimethylene-2,11,20-trithia[3$_3$](1,3,5)cyclophane 2,11,20-trioxide (**49**; 300 MHz, CDCl$_3$) δ 7.2−6.6 (m, 6H, ArH), 6.2−6.0 (m, 6H, 3 × =CH$_2$), 4.5−3.8 (m, 6H, H$_2$-3,10,21).

1,12,19-Trimethylene-2,11,20-trithia[3$_3$](1,3,5)cyclophane 2,2,-11,11,20,20-Hexaoxide (50). A mixture of trisulfoxides **48** and **49** (0.1 g, 0.24 mmol) was oxidized following the general procedure B. Trisulfone **50** was obtained as a white solid (0.1 g, 0.22 mmol, 92%) decomposing at 250 °C. TLC R_f 0.78; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.78 and 7.50 (two s, 6H, ArH), 6.69 and 6.09 (two s, 6H, 3 × =CH$_2$), 4.39 (s, 6H, 3 × SCH$_2$); MS (70 eV, EI) *m/z* (%) 462 (7) [M$^+$], 270 (29), 239 (23), 104 (31), 57 (25), 55 (21), 44 (93), 43 (35), 41 (21), 32 (100); Elem anal. Calcd (%) for C$_{21}$H$_{18}$O$_6$S$_3$ (462.56): C, 54.53; H, 3.92. Found: C, 54.31; H, 4.00.

(*R*,*R*,*R*)-5,7,9-Trimethyl-1,12,19-trimethylene-2,11,20-trithia-[3$_3$](1,3,5)cyclophane 2,11,20-Trioxide (51). Cage **51** was prepared, together with its diastereoisomer **52**, from 1,3,5-triethynyl-benzene and trisulfoxide **15** [(via 2,4,6-trimethyl-1,3,5-benzenetrimethanesulfenic acid (**20**)] following procedure C (entry 17 in Table 1). The more mobile adduct **51** was isolated after chromatographic separation as a white solid decomposing at 180 °C. TLC R_f (EtOAc/petrol 9:1) 0.05; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.24 (s, 3H, ArH), 6.20 and 6.10 (two s, 6H, 3 × =CH$_2$), 4.60 and 4.17 (AB system, $^2J_{gem}$ = 12.6 Hz, 6H, H$_2$-3,-

10,21), 2.40 (s, 9H, 3 × Me); Elem anal. Calcd (%) for $C_{24}H_{24}O_3S_3$ (456.64): C, 63.13; H, 5.30. Found: C, 63.26; H, 5.65.

(R*,R*,S*)-5,7,9-Trimethyl-1,12,19-trimethylene-2,11,20-trithia-[3$_3$](1,3,5)cyclophane 2,11,20-Trioxide (52). Cage **52** was prepared, together with its diastereoisomer **51**, from 1,3,5-triethynylbenzene and trisulfoxide **15** [(via 2,4,6-trimethyl-1,3,5-benzenetrimethanesulfenic acid (**20**)] following procedure C (entry 17 in Table 1). The less mobile adduct **52** was isolated after chromatographic separation as a white solid decomposing at 180 °C. TLC R_f (EtOAc/petrol 9:1) 0.04; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−6.9 (m, 3H, ArH), 6.30, 6.19, 6.13, 6.12, 6.08, and 6.05 (six s, 6H, 3 × =CH$_2$), 4.8−4.0 (m, 6H, H$_2$-3,10,21), 2.72, 2.11, and 2.05 (three s, 9H, 3 × Me); Elem anal. Calcd (%) for $C_{24}H_{24}O_3S_3$ (456.64): C, 63.13; H, 5.30. Found: C, 63.10; H, 5.37.

5,7,9-Trimethyl-1,12,19-trimethylene-2,11,20-trithia[3$_3$](1,3,5)-cyclophane 2,2,11,11,20,20-Hexaoxide (53). A mixture of trisulfoxides **51** and **52** (0.2 g, 0.44 mmol) was oxidized following the general procedure B. Trisulfone **53** was obtained as a white solid (0.2 g, 0.40 mmol, 91%), decomposing at 250 °C. TLC R_f 0.80; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10 (s, 3H, ArH), 6.71 and 6.19 (two d, $^2J_{gem}$ = 0.8 Hz, 6H, 3 × =CH$_2$), 4.73 (s, 6H, 3 × SCH$_2$), 2.50 (s, 9H, 3 × Me); Elem anal. Calcd (%) for $C_{24}H_{24}O_6S_3$ (504.64): C, 57.12; H, 4.79. Found: C, 57.31; H, 4.55.

C_3sym-1,3,5-Tris{[1-(4-ethynylphenyl)ethenylsulfinyl]methyl}-benzene (46). Compound **46** was prepared, together with its diastereoisomer **47**, from 1,4-diethynylbenzene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 15 in Table 1). The more mobile adduct **46** was isolated after chromatographic separation as a yellow solid melting at 95 °C. TLC R_f (EtOAc/petrol 9:1) 0.77; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.57 and 7.48 (AA′BB′ system, $^3J_{ortho}$ = 8.5 Hz, 12H, 3 × H-2′,3′,5′,6′), 6.73 (s, 3H, H-2,4,6), 6.02 and 5.69 (two s, 6H, 3 × =CH$_2$), 3.93 and 3.47 (AB system, $^2J_{gem}$ = 13.3 Hz, 6H, 3 × SCH$_2$), 3.21 (s, 3H, 3 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 149.8 (3 × C=CH$_2$), 134.1 (C-1,3,5), 133.0 (3 × C-3′,5′), 132.8 (C-2,4,6), 128.9 (3 × C-1′), 126.5 (3 × C-2′,6′), 123.4 (3 × C-4′), 119.4 (3 × =CH$_2$), 82.8 (3 × C≡CH), 79.1 (3 × ≡CH), 56.3 (3 × SCH$_2$); MS (FAB) m/z (%) 643 (9) [M + 1], 391 (19), 155 (46), 149 (27), 139 (21), 138 (54), 137 (100), 120 (19), 107 (32), 89 (29), 77 (25); Elem anal. Calcd (%) for $C_{39}H_{30}O_3S_3$ (642.85): C, 72.87; H, 4.70. Found: C, 73.26; H, 4.68.

noC_3sym-1,3,5-Tris{[1-(4-ethynylphenyl)ethenylsulfinyl]methyl}benzene (47). Compound **47** was prepared, together with its diastereoisomer **46**, from 1,4-diethynylbenzene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 15 in Table 1). The less mobile adduct **47** was isolated after chromatographic separation as a yellow solid melting at 97 °C. TLC R_f (EtOAc/petrol 9:1) 0.73; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−7.4 (m, 12H, 3 × H-2′,3′,5′,6′), 6.80 (s, 2H) and 6.75 (s, 1H) (H-2,4,6), 6.02 and 5.86 (two s, 2H, =CH$_2$), 6.00 and 5.77 (two s, 4H, 2 × CH$_2$), 3.90 and 3.51 (AB system, $^2J_{gem}$ = 13.1 Hz, 4H, 2 × SCH$_2$), 3.87 and 3.54 (AB system, $^2J_{gem}$ = 13.1 Hz, 2H, SCH$_2$), 3.21 (s, 2H, 2 × ≡CH), 3.20 (s, 1H, ≡CH);

^{13}C NMR (75 MHz, CDCl$_3$) δ 151.0 and 150.4 (3 × C=CH$_2$), 134.1 (C-1,3,5), 133.0 (3 × C-3′,5′), 132.3 and 132.1 (C-2,4,6), 130.1 and 129.8 (3 × C-1′), 126.6 and 126.5 (3 × C-2′,6′), 123.4 (3 × C-4′), 119.2 and 118.9 (3 × =CH$_2$), 82.7 (3 × C≡CH), 79.1 (3 × ≡CH), 58.1 and 57.1 (3 × SCH$_2$); Elem anal. Calcd (%) for $C_{39}H_{30}O_3S_3$ (642.85): C, 72.87; H, 4.70. Found: C, 72.62; H, 4.85.

C_3sym-1,3,5-Tris{[1-(3,5-diethynylphenyl)ethenylsulfinyl]-methyl}benzene (44). Compound **44** was prepared, together with its diastereoisomer **45** and the cages **48/49**, from 1,3,5-triethynylbenzene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 14 in Table 1). The more mobile adduct **44** was isolated after chromatographic separation as a yellow solid melting at 94 °C. TLC R_f (EtOAc/petrol 9:1) 0.80; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−7.5 (m, 9H, 3 × H-2′,3′,5′), 6.70 (s, 3H, H-2,4,6), 5.98 and 5.73 (two d, $^2J_{gem}$ = 0.6 Hz, 6H, 3 × =CH$_2$), 3.95 and 3.54 (AB system, $^2J_{gem}$ = 13.2 Hz, 6H, 3 × SCH$_2$), 3.18 (s, 6H, 6 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 149.2 (3 × C=CH$_2$), 136.2 (3 × C-4′), 134.6 (C-1,3,5), 132.6 (3 × C-2′,6′), 130.3 (C-2,4,6), 129.0 (3 × C-1′), 123.6 (3 × C-3′.5′), 120.4 (3 × =CH$_2$), 81.7 (3 × C≡CH), 79.3 (3 × ≡CH), 56.5 (3 × SCH$_2$); Elem anal. Calcd (%) for $C_{45}H_{30}O_3S_3$ (714.92): C, 75.60; H, 4.23. Found: C, 75.66; H, 4.55.

noC_3sym-1,3,5-Tris{[1-(3,5-diethynylphenyl)ethenylsulfinyl]-methyl}benzene (45). Compound **45** was prepared, together with its diastereoisomer **44** and the cages **48/49**, from 1,3,5-triethynylbenzene and trisulfoxide **14** [(via 1,3,5-benzenetrimethanesulfenic acid (**19**)] following procedure C (entry 14 in Table 1). Compound **45** was isolated after chromatographic separation as a yellow solid melting at 110 °C. TLC R_f (EtOAc/petrol 9:1) 0.76; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.6−7.5 (m, 9H, 3 × H-2′,3′,5′), 6.78 (s, 2H) and 6.75 (s, 1H) (H-2,4,6), 6.00 and 5.90 (two d, $^2J_{gem}$ = 0.6 Hz, 2H, =CH$_2$), 5.99 and 5.83 (two d, $^2J_{gem}$ = 0.8 Hz, 4H, 2 × =CH$_2$), 3.91 and 3.59 (AB system, $^2J_{gem}$ = 13.2 Hz, 4H, 2 × SCH$_2$), 3.87 and 3.61 (AB system, $^2J_{gem}$ = 13.1 Hz, 2H, SCH$_2$), 3.18 (s, 6H, 6 × ≡CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.0 and 149.6 (3 × C=CH$_2$), 136.2 (3 × C-4′), 134.6 (C-1,3,5), 132.4 and 132.0 (3 × C-2′,6′), 130.4 and 130.3 (C-2,4,6), 129.8 and 129.7 (3 × C-1′), 123.63 and 123.61 (3 × C-3′,5′), 120.3 (3 × =CH$_2$), 81.7 (3 × C≡CH), 79.3 (3 × ≡CH), 58.0 and 57.4 (3 × SCH$_2$); Elem anal. Calcd (%) for $C_{45}H_{30}O_3S_3$ (714.92): C, 75.60; H, 4.23. Found: C, 75.42; H, 4.33.

Supporting Information Available: Experimental details of X-ray crystallographic analyses, crystallographic data, and CIF files of compounds **21** and **39** and ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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