Preparation and Structures of Cyclic Tetrathiadienes and Tetrathiaenynes

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Through the use of diisobutylaluminium hydride (DIBAH) we were able to reduce selectively the triple bond(s) of the following cyclic diynes: 1,4,7,10-tetrathiacyclodeca-2,8-diyne (**1**), 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (**2**), 1,4,9,12-tetrathiacyclohexadeca-2,10-diyne (**3**), 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**4**), 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (**5**), 1,4,8,11-tetrathiacycloheptadeca-2,9-diyne (**6**), and 7,16-dioxa-1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**7**). The resulting cyclic enynes **8**–**14** and cyclic dienes **15**–**20** were isolated and characterized by their analytical data. In the cases of **8**, **10**, **11**, **14**, and **15**–**20** we were able to isolate single crystals, which were investigated by X-ray diffraction. For all molecular structures we found stair-like conformations. These shapes of the molecules were traced back to the zigzag arrangements of the hydrocarbon chains and the rigid building units (S–CH=CH–S) and/or (S–C≡C–S). In the solid-state forms of **11**, **16**, **17**, and **19** we encountered columnar structures caused by close contacts between sulfur centers of neighboring rings.

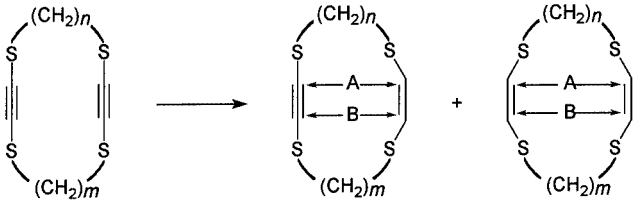
Introduction

Supramolecular chemistry provides many examples of relatively weak directional forces determining the structures of aggregates in the solid state.[1,2] Hydrogen bonding and π-π stacking, to name the most important ones, are such forces; both have been used to form channel-like structures. Moore et al. used macrocyclic rigid rings as building blocks,[3] hydrogen bonds between phenolic OH groups and π-π stacking of aromatic rings being used to stack the rings on top of one another. Ghadiri's approach[4] used flat cyclic peptides built from an even number of D- and L-amino acids. The cycles associate in stacks in an antiparallel fashion through the formation of hydrogen bonds between neighboring rings within one column. Close contacts between chalcogen centers in the solid state have also been reported as directional forces,[5−11] above all in the investigation of organic conductive materials.[8−11] In most cases the short S···S contacts go along with close CH···S, C−H···π-contacts, and π-π stacking.

On examination of the structures of cyclic tetrathiadiynes[12] and tetraselenadiynes[13] in the solid state we realized that weak interactions between chalcogen centers alone were able to give rise to columnar structures.[14] To examine whether tetrathiadienes could also form columnar structures due to van der Waals forces in the solid state, we reduced a series of cyclic tetrathiadiynes to the corresponding enynes and dienes, respectively. Moreover, the reduction of triple bonds of tetrathiadiynes also opens a new route to cyclic thiacrown ethers with C_2H_2 and possibly C_2H_4 bridges between the sulfur atoms.[15−17] Such a new route is of interest because medium-sized and macrocyclic rings with small bridges between the sulfur atoms are not readily accessible.[16]

Results

To reduce the triple bonds of cyclic tetrathiadiynes selectively to double bonds we used diisobutylaluminium hydride (DIBAH) as the reducing agent. The addition of this reagent to alkynes with subsequent hydrolysis constitutes a mild method for reduction to the corresponding olefin.[18,19] In most cases the *cis* products are found, but in certain cases the *trans* isomer is observed.[20,21] Depending on the



n	*m*			
2	2	**1**	**8**	**15**
3	3	**2**	**9**	**16**
4	4	**3**	**10**	**17**
5	5	**4**	**11**	**18**
6	6	**5**	**12**	**19**
3	6	**6**	**13**	**20**
$(CH_2CH_2)_2O$		**7**	**14**	

Scheme 1

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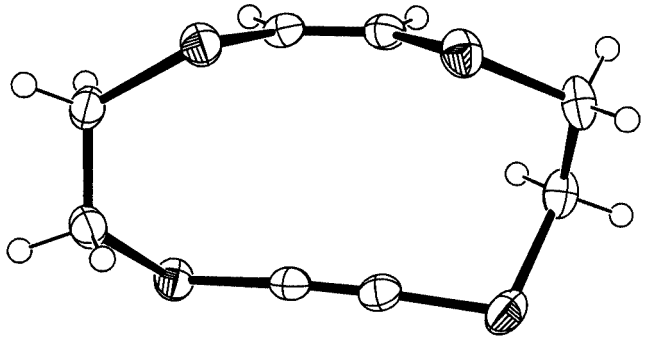
amount of reducing agent, we were able to steer the reaction to yield either the monoenes or the dienes (Scheme 1).

With 0.4−2 equiv. of DIBAH per triple bond we obtained mainly the monoenes **8**−**14**. With an excess of DIBAH (4 equiv. per triple bond) the major components of the reaction product were the dienes **15**−**20** (Scheme 1). Treatment of **7** resulted only in the enyne **14**, even when a fourfold excess of the reducing agent was used. The yields for the monoenes were mostly moderate, whereas those of the dienes varied between 50 and 100%.

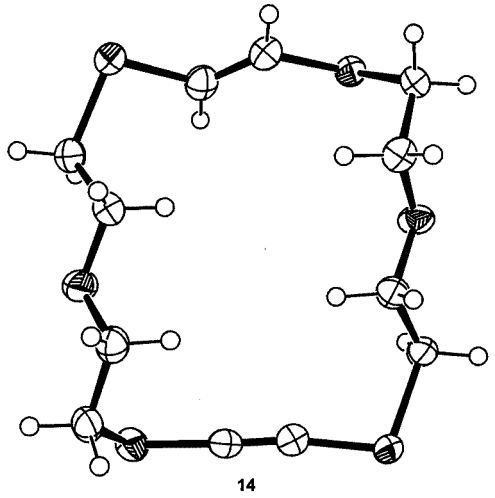
Structural Investigations

a) Molecular Structures

Because of the symmetry of the resulting cycles the structures were assigned on the basis of their analytical data, especially by NMR spectroscopy with correlation techniques. In the cases of **8**, **10**, **11**, and **14**, and also **15**−**20** we were able to isolate single crystals that were investigated by X-ray diffraction.



8



14

Figure 1. Molecular structures of **8** and **14** (ORTEP plot; thermal ellipsoids at 50% probability level; heteroatoms are indicated by shaded ellipsoids)

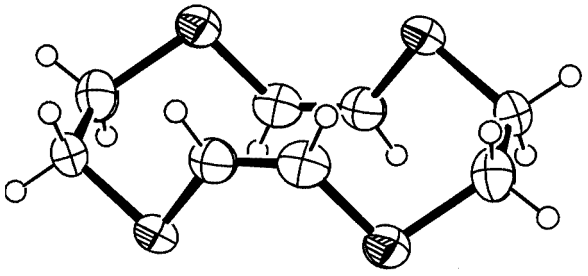
In Figure 1 we show the molecular structures of **8** and **14** as representative cyclic tetrathiaenynes. In Table 1 we list some distances and angles of all the four tetrathiaenynes investigated. Important for the conformations of the rings are the large torsion angles between the CH_2−S bonds adjacent to the alkyne unit; these vary between 75 and 90°. These values are close to those reported for the cyclic tetrathiadiynes.[12] The large torsion angles are due to repulsion between the 3p lone pairs on the sulfur centers through the triple bond. In contrast, the interactions between the 3p lone pairs of the sulfur centers adjacent to the double bond are much less pronounced. The CH_2−S−CH=CH torsion angles vary from 3 to 57° (Table 1). Neither repulsion nor conjugation between the 3p lone pairs of the sulfur atoms and the double bond can be assumed from these values. The torsion angles between the CH_2−S bonds adjacent to the double bond adopt small values for those rings with a *cis* double bond (**8**, **10**, **11**). For **14**, the torsion angle between the CH_2−S bonds adjacent to the double bond amounts to 87.7°. From these results, the molecular structures of the cyclic tetrathiaenynes can be described as cycles with two rigid building blocks: the S−C≡C−S and the S−CH=CH−S moieties. The first is linear, and adopts torsion angles of the adjacent CH_2−S bonds between 75 and 90°, whereas the second maintains planarity, except for **14** at nearly 90°. The alkane chains in between try to adopt a strain-free zigzag conformation,[22] including the sulfur centers if possible. This is the case in **11**. In **10** and **14** the chains adopt a zigzag arrangement including one sulfur atom, whereas the other C−S bond assumes an anticlinal conformation with respect to the adjacent C−C bond.

Table 1. Selected distances [Å] and angles [°] of **8**, **10**, **11** and **14**; for the definition of A and B see Scheme 1

	8	**10**	**11**	**14**
Torsion angle CH_2−S···S−CH_2 on triple bond	85.5	84.7	75.1	88.7
Torsion angle CH_2−S···S−CH_2 on double bond	14.1	4.8	6.7	87.7
Torsion angle	24.0	18.1	57.4	40.0
CH_2−S−CH=CH	30.5	14.3	2.7	43.6
Bond angle	176.7	178.7	175.5	175.0
C≡C−S	169.7	171.9	179.9	169.0
Transannular distances				
A	3.40	5.24	7.86	6.40
B	3.32	5.26	7.89	6.80
C=C	1.33	1.33	1.32	1.28
C≡C	1.21	1.20	1.20	1.19

The structural variety of the dienes is represented in Figure 2. It shows one of the four independent molecules of **15** and one of two different modifications of **19** (α modification) as examples. In all cases we observe the *cis* configuration of the double bond with an almost planar S−CH=CH−S moiety. Table 2 lists the most relevant angles and distances for all the solid-state structures found for **15**−**20**.

Here, the CH_2−S−CH=CH torsion angles vary between 5 and 40°. To obtain conformations of low energy the chains preferentially adopt zigzag arrangements in the alkane parts.[22] In the 12-membered ring of **15** the planar



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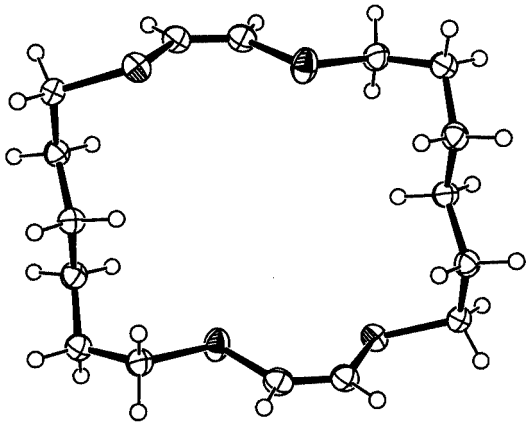

19

Figure 2. Molecular structures of **15** (one independent molecule out of four) and the α modification of **19** (ORTEP plot; thermal ellipsoids at 50% probability level; heteroatoms are indicated by shaded ellipsoids)

S−CH=CH−S fragments are oriented *anti* to each other. In the solid state we found four independent molecules, all with small CH_2−S···S−CH_2 torsion angles and staggered conformations for the ethano bridges. In the case of the 14-membered ring of **16** we also find the *anti* orientation of the two S−CH=CH−S groups and a zigzag arrangement of the propano groups including one sulfur center whereas the other C−S bond assumes an anticlinal conformation to the neighboring C−C bond. The torsion angles between the S−CH_2 bonds amount to 62°. The *anti* orientation of the two S−CH=CH−S fragments is also found in **17** and **20**, with small torsion angles between the CH_2−S···S−CH_2 bonds. The S−CH=CH−S fragments in the two independent molecules of **18** adopt the *syn* arrangement, those in **19** the *anti*. In order to allow zigzag arrangements of the penta- and hexamethylene chains, respectively, the CH_2−S···S−CH_2 torsion angles vary considerably in these structures (Table 2). In the cases of **17** and **18**, four C−S bonds assume an anticlinal conformation with respect to adjacent C−C bonds. In **19**, two C−S bonds and two C−C bonds adopt an anticlinal orientation with respect to the neighboring C−C bonds. In **20**, the propano bridge adopts a zigzag arrangement with the adjacent sulfur atoms, whereas the C−S bonds in the longer bridge assume an anticlinal conformation with respect to the adjacent C−C bonds.

b) Packing in the Crystals

Our investigations of **2** and **4** revealed close contacts between the chalcogen centers.[14] In the case of **4**, the 3p lone pair of the sulfur atom coincides with the direction of the C−S bond of the neighboring ring. This directionality[5,6]

Table 2. Selected distances [Å] and angles [°] of **15**−**20**; for the definition of A and B see Scheme 1

	15[a,b]	**16**[b]	**17**[b]	**18**[c]	**19α**[b,d]	**19β**[b,d]	**20**
Torsion angle	1.4	61.9	8.2	16.9	39.0	61.9	5.9
CH_2−S···S−CH_2	0.5			9.2			0.6
on double bond	0.9			40.0			
	2.5			32.9			
Torsion angle	28.2, 28.1	45.6	17.7	12.6, 17.6	24.3	45.6	38.4
CH_2−S−CH=CH	27.9, 29.8	5.7	24.0	10.9, 15.2	5.2	5.7	36.1
	28.6, 27.8			22.4, 4.0			35.7
	29.4, 28.2			19.6, 5.1			40.1
Transannular distances							
A	3.52	5.52	5.60	6.21	7.10	7.52	6.27
	3.61			6.13			
	3.54						
	3.58						
B	3.52	5.52	5.60	6.27	7.10	7.52	7.20
	3.61			6.15			
	3.54						
	3.58						
C=C	1.33	1.33	1.32	1.32	1.33	1.33	1.30
	1.33			1.33			1.31
	1.33			1.31			
	1.32			1.32			

[a] Four independent halves of the molecule. [b] Crystallographically centrosymmetric molecule. [c] Two independent molecules. [d] Two different modifications of the same compound were found.

creates columnar structures in the solid state.[14] These structures arise by stacking of the rigid rings on top of one another. The most common motif of association is that one sulfur center of one ring keeps close contact with two sulfur centers of two neighboring rings (which are stacked on top of each other). As a result, a zigzag arrangement of the chalcogen atoms arises. A schematic drawing is shown in Figure 3.

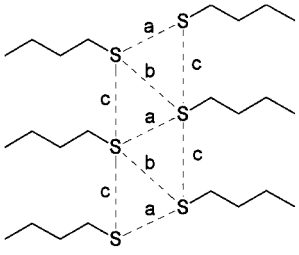

Figure 3. Schematic plot of the zigzag arrangement due to close chalcogen contacts in the columnar structures; definition of the distances between chalcogen centers of neighboring rings (*a* and *b*) and within the stack (*c*)

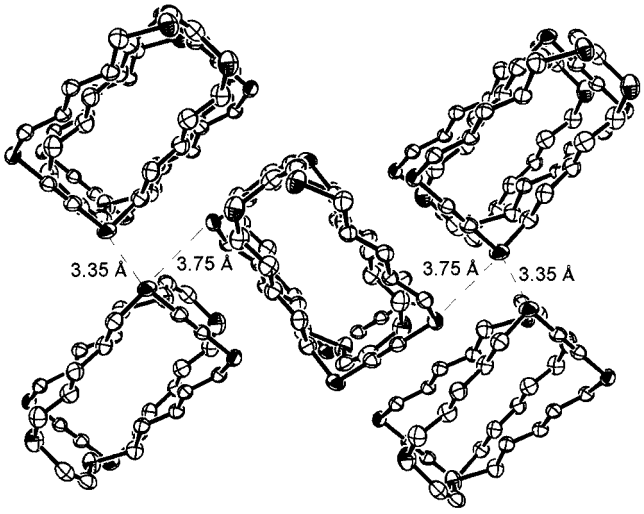

Figure 4. Columnar structure of **11**; shortest distances of sulfur atoms are indicated by dashed lines (ORTEP plot; thermal ellipsoids at 50% probability level; heteroatoms are indicated by shaded ellipsoids)

Usually, the distances between the neighboring rings are not equal (*a*, *b* in Figure 3) and are also different from the distances within the stack (*c* in Figure 3).

For the enynes **8**, **11**, and **14** we find contacts between the chalcogen atoms close to the sum of the van der Waals radii (S···S = 3.7 Å[23]) or even shorter. In the case of **11** these contacts give rise to columnar structures. Table 3 lists the shortest distances between chalcogen atoms. In **14**, the rings are displaced in pairs with four close contacts between the sulfur centers, but no columnar structures are seen. Figure 4 shows the columnar structure of **11**. The rings are stacked on top of one another in such a way that the alkyne and alkene units alternate. In most of the synthesized dienes we encountered close contacts between the sulfur centers. In the unit cells of **15** we found four independent molecules with close intermolecular contacts (Table 3) that did not give rise to any columnar structures. For **16** the rings were displaced in pairs and the nearest S···S distances between the rings were still large, the same holding for **18**. The tubular structures of **17** and of the β modification of **19** have already been discussed in a preliminary publication.[14] Figure 5 shows the α modification of **19**, showing close distances between neighboring rings as outlined in Figure 3. Each ring is part of four zigzag arrangements of two different kinds (*a*, *b* and *a′*, *b′* in Table 3 and Figure 3). The distances between nearest neighbors (*a*, *b* and *a′*, *b′* in Table 3) and within the stacks (*c* in Table 3) are relatively large compared to those in the β modification.[14] The directionality of the sulfur−sulfur interactions is unspecific in most cases.

Conclusion

Through the use of DIBAH as reducing agent we have been able to reduce a series of cyclic tetrathiadiynes selectively to the corresponding enynes and dienes. The cyclic enynes and the cyclic dienes preferentially adopt stair-like conformations, due to the fact that two rigid building units are connected by hydrocarbon chains. The stair-like shapes of the cycles result because the rigid building units force the chains in the same direction (S−CH=CH−S) or into conformations with torsion angles of between 70 and 90° (S−C≡C−S) and because the chains preferentially adopt

Table 3. Closest intramolecular distances between sulfur centers in the solid-state forms of enynes **8**, **10**, **11**, and **14** and the dienes **15**−**20**; all values in Å; for definition of *a*, *b*, and *c* see text and Figure 3

Compound	Shortest distances between chalcogen centers in the solid state				
8	3.76	3.97	3.98		
10	4.18	4.26	4.32		
11	3.35	3.75			
14	3.67	3.83	3.85	4.02	
15	3.78	3.93	3.94	3.95	
16	4.05	4.08	4.12		
17	3.47 (*a*)	4.13 (*b*)	5.22 (*c*)		
18	4.06	4.11			
19α	4.30 (*a*)	4.37 (*b*)	4.26 (*a′*)	4.92 (*b′*)	5.24 (*c*)
19β	4.07 (*a*)	4.07 (*b*)	4.18 (*a′*)	4.18 (*b′*)	5.24 (*c*)
20	4.20				

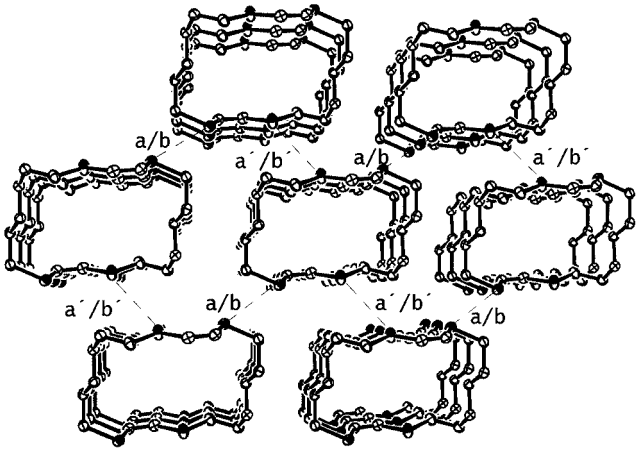

Figure 5. Columnar structure of the α modification of **19**; shortest distances of sulfur atoms are indicated by dashed lines (ORTEP plot; thermal ellipsoids at 50% probability level; heteroatoms are indicated by shaded ellipsoids); for definition of *a* and *b* see Figure 3

anti-periplanar conformations, resulting in a zigzag arrangement of the chains. The same shape is also encountered in medium-sized cyclic dienes.[22] Our investigations into the enynes **8**, **10**, **11**, and **14**, and the dienes **15**−**20** in most cases found close intermolecular contacts that in some cases gave rise to columnar structures. These examples show that close contacts between chalcogen centers[14] may exert a steering effect similar to those reported for hydrogen bonds and π-π stacking[1,2] to produce columnar structures in the solid state.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 300 (300 and 75 MHz, respectively) or Bruker Avance 500 spectrometers (500 and 125 MHz, respectively). The chemical shifts are quoted in ppm on the δ scale, using the residual protonated solvent as the internal standard. IR spectra were obtained with a Bruker Vector 22 FT-IR spectrometer, UV spectra with a Hewlett−Packard HP 8452A spectrometer. Absorption maxima of IR spectra are quoted in cm^{-1} and those of UV spectra in nm, with log ε quoted in 1000 cm^2mol^{-1}. Elemental analyses were performed by the Mikroanalytisches Labor der Chemischen Institute der Universität Heidelberg. Mass spectrometry was performed with a ZAB-2F spectrometer (Vacuum Generators) and with a Hewlett−Packard HP 59970 CD GC/MS-MSD workstation. Melting points (m.p.) were determined with a melting point determination apparatus as described by Dr. Tottoli (Büchi) and are uncorrected. Material used for column chromatography: Macherey−Nagel 60 silica gel (40−63 mesh); 3% (v/v) triethylamine was added.

Starting Materials: 1,4,7,10-Tetrathiacyclododeca-2,8-diyne (**1**), 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (**2**), 1,4,9,12-tetrathiacyclohexadeca-2,10-diyne (**3**), 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**4**), 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (**5**), 1,4,8,11-tetrathiacycloheptadeca-2,9-diyne (**6**), and 7,16-dioxa-1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**7**) were prepared by literature methods.[12] Diisobutylaluminium hydride (DIBAH) was purchased from Aldrich as a 1.0 M solution in hexane.

General Procedure: All reactions were carried out under argon. Solvents were dried and distilled prior to use. A solution of diisobutylaluminium hydride (DIBAH) in hexane was added dropwise at room temperature to a solution of tetrathiacyclodiyne in the solvent given below. The resulting mixture was stirred at room temperature for 2 d, followed by addition of 5 mL of water. The product was purified by column chromatography (SiO_2, *n*-hexane/toluene, 1:1).

(*Z*)-1,4,7,10-Tetrathiacyclododeca-2-en-8-yne (8): This compound was produced from 1,4,7,10-tetrathiacyclododeca-2,8-diyne (**1**, 116 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 0.55 mL, 0.55 mmol). Yield: 76 mg (65%) of **8** as a yellow solid, m.p. 127 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.99 (m, 4 H, $CH_2SC=$), 3.17 (m, 4 H, $CH_2SC\equiv$), 6.30 (s, 2 H, =CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.9 ($CH_2SC=$), 38.3 ($CH_2SC\equiv$), 86.6 (C≡), 125.0 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 3015 cm^{-1}, 2953, 2902, 1631, 1544, 1403. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 nm (3.68). MS (EI+): *m*/*z* = 234 [M^+], 208 [$M^+ - C_2H_2$]. HRMS (EI, 70 eV): calcd. 233.9666 [M^+]; found 233.9648.

(*Z*)-1,4,8,11-Tetrathiacyclotetradeca-2-en-9-yne (9): This compound was produced from 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (**2**, 130 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 0.55 mL, 0.55 mmol). Yield: 42 mg (36%) of **9** as a colorless solid, m.p. 84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 [tt, $^3J(SCH_2,SCH_2CH_2)$ = 6.8 Hz, 4 H, $SCH_2CH_2CH_2S$], 2.72 [t, $^3J(SCH_2CH_2,SCH_2)$ = 7.2 Hz, 4 H, $\equiv CSCH_2$), 2.74 [t, $^3J(SCH_2CH_2,SCH_2)$ = 6.7 Hz, 4 H, $=CSCH_2$], 6.36 (s, 2 H, $=CH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.7 ($SCH_2CH_2CH_2S$), 33.2 ($CH_2SC=$), 35.0 ($CH_2SC\equiv$), 85.7 (C≡), 128.8 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 3001 cm^{-1}, 2922, 2853, 1626, 1550, 1423. MS (EI+): *m*/*z* = 262 [M^+]. HRMS (EI, 70 eV): calcd. 261.9978 [M^+]; found 261.9962.

(*Z*)-1,4,9,12-Tetrathiacyclohexadeca-2-en-10-yne (10): This compound was produced from 1,4,9,12-tetrathiacyclohexadeca-2,10-diyne (**3**, 144 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 0.55 mL, 0.55 mmol). Yield: 63 mg (43%) of **10** as a colorless solid, m.p. 122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (m, 4 H, $CH_2CH_2SC=$), 1.90 (m, 4 H, $CH_2CH_2SC\equiv$), 2.61 [t, $^3J(SCH_2CH_2,SCH_2)$ = 7.1 Hz, 4 H, $CH_2SC\equiv$], 2.82 (t, $^3J(SCH_2CH_2,SCH_2)$ = 6.1 Hz, 4 H, $CH_2SC=$], 6.10 (s, 2 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.9 ($CH_2CH_2SC\equiv$), 29.1 ($CH_2CH_2SC=$), 33.9 ($CH_2SC=$), 36.5 ($CH_2SC\equiv$), 85.8 (C≡), 124.4 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 3013 cm^{-1}, 2924, 2851, 1630, 1537, 1449, 1415, 1364. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 256 nm (3.90). MS (EI+): *m*/*z* = 290 [M^+]. HRMS (EI, 70 eV): calcd. 290.0291 [M^+]; found 290.0288. $C_{12}H_{18}S_4$ (290.0): calcd. C 49.61, H 6.24, S 44.15; found C 49.70, H 6.28, S 44.15.

(*Z*)-1,4,10,13-Tetrathiacyclooctadeca-2-en-11-yne (11): This compound was produced from 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**4**, 96 mg, 0.3 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 0.36 mL (0.36 mmol). Yield: 22 mg (23%) of **11** as a colorless solid, m.p. 74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56−1.66 (m, 8 H, $CH_2CH_2CH_2S$, $CH_2CH_2SC=$), 1.76−1.81 (m, 4 H, $CH_2CH_2SC\equiv$), 2.64 (t, $CH_2SC\equiv$), 2.69 (t, $CH_2SC=$), 6.23 (s, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6 ($CH_2CH_2CH_2S$), 29.1 ($CH_2CH_2SC\equiv$), 30.4 ($CH_2CH_2SC=$), 34.3 ($CH_2SC=$), 36.3 ($CH_2SC\equiv$), 86.0 (C≡), 127.5 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2853, 1631, 1543, 1453, 1422. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 nm (3.79). MS (EI+): *m*/*z* = 318 [M^+]. HRMS (EI, 70 eV): calcd. 318.0606 [M^+]; found 318.0624.

(*Z*)-1,4,11,14-Tetrathiacycloeicosa-2-en-12-yne (12): This compound was produced from 1,4,11,14-tetrathiacycloeicosa-2,12-di-

yne (**5**, 172 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 0.4 mL, 0.4 mmol). Yield: 38 mg (27%) of **12** as a colorless solid, m.p. 87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45−1.51 (m, 8 H, CH_2CH$_2$CH$_2$C≡, CH_2CH$_2$CH$_2$C=), 1.62−1.66 (m, 4 H, CH_2CH$_2$SC=), 1.74−1.80 (m, 4 H, CH_2CH$_2$SC≡), 2.63 (t, CH$_2$SC≡), 2.75 (t, CH$_2$SC=), 6.11 (s, = CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.6 (*C*H$_2$CH$_2$CH$_2$SC=), 28.3 (*C*H$_2$CH$_2$CH$_2$SC≡), 29.5 (*C*H$_2$CH$_2$SC≡), 30.0 (*C*H$_2$CH$_2$SC=), 34.3 (*C*H$_2$SC=), 36.5 (*C*H$_2$SC≡), 86.0 (s, C≡), 125.3 (d, C=) ppm. IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 2852, 1630, 1544, 1445, 1420. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 256 nm (3.96). MS (EI+): *m*/*z* = 346 [M$^+$], 313 [M$^+$ − SH]. HRMS (EI, 70 eV): calcd. 346.0917 [M$^+$]; found 346.0910. $C_{16}H_{26}S_4$ (346.1): calcd. C 55.44, H 7.56; found C 55.21, H 7.47.

(*Z*)-1,4,8,11-Tetrathiacycloheptadeca-2-en-9-yne (13): This compound was produced from 1,4,8,11-tetrathiacycloheptadeca-2,9-diyne (**6**, 90 mg, 0.3 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 0.3 mL, 0.3 mmol). Yield: 40 mg (44%) of **13** as a colorless solid, m.p. 82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39−1.66 (m, 6 H, CH_2CH$_2$CH$_2$SC=, CH_2CH$_2$CH$_2$SC≡, CH_2CH$_2$SC=), 1.70−1.80 (m, 2 H, CH_2CH$_2$SC≡), 2.00−2.11 (m, 2 H, SCH$_2$CH_2CH$_2$S), 2.55−2.76 (m, 8 H, CH$_2$S), 6.11 [d, ^3J(=CH, =CH) = 8.0 Hz, 1 H, =CH], 6.18 [d, ^3J(=CH, =CH) = 8.0 Hz, 1 H, =CH] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.0 (CH$_2$), 27.5 (CH$_2$), 28.6 (CH$_2$), 29.5 (CH$_2$), 31.4 (CH$_2$), 33.0 (CH$_2$), 34.1 (CH$_2$), 34.3 (CH$_2$), 35.8 (CH$_2$), 85.2 (C≡), 86.4 (C≡), 125.0 (C=), 127.0 (C=). MS (EI+): *m*/*z* = 304 [M$^+$], 271 [M$^+$ − SH].

(*E*)-7,16-Dioxa-1,4,10,13-tetrathiacyclooctadeca-2-en-11-yne (14): This compound was produced from 7,16-dioxa-1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**7**, 200 mg, 0.62 mmol) in THF (10 mL), by treatment with DIBAH (1.0 M in hexane, 2.5 mL, 2.5 mmol). Yield: 87 mg (43%) of **14** as a colorless solid, m.p. 97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.78 [t, ^3J(OCH_2CH$_2$SC≡, OCH$_2$CH_2SC≡) = 6.6 Hz, 4 H, OCH$_2$CH_2SC≡], 2.83 [t, ^3J(OCH_2CH$_2$SC=, OCH$_2$CH_2SC=) = 7.0 Hz, 4 H, OCH$_2$CH_2SC=], 3.65 [t, ^3J(OCH$_2$CH_2SC=, OCH_2CH$_2$SC=) = 7.0 Hz, 4 H, OCH_2CH$_2$SC=], 3.78 [t, ^3J(OCH$_2$CH_2SC≡, OCH_2CH$_2$SC≡) = 7.0 Hz, 4 H, OCH_2CH$_2$SC≡], 6.22 (s, 2 H, = CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.3 (OCH$_2$*C*H$_2$SC≡), 35.1 (OCH$_2$*C*H$_2$SC=), 69.1 (O*C*H$_2$CH$_2$SC=), 70.6 (O*C*H$_2$CH$_2$SC≡), 85.6 (C≡), 124.4 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1}, 2921, 2876, 2854, 1631, 1474, 1400. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 270 nm (3.84). MS (EI+): *m*/*z* = 322 [M$^+$]. HRMS (EI, 70 eV): calcd. 322.0190 [M$^+$]; found 322.0197.

(2*Z*,8*Z*)-1,4,7,10-Tetrathiacyclododeca-2,8-diene (15): This compound was produced from 1,4,7,10-tetrathiacyclododeca-2,8-diyne (**1**, 116 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 4.0 mL, 4.0 mmol). Yield: 62 mg (52%) of **15** as a colorless solid, m.p. 179 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.02 (s, 8 H, SCH$_2$), 6.12 (s, 4 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.3 (t, SCH$_2$), 127.1 (d, C=) ppm. IR (KBr): $\tilde{\nu}$ = 3011 cm^{-1}, 2909, 1629, 1561, 1407, 1317. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 246 nm (4.00), 254 (4.02). MS (EI+): *m*/*z* = 236 [M$^+$], 208 [M$^+$ − C$_2$H$_4$], 176 [M$^+$ − SC$_2$H$_4$]. HRMS (EI, 70 eV): calcd. 235.9822 [M$^+$]; found 235.9826. $C_8H_{12}S_4$ (236.0): calcd. C 40.64, H 5.12, S 54.25; found C 40.77, H 5.16, S 53.47.

(2*Z*,9*Z*)-1,4,8,11-Tetrathiacyclotetradeca-2,9-diene (16): This compound was produced from 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (**2**, 130 mg, 0.5 mmol) in dichloromethane (10 mL), by treatment with DIBAH (1.0 m in hexane, 4.0 mL, 4.0 mmol). Yield: 102 mg (77%) of **16** as a colorless solid, m.p. 141 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 [quint., ^3J(SCH$_2$,SCH$_2$CH_2) = 6.9 Hz, 4 H, SCH$_2$CH_2CH$_2$S], 2.84 [t, ^3J(SCH$_2$CH_2,SCH$_2$) = 6.9 Hz, 8 H, SCH$_2$], 6.26 (s, 4 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.2 (SCH$_2$*C*H$_2$), 32.4 (SCH$_2$), 127.4 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 1735, 1631, 1536, 1431. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 260 nm (3.92). MS (EI+): *m*/*z* = 264 [M$^+$]. HRMS (EI, 70 eV): [M$^+$] calcd. 264.0135; found 264.0119. $C_{10}H_{16}S_4$ (264.5): calcd. C 45.41, H 6.10, S 48.49; found C 45.51, H 6.15, S 47.90.

(2*Z*,10*Z*)-1,4,9,12-Tetrathiacyclohexadeca-2,10-diene (17): This compound was produced from 1,4,9,12-tetrathiacyclohexadeca-2,10-diyne (**3**, 144 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 4.0 mL, 4.0 mmol). Yield: 130 mg (89%) of **17** as a colorless solid, m.p. 165 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73 (m, 4 H, SCH$_2$CH_2), 2.70 (m, 8 H, SCH$_2$), 6.04 (s, 4 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.8 (SCH$_2$*C*H$_2$), 34.8 (SCH$_2$), 125.5 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1}, 2947, 2923, 2842, 1634, 1548, 1448, 1422, 1361. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 252 nm (4.38). MS (EI+): *m*/*z* = 292 [M$^+$], 259 [M$^+$ − SH]. HRMS (EI, 70 eV): calcd. 292.0448 [M$^+$]; found 292.0476. $C_{12}H_{20}S_4$ (292.0): calcd. C 49.27, H 6.89, S 43.84; found C 49.32, H 6.83, S 42.95.

(2*Z*,11*Z*)-1,4,10,13-Tetrathiacyclooctadeca-2,11-diene (18): This compound was produced from 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**4**, 60 mg, 0.19 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 m in hexane, 1.52 mL, 1.52 mmol). Yield: 39 mg (64%) of **18** as a colorless solid, m.p. 254 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58−1.68 (m, 12 H, SCH$_2$CH_2 and SCH$_2$CH$_2$CH_2), 2.74 (m, 8 H, SCH$_2$), 6.10 (s, 4 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1 (SCH$_2$CH$_2$*C*H$_2$), 29.7 (SCH$_2$*C*H$_2$), 34.3 (SCH$_2$), 125.2 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 3019 cm^{-1}, 2915, 2845, 1631, 1542, 1417. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 254 nm (4.34). MS (EI+): *m*/*z* = 320 [M$^+$], 287 [M$^+$ − SH]. HRMS (EI, 70 eV): calcd. 320.0761 [M$^+$]; found 320.0734. $C_{14}H_{24}S_4$ (320.1): calcd. C 52.45, H 7.54; found C 52.51, 7.63.

(2*Z*,12*Z*)-1,4,11,14-Tetrathiacycloeicosa-2,12-diene (19): This compound was produced from 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (**5**, 175 mg, 0.5 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 4.0 mL, 4.0 mmol). Yield: 157 mg (90%) of **19** as a colorless solid, m.p. 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58−1.68 (m., 16 H, SCH$_2$CH_2 and SCH$_2$CH$_2$CH_2), 2.74 (m, 8 H, SCH$_2$), 6.10 (s, 4 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ =26.1 (SCH$_2$CH$_2$*C*H$_2$), 29.7 (SCH$_2$*C*H$_2$), 34.3 (SCH$_2$), 125.2 (C=) ppm. IR (KBr): $\tilde{\nu}$ = 3009 cm^{-1}, 2924, 2850, 1631, 1547, 1459, 1422. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 256 nm (4.28). MS (EI+): *m*/*z* = 348 [M$^+$], 315 [M$^+$ − SH]. HRMS (EI, 70 eV): calcd. 348.1074 [M$^+$]; found 348.1043. $C_{16}H_{28}S_4$ (348.1): calcd. C 55.12, H 8.09; found C 55.20, H 8.16.'"5

(2*Z*,9*Z*)-1,4,8,11-Tetrathiacycloheptadeca-2,9-diene (20): This compound was produced from 1,4,8,11-tetrathiacycloheptadeca-2,9-diyne (**6**, 90 mg, 0.3 mmol) in toluene (10 mL), by treatment with DIBAH (1.0 M in hexane, 2.4 mL, 2.4 mmol). Yield: 88 mg (96%) of **20** as a colorless solid, m.p. 86 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37−1.43 (m, 8 H, SCH$_2$CH$_2$CH_2, SCH$_2$CH_2CH$_2$), 1.49−1.56 (m, 4 H, SCH_2CH$_2$CH$_2$), 1.79−1.90 (m, 2 H, SCH$_2$CH_2CH$_2$S), 2.61−2.66 (m, 8 H, SCH$_2$), 6.15 [d, ^3J(=CH, =CH) = 7.9 Hz, 2 H, =CH], 6.19 [d, ^3J(=CH, =CH) = 7.9 Hz, 2 H, =CH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4 (SCH$_2$CH$_2$*C*H$_2$), 29.7 (SCH$_2$*C*H$_2$CH$_2$), 31.9 (SCH$_2$*C*H$_2$CH$_2$S), 32.8 (SCH$_2$), 34.6 (SCH$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2923, 2851, 1528, 1461, 1441,

Table 4. Crystallographic data for enynes **8**, **10**, **11**, and **14**

Compound	**8**	**10**	**11**	**14**
Empirical formula	$C_8H_{10}S_4$	$C_{12}H_{18}S_4$	$C_{14}H_{22}S_4$	$C_{12}H_{18}O_2S_4$
Formula mass [g/mol]	234.40	290.50	318.56	322.50
Crystal size [mm]	0.40 × 0.36 × 0.28	0.40 × 0.20 × 0.14	0.38 × 0.20 × 0.18	0.30 × 0.20 × 0.14
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a [Å]	11.5302(1)	9.0049(3)	10.6359(3)	10.9738(1)
b [Å]	8.3109(1)	10.1253(3)	14.8346(3)	16.3355(2)
c [Å]	11.7249(1)	15.9809(5)	10.5146(2)	8.6030(1)
β [°]	110.849(1)	90	90.196(1)	94.368(1)
V [Å^3]	1049.985(18)	1457.10(8)	1658.98(7)	1537.72(3)
$D_{calcd.}$ [g/cm^3]	1.483	1.324	1.275	1.393
Z	4	4	4	4
F(000)	488	616	680	680
$h_{min.}/h_{max}$	−14/14	−11/11	−13/13	−14/14
$k_{min.}/k_{max}$	−10/10	−13/13	−19/19	−21/21
$l_{min.}/l_{max}$	−15/15	−20/20	−13/13	−11/11
μ [mm^{-1}]	0.848	0.848	0.555	0.609
Refl. collected	10438	15115	16793	15544
Refl. unique	2406	3349	3807	3525
Refl. observed	2188	2954	2879	2698
Variables	149	146	252	235
$R(F^2)$	0.025	0.035	0.041	0.032
$R_w(F^2)$	0.062	0.087	0.094	0.070
S (Gof) on F^2	1.12	1.04	1.03	1.01
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.26	0.41	0.79	0.30
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.30	−0.23	−0.43	−0.21

Table 5. Crystallographic data for dienes **15**, **16**, **18**, the α modification of **19**, and **20**

Compound	**15**	**16**	**18**	**19α**	**20**
Empirical formula	$C_8H_{12}S_4$	$C_{10}H_{16}S_4$	$C_{14}H_{24}S_4$	$C_{16}H_{28}S_4$	$C_{13}H_{22}S_4$
Formula mass [g/mol]	236.42	264.47	320.57	348.62	306.55
Crystal size [mm]	0.39 × 0.14 × 0.12	0.61 × 0.22 × 0.06	0.41 × 0.18 × 0.08	0.28 × 0.20 × 0.18	0.40 × 0.20 × 0.18
Crystal system	triclinic	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	$P\bar{1}$	$Pbca$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a [Å]	9.0182(3)	9.4692(2)	10.4526(2)	5.5202(3)	10.1105(1)
b [Å]	9.0612(3)	9.9459(2)	17.6098(2)	8.4666(5)	10.7869(1)
c [Å]	13.5966(4)	13.2848(1)	19.3207(3)	10.8787(6)	15.4064(1)
α [°]	101.089(1)	90	90	108.054(1)	90
β [°]	100.393(1)	90	90	99.234(1)	98.716(1)
γ [°]	91.672(1)	90	90	95.964(1)	90
V [Å^3]	1070.07(6)	1251.16(4)	3556.33(10)	470.71(5)	1660.83(2)
$D_{calcd.}$ [g/cm^3]	1.467	1.404	1.197	1.230	1.226
Z	4	4	8	1	4
F(000)	496	560	1376	188	656
$h_{min.}/h_{max}$	−11/11	−12/12	−13/13	−7/7	−13/13
$k_{min.}/k_{max}$	−11/11	−12/12	−22/22	−10/10	−14/14
$l_{min.}/l_{max}$	−17/17	−17/17	−25/25	−14/14	−19/19
μ [mm^{-1}]	0.833	0.720	0.518	0.495	0.552
Refl. collected	11172	11780	36692	4877	16627
Refl. unique	4900	1435	8122	2144	3797
Refl. observed	3619	1225	5093	1852	2394
Variables	218	96	325	91	242
$R(F^2)$	0.051	0.028	0.045	0.032	0.036
$R_w(F^2)$	0.131	0.067	0.079	0.080	0.082
S (Gof) on F^2	1.03	1.07	1.00	1.07	1.00
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.83	0.40	0.29	0.31	0.24
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.33	−0.32	−0.25	−0.29	−0.25

1415. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 256 nm (4.44). MS (EI+): m/z = 306 [M$^+$]. HRMS (EI, 70 eV): calcd. 306.0604 [M$^+$]; found 306.0594. $C_{13}H_{22}S_4$ (306.6): calcd. C 50.93, H 7.23; found C 50.64, H 7.35.

X-ray Diffraction Analyses: All X-ray studies were performed with a Bruker Smart CCD diffractometer (Mo-K_α radiation, graphite monochromator). Frames corresponding to a complete sphere of data were collected by using 0.3° ω-scans. The structures were

solved by direct methods (SHELXTL V5.10[24]). The structural parameters of the non-hydrogen atoms were refined anisotropically by a full-matrix, least-squares technique (F^2). The refinement was carried out with SHELXTL V5.10.[24] Table 4 and Table 5 contain the crystallographic data and details of the refinement procedure for compounds **8**, **10**, **11**, **14**−**16**, **18**, the α modification of **19**, and **20**. The data for **17** and the β modification of **19** have already been published.[14] All isolated single crystals were colorless and polyhedral in shape. The X-ray studies were performed at 200(2) K. For the achiral products **10** and **18** the chiral space group $P2_12_12_1$ was found. The absolute structure parameter for **10** is 0.3(1) and for **18** it is 0.55(7). CCDC-171188, -171189 and -181342 to -181350 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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