Base-Catalyzed Reactivity of Sulfur- and Selenium-Bridged Cyclic Alkynes: Tandem Isomerization and Cycloaromatization versus Isomerization and Nucleophilic Addition

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The synthesis and base-catalyzed reactivity of some novel sulfur- and selenium-bridged cyclic di- and tetralkynes, derived from 1,2- and 1,4-dihydroxybenzene and 1,2-bis(bromomethyl)benzene, are described. The cyclic propargylic sulfides and selenides undergo base-induced isomerization to the corresponding allenes, followed by cycloaromatization of the latter by diradical or anionic mechanisms, depending on the nature of the base. Because of the lack of stability of the expected diradical intermediate, the corresponding allenic sulfones undergo nucleophilic addition, which is responsible for their DNA-cleaving properties.

Introduction

The so-called enediyne antibiotics, such as calicheamicin or esperamicin, are amongst the most potent antitumor agents known to date.[1−4] Formation of a diradical intermediate with accompanying cycloaromatization has been postulated as the key step in the DNA-cleavage activity of these natural products. However, because of the complexity, scarcity, and difficult synthesis of the natural enediynes, a variety of model enediynes have been prepared and tested for their biological activity during the last decade. Thus, the cyclization of bis(γ,γ-dimethylallenyl) sulfone was used by Nicolaou[5] as a model for the design of a new class of DNA-cleaving molecules that could mimic the activity of the natural enediynes. This was in turn based on the thermal cyclization of diallenyl sulfones, a reaction discovered by us some three decades ago and demonstrated to involve a diradical intermediate.[6] However, subsequent mechanistic studies by Nicolaou[7] and others[8−12] resulted in the conclusion that their biological activity was due to an alternative mechanism, the Maxam-Gilbert[13] mechanism, involving nucleophilic addition of DNA to the diallenyl sulfones. In fact, this conclusion is hardly surprising in view of the relatively high temperature required for the diallenyl sulfone cyclization.[6]

It is well documented that introduction of various functional groups such as crown ethers or β-dicarbonyl moieties into intercalating molecules, which can form cationic complexes with metal ions, may increase the overall binding properties of these molecules to DNA, which is an anionic polymer.[14−19] This so-called metal ion assisted DNA intercalation gave chemists a new tool for modification of the DNA-cleaving ability of commonly known enediynes[20−24] and propargyl sulfones.[25−27] Konig and Pitsch, for example, reported activation of enediyne macrocycles towards Bergman cyclization by mercury(II) coordination,[28] the cyclization temperature of the coordinated macrocycle being nearly 100 °C lower than that required for the macrocyclic enediyne itself. Subsequently, Basak and Shain reported a similar decrease in temperature for a Bergman cyclization upon complexation.[29]

During the last decade, an interesting cyclization process for nonconjugated diynes has been thoroughly studied, both chemically and by quantum mechanical methods, by Gleiter et al.[30−33] Thus, thermally induced transannular alkyne coupling of strained ten-membered cyclic diynes in the presence of various H-donors affords bicyclic *s-trans*-butadiene products by generation of the corresponding 1,4-diradicals.

We have recently investigated base-catalyzed rearrangements of appropriately substituted π-conjugated bis(propargyl) sulfones and tested their biological activities.[34,35] We have thus found that, in the presence of triethylamine in $CHCl_3$ at room temperature, bis(γ-phenylpropargyl) sulfone (**1**) undergoes a spontaneous and quantitative tandem rearrangement, cyclization, and aromatization to the naphthalene derivative **3**, apparently through formation of a diradical intermediate **2** (Scheme 1). As one may expect from its facile base-catalyzed diradical cyclization, sulfone **1** exhibits DNA-cleaving activity.[35]

In view of these results, and keeping in mind the possibility of a Maxam-Gilbert mechanism for the DNA-cleaving activity of diallenyl sulfones, we decided to extend the scope

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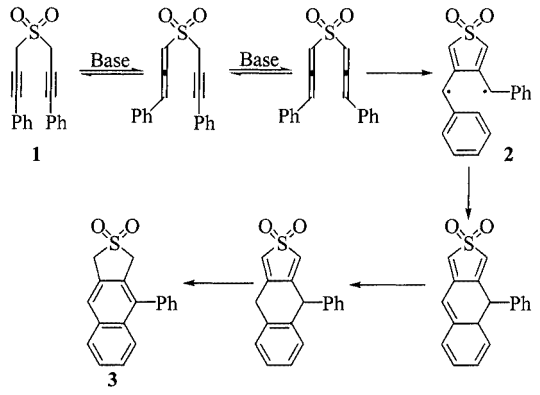


Scheme 1

of our investigations by incorporation of the dipropargylic system into suitable medium-sized cyclic structures (**4**−**8**; Figure 1) in order to compare their reactivities with those of the acyclic sulfur-bridged propargylic systems. Furthermore, we also wished to study the effect of the nature of the bridge and the size of the cycle on the reactivity of these systems.

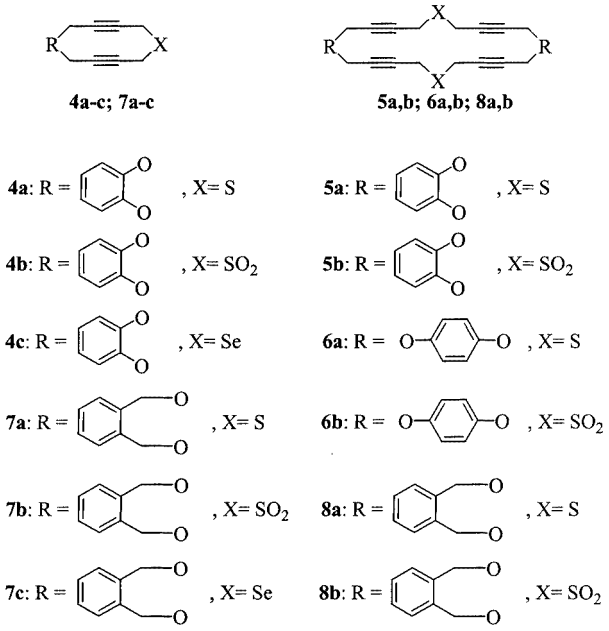


Figure 1. Sulfur and selenium-bridged cyclic alkynes

Base-Catalyzed Reactivity of Cyclic Dipropargyl Sulfones and Bis(dipropargyl) Disulfones

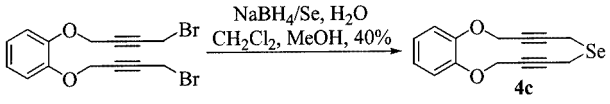
Examination of the base-catalyzed reactivities of the dipropargyl and bis(dipropargyl) compounds presented in Figure 1 revealed that their reactivity strongly depended on the nature of the bridge as well as on the nature of the base and solvent used (Table 1). As far as the first quality is concerned, the remarkable differences in the reactivities of the sulfones **4b**−**8b** (Table 1, Entries 3, 8, 9, and 14) and corresponding sulfides (Table 1, Entries 1, 6, 10, 12, and 17) and selenides (Table 1, Entries 4 and 15) are worthy of note. Bis(sulfone) **8b** decomposed even in the presence of weak bases such as Et_3N or DABCO in $CHCl_3$, apparently due to nucleophilic attack of the base on the allenic intermediate. Treatment of monosulfones **4b** and **7b** even with 0.2 equiv. of DBU in chloroform also resulted in very fast decomposition. However, use of triethylamine resulted in the fast formation of an inseparable mixture of mono- and bis(allenyl) derivatives **9**, **10** and **11**, **12** (Scheme 3). Interestingly, unlike the case of acyclic dipropargyl sulfones,[35] we were able not only to detect these allenyl sulfones, but even to isolate them.

Bis(allenyl) derivatives **11** and **12** were in turn formed as mixtures of *dl* and *meso* isomers. For compounds **9**, *meso*-**11**, and *dl*-**11**, full structural assignments were made by 2D NMR experiments.

No diradical cyclization was achieved under any set of conditions. Apparently, these sulfones could not be cyclized to the corresponding thiophene dioxides, due to the lack of stability of the expected diradical intermediate. As regards sulfone **5b**, treatment with triethylamine or DABCO (Table 1, Entries 8 and 9) resulted in the formation of a new product, identified by 2D NMR experiments as bis[methylene-2-(2*H*-1,5-benzodioxepinyl)] sulfone (**13**) (Scheme 4).

Results and Discussion

The cyclic propargyl sulfides **4a**, **6a**, and **7a** were synthesized by treatment of the corresponding dibromides with sodium sulfide nonahydrate under high-dilution conditions.[36] The cyclic bis(dipropargyl) disulfides **5a** and **8a** were prepared by a base-induced reaction between the corresponding bis(mesylates) and bis(thioacetates).[36] All these sulfides (**4a**−**8a**) were then oxidized with MCPBA in high yields to the corresponding sulfones **4b**−**8b**. The 13-membered cyclic selenide **4c** and the 15-membered cyclic selenide **7c** were obtained by treatment of a CH_2Cl_2/MeOH solution of the corresponding dipropargyl dibromide with an aqueous solution of sodium hydroselenide under high-dilution conditions (Scheme 2).[37]



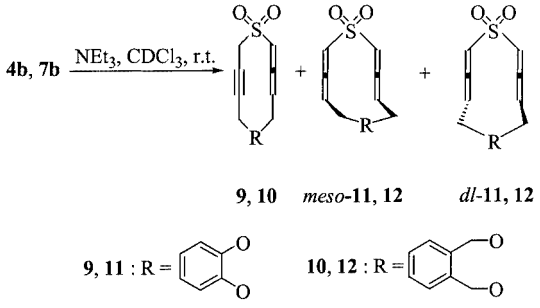
Scheme 2

No experimental evidence in support of a detailed mechanism for the conversion of bis(dialkynyl) disulfone **5b** into **13** was obtained. However, the formation of the latter by a double intramolecular nucleophilic addition of the bis(phenolate) anion precursor **15** is not unreasonable in view of the well-known reactivity of allenyl sulfones in heteroconjugate addition reactions in general.[38,39] We assume that the intermediate **15** may in turn arise from a tandem base-induced isomerization of **5b** to **14**, with subsequent

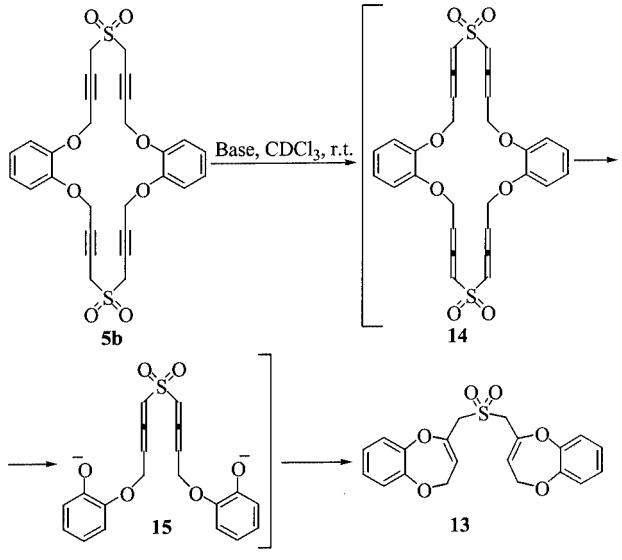
Table 1. Base-catalyzed reactivities of *S*- and *Se*-bridged cyclic alkynes at room temperature

Entry	Alkyne	Base	Solvent	Time [h]	Product (ratio)	Yield (%)
1	**4a**	DBU	DMSO	4	*Z*-**16** + *E*-**16** (9:1)	82[a]
2	**4a**	*t*BuOK	THF	1	**28**	81
3	**4b**	Et_3N	$CHCl_3$	4	**9** + *meso*-**11** + *dl*-**11** (2.6:2.2:1)	40[a] [b]
4	**4c**	DBU	DMSO	48	**18**	74
5	**4c**	*t*BuOK	THF	1	**29**	65
6	**5a**	DBU	DMSO	15	**20** + **21** (1:1)	82[a]
7	**5a**	*t*BuOK	THF	0.5	**28**	75
8	**5b**	DABCO[c]	DMSO	0.25	**13**	35
9	**5b**	Et_3N [c]	DMSO	4	**13**	39
10	**6a**	DBU	DMSO	6	**22** + **23** (1:1)	80[a]
11	**6a**	*t*BuOK	THF	0.75	**22** + **23** + **28** (1:10:6)	65[a]
12	**7a**	DBU	DMSO	48	*E*-**17**	55
13	**7a**	*t*BuOK	THF	0.25	*Z*-**26** + *E*-**26** (9:1)	78[a]
14	**7b**	Et_3N	$CDCl_3$	8	**10** + **12** (3:7)	80[a] [b]
15	**7c**	DBU	DMSO	120	**19**	67
16	**7c**	*t*BuOK	THF	0.25	**27**	76
17	8a	DBU	DMSO	19	**24** + **25** (0.9:1)	80[a]
18	**8a**	*t*BuOK	THF	1	**24** + **25** (0.9:1)	71[a]

[a] Total yield for all products. [b] The ratio of the products was determined by NMR. [c] 2.5 equiv. of base was used.



Scheme 3



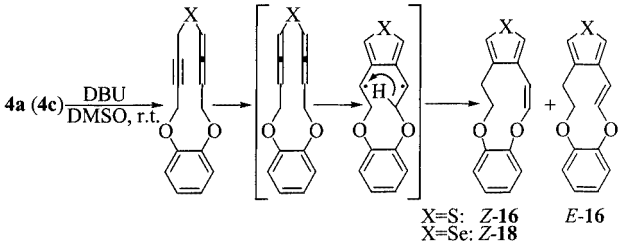
Scheme 4

fragmentation of the latter to **15**. It should be noted that, in the presence of DABCO, a weaker base but a stronger nucleophile, the reaction was practically instantaneous (Table 1, Entry 8), whereas with Et_3N it took about 4 h to be completed (Table 1, Entry 9).

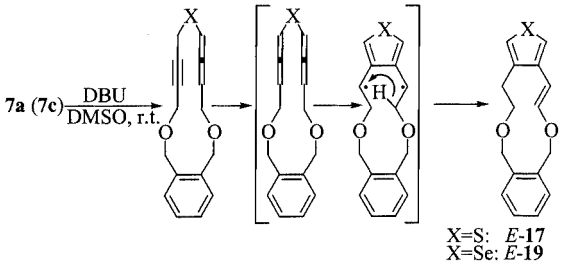
It should also be noted that allenyl sulfones **4b**, **5b**, and **7b** exhibit DNA-cleaving properties (vide infra).

Base-Catalyzed Reactivity of Cyclic Dipropargyl Sulfides and Selenides and Bis(dipropargyl) Disulfides and Diselenides: Radical Cyclization

As mentioned previously, sulfides **4a**−**8a** differ sharply from the corresponding sulfones in their base-catalyzed reactivity. We have thus found that the nature of base used has a drastic effect on the mechanism of the tandem isomerization and cyclization reaction. Because of their much lower α-hydrogen acidity relative to the corresponding sulfones, the sulfides all underwent no change in the presence of triethylamine for several days. However, treatment of sulfides **4a** and **7a** with DBU in DMSO (Table 1, Entries 1 and 12) at room temperature resulted in tandem isomerization and cyclization, with formation of the tricyclic thiophene derivatives **16** and **17**, respectively (Schemes 5 and 6). The mechanism of these reactions is shown in the Schemes and is postulated to involve diradical intermediates, stabilized by the formation of the aromatic thiophene ring. Formation of monoallenic species was detected by NMR during the course of the reactions.



Scheme 5



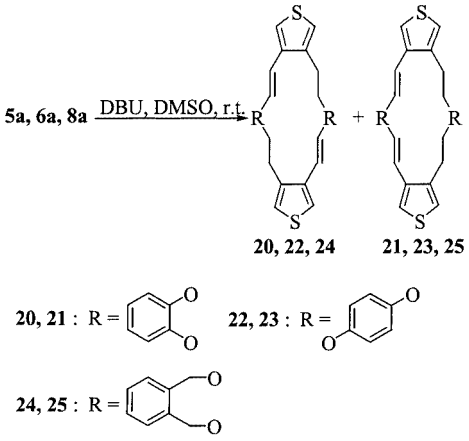
Scheme 6

Selenides **4c** and **7c** reacted with DBU in DMSO in a similar manner to sulfides **4a** and **7a**, with the formation of selenophene derivatives **18** and **19**, respectively, but the reaction was much slower (Schemes 5 and 6). Whilst the reaction between sulfide **4a** and DBU had required 4 h (Table 1, Entry 1), the analogous reaction of selenide **4c** was complete only after 2 d (Table 1, Entry 4). This may be explained by the lower acidity of the α-hydrogen atoms relative to those in the sulfur analogs.[40]

The presence of the methylene spacers in sulfide **7a** had a great effect on the rate of the reaction. Thus, the reaction of sulfide **4a** was complete after 4 h, whereas the analogous reaction of **7a** required 2 d (Table 1, Entry 12). We had previously shown[34,35] that acetylene/allene isomerization of sulfur-bridged acyclic systems depends on substitution at the γ-position of the propargyl unit, steric hindrance slowing down the reaction. The additional methylene groups in **7a** provide more flexibility to the molecule, and the γ-position is therefore sterically more hindered.

The presence of the methylene groups in **7a** affects the stereochemical outcome of the reaction as well. Thus, while the tricyclic compound **16** was obtained as a mixture of (*Z*) and (*E*) isomers in a ratio of 9:1, only the (*E*) isomer was isolated with compound **17**. In compound **16**, formation of the (*Z*) isomer is favored by the more strained central 10-membered ring, with 6 sp^2-carbon atoms. In compound **17**, on the other hand, the flexibility of the 12-membered central ring facilitates the formation of the (*E*) isomer.

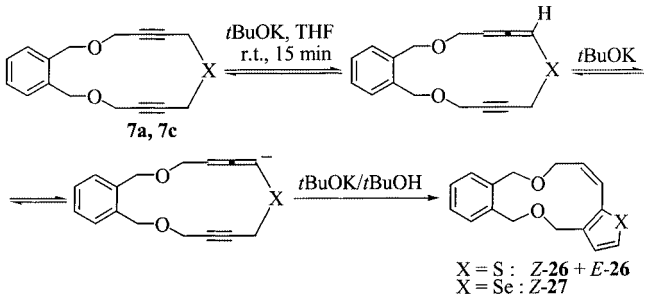
The bis(sulfides) **5a**, **6a**, and **8a** reacted with DBU (Table 1, Entries 6, 10, 17) in the same manner as described above for the monosulfides **4a** and **7a**, by tandem isomerization and radical cyclization to form the bis(thiophene) derivatives **20**−**25** (Scheme 7). In all cases the double bond had the (*E*) configuration. These bis(thiophene) derivatives, which were formed as mixtures of regioisomers, differ in the position of the double bonds in the central ring. Since compounds **21** and **23** are much more soluble in acetone than their partners **20** and **22**, we successfully achieved the separation of the corresponding regioisomers by fractional crystallization from acetone. In the case of benzylic derivatives, however, the pair **24**/**25** was obtained as an inseparable mixture of isomers. For the structural assignment of these compounds we used 2D NMR analysis, and here the AA′BB′ pattern of the symmetrically *o*-disubstituted benzene rings in **25** was of great assistance.



Scheme 7

Base-Catalyzed Reactivities of Cyclic Dipropargyl Sulfides and Selenides and Bis(dipropargyl) Disulfides and Diselenides: Anionic Cyclization

Surprisingly, we have found that a different kind of cycloaromatization takes place on use of a stronger base, *t*BuOK in dry THF. Sulfide **7a** (Table 1, Entry 13) and selenide **7c** (Table 1, Entry 16) react almost spontaneously, with formation of 2-vinylthiophene **26** and 2-vinylselenophene **27**, respectively (Scheme 8). The same kind of products were first observed on treatment of sulfur- and selenium-bridged acyclic dipropargylic systems with *t*BuOK, and an anionic mechanism was suggested for this reaction.[41] Although the full details of this unusual cycloaromatization are still under investigation, we assume that the reaction involves a series of steps, initiated by a base-catalyzed acetylene-to-allene isomerization and followed by deprotonation of the allenyl group, similarly to what has been observed by Brandsma et al. with allenyl sulfides.[42−44] The generated allenyl anion may than undergo cyclization through intramolecular attack on the second acetylenic group, similarly to that recently observed by Schwan et al. during the cyclization of benzyl propargyl sulfides to 2-aryl-2,3-dihydrothiophenes.[45] A base-catalyzed rearrangement of a bis(allenyl) system, bis(γ,γ-dimethylallenyl) sulfone, had been observed by us previously, this compound undergoing cyclodimerization to an adamantane derivative, 2,4,6,8-tetrakis(2-methylpropen-1-yl)-9λ^6,10λ^6-dithiatricyclo[3.3.1.1^{3,7}]decane-9,10-tetraone in the presence of *n*-butyllithium.[46] In a similar manner to that described above, the formation of

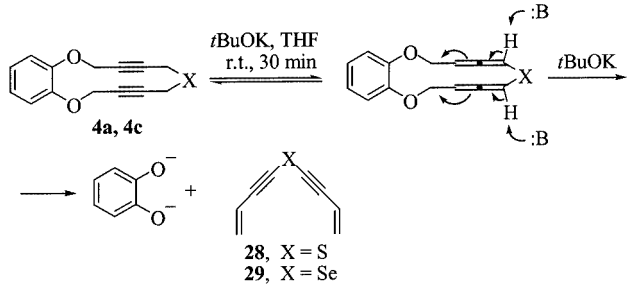


Scheme 8

the adamantane derivative is initiated by the formation of α-sulfonyl carbanion. In this case, however, deprotonation is followed by an intermolecular nucleophilic attack of α-sulfonyl carbanion onto one of the β-allenyl carbon atoms in the second molecule.

Interestingly, 2-vinylthiophene **26** was obtained as a mixture of (*Z*) and (*E*) isomers in a 9:1 ratio, whereas for 2-vinylselenophene **27** only the (*Z*) isomer could be detected in the ^{1}H NMR spectrum of the crude reaction mixture. The same preference for the formation of (*Z*) isomers was observed for the acyclic bridged dipropargylic systems.[41] One should note that, under the same set of conditions (*t*BuOK/THF), benzyl bis(sulfide) **8a** reacts by an usual radical mechanism with the formation of a mixture of **24** and **25** (Table 1, Entry 18). Most probably, the geometry of the less hindered bis(benzylic) derivative in this case is more favorable to the cycloaromatization process by the free radical mechanism. It is noteworthy that, although bridged dipropargylic systems have been investigated in the past by Garratt et al.,[47−49] Iwai et al.,[50] and Ollis et al.[51−53] under practically identical conditions, this kind of cycloaromatization has never been observed before.

Finally, and in contrast to the results described above, sulfide **4a** and selenide **4c** reacted with *t*BuOK in dry THF with formation of bis(3-buten-1-ynyl) sulfide and selenide (**28** and **29**), respectively (Scheme 9). In this case, the good leaving group ability of the pyrocatechol dianion is of crucial importance for the reaction mechanism and results in fragmentation of the deprotonated bis(allene) rather than the intramolecular nucleophilic attack (Scheme 9).

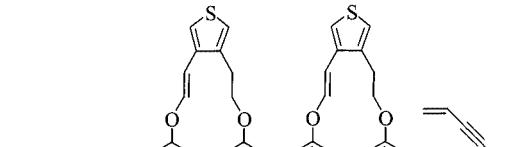


Scheme 9

The behaviour of bis(sulfides) under the same conditions was also investigated. Whereas bis(sulfide) **5a** reacted with *t*BuOK in exactly the same manner as **4a**, affording **28** in good yield, bis(sulfide) **6a** afforded a mixture of **28** together with the diradical cyclization products **22** and **23** (Table 1, Entry 11; Scheme 10). The formation of **22** and **23** is presumed to take place in a similar way to the behaviour of benzyl derivative **8a**, by a free radical process that is enhanced by a favorable geometry of the intermediate allenic species.

DNA-Cleaving Activity

The DNA-cleaving properties of the dipropargyl sulfones **4b** and **7b** and the bis(dipropargyl) disulfone **5b** were assayed with double-stranded supercoiled ΦX174 form I DNA in 10% DMSO-Tris-HCl at pH = 8.5. Aerobic incubation of all three tested sulfones with ΦX174 form I DNA at 37 °C produced cleaved DNA, as shown by gel electrophoresis analysis (Figure 2). Bis(sulfone) **5b**, which is most reactive under basic conditions (DABCO, $CHCl_3$) and the reactivity of which is explained in the terms of nucleophilic addition, is also the compound with the best DNA-cleaving properties. Since these sulfones **4b**, **7b**, and **5b** do not undergo cycloaromatization under any set of basic conditions, a diradical mechanism of DNA cleavage can be ruled out. The Maxam-Gilbert mechanism, involving nucleophilic addition of DNA to the diallenyl sulfones, indeed appears to be responsible for their biological activity.



Scheme 10

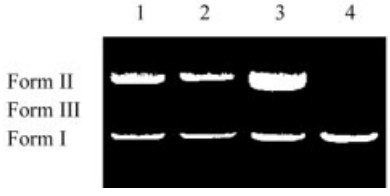


Figure 2. DNA cleavage by sulfones **4b**, **7b**, and **5b**; ΦX 174 form I DNA (50 μM per base pair) was incubated for 24 h at 37 °C with compounds **4b**, **7b**, and **5b** in 10% DMSO in tris-HCl buffer (pH = 8.5, 50 mM) and analyzed by electrophoresis (1% agarose gel, ethidinium bromide stain); lanes 1−3 correspond to DNA and sulfone **4b**, **7b** and **5b**, respectively; lane 4 corresponds to DNA alone; forms I, II, and III correspond to supercoiled, relaxed, and linear DNA, respectively

Experimental Section

General Remarks: Melting points were obtained with a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded with a Nicolet 60 SXB FTIR. ^{1}H NMR and ^{13}C NMR were recorded with Bruker DPX 300 or DMX 600 spectrometers with TMS as internal standard. Chemical shifts are reported in ppm downfield from tetramethylsilane. High-resolution mass spectra were obtained with a VG-Fison AutoSpec instrument and other mass spectra with a Finnigan GC/MS 4021 instrument by chemical ionization (CI) or electron impact (EI). Column chromatography was performed with Merck 60 silica gel (230−240 mesh), and preparative thin layer chromatography was carried out on glass sheets precoated with Merck 60 F254 silica gel (0.25 mm). All solv-

ents and reagents were obtained from Aldrich or Fluka and used without further purification, with the exception of THF, which was distilled from Na under nitrogen.

General Procedure for the Preparation of Cyclic Sulfides: The cyclic sulfides were prepared by two alternative methods. Sulfides **4a**, **6a**, and **7a** were prepared by method A and sulfides **5a** and **8a** by method B.

Method A: This method is illustrated with the preparation of sulfide **4a**: A solution of $Na_2S\ 9H_2O$ (0.24 g, 1 mmol) in H_2O (50 mL) was added whilst stirring, over a period of 6 h, to a solution of 1,2-bis(4-bromobut-2-ynyloxy)benzene (0.37 g, 1 mmol) in CH_2Cl_2/MeOH (1:1, 500 mL). The mixture was stirred at room temperature for 24 h and then concentrated under reduced pressure to the volume of ca. 50 mL. Extraction with CH_2Cl_2 (2 × 50 mL) followed by washing with water (2 × 50 mL) and drying with $MgSO_4$ gave the crude product, which was purified by column chromatography on silica gel with CH_2Cl_2/hexane (2:1) as eluent. An analytical sample was obtained by recrystallization from $CHCl_3$/hexane; m.p. 93−94 °C (white crystals), yield 0.073 g (30%). IR (KBr): $\tilde{\nu}$ = 1506, 1450, 1374, 1250, 1209, 1123, 1014, 738 cm^{-1}. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 3.39 (t, *J* = 2.0 Hz, 4 H), 4.91 (t, *J* = 2.0 Hz, 4 H), 6.97 & 7.08 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 21.1 (CH_2S), 57.5 (CH_2O), 77.6 & 84.4 (C≡C), 118.6 & 122.5 (CH_{arom}), 148.5 (C-*ipso*) ppm. MS (EI): *m*/*z* (%) = 244(100) [M^+], 198 (27), 160 (25), 136 (51), 103 (35), 91 (86). HRMS ($C_{14}H_{12}O_2S$): calcd. 244.055802; found 244.054000. $C_{14}H_{12}O_2S$ (244.3): calcd. C 68.83, H 4.95, S 13.13; found C 68.62, H 4.99, S 12.96.

Compound 6a: M.p. 216 °C (white crystals, from $CHCl_3$), yield 0.17 g (35%) [flash chromatography, CH_2Cl_2/hexane (3:1)]. IR (KBr): $\tilde{\nu}$ = 1507, 1376, 1200, 1007, 818 cm^{-1}. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 3.37 (t, *J* = 2.2 Hz, 8 H), 4.79 (t, *J* = 2.2 Hz, 8 H), 6.99 (s, 8 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 18.2 (CH_2S), 56.1 (CH_2O), 78.7 & 82.6 (C≡C), 116.1 (CH_{arom}), 151.5 (C-*ipso*) ppm. MS (CI NH_3): *m*/*z* (%) = 506 (100) [MNH_4^+], 489 (6.5) [MH^+], 374 (8), 212 (7), 161 (7.2). HRMS ($C_{28}H_{24}O_4S_2$): calcd. 488.111603; found 488.111585. $C_{28}H_{24}O_4S_2$ (488.6): calcd. C 68.83, H 4.95, S 13.13; found C 68.70, H 4.89, S 13.02.

Compound 7a: Yield 0.19 g (70%) [viscous oil, flash chromatography, eluent CH_2Cl_2/hexane (2:1)]. IR (neat): $\tilde{\nu}$ = 1713, 1352, 1069, 757 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.61 (t, *J* = 2.0 Hz, 4 H), 4.29 (t, *J* = 2.0 Hz, 4 H), 4.75 (s, 4 H), 7.32 & 7.42 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.3 (CH_2S), 57.6 (CH_2), 68.0 (CH_2), 80.2 & 81.9 (C≡C), 128.1 & 129.3 (CH_{arom}), 136.0 (C-*ipso*). MS (CI CH_4): *m*/*z* (%) = 272 (7) [M^+], 225 (10), 179 (18), 171 (59), 153 (17), 151 (21), 135 (21), 119 (48), 104 (82), 91 (100). HRMS ($C_{16}H_{16}O_2S$): calcd. 272.087102; found 272.086319.

Method B: This method is illustrated with the preparation of sulfide **5a**. A solution of KOH (0.5 g, 9 mmol) in MeOH (100 mL) was added dropwise to a solution of 1,2-bis[4-(mesyloxy)but-2-ynyloxy]benzene (0.9 g, 2.25 mmol) and 1,2-bis[4-(thioacetyloxy)but-2-ynyloxy]benzene (0.82 g, 2.25 mmol) in THF/MeOH (1:1, 1000 mL), and the mixture was stirred at room temp. for 4 h and then concentrated under reduced pressure to a volume of ca. 50 mL. Extraction with CH_2Cl_2 (2 × 50 mL) followed by washing with water (2 × 50 mL) and drying with $MgSO_4$ gave a crude product, which was recrystallized from $CHCl_3$. M.p. 141−142 °C; yield 0.35 g (32%). IR (KBr): $\tilde{\nu}$ = 1591, 1502, 1375, 1251, 1214, 1122, 1008, 736 cm^{-1}. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 3.39 (t, *J* = 2.1 Hz, 8 H), 4.8 (t, *J* = 2.1 Hz, 8 H), 6.94 & 7.05 (AA′BB′ system, 8 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 18.5 (CH_2S), 56.7 (CH_2O), 78.4 & 82.5 (C≡C), 115.6 (C-*ortho*), 121.9 (C-*meta*), 146.9 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 489 (33) [MH^+], 447 (10), 211 (27), 161 (100), 111 (37). HRMS ($C_{28}H_{25}O_4S_2$): calcd. 489.119428; found 489.117173. $C_{28}H_{24}O_4S_2$ (488.6): calcd. C 68.83, H 4.95, S 13.13; found C 68.67, H 4.87, S 12.94.

Compound 8a: Yield 0.24 g (20%) [viscous oil, flash chromatography, eluent EtOAc/hexane (1:5)]. IR (neat): $\tilde{\nu}$ = 1452, 1355, 1225, 1175, 1132, 1073, 947, 756 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.53 (t, *J* = 2.1 Hz, 8 H), 4.27 (t, *J* = 2.1 Hz, 8 H), 4.69 (s, 8 H), 7.29 & 7.37 (AA′BB′ system, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.4 (CH_2S), 57.8 (CH_2), 69.0 (CH_2), 79.3 & 81.7 (C≡C), 128.1 &129.1 (CH_{arom}), 135.9 (C-*ipso*) ppm. MS (CI CH_4): *m*/*z* (%) = 545 (4) [MH^+], 225 (11), 171 (14), 141 (34), 135 (31), 128 (16), 119 (100), 105 (46), 91 (64). HRMS ($C_{32}H_{33}O_4S_2$): calcd. 545.182028; found 545.183405.

General Procedure for the Preparation of Cyclic Sulfones: A solution of MCPBA (1.5 mmol, 65%) in CH_2Cl_2 (5 mL) was added dropwise, whilst stirring, to a solution of cyclic sulfide (0.5 mmol) in CH_2Cl_2 (10 mL). After 12 h at room temp., the reaction mixture was washed with a solution of 5% KI (2 × 10 mL), then 5% $Na_2S_2O_3$ (2 × 10 mL) and 5% $NaHCO_3$ (2 × 10 mL), and finally with water. The organic solution was dried with anhydrous $MgSO_4$ and the solvents were evaporated to give crude sulfone as a white solid, which was purified by recrystallization.

Cyclic Sulfone 4b: M.p. 176−177 °C (white crystals, from $CHCl_3$), yield 0.11 g (82%). IR (KBr): $\tilde{\nu}$ = 1494, 1329, 1271, 1239, 1125, 974, 769 cm^{-1}. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 4.19 (t, *J* = 2.0 Hz, 4 H), 4.97 (t, *J* = 2.0 Hz, 4 H), 6.99 & 7.07 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 46.2 (CH_2SO_2), 57.5 (CH_2O), 75.9 & 82.2 (C≡C), 119.6 (C-*ortho*), 122.9 (C-*meta*), 149.2 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 276 (100) [M^+], 183 (11), 160 (42), 121 (13), 110 (12). HRMS ($C_{14}H_{12}O_4S$): calcd. 276.045631; found 276.046424. $C_{14}H_{12}O_4S$ (276.3): calcd. C 60.86, H 4.38, S 11.61; found C 60.59, H 4.25, S 11.38.

Cyclic Sulfone 5b: M.p. 231−232 °C (white crystals, from acetone), yield 0.112 g (86%). IR (KBr): $\tilde{\nu}$ = 1592, 1500, 1457, 1325, 1250.1123, 1006, 745 cm^{-1}. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 4.08 (t, *J* = 1.8 Hz, 8 H), 4.88 (t, *J* = 1.8 Hz, 8 H), 6.98 & 7.08 (AA′BB′ system, 8 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 44.2 (CH_2SO_2), 57.4 (CH_2O), 76.1 & 83.7 (C≡C), 116.5 (C-*ortho*), 123.1 (C-*meta*), 148.5 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 552 (45) [M^+], 387 (10), 298 (25), 260 (100), 186 (92). HRMS ($C_{28}H_{24}O_8S_2$): calcd. 552.091262; found 552.095367. $C_{28}H_{24}O_8S_2$ (552.6): calcd. C 60.86, H 4.38, S 11.61; found C 60.63, H 4.19, S 11.45.

Cyclic Sulfone 6b: M.p. 209−210 °C (dec.) (white crystals, from $CHCl_3$); yield 0.12 g (89%). IR (KBr): $\tilde{\nu}$ = 1506, 1332, 1234, 1199, 1133, 1031, 984 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 4.24 (t, *J* = 2.0 Hz, 4 H), 4.81 (t, *J* = 2.0 Hz, 4 H), 6.94 (s, 4 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 43.8 (CH_2SO_2), 56.5 (CH_2O), 75.7 & 83.3 (C≡C), 116.6 (CH_{arom}), 152.1 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 552 (15) [M^+], 298 (29), 260 (95), 186 (100). HRMS ($C_{28}H_{24}O_8S_2$): calcd. 552.091262; found 552.093754. $C_{28}H_{24}O_8S_2$ (552.6): calcd. C 60.86, H 4.38, S 11.61; found C 60.68, H 4.30, S 11.39.

Cyclic Sulfone 7b: M.p.161−163 °C (white crystals, from $CHCl_3$/hexane); yield 0.14 g (60%). IR (neat): $\tilde{\nu}$ = 1318, 1248, 1141, 1123,

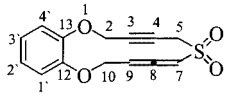
1071, 754 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.24 (t, *J* = 2.0 Hz, 4 H), 4.33 (t, *J* = 2.0 Hz, 4 H), 4.72 (s, 4 H), 7.33 & 7.39 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 44.7 (CH_2SO_2), 57.4 (CH_2), 69.1 (CH_2), 74.5 & 84.9 (C≡C), 128.5 & 129.6 (CH_{arom}), 135.5 (C-*ipso*) ppm. MS (CI, CH_4): *m*/*z* (%) = 305 (5) [MH^+], 171 (62), 143 (53), 119 (100), 91 (70). HRMS ($C_{16}H_{17}O_4S$): calcd. 305.084756; found 305.083008. $C_{16}H_{16}O_4S$ (304.3): calcd. C 63.14, H 5.30, S 10.54; found C 62.94, H 5.21, S 10.26.

Cyclic Sulfone 8b: M.p.182−183 °C (white crystals, from acetone); yield 0.09 g (83%). IR (neat): ṽ = 1322, 1130, 1078, 751 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 4.31 (t, *J* = 2.0 Hz, 8 H), 4.49 (t, *J* = 2.0 Hz, 8 H), 4.60 (s, 8 H), 7.30 & 7.35 (AA′BB′ system, 8 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 44.3 (CH_2SO_2), 57.7 (CH_2), 68.8 (CH_2), 74.9 & 84.3 (C≡C), 128.2 &129.0 (CH_{arom}), 136.3 (C-*ipso*) ppm. $C_{32}H_{32}O_8S_2$ (608.7): calcd. C 63.14, H 5.30, S 10.54; found C 62.91, H 4.99, S 10.26.

Cyclic Selenide 4c: A solution of NaHSe, obtained by addition, under N_2, of a solution of $NaBH_4$ (0.120 g) in water (10 mL) to a suspension of Se (0.115 g) in H_2O (15 mL), was added under N_2 to a solution of 1,2-bis(4-bromobut-2-ynyloxymethyl)benzene (1 mmol) in CH_2Cl_2/MeOH (1:2, 150 mL) over 1 h at room temp. The reaction mixture was stirred at room temp. overnight, extracted with CH_2Cl_2 (2 × 25 mL), washed with H_2O, and dried with $MgSO_4$, and the solvents were evaporated under reduced pressure to give the product; m.p. 220−221 °C (dec.), 0.12 g (40%) [yellow pale crystals, column chromatography with CH_2Cl_2/hexane (3:1) as eluent]. IR (KBr): ṽ = 1495, 1362, 1234, 1189, 1110, 984 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.33 (t, *J* = 2.0 Hz, 4 H), 4.87 (t, *J* = 2.0 Hz, 4 H), 6.99 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 10.2 (CH_2Se, $J_{C\text{-}Se}$ = 32.5 Hz), 58.5 (CH_2O), 78.1 & 84.8 (C≡C), 118.4 (C-*ortho*), 122.9 (C-*meta*), 148.6 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 291.2 (17) [M^+], 280 (31), 231 (47), 219 (62), 175 (65), 169 (67), 131 (68), 117 (100). HRMS ($C_{14}H_{12}O_2{}^{80}Se$): calcd. 292.000250; found 291.999106. $C_{14}H_{12}O_2Se$ (291.2): calcd. C 57.74, H 4.15; found C 57.55, H 4.02.

Cyclic Selenide 7c: This compound was obtained by the above procedure as a viscous oil, yield 0.25 g (77%), and used without any purification; an analytically pure sample was obtained by flash chromatography on silica gel with CH_2Cl_2/hexane (3:1) as eluent. IR (KBr): ṽ = 1360, 1325, 1193, 1095, 760 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.56 (t, *J* = 2.0 Hz, 4 H), 4.30 (t, *J* = 2.0 Hz, 4 H), 4.76 (s, 4 H), 7.31 & 7.39 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 8.5 (CH_2Se, $J_{C\text{-}Se}$ = 32.5 Hz), 57.6 (CH_2), 68.0 (CH_2), 80.0 & 83.1 (C≡C), 128.2 &129.1 (CH_{arom}), 136.0 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 321 (5) [MH^+], 251 (59), 209 (52), 199 (60), 193 (42), 181 (44), 171 (100), 159 (40). HRMS ($C_{16}H_{17}O_2{}^{80}Se$): calcd. 321.039375; found 321.039688.

General Procedure for Base-Catalyzed Isomerization, Cyclization, and Aromatization: This procedure refers to all of the sulfur- or selenium-bridged propargylic systems **4**−**8**, while the exact conditions and reaction times are as shown in Table 1. The base (2 or 4 equiv. unless otherwise specified) was added to a solution of the appropriate dipropargylic or bis(dipropargylic) system, respectively (1 mmol), in 10 mL of solvent. After stirring at room temperature for the appropriate time, the reaction mixture was diluted with dichloromethane (when DMSO or THF were used as a solvent) and washed three times with water. The organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The products were purified by column or preparative thin layer chromatography. The data for all products are listed below.



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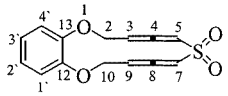

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Compound 9: IR (neat): ṽ = 1967, 1501, 1454, 1317, 1262, 1126, 1048, 755 cm^{-1} (IR of the mixture **9**, *dl*-**11** and *meso*-**11**). ^1H NMR ([D$_6$]acetone, 600 MHz): δ = 4.00 (dtd, *J* = 17.5, 2.0, 1.0 Hz, 1 H, 5-H), 4.13 (dt, *J* = 17.5, 2.5 Hz, 1 H, 5-H), 4.83 (dd, *J* = 16.0, 2.5 Hz, 1 H, 2-H), 4.86 (dd, *J* = 16.0, 2.0 Hz, 1 H, 2-H), 4.88 (dt, *J* = 15.5, 4.0 Hz, 1 H, 10-H), 4.93 (dtd, *J* = 15.5, 4.5, 4.0 Hz, 1 H, 10-H), 6.26 (m, 2 H, 7-H & 9-H), 6.93 (m, 1 H, 3′-H), 7.01 (m, 2 H, 1′,2′-H), 7.09 (m, 1 H, 4′-H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 46.6 (C-5), 59.7 (C-2), 63.1 (C-10), 75.8 & 82.9 (C-4 & C-3), 97.2 (C-9), 98.8 (C-7), 115.0 (C-1′), 120.7 (C-4′), 121.7 (C-3′), 123.8 (C-2′), 147.5 (C-13), 149.7 (C-12), 206.7 (C-8) ppm.

Compound *dl*-11: ^1H NMR ([D$_6$]acetone, 600 MHz): δ = 4.70 (t, *J* = 4.0 Hz, 2 H, 10-H), 6.29 (dt, *J* = 6.0, 4.0 Hz, 1 H, 9-H), 6.62 (dt, *J* = 6.0, 4.0 Hz, 1 H, 7-H), 6.98 & 7.06 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 65.4 (C-10), 98.5 (C-9), 102.6 (C-7), 116.8 (C-4′, 1′), 122.7 (C-3′, 2′), 148.9 (C-12, 13), 204.3 (C-8) ppm.

Compound *meso*-11: ^1H NMR ([D$_6$]acetone, 600 MHz): δ = 4.44 (ddd, *J* = 14.0, 4.5, 3.5 Hz, 1 H, 10-H), 4.93 (ddd, *J* = 14.0, 4.5, 3.0 Hz, 1 H, 10-H), 6.29 (ddd, *J* = 6.0, 4.5, 3.0 Hz, 1 H, 9-H), 6.66 (ddd, *J* = 6.0, 4.5, 3.5 Hz, 1 H, 7-H), 6.95 & 7.04 (AA′BB′ system, 4 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 64.7 (C-10), 98.0 (C-9), 103.0 (C-7), 114.6 (C-1′, 4′), 121.8 (C-3′, 2′), 148.8 (C-12, 13), 205.5 (C-8) ppm.

Bis[methylene-2-(2-*H*-1,5-benzodioxepinyl)] Sulfone (13): M.p. 84−85 °C (white crystals, from methanol), yield 0.15 g (39%). IR (neat): ṽ = 1597, 1494, 1327, 1252, 1119, 759 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 4.19 (s, 4 H, CH_2SO_2), 4.62 (d, *J* = 4.0 Hz, 4 H, 4-H), 5.40 (t, *J* = 4.0 Hz, 2 H, 3-H), 7.07 (m, 6 H, H_{arom}), 7.17 (m, 2 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 60.1 (CH_2SO_2), 70.0 (C-4), 111.1 (C-3), 122.3, 123.5, 125.2 & 125.9 (C_{ar}), 144.9 (C-2), 151.0 & 151.1 (C-*ipso*) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) =386 (18) [M^+], 322 (15) [$M^+ - SO_2$], 277 (6), 213 (11), 161 (14), 147 (100). HRMS ($C_{20}H_{18}O_6S$): calcd. 386.082410; found 386.082720. $C_{20}H_{18}O_6S$ (386.4): calcd. C 62.16, H 4.70, S 8.30; found C 61.90, H 4.52, S 8.04.

2,12-Dioxa-7-thiatricyclo[11.4.0^{1,13}.0^{5,9}]heptadeca-3,5,8,13,15,17-hexaene (16): Viscous oil, yield 0.2 g (82%) [total for (*Z*) and (*E*) isomers]. **(*Z*) Isomer:** IR (neat): ṽ = 2926, 1650, 1493, 1440, 1379, 1257, 1190, 1127, 1044, 1010, 752 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.03 (t, *J* = 5.5 Hz, 2 H, 10-H), 4.44 (t, *J* = 5.5 Hz, 2 H, 11-H), 5.70 (d, *J* = 6.5 Hz, 1 H, 4-H), 6.71 (d, *J* = 6.5 Hz, 1 H, 3-H), 6.93 (ddd, *J* = 8.0, 6.0, 3.5 Hz, 1 H, 16-H), 6.98 (m, 3 H, 8-H, 14, 15), 7.00 (dd, *J* = 3.0, 2.1 Hz, 1 H, 6-H), 7.12 (ddd, 1 H, 17-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.5 (C-10), 73.7 (C-11), 105.3 (C-4), 119.5 (C-17), 121.4 (C-14), 122.3 (C-8), 122.7 (C-16), 123.5 (C-6), 124.9 (C-15), 135.4 (C-5), 138.4 (C-9), 143.3 (C-3), 146.9 (C-11), 149.3 (C-13) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 245 (21) [MH^+], 244 (100), 231 (20), 219 (26), 181 (33), 169 (58), 135 (69), 119 (37). HRMS ($C_{14}H_{12}O_2S$): calcd. 244.056187; found 244.055802.

3,13-Dioxa-8-thiatricyclo[13.4.0^{1,15}.0^{6,10}]nonadeca-4,6,9,15,17,19-hexaene (17): Yield 0.15 g (55%) [viscous oil, flash chromatography,

CH_2Cl_2/hexane (2:1)]. IR (neat): $\tilde{\nu}$ = 2952, 2863, 1712, 1431, 1350, 1024, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.91 (t, *J* = 5.5 Hz, 2 H), 3.51 (t, *J* = 5.5 Hz, 2 H), 4.65 (s, 2 H), 5.01 (s, 2 H), 6.23 (d, *J* = 13.0 Hz, 1 H), 6.75 (d, *J* = 13.0 Hz, 1 H), 6.8 (ABq, *J* = 3.5 Hz, 2 H), 7.23 (m, 3 H), 7.45 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.0 (C-11), 67.6, 67.8 & 68.8 (C-2,12,14), 105.2 (C-5), 118.6 (CH), 122.4 (CH), 127.7 (Cq), 128.7 (CH), 130.8 (CH), 131.0 (CH), 135.4 (Cq), 135.6 (Cq), 138.5 (Cq), 146.4 (C-4) ppm. MS (CI, CH_4): *m*/*z* (%) = 272 (100) [MH^+], 254 (47), 227 (78), 225 (51), 213 (45), 171 (35), 137 (41), 123 (40), 119 (47), 104 (90). HRMS ($C_{16}H_{16}O_2S$): calcd. 272.087102; found 272.086539.

2,12-Dioxa-7-selenatricyclo[11.4.0^{1,13}.0^{5,9}]heptadeca-3,5,8,13,15,17-hexaene (18): Yield 0.21 g (71%) [viscous oil, preparative TLC, eluent CH_2Cl_2/hexane (2:1)]. IR (neat): $\tilde{\nu}$ = 3291, 2929, 1598, 1495, 1259, 755 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.99 (t, *J* = 6.0 Hz, 2 H, 10-H), 4.49 (t, *J* = 6.0 Hz, 2 H, 11-H), 5.64 (d, *J* = 6.5 Hz, 1 H, 4-H), 6.73 (d, *J* = 6.5 Hz, 1 H, 3-H), 6.91 (m, 6 H, 6,8,14,15,16,17-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 31.9 (C-10), 73.7 (C-11), 106.2 (C-4), 120.9 (CH_{ar}), 121.1 (CH_{ar}), 121.9 (CH_{ar}), 122.1 (CH_{ar}), 125.1 (CH_{ar}), 138.0 & 140.9 (C-9 & C-5), 143.7 (C-3), 146.8 & 149.5 (C-11 & C-13) ppm. MS (EI): *m*/*z* (%) = 292 (98) [M^+], 269 (18), 219 (16), 183 (100), 121 (75), 102 (25). HRMS ($C_{14}H_{12}O_2{}^{80}Se$): calcd. 292.000250; found 292.001000.

3,13-Dioxa-8-selenatricyclo[13.4.0^{1,15}.0^{6,10}]nonadeca-4,6,9,15,17,19-hexaene (19): Yield 0.17 g (52%) [viscous oil, preparative TLC, eluent CH_2Cl_2/hexane (2:1)]. IR (neat): $\tilde{\nu}$ = 2921, 2851, 1723, 1456, 1353, 1085 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.87 (t, *J* = 6.0 Hz, 2 H), 3.47 (t, *J* = 6.0 Hz, 2 H), 4.64 (s, 2 H), 5.08 (s, 2 H), 6.21 (d, *J* = 1 3.0 Hz, 1 H), 6.86 (d, *J* = 1 3.0 Hz, 1 H), 7.31 (m, 4 H), 7.68 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 29.2 (C-11), 68.5, 69.9, 79.2 (CH_2, C-2,12,14), 99.3 (C-5), 117.1 (CH_{ar}), 122.1 (CH_{ar}), 127.2 (C_q), 127.6 (CH_{ar}), 127.9 (CH_{ar}), 128.2 (CH_{ar}), 128.8 (CH_{ar}), 136.2 (C_q), 136.5 (C_q), 137.2 (C_q), 148.1 (C-4) ppm. MS (EI): *m*/*z* (%) = 320 (12) [M^+], 292 (12), 269 (11), 219 (12), 202 (21), 174 (10), 159 (22), 121 (23), 119 (57), 105 (37), 91 (100). HRMS ($C_{16}H_{16}O_2{}^{80}Se$): calcd. 320.031550; found 320.032188.

2,12,19,29-Tetraoxa-7,24-dithiapentacyclo[28.4.0.0^{5,9}.0^{13,18}.0^{22,26}]-tetratriaconta-3,5,8,13,15,17,20,22,25,30,32,34-dodecene (20): Yield 0.2 g (41%), m.p. 231−232 °C (white crystals, from acetone). IR (KBr): $\tilde{\nu}$ = 1635, 1504, 1199, 1083, 1026, 834 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 600 MHz): δ = 3.03 (t, *J* = 7.0 Hz, 4 H, 10,27-H), 4.14 (t, *J* = 7.0 Hz, 4 H, 11,28-H), 6.90 (m, 2 H, 16,33-H), 7.00 (m, 4 H, 14,15,32,33-H), 7.06 (dd, *J* = 12.5, 0.8 Hz, 2 H, 4,21-H), 7.13 (m, 2 H, 17,34-H), 7.17 (d, *J* = 12.5, Hz, 2 H, 3,20-H), 7.33 (m, 2 H, 8,25-H), 7.42 (m, 2 H, 6,23-H) ppm. ^{13}C NMR ([D$_6$]DMSO, 150 MHz): δ = 29.1 (C-10), 69.8 (C-11), 107.8 (C-4), 112.8 (C-14), 116.0 (C-17), 118.9 (C-6), 121.7 (C-16), 123.5 (C-8), 123.7 (C-15), 136.3 (C-9), 139.9 (C-5), 144.1 (C-3), 148.6 (C-13), 148.9 (C-1) ppm. MS (CI, CH_4): *m*/*z* (%) = 488 (45) [M^+], 331 (24), 281 (44), 231 (42), 219 (60) 181 (67), 169 (100), 131 (56). HRMS ($C_{28}H_{24}O_4S_2$): calcd. 488.111603; found 488.110000. $C_{28}H_{24}O_4S_2$ (488.6): calcd. C 68.83, H 4.95, S 13.13; found C 68.68, H 4.79, S 12.90.

2,12,19,29-Tetraoxa-7,24-dithiapentacyclo[28.4.0.0^{5,9}.0^{13,18}.0^{22,26}]-tetratriaconta-3,5,8,13,15,17,22,25,27,30,32,34-dodecene (21): Yield 0.2 g (41%), m.p. 144−145 °C (white crystals, from acetone). IR (KBr): $\tilde{\nu}$ = 1651, 1593, 1499, 1255, 1214, 1135, 1025, 933, 735 cm^{-1}. ^1H NMR ([D$_6$]acetone, 600 MHz): δ = 3.15 (t, *J* = 7.0 Hz, 4 H, 10, 21-H), 4.28 (t, *J* = 7.0 Hz, 4 H, 11,20-H), 6.50 (dd, *J* = 12.5, 0.5 Hz, 2 H, 4,27-H), 6.88 & 7.00 (AA′BB′ system, 4 H, 14,15,16,17-H), 7.08 (d, *J* = 12.5, Hz, 2 H, 3,28-H), 7.18 & 7.27 (AA′BB′ system, 4 H, 31,32,33,34-H), 7.28 (m, 4 H, 6,8,23,25-H) ppm. ^{13}C NMR ([D$_6$]acetone, 150 MHz): δ = 30.0 (C-10), 70.5 (C-11), 107.2 (C-4), 115.2 (C-14), 121.0 (C-8), 121.1 (C-6), 122.1 (C-15), 123.0 (C-34), 125.8 (C-33), 137.3 (C-5), 138.8 (C-9), 148.1 (C-1,3), 150.0 (C-13) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 489 (28) [MH^+], 431 (45), 380 (30), 331 (60), 281 (49), 263 (54), 245 (99), 206 942), 161 (64), 110 (100). HRMS ($C_{28}H_{25}O_4S_2$): calcd. 489.119428; found 489.119962. $C_{28}H_{24}O_4S_2$ (488.6): calcd. C 68.83, H 4.95, S 13.13; found C 68.72, H 4.84, S 12.84.

2,12,17,27-Tetraoxa-7,22-dithiapentacyclo[26.2.2.2^{13,16}.0^{5,9}.0^{20,24}]-tetratriaconta-3,5,8,13,15,18,20,23,28,30,31,33-dodecene (22): Yield 0.19 g (40%), m.p. 217−218 °C (white crystals, from acetone). IR (KBr): $\tilde{\nu}$ = 2962, 1504, 1261, 1094, 1021, 800 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 600 MHz): δ = 2.99 (t, *J* = 7.5 Hz, 4 H), 4.06 (t, *J* = 7.5 Hz, 4 H), 6.08 (dd, *J* = 12.5, 0.7 Hz, 2 H), 6.82 (d, *J* = 8.2 Hz, 4 H), 6.99 (d, *J* = 8.2 Hz, 4 H), 7.20 (d, *J* = 12.5, Hz, 2 H), 7.40 (m, 2 H), 7.46 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 150 MHz): δ = 28.8 (C-10), 67.7 (C-11), 106.8 (C-4), 115.5 (C-14, 33), 119.2 (C-15, 34), 120.2 (C-6), 123.9 (C-8), 135.2 (C-9), 136.1 (C-5), 146.0 (C-3), 149.3 (C-13), 154.1 (C-1) ppm. MS (CI, CH_4): *m*/*z* (%) = 488 (100) [M^+], 295 (15), 255 (14), 135 (12). HRMS ($C_{28}H_{24}O_4S_2$): calcd. 488.111603; found 488.110000. $C_{28}H_{24}O_4S_2$ (488.6): calcd. C 68.83, H 4.95, S 13.13; found C 68.72, H 4.83, S 12.98.

2,12,17,27-Tetraoxa-7,22-dithiapentacyclo[26.2.2.2^{13,16}.0^{5,9}.0^{20,24}]-tetratriaconta-3,5,8,13,15,20,23,25,28,30,31,33-dodecene (23): Yield 0.19 g (40%), m.p. 168−169 °C (white crystals, from acetone). IR (KBr): $\tilde{\nu}$ = 1652, 1506, 1230, 1205, 1106, 1030, 926 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 600 MHz): δ = 3.03 (t, *J* = 7.0 Hz, 4 H), 4.11 (t, *J* = 7.0 Hz, 4 H), 6.27 (dd, *J* = 12.7, 0.7 Hz, 2 H), 6.80 (s, 4 H), 6.92 (s, 4 H), 7.03 (d, *J* = 12.7 Hz, 2 H), 7.41 (m, 2 H), 7.44 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 150 MHz): δ = 28.9 (C-10), 67.8 (C-11), 108.5 (C-4), 115.6 (C-14, 15), 118.1 (C-29, 30), 121.7 (C-8), 123.8 (C-6), 136.0 (C-5), 136.2 (C-9), 144.1 (C-3), 151.7 (C-1), 152.1 (C-13) ppm. MS (CI, iC_4H_{10}): *m*/*z* (%) = 488 [M^+] (65), 245 (20), 219 (36), 169 (33), 139 (27), 135 (35), 110 (100). HRMS ($C_{28}H_{24}O_4S_2$): calcd. 488.111603; found 488.110083. $C_{28}H_{24}O_4S_2$ (488.6): calcd. C 68.83, H 4.95, S 13.13; found C 68.76, H 4.90, S 12.96.

3,13,22,32-Tetraoxa-8,27-dithiapentacyclo[32.4.0.0^{6,10}.0^{15,20}.0^{25,29}]-octatriaconta-4,6,9,15,17,19,23,25,28,34,36,38-dodecene (24): ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.87 (t, *J* = 7.0 Hz, 4 H, 11,30-H), 3.70 (t, *J* = 7.0 Hz, 4 H, 12,31-H), 4.56 (s, 4 H, 14,33-H), 4.78 (s, 4 H, 2,21-H), 5.81 (d, *J* = 13.0 Hz, 2 H, 5,24-H), 6.79 (d, *J* = 1 3.0 Hz, 2 H, 4,23-H), 6.96 (m, 4 H, 7,26-H and 9,28-H), 7.30 (m, 2 H, 18,37-H), 7.31 (m, 2 H, 17,36-H), 7.33 (m, 2 H, 16,35-H), 7.40 (m, 2 H, 19,38-H) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 29.6 (C-11,30), 69.4 (C-2,21), 70.0 (C-12,31), 71.4 (C-14,33), 99.8 (C-5,24), 117.4 (C-7,26), 121.9 (C-9,28), 128.2 (C-18,37), 128.6 (C-16,35), 129.0 (C-19,38), 129.5 (C-17,36), 135.0 & 135.4 (C-1,20 & C-1,20 from isomer **25**), 136.2 & 136.5 (C-15,34 & C-15,34 from isomer **25**), 136.5 & 136.6 (C-10,29 & C-10,29 from isomer **25**), 137.4 & 137.5 (C-6,25 & C6,25 from isomer **25**), 148.1 (C-4,25) ppm. MS (EI) (for the mixture of **24** and **25**): *m*/*z* (%) = 544 [M^+] (58), 531 (75), 508 (40), 481 (100), 445 (29), 407 (25), 381 (64), 367 (30). HRMS ($C_{32}H_{32}O_4S_2$): calcd. 544.174203; found 544.174965.

3,13,22,32-Tetraoxa-8,27-dithiapentacyclo[32.4.0.0^{6,10}.0^{15,20}.0^{25,29}]-octatriaconta-4,6,9,15,17,19,25,28,30,34,36,38-dodecene (25): ^1H NMR ($CDCl_3$, 600 MHz): δ = 2.84 (t, *J* = 7.0 Hz, 4 H, 11,24-H), 3.61 (t, *J* = 7.0 Hz, 4 H, 12,23-H), 4.47 (s, 4 H, 14,21-H), 4.89 (s, 4 H, 2,33-H), 5.88 (d, *J* = 13.0 Hz, 2 H, 5,30-H), 6.94 (d, *J* =

13.0 Hz, 2 H, 4,31-H), 6.95 (m, 2 H, 9,26-H), 6.98 (m, 2 H, 7,28-H), 7.21 & 7.31 (AA′BB′ system, 4 H, 16,17,18,19-H), 7.37 & 7.44 (AA′BB′ system, 4 H, 35,36,37,38-H) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 29.7 (C-11,24), 69.4 (C-2,33), 70.2 (C-12,23), 70.6 (C-14,21), 100.1 (C-5,30), 117.4 (C-7,28), 122.1 (C-9,26), 127.7 (C-16,19), 128.3 (C-17,18), 128.6 (C-36,37), 129.3 (C-35,38), 135.0 & 135.4 (C-1,20 & C-1,20 from isomer **24**), 136.2 & 136.5 (C-15,34 & C-15,34 from isomer **24**), 136.5 & 136.6 (C-10,29 & C-10,29 from isomer **24**), 137.4 & 137.5 (C-6,25 & C6,25 from isomer **24**), 147.8 (C-4,31) ppm. MS (EI) (for the mixture of **24** and **25**): *m/z* (%) = 544 [M$^+$] (58), 531 (75), 508 (40), 481 (100), 445 (29), 407 (25), 381 (64), 367 (30). HRMS ($C_{32}H_{32}O_4S_2$): calcd. 544.174203; found 544.174965.

3,13-Dioxa-8-thiatricyclo[13.4.0^{1,15}.0^{7,11}]nonadeca-5,7(11),9,15,17,19-hexaene (26): Yield 0.2 g (75%) [viscous oil, preparative TLC, eluent CH_2Cl_2/hexane (2:1)]; this compound was obtained as an inseparable mixture of (*Z*) and (*E*) isomers in 9:1 ratio, and the full NMR assignments were done for the (*Z*) isomer by 2D NMR experiments. **(*Z*) Isomer:** IR (neat): ṽ = 2929, 2843, 1431, 1215, 1050, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 4.15 (dd, *J* = 7.0, 1.0 Hz, 2 H, 4-H), 4.46 (s, 2 H, 12-H), 4.63 (s, 2 H, 2-H), 4.67 (s, 2 H, 14-H), 5.98(dt, *J* = 11.0, 7.0, 1 H, 5-H), 6.41 (br. d, *J* = 11.0, 1 H, 6-H), 7.05 (d, *J* = 5.0 Hz, 1 H, 10-H), 7.20 (d, *J* = 5.0 Hz, 1 H, 9-H), 7.27 (m, 4 H, CH_{arom}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 65.3 (C-12), 66.4 (C-4), 70.2 (C-2), 70.4 (C-14), 124.2 (C-6), 124.6 (C-9), 127.8 & 128.0 (C-17 & C-18), 129.5 (C-10), 130.0 (C-16 & C-19), 134.1 (C-5), 135.0 (C-11), 136.7 (C-15), 136.9 (C-7), 137.6 (C-1) ppm. **(*E*) *Isomer*:** ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 4.18 (dd, *J* = 5.8, 1.0, 2 H, 4-H), 4.54 (s, 2 H, 12-H), 4.58 (s, 2 H, 2-H), 4.75 (s, 2 H, 14-H), 5.92 (dt, *J* = 15.0, 5.8 Hz, 1 H, 5-H), 6.68 (br. d, *J* = 15.0, 1 H, 6-H), 6.95 (d, *J* = 5.0, 1 H, 10-H), 7.13 (d, *J* = 5.0, 1 H, 9-H), 7.27 (m, 4 H, CH_{arom}) ppm. MS (CI, CH_4): *m/z* (%) = 272 (7.23) [MH$^+$], 212 (15), 151 (41), 135 (20), 123 (93), 104 (100), 91 (70). HRMS ($C_{16}H_{16}O_2S$): calcd. 272.087102; found 272.086199.

3,13-Dioxa-8-selenatricyclo[13.4.0^{1,15}.0^{7,11}]nonadeca-5,7(11),9,15,17,19-hexaene (27): Yield 0.24 g (76%) [viscous oil, preparative TLC, eluent CH_2Cl_2/hexane (3:1)]. IR (neat): ṽ = 2918, 2856, 1453, 1362, 1207, 1086, 1001, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.17 (dd, *J* = 7.0, 1.0 Hz, 2 H, 3-CH_2), 4.41 (s, 2 H, 10-CH_2), 4.62 (s, 2 H, CH_2), 4.65 (s, 2 H), 5.91(dt, *J* = 11.0, 7.0 Hz, 1 H, 4-H), 6.41 (br. d, *J* = 11.0, 1 H, 5-H), 7.29 (m, 5 H,), 7.88 (d, *J* = 5.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 66.1 (CH_2), 66.5 (CH_2), 70.2 (CH_2), 70.3 (CH_2), 126.3 (CH), 127.8 (CH), 128.0 (CH) 129.8 (CH), 130.0 (CH), 130.1 (CH), 132.3 (CH), 133.3 (CH), 136.7 (C_q), 136.9 (C_q), 137.8 (C_q), 142.9 (C_q) ppm. MS (CI, *i*C_4H_{10}): *m/z* (%) = 321 (3) [MH$^+$], 281 (12), 260 (28), 219 (24), 199 (28), 185 (37), 171 (100), 119 (50). HRMS ($C_{16}H_{16}O_2{}^{80}Se$): calcd. 320.031550; found 320.031609.

Bis(3-buten-1-ynyl) Sulfide (28): Oil, yield 0.11 g (82%) (flash chromatography, hexane). IR (neat): ṽ = 2917, 2161, 1594, 1496, 1260, 1104 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.55 (dd, *J* = 11.0, 2.0 Hz, 1 H, 4-H$_{cis}$), 5.73 (dd, *J* = 17.5, 2.0 Hz, 1 H, 4-H$_{trans}$), 5.89 (dd, *J* = 17.5, 11.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.5 & 93.7 (C≡C), 116.3 (C-3), 128.0 (C-4) ppm. MS (CI, *i*C_4H_{10}): *m/z* (%) = 134 (100) [M$^+$], 108 (8), 102 (5). HRMS (C_8H_6S): calcd. 134.019022; found 134.017978.

Bis(3-buten-1-ynyl) Selenide (29): Oil, yield 0.15 g (81%) (flash chromatography, hexane). IR (neat): ṽ = 2920, 1580, 1489, 1220, 1098 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.53 (dd, *J* = 11.0, 2.0 Hz, 1 H, 4-H$_{cis}$), 5.70 (dd, *J* = 18.0, 2.0 Hz, 1 H, 4-H$_{trans}$), 5.91 (dd, *J* = 18.0, 11.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.0 & 99.2 (C≡C), 116.5 (C-3), 128.1 (C-4) ppm. MS (CI, *i*C_4H_{10}): *m/z* (%) = 183 (8) [MH$^+$], 169 (24), 147 (18), 131 (34), 102 (100). HRMS ($C_8H_6{}^{80}Se$): calcd. 181.963471; found 181.961926.

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