Synthesis of substituted bis(allyl) polythioethers: Application for the synthesis of crown thioethers

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Abstract: Present study describes the synthesis of a novel substituted bis (allyl) thioethers by the condensation of thioetherdithiols with different allylchlorides. Representative example of the cyclization of the diallylpolythioethers *via* intramolecular radical reaction is presented. The corresponding crown thioetheris is obtained in good yield and high purity.

Keywords: Polythioethers, crown thioethers, allyl thioethers.

INTRODUCTION

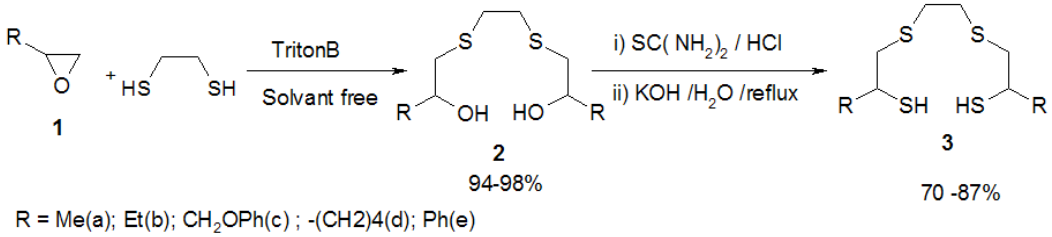
Diallylicthioethers are useful intermediates in organic chemistry [1-8].They display a wide variety of biological applications, including antivirals [9-13], antioxidants [14-21], antitumorals [12,21-23], antidiabetics [24] and other biological applications [25-29]. The reaction of diallylic sulfuric compounds with unsaturated compounds was reported to undergo Diels-Alder condensation to yield different thio-heterocyclic compounds [30] .They were also used as intermediates for the generation of crown thioethers via ring-closing metathesis (RCM) [31,32].

In continuity with the previously reported synthesis of different thioetherdithiols as polydentate ligands [33], we describe herein, an efficient approach toward the synthesis of new bis (allyl)thioethers through the allylation of thioetherthiol with different allyl chlorides.

RESULTS AND DISCUSSION

1. Synthesis of bis (allyl) polythioethers

To access to the type of this product we used dithioetherdithiols **3** (Scheme 1) as intermidiate obtained from β,β'-dihydroxythioethers **2**. These compounds were prepared from the reaction of etanedithiol with epoxides in the presence of Triton B using the method described previously [34]. They have been converted into dithioethers dithiols in good yields. The thiolation of the two hydroxyl groups was attempted according to the literature [35]. The condensation of alcohols in concentrated hydrochloric acid with thiourea followed by hydrolysis of the thiouronium salt



Scheme 1

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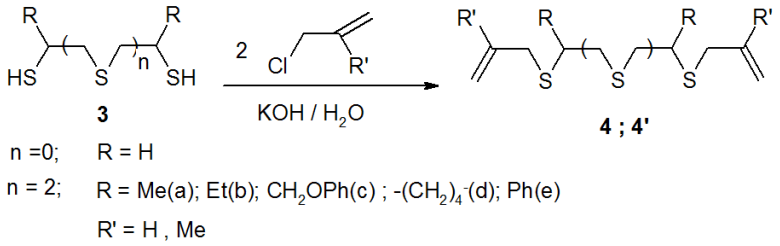


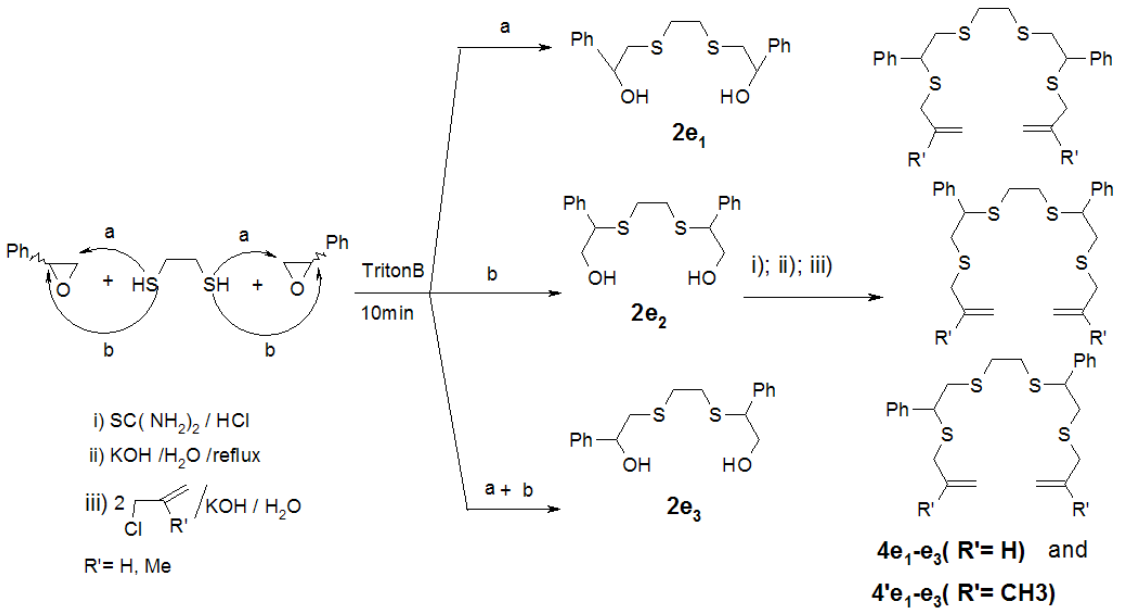
Scheme 2

intermediate under basic conditions is considered to be a good thiolation method, which is widely used for the preparation of primary and secondary thiols. Therefore, the new symmetric disubstituted dithioetherdithiols **3** have been prepared in this way.

The thioetherdithiols **3** have been served as intermediates for the synthesis of substituted diallylpolythioethers **4** and **4'** through treatment with allyl chloride (Scheme 2).

As shown in Tables 1, the diallylpolythioethers were obtained in good yields. These compounds described here were obtained and characterized as diastereomeric mixtures. Compounds **4** and **4'** should be obtained as mixtures of diastereomers. However, since the two stereogeniccenters within the molecule are far from each other, the diastereoisomers could not be discerned by NMR techniques as in the case of their precursors **2** [34]. The ^{1}H NMR spectrum shows a sharp singlet for the two methylene groups of the dimercaptoethane moiety (-SCH_2-CH_2S-) at around δ = 2.80 ppm. As the compounds **3a**, **3b**, and **3d** are symmetric, the ^{13}C NMR spectra show the existence of only three different signals corresponding to the three aliphatic carbon atoms of one isomer, besides the peaks related to the carbon atoms of the alkyl groups.

Dealing with the styrene oxide, we showed in a previous letter [34] that the ring opening of this epoxide with dimercaptoethane using benzyltrimethylammonium hydroxide (Triton B) as catalyst led to a mixture of three regioisomers of *β,β'*-dihydroxydithioethers **2e$_1$–e$_3$** (Schema 3). The three isomers were converted into their homologous thioetherthiols **3e$_1$–e$_3$**. These latters are subsequently transformed to their homologues polythioétherdiallyliques **4e$_1$–e$_3$** and **4'e$_1$–e$_3$**.The mixture of isomers was purified using a column chromatography whereas the ratio of the three isomers was determined by^{1}H NMR spectroscopy.



Scheme 3

2. Radical Reaction

We attempted to synthesize crown thioether molecules via intramolecular radical cyclization. As schown in Scheme 4, operating in the presence of one equivalent of diallylthioether **4i** with a slight excess of 1,2-ethanedithiol in the presence of 2,2'-azobis (2-methylpropionitrile) (AIBN) according to the method described in the literature [36,37], the reaction leads to the desired thioéthercouronne **5** in 55% yield . The latter is likely to present some very interesting complexing properties. The radical addition reaction is regiospecific; it only leads to anti-Markovnikov product where the sulfur atom attacks the less substituted carbon atom in alkene. Besides the desired product, other products were detected by gas chromatography (GC). This result is expected since the presence of radicals that support the existence of other competitive reactions.

CONCLUSION

The synthesis of a variety of new symmetric di and tetrasubstituted diallylpolythioethers was described. The desired compounds were obtained in good yields and high purity. Compound **5** is prepared via intramolecular radical reactions using **4i** as precursseur. The results show that compounds **4** and **4'** can be used as intermediates for the generation of interesting crown thioethers.

EXPERIMENTAL

The products were characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent for molecules **4** and **4´** and in CD_2Cl_2 for molecule **5**, on a Bruker AC 300 spectrometer. The chemical shifts were reported in δ-values relative to TMS (internal reference). For the ^{1}H NMR,the multiplicities of signals are indicated by the following abbreviations: s: singlet, d: doublet, t:triplet, m: multiplet. HRMS spectra were obtained using MAT 95 SBE instrument.

1. General procedure for the synthesis of diallyls polythioethers 4 and 4'

In three-necked flask equipped with a refrigerant and a funnel, 3g (0.053 mol) of KOH in 3 mL of H_2O was placed at room temperature. Thioetherdithiols **3** (0.015 mol) were added dropwise over 30 min to a stirred solution. Allyl Chloride (0.045 mol) was then added and the solution was stirred over 10 min. The progress of this reaction was monitored by TLC. Then the mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (3x50 mL). The organic layer was washed with $MgSO_4$ and concentrated. The residue obtained was purified by column chromatography (Cyclohexane/ ethyl acetate 80/20).

2. General procedure for thepreparation of 1, 4, 8, 11-tetrathiatetradecane 5

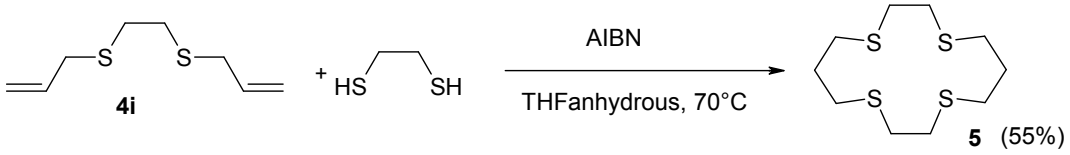
In a 25 mL two-necked flask are placed under a nitrogen atmosphere (5 mmol) diallylthioether 4**i**, (11 mmol) of 1,2- ethanedithiol and (0.3 g) of 2,2'-azobis (2-methylpropionitrile) (AIBN). The mixture is maintained stirring at 70 °C. The progress of the reaction is monitored by TLC. At the end of the reaction, the product obtained is purified by column chromatography using chloroform as eluant.

5, 12-Dimethyl-4, 7, 10, 13-tetrathiahexadeca-1,15-diene 4a

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.25 (d, J = 6.3 Hz, 6H), 2.51-2.73 (m, 4H), 2.78(s, 4H), 2.98 (m, 2H), 3.10 (d, J = 9.0 Hz, 4H), 5.12 (m, 4H), 5.96 (tdd, *J* = 6.8, 9.9, 18.2 Hz,2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.9, 32.4, 34.2, 40.5, 41.4, 117.2, 133.1; HRMS: calculated for $C_{14}H_{26}S_4$: 345.0815. found 345.0817.

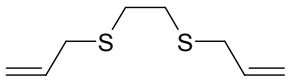
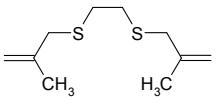
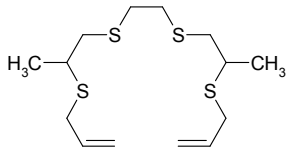
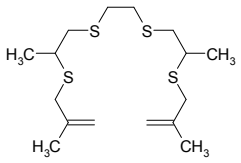
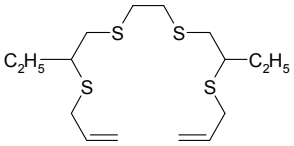
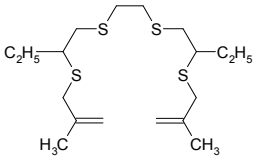
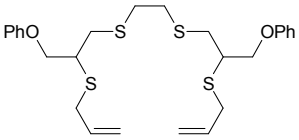
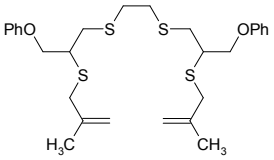
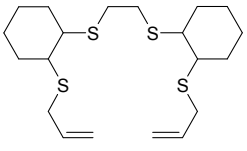
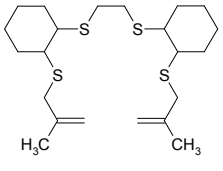
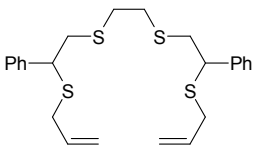
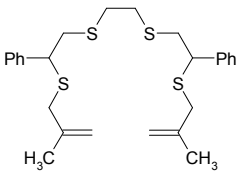
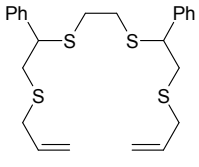
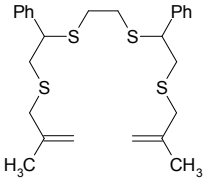
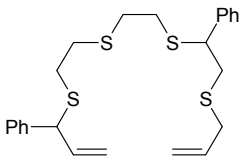
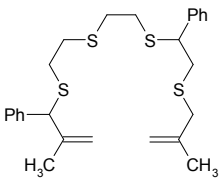
2, 5, 12, 15-Tetramethyl-4, 7, 10, 13-tetrathiahexadeca-1,15-diene 4a'

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.34 (d, *J* = 9.0 Hz, 6H), 1.83 (s, 6H), 2.51-2.76 (m, 4H), 2.79 (s, 4H), 2.98 (m, 2H), 3.15 (d, *J* = 12.0 Hz, 4H), 4.84 (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75



Scheme 4

Table I: Synthesis of diallylspolythioethers for n = 0; 2.

	Bis(allyl)thioethers[a] (R'= H)	Yield(%)	Bis(allyl)thioethers[a] (R' = CH_3)	Yield (%)
n=0	 **4i**	98	 **4ii**	98
	 **4a**	98	 **4'a**	97
	 **4b**	95	 **4'b**	98
	 **4c**	70	 **4'c**	75
n = 2	 **4d**	70	 **4'd**	80
	 **4e 1** 53%		 **4'e1** 52%	
	 **4e 2** 30%	70[b]	 **4'e2** 29%	75[b]
	 **4e 3** 17%		 **4'e3** 19%	

[a] The ratio of the three isomers was determined by ^{1}H NMR. [b]Total yield of three isomers.

MHz, $CDCl_3$) δ = 21.1, 22.5, 34.3, 40.9, 41.2, 112.1, 141.1; HRMS: calculated for $C_{16}H_{30}NaS_4$: 373.1128. found 373.1127.

5,12-Diethyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4b

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.97 (t, *J* = 7.5 Hz 6H), 1.54 (m, 4H), 2.71 (m, 4H), 2.78 (s, 4H), 3.61 (m, 2H), 5.12 (m, 4H), 5.96 (tdd, *J* = 6.6, 9.2, 18.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.23, 28.8, 32.2, 33.1, 38.8, 46.3, 117.2, 133.1; HRMS: calculated for $C_{16}H_{30}NaS_4$: 373.1128. found 373.1125.

5,12-Diethyl- 2,15-dimethyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4b'

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.96 (t, *J* = 7.5 Hz, 6H), 1.66 (m, 4H), 1.71 (s, 6H), 2.64 -2.89 (m, 4H), 2.80 (m, 2H), 2.81 (s, 4H), 3.11 (s, 4H), 4.84 (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.1, 22.7, 27.3, 32.9, 40.5, 41.4, 46.4, 112.1, 142.1; HRMS: calculated for $C_{18}H_{34}NaS_4$: 401.1441. found 401.1438.

5,12-Diphenoxymethyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4c

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.58-2.83 (m, 4H), 2.81 (s, 4H), 3.35 (m, 2H), 3.56 (d, *J* = 6.8 Hz, 4H), 4.02-4.30 (m, 4H), 5.12 (m, 2H), 5.90 (tdd, *J* = 6.8, 9.9, 16.9 Hz, 2H), 6.80-7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 32.1, 32.9, 35.4, 44.2, 77.8, 114.4, 117.9, 120.5, 129.3, 133.1, 157.5; HRMS: calculated for $C_{26}H_{34}NaO_2S_4$: 529.1339. found 529.1342.

5,12-Diphenoxymethyl-2,15-dimethyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4c'

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.70 (s, 6H), 2.60-2.84 (m, 4H), 2.81 (s, 4H), 3.12 (s, 4H), 3.36 (m, 2H), 4.08-4.32 (m, 4H), 4.85 (d, *J* = 9.2 Hz, 4H), 6.80-7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 22.5, 32.8, 35.4, 37.1, 43.5, 74.1, 114.9, 117.9, 120.5, 129.2, 142.1, 159.3; HRMS: calculated for $C_{28}H_{38}NaO_2S_4$: 557.1652. found 557.1658

1,2-Bis(2-(allylthio)cyclohexylthio) ethane 4d

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.39-1.49 (m, 8H), 1.64-1.89 (m, 8H), 2.72 (m, 4H), 2.81 (s, 4H), 3.52 (d, *J* = 6.8 Hz, 4H), 5.16 (4H, m, J = 16.9 Hz,), 5.90 (2H, tdd, *J* = 6.8, 9.9, 16.8 Hz,); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 24.3, 25.9, 31.7, 32.9, 33.7, 36.5, 45.2, 46.7, 117.9, 133.1; HRMS: calculated for $C_{20}H_{34}NaS_4$: 425.1441. found 425.1447.

1,2-Bis(2-(2-methylallylthio)cyclohexylthio) ethane 4d'

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.39-1.49 (m, 8H), 1.64-1.89 (m, 8H), 1.70 (s, 6H), 2.72 (m, 4H), 2.81 (s, 4H), 3.11 (s, 4H), 4.84 (d, *J* = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 20.7, 24.3, 31.3, 31.7, 32.9, 40.5, 45.1, 46.6, 113.6, 141.2; HRMS: calculated for $C_{22}H_{38}NaS_4$: 453.1754. found 453.1760.

5,12-Diphenyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4e$_1$

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.80 (s, 4H), 2.75-3.10 (m, 4H), 3.54 (d, *J* = 6.8 Hz, 4H), 3.98 (m, 2H), 5.12 (m, *J* = 16.9 Hz, 4H), 5.90 (tdd, *J* = 6.8, 9.9, 16.9 Hz, 2H), 6.90-7.50 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 33.5, 34.5, 40.0, 43.0, 117.2, 127.2, 128.7, 128.8, 133.1, 139.0; HRMS: calculated for $C_{24}H_{30}NaS_4$: 469.1128. found 469.1133.

5,12-Diphenyl-2,15-dimethyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4'e$_1$

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1,70 (s,6H),2.81 (s, 4H), 2.97-3.40 (m, 4H), 3,12 (s, 4H), 4.15(m,2H, 4.84 (d, *J*= 9 Hz, 4H), 6.90-7.50 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 22.5, 34.4, 41.9, 48.7, 117.7, 127.1, 128.6, 128.7, 133.1, 141.1; HRMS: calculated for $C_{24}H_{30}NaS_4$: 497.1441. found 497.1446.

6,11-Diphenyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4e$_2$

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.81 (s, 4H), 3.10-3.40 (m, 4H), 3.54 (d, J = 6.8 Hz, 4H), 4.10 (m, 2H), 5.12 (m, *J* = 16.9 Hz, 4H), 5.89 (tdd, *J* = 6.8, 9.9, 16.9 Hz, 2H); 6.90-7.50 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 31.4, 35.4, 41.9, 48.7, 117.2, 127.2, 128.7, 128.8, 133.1, 139.0; HRMS: calculated for $C_{24}H_{30}NaS_4$: 469.1128. found 469.1133.

6,11-Diphenyl-2,15-dimethyl-4,7,10,13-tetrathiahexadeca-1,15-diene 4'e$_2$

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.70 (s, 6H), 2.80 (s, 4H), 2.75-3.10 (m, 4H), 3.12 (s, 4H), 3.98 (m, 2H), 4.85 (d, *J* = 9.1 Hz, 4H), 6.90-7.50 (m,10H); ^{13} C NMR (75 MHz, $CDCl_3$) δ = 22.5, 33.5, 38.5, 40.0, 46.7, 117.2, 127.2, 128.7, 128.8, 139.0, 142.1; HRMS: calculated for $C_{26}H_{34}NaS_4$: 497.1441. found 497.1446.

5,11-Diphenyl -4,7,10,13-tetrathiahexadeca-1,15-diene 4e$_3$

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.81 (s, 4H), 3.10-3.30 (m, 4H), 3.54 (d, *J* = 6.8 Hz, 4H), 4.10 (m, 2H), 5.12 (m, *J* = 16.9 Hz, 4H), 5.89 (tdd, *J* = 6.8, 9.9, 16.9 Hz, 2H), 6.90-7.50 (m,10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 22.5,

31.3, 40.9, 41.3, 42.3, 43.7, 48.1, 117.2, 133.1, 127.2, 128.7, 128.8, 139.0; HRMS: calculated for $C_{26}H_{34}NaS_4$: 469.1128. found 469.1133.

5,11-Diphenyl-2, 15-dimethyl-4, 7, 10, 13-tetrathiahexadeca-1,15-diene4'e$_3$

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.70 (s, 6H), 2.81 (s, 4H), 3.10-3.30 (m, 4H), 3.40 (d, *J* = 6.8 Hz, 4H), 4.09 (m, 2H), 4.85 (d, *J* = 9.1Hz, 4H), 6.90-7.50 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 22.5, 31.4, 41.9, 43.8, 48.7, 112.4, 127.1, 128.6, 128.7, 139.0, 142.2; HRMS: calculated for $C_{26}H_{34}NaS_4$: 497.1441. found 497.1446.

1, 4, 8, 11-Tetrathiacylotetradecane (5)

Yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 2.13 (m, 4H), 2.50 (m, 8H), 2.79 (s, 8H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 27.1, 30.0, 31.9; HRMS: calculated for $C_{10}H_{20}NaS_4$: 291.0300. found 291.0100.

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