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RESEARCH ARTICLE

Preparation and reactivity of unsymmetrical di- and trisulfides

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Triphenylmethanesulfenyl chloride TrSCl (**6**) and triphenylmethanethiosulfenyl chloride TrSSCl (**7**) react with various thiols RSH to give the corresponding unsymmetrical polysulfides TrSSR **9** and TrSSSR **10**, respectively. Compounds **9** and **10** were obtained in excellent yield and identified by ^{1}H- and ^{13}C-NMR as well as by elemental analysis. *p*-Methoxybenzyl trityl trisulfide **10c** was characterized by X-ray crystallography. Preliminary experiments showed an interesting reactivity of trisulfides TrSSSR **10** with electrophiles to give polysulfides RS_XR; the use of elemental iodine results in the formation of the corresponding hexasulfides RS_6R, **15** in high yield and with higher than 90% selectivity.

Keywords: Trityl; Thiol; Disulfides; Trisulfides; Sulfenyl chloride; Thiosulfenyl chloride; Polysulfides; Sulfur transfer reagent

1. Introduction

One of the main classes of organic sulfur compounds is characterized by structure **1**, in which chains of sulfur atoms are terminated by two groups that can be the same, different or connected as cyclic polysulfides.

1

Alkyl and aryl mono- and disulfides are relatively easy to prepare and are generally stable, easily characterized compounds. In the synthesis of trisulfides, polysulfides are often obtained as impurities. Thus the isolation, purification and characterization of individual

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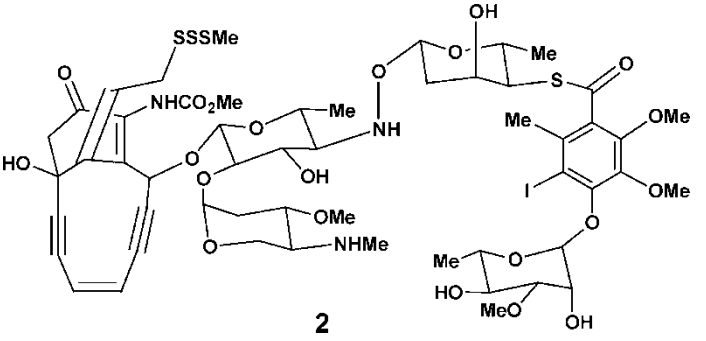
di- and trisulfides can be difficult as their properties are often similar. In other cases, clean-cut separations are all but impossible.

Sustained research activity on organopolysulfides has resulted in a plethora of new methods for their preparation, opening the way to both naturally-occurring as well as unknown polysulfides [1–3]. Often, interest in the chemistry of this class results from their prevalence in nature and diverse roles played in living organisms.

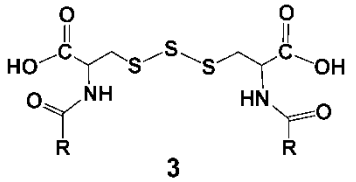
For instance, dimethyl trisulfide, CH_3SSSCH_3, has been found to function as a communicative secretion of the mandibular gland of the ponerine ant *paltothyreus tarsatus* [4]. This trisulfide has been also identified as a volatile compound produced by the bacteria *pseudomonas putrefaciens* [5] and is present in sterile fish muscle and as a trace component with dimethyl tetrasulfide in the volatiles of swine manure [6].

Several organic polysulfides have been found in plant sources [7–11]. Among these are examples from the onion family (*genus allium*) [12, 13]. Diallyl di- and trisulfides are considered as the main materials for the preparation of the insecticidal principles of garlic and allyl methyl trisulfide is a component of garlic oil [14]. During the last decade, the enediyne class of compounds received great attention because of their powerful anti-cancer activity [15]. Among this class, is the unusual trisulfide, calicheamicin γ_1^I **2** [16, 17]. For this family of compounds and their bacterial sources, the biological mode of action and synthesis have been reviewed by Nicolaou [15] and Danishefsky [18].



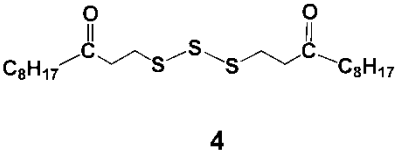
2

Cysteine trisulfide derivatives **3** have an immunostimulating effect and are useful in the treatment of artheriosclerosis [19]. Bis(3-oxoundecyl) trisulfide **4**, found in brown algae *Dictyopteris plagiogramma* [20, 21], is another example of naturally occurring trisulfide.



3

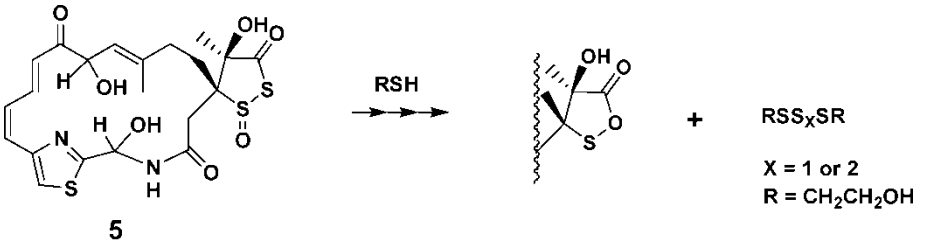
R = unbranched alkyl



4

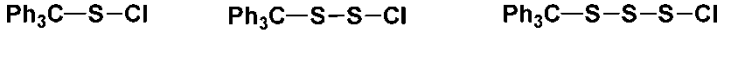
In addition, the synthesis, properties, and uses of industrial application of polysulfide polymers have been reported [22–26]. A variety of methods have been utilized for the synthesis of the above and other symmetrical and unsymmetrical trisulfides [27–32].

Other compounds like leinamycin **5** generate *in situ* polysulfides upon treatment with thiols [33] or other nucleophiles. Polysulfides mediate formation of oxygen radicals that cleave DNA. This action is observed for both polysulfides generated *in situ* and prepared independently.



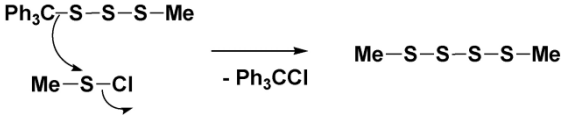
5

Recently, we reported [34–36] the reaction of sulfenyl chloride **6** (and its thio- **7** and dithio homologue **8**) with disulfides to give tri-, tetra-, and pentasulfides RS_XR, respectively, in good to excellent yields.



6 **7** **8**

The formation of the corresponding trityl polysulfide intermediate TrS_XR (**9** or **10**) was a common feature in these reactions [34–36]. Compounds **9** and **10** underwent a series of reactions to give the final product (scheme 1).

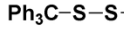


SCHEME 1

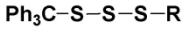
The ease with which these trityl intermediates reacted was verified in some reactions and their clean conversion (due to the excellent properties of the trityl moiety as a leaving group) attracted our interest. We have investigated the synthetic utility of this reaction and describe our findings.

2. Results and discussion

Trityl substituted polysulfides used here as starting materials were prepared using a long-known reaction of the corresponding sulfenyl chlorides and thiols. Indeed, the preparation of a series of TrS_XBu and TrS_XTr (x = 1 to 4) polysulfides using this method was reported earlier [37]. By using our significantly improved procedure (reaction times decreased from 8 to 1 h, with improved purity and yield), we obtained various benzyl and aryl substituted trityl polysulfides for further studies. The reaction products were established on the basis of their ^{1}H- and ^{13}C-NMR spectra and elemental analysis.



9a: R = *p*-chlorobenzyl
9b: R = *p*-methoxybenzyl
9c: R = *p*-nitrophenyl



10a: R = benzyl
10b: R = *p*-chlorobenzyl
10c: R = *p*-methoxybenzyl
10d: R = phenylethylene
10e: R = *p*-chlorophenyl
10f: R = *p*-methoxyphenyl
10g: R = *p*-nitrophenyl
10h: R = *p*-bromophenyl
10i: R = 2-naphthyl

Both **9** and **10** were inert towards *p*-nitrobenzyl bromide, mesyl chloride and benzoyl chloride. No trace of the desired nucleophilic substitution reaction was observed even after 24 h reflux in acetonitrile. Only small amounts of decomposition products (mainly RS_XR) were formed. The reported reaction with 2,4-dinitrophenylsulfenyl chloride was also slow [38, 39]. However, more REACTIVE electrophiles such as thionyl chloride, sulfur dichloride and iodine reacted with trityl polysulfides TrS_XR, but with poor selectivity (table 1). Reactions were complete in 14 h (depending on conditions) forming a mixture of polysulfides RS_XR with x ranging from 2 to 6. Only in the presence of acetic acid did the selectivity improve, resulting in the formation mainly of tetra- and pentasulfides.

The reaction became rapid and cleaner in the presence of methanol. Unfortunately, the separation of hexasulfides **15** from trityl methyl ether (TrOMe) that formed during the reaction was not achieved due to very similar retention factors of the two compounds. The use of glycol did not solve the problem even with a 100-fold excess; some disubstituted dityrl ethers, $TrOCH_2CH_2OTr$ formed and separation of the polysulfide was impossible. Fortunately, the use of silica gel as a heterogeneous source of the OH group resulted in a fast and clean separation.

It was discovered that the reaction requires the presence of some alcohol and an excess of iodine (table 2). With stoichiometric or smaller amounts of iodine, yields were low. With silica gel, the reaction time had to be extended, likely due to the less efficient heterogeneous conditions of the reaction.

The use of excess iodine required its removal with sodium thiosulfate. Additionally, the reaction was slowed from 1–3 to 10 min as a result of heterogeneous conditions. The organic layer was washed with 0.1% hydrochloric acid before proceeding. Failure to do so resulted in the partial decomposition of the hexasulfide during purification on the column, likely caused by some sulfur species formed from sodium thiosulfate. Column chromatography did not separate hexasulfides from other polysulfides.

Table 1. Yields of polysulfides formed in a reaction of TrS_XR (R = benzyl) with electrophiles under various conditions.

	Yields [%][a]				
Conditions	RS_2R **11**	RS_3R **12**	RS_4R **13**	RS_5R **14**	RS_6R **15**
SO_2Cl_2/CH_2Cl_2 (excess)	2	5	15	27	46
I_2 (3 eq)/CH_2Cl_2	12	22	15	5	8
I_2 (3 eq)/CH_2Cl_2 C_5H_5N		15	14	9	15
I_2 (4 eq)/CH_2Cl_2 AcOH	1	6	51	40	

[a]Determined by NMR with bibenzyl as internal standard.

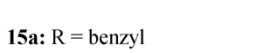
Table 2. Yields of polysulfides formed in a reaction of TrS_3R (R = benzyl) with various amounts of iodine.

	Ratios[a]				
Conditions	RS_2R **11**	RS_3R **12**	RS_4R **13**	RS_5R **14**	RS_6R **15**
I_2 (0.5 eq)/MeOH (1 min)		2	10		
I_2 (2 eq)/MeOH (3 min)		2	5	66	10
I_2 (3 eq)/MeOH (1 min)		2	5	91	
I_2 (3 eq)/$(CH_2OH)_2$ (1 min)			3	90	
I_2 (4 eq)/silica (SiOH) (10 min)		4	5	91	

[a]Determined by NMR.

The reaction described here provides one main product (hexasulfide **15** for corresponding TrS_3R and tetrasulfides **13** for corresponding TrS_2R), however, the reactions are accompanied by varying amounts of other polysulfides. The best results in terms of selectivity and yield were obtained for benzyl derivatives. Apparently, the substitution in the ring does not play a significant role in the reaction outcome. *p*-Nitrophenyltrityl trisulfide (**10g**) resulted in a much less selective formation of the corresponding hexasulfide that had been accompanied by tetra- and pentasulfides. Similarly, *p*-methoxybenzyl trityl disulfide (**9b**) gave a mixture containing three products, mainly tetrasulfide (table 3).

All attempts to crystallize the hexasulfides were futile. This is not surprising as dibenzyl hexasulfide is reported to be an oil [40]. Hexasulfides **15** were characterized by NMR and elemental analysis. The prepared dibenzyl hexasulfide (**15a**) was desulfurized with triphenylphosphine to the corresponding pentasulfide **14a**. This conversion was confirmed by comparison with separately prepared benzyl pentasulfide (**14a**) [35].



15a: R = benzyl
15b: R = *p*-chlorobenzyl
15c: R = *p*-methoxybenzyl

To learn more about the origins of the observed reactivity of TrSSSR, an X-ray crystal structure of *p*-methoxybenzyltrityl trisulfide **10c** was obtained [41]. The ORTEP drawing is shown in figure 1. Selected bond lengths, bond angles and dihedral angles are shown in table 4.

The weak C(1)-S(1) bond predestines it to be cleaved most easily when S(1) acts as a nucleophile. The trityl cation is a good leaving group due to extensive delocalization.

Table 3. Yields of polysulfides obtained from trityl di- and trisulfides.

		Yields [%][a]				
Starting material		R_2S_2 **11**	R_2S_5 **12**	R_2S_4 **13**	R_2S_5 **14**	R_2S_6 **15**
p-MeO-$C_6H_4CH_2S_2Tr$	**9b**	4	26	60	12	
$C_6H_5CH_2S_3Tr$	**10a**			4	2	81
p-Cl-$C_6H_4CH_2S_3Tr$	**10b**			4		91
p-MeO-$C_6H_4CH_2S_3Tr$	**10c**			9		80
p-O_2N-$C_6H_4S_3Tr$	**10g**			15	12	66

[a]Determined by NMR with bibenzyl as internal standard, after isolation.

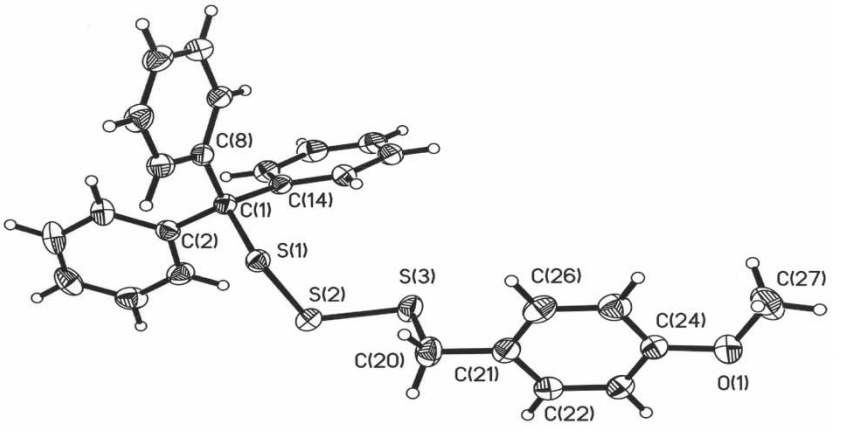


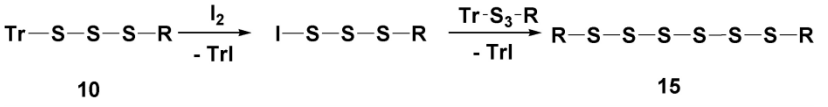
Figure 1. ORTEP Representation of *p*-methoxybenzyltrityl trisulfide **10c**.

Most likely, the reaction is initiated when I_2 is attacked by the sulfur atom adjacent to the trityl group (scheme 2). The dithiosulfenyl iodide that forms likely reacts with another molecule of TrS_3R in a manner similar to the mechanism rationalizing insertion of TrS_XCl into the S-S bonds [34, 35]. As a result, the corresponding RS_XR and trityl iodide (TrI) form.

Apparently the presence of TrI is detrimental for both yield and selectivity of the reaction. This effect is likely caused by an easy dissociation of iodide ion from the molecule. The resulting trityl cation might combine with the polysulfides and lead to the redistribution of sulfur in the products significantly lowering yield and selectivity as well as leading to the formation of some undesired side products. Reaction times varied depending on the reagent, from 5+ minutes with iodine and up to 1 h with SO_2Cl_2 that was the slowest acting even when present in excess. By adding an excess of alcohol, the trityl cation is trapped in as $TrOCH_3$ [42, 43]. Due to the separation problem (similar rf of both TrOR and RS_XR) it is advantageous to use a solid source of the hydroxyl group. Here, silica gel has proved to be an excellent trityl trapping agent permanently removing this cation from the reaction medium. The hexasulfides prepared according to the above method were surprisingly stable, and could be handled at

Table 4. Selected bond lengths, bond angles, and dihedral angles from the X-ray structure of *p*-methoxybenzyltrityl trisulfide **10c**.

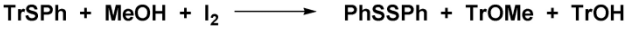
Bond Lengths (Å)			
Bond		Bond	
S(1)-S(2)	2.0423(2)	S(2)-S(3)	2.0409(1)
S(1)-C(1)	1.904(2)	C(20)-C(21)	1.949(3)
S(3)-C(20)	1.829(3)	C(1)-C(2)	1.529(3)
Bond Angles (deg)			
Angle		Angle	
S(1)-S(2)-S(3)	107.72(5)	C(2)-C(1)-S(1)	107.62(1)
C(1)-S(1)-S(2)	107.55(8)	S(3)-C(20)-C(21)	107.61(2)
C(20)-S(3)-S(2)	102.24(9)	C(24)-O(1)-C(27)	116.8(3)
Dihedral Angles (deg)			
Angle		Angle	
C(1)-S(1)-S(2)-S(3)	106.88(8)	S(2)-S(3)-C(20)-C(21)	176.18(2)
S(1)-S(2)-S(3)-C(20)	82.46(1)	S(1)-C(1)-C(2)-C(3)	112.1(2)
S(2)-S(1)-C(1)-C(2)	73.95(1)	S(2)-S(1)-C(1)-C(8)	−167.37(1)



SCHEME 2

room temperature for hours without any change. For extended times they were stored in the freezer. On the other hand, they partially decomposed during preparation on the silica gel column (likely *via* sulfur extrusion to form lower polysulfides). This adverse reaction was easily prevented with a diluted hydrochloric acid as described earlier. Addition of a small amount of acetic acid prior to purification on the column was equally protective.

The described reaction has some literature precedent [44]. It is known that treatment of TrSPh with methanolic iodine solution gives diphenyl disulfide (scheme 3).



SCHEME 3

The above reaction was never applied in the preparation of higher polysulfides. Alternative conversions of thiols to polysulfides are rather tedious [40], thus this approach allows for faster access to these compounds.

3. Conclusion

The optimized reaction of triphenylmethanesulfenyl chloride **6** and its thio homolog **7** with thiols provides a simplified route for the preparation of unsymmetrical trityl di- **9** and trisulfides **10**. Both types of compound possess nucleophilic properties and are capable of reacting with iodine or thionyl chloride to give mainly symmetrical hexa- and tetrasulfides, respectively. This approach is presently being extended to other polysulfides [45].

4. Experimental

Nuclear magnetic resonance spectra were recorded at 400 MHz (Varian Mercury 400) spectrometer. Deuteriochloroform ($CDCl_3$) was used as solvent along with TMS as an internal standard. Thiols were obtained from Aldrich Chemical Company (Milwaukee, WI 53233 USA) and used directly.

4.1 *General procedure for the preparation of TrS_XR*

To a stirred suspension of 2.90 mmol of sulfenyl chloride **6** or **7** in 100 mL of anhydrous diethyl ether, a solution of 3.0 mmol of the thiol in 30 mL of anhydrous diethyl ether was added dropwise during 30 min under nitrogen atmosphere at −78°C. The reaction was warmed to room temperature over 1.5 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 15% chloroform in hexane afforded an oily product which solidified upon treatment with 35–60°C petroleum ether. Recrystallization from hexanes gave high yields of the corresponding polysulfides **9** or **10**.

4.2 *General procedure for the preparation of RS_XR*

A solution of benzyltrityl di- or trisulfide (0.125 mmol) in CH_2Cl_2 (5 mL) was added rapidly into a suspension of silica gel in a solution of iodine (64 mg, 0.5 mmol) in Et_2O (2.5 mL). After 10 min of stirring, the solution was filtered (silica gel was washed with CH_2Cl_2). A concentrated aqueous solution of $Na_2S_2O_3$ (excess, 1–2 mL) was added to a stirred organic layer in order to remove iodine (*ca*. 1–2 min of stirring). The colorless mixture was partitioned between hexanes and water. The organic layer was washed with HCl (0.1 M, 25 mL). After workup, the residue was chromatographed on silica gel with 0.25–0.5% AcOEt in hexanes to give the product (see table 3).

4.2.1 *p*-Chlorobenzyltrityl disulfide 9a. Yield: 85%; mp: 97–98°C. ^{1}H NMR ($CDCl_3$): δ 2.77 (s, 2H), 6.85–7.47 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 40.67, 71.22, 126.85, 127.78, 128.34, 130.01, 130.38, 132.90, 135.12, 143.53 ppm. Anal. calcd for $C_{26}H_{21}S_2Cl$: C, 72.16; H, 4.86%. Found C, 72.14; H, 4.86%.

4.2.2 *p*-Methoxybenzyltrityl disulfide 9b. Yield: 90%; mp: 112–114°C. ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 2H), 3.72 (s, 3H), 6.70–7.47 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 41.15, 55.21, 55.23, 71.10, 113.64, 126.27, 127.71, 128.41, 130.06, 130.23, 143.69, 158.56 ppm. Anal. calcd for $C_{27}H_{24}OS_2$: C, 75.70; H, 5.61%. Found C, 75.33; H, 5.70%.

4.2.3 *p*-Nitrophenyltrityl disulfide 9c. Yield: 78%; mp: 108–109°C. ^{1}H NMR ($CDCl_3$): δ 7.10–7.85 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 73.04, 122.98, 126.97, 127.16, 127.74, 129.83, 142.52, 145.65, 146.09 ppm. Anal. calcd for $C_{25}H_{19}$ NO_2S_2: C, 69.93; H, 4.43%. Found C, 70.08; H, 4.43%.

4.2.4 Benzyltrityl trisulfide 10a. Yield: 96%; mp: 109–110°C. ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 2H), 7.16–7.33 (m, 20H) ppm. ^{13}C NMR ($CDCl_3$): δ 43, 80, 73.19, 127.02, 127.31, 127.75, 128.35, 129.21, 130.25, 136.42, 143.27 ppm. Anal. calcd for $C_{26}H_{22}S_3$: C, 72.56; H, 5.12%. Found C, 71.97; H, 5.36%.

4.2.5 *p*-Chlorobenzyltrityl trisulfide 10b. Yield: 88%; mp: 125–127°C. ^{1}H NMR ($CDCl_3$): δ 3.74 (s, 2H), 7.08–7.31 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 42.88, 73.22, 127.07, 127.78, 128.50, 130.22, 130.52, 133.15, 135.07, 143.18 ppm. Anal. calcd for $C_{26}H_{21}S_3Cl$: C, 67.19; H, 4.52%. Found C, 66.99; H, 4.64%.

4.2.6 *p*-Methoxybenzyltrityl trisulfide 10c. Yield: 96%; mp: 116–118°C. ^{1}H NMR ($CDCl_3$): δ 3.76 (s, 5H, -OCH_3 and -CH_2SSS), 6.78–7.32 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 43.32, 55.29, 73.20, 113.82, 127.03, 127.76, 128.38, 130.29, 130.38, 143.34, 158.81 ppm. Anal. calcd for $C_{27}H_{24}OS_3$: C, 70.44; H, 5.22%. Found C, 70.54; H, 5.54%. The X-ray crystallographic structure of trisulfide 10c was carried out (figure 1).

4.2.7 Phenylethylenetrityl trisulfide 10d. Yield: 92%; mp: 72–73°C. ^{1}H NMR ($CDCl_3$): δ 2.83, 2.92 (m, 4H, –CH_2-Ph and –CH_2-S), 7.11–7.33 (m, 20H) ppm. ^{13}C NMR ($CDCl_3$): δ 35.46, 40.77, 73.27, 126.21, 127.03, 127.76, 128.28, 128.52, 130.25, 139.62, 143.26 ppm. Anal. calcd for $C_{27}H_{24}S_3$: C, 72.97; H, 5.41%. Found C, 72.68; H, 5.69%.

4.2.8 *p*-Chlorophenyltrityl trisulfide 10e. Yield: 88%; mp: 95–96°C. ^{1}H NMR ($CDCl_3$): δ 7.19–7.32 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 73.62, 127.14, 127.83, 128.92, 130.19, 131.02, 133.83, 135.71, 142.91 ppm. Anal. calcd for $C_{25}H_{19}S_3Cl$: C, 66.67; H, 4.22%. Found C, 66.84; H, 4.14%.

4.2.9 *p*-Methoxyphenyltrityl trisulfide 10f. Yield: 93%; mp: 108–110°C. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 3H), 6.77–7.37 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 55.40, 73.42, 114.47, 127.02, 127.77, 128.11, 130.27, 133.44, 143.16, 160.01. Anal. calcd for $C_{26}H_{22}OS_3$: C, 69.96; H, 4.93%. Found C, 69.83; H, 5.22%.

4.2.10 *p*-Nitrophenyltrityl trisulfide 10g. Yield: 90%; mp: 106–107°C; ^{1}H NMR ($CDCl_3$): δ 7.02–7.80 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 73.92, 123.76, 127.34, 127.36, 127.94, 130.10, 142.57, 146.20 ppm. Anal. calcd for $C_{25}H_{19}N\,O_2S_3$: C 65.08, H 4.12%; found C, 65.36; H, 4.21%.

4.2.11 *p*-Bromophenyltrityl trisulfide 10h. Yield: 95%; mp: 104–105°C. ^{1}H NMR ($CDCl_3$): δ 7.20–7.34 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$): δ 73.63, 127.16, 127.84, 130.18, 131.13, 131.84, 136.37, 142.89 ppm. Anal. calcd for $C_{25}H_{19}S_3$ Br: C, 60.62; H, 3.84%. Found C, 60.91; H, 4.10%.

4.2.12 2-Naphthyltrityl trisulfide 10i. Yield: 86%; mp: 99–101°C. ^{1}H NMR ($CDCl_3$): δ 7.10–7.36 (m, 22H) ppm. ^{13}C NMR ($CDCl_3$): δ 73.56, 126.29, 126.50, 127.09, 127.16, 127.50, 127.58, 127.81, 128.65, 130.23, 132.51, 133.12, 134.34, 143.04 ppm. Anal. calcd for $C_{29}H_{22}S_3$: C, 74.68; H, 4.72%. Found C, 74.63; H, 5.00%.

4.2.13 Dibenzylhexasulfide 15a. Yield: 81%; oil. ^{1}H NMR ($CDCl_3$): δ 4.19 (s, 4H), 7.31–7.35 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ 44.09, 127.82, 128.72, 129.54, 135.94 ppm. Anal. calcd for $C_{14}H_{14}S_6$: C, 44.88; H, 3.77%. Found C, 44.71; H, 3.63%.

4.2.14 Di(p-chlorobenzyl)hexasulfide 15b. Yield: 91%; oil. ^{1}H NMR ($CDCl_3$): δ 4.11 (s, 4H), 7.19–7.32 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$): δ 43.17, 128.90, 130.85, 133.81, 134.47 ppm. Anal. calcd for $C_{14}H_{12}Cl_2S_6$: C, 37.91; H, 2.73%. Found C, 37.05; H, 2.51%.

4.2.15 Di(p-methoxybenzyl)hexasulfide 15c. Yield: 80%; oil. ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 6H), 4.15 (s, 4H), 6.84 (d, J = 8.8 Hz, 4H), 7.24 (d, J = 8.8 Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 43.66, 55.27, 114.15, 127.82, 130.74, 159.320 ppm. Anal. calcd for $C_{16}H_{18}O_2S_6$: C, 44.21; H, 4.17%. Found C, 44.89; H, 4.38%.

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