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Liquid Crystal Materials with Sulfur Atoms Incorporated in the Principal Structure. IV. New Liquid Crystal Compounds; 2-(*p*-Substituted phenyl)-5-alkyl-1,3-oxathianes

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2-(*p*-Substituted phenyl)-5-alkyl-1,3-oxathianes, new liquid crystal compounds, were synthesized by the acetal-formation reaction of the corresponding aldehydes and 2-alkyl-3-mercapto-1-propanols. The mesomorphic behaviors of these 1,3-oxathiane compounds were compared with those of the corresponding 1,3-dithianes and 1,3-dioxanes. Some of 2-(*p*-cyanophenyl)-5-alkyl-1,3-oxathianes exhibit monotropic nematic liquid crystal phase at room temperature, whereas 2-(*p*-alkoxyphenyl)-5-alkyl-1,3-oxathianes tend hardly to exhibit liquid-crystal phase. These mesomorphic characters seem to originate in the molecular width and bending at the 1,3-oxathiane ring.

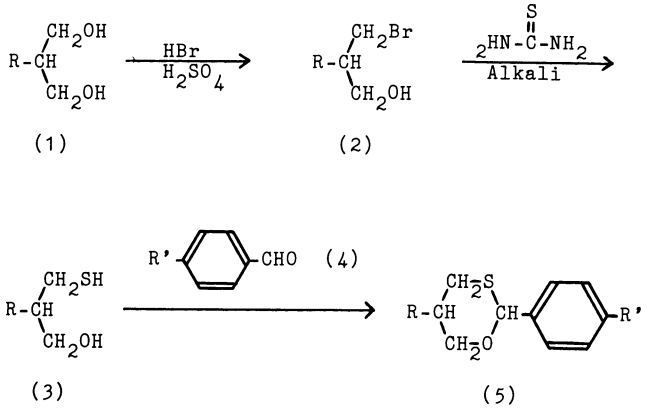
In recent years, 2,5-disubstituted 1,3-dithianes and several 2,5-disubstituted 1,3-oxathianes, new types of liquid-crystalline compounds, have been reported.[1-5] The present study relates to the synthesis and mesomorphic behavior of 2-(*p*-substituted phenyl)-5-alkyl-1,3-oxathianes having the systematically changed chain length of alkyl groups. The features concerning about appearance of mesophase of these 1,3-oxathianes were compared with those of the corresponding 1,3-dithianes and 1,3-dioxanes.

Results and Discussion

2-(*p*-Substituted phenyl)-5-alkyl-1,3-oxathianes were synthesized *via* the following route.

In step **1**→**2**, the reaction temperature must be kept between 70 and 75 °C. At a temperature between 90 and 95 °C, the main product was the disubstituted bromide contrary to the purpose. As compounds **3** were susceptible to oxidation, step **2**→**3** required nitrogen atmosphere. In **3**→**5**, both trans and cis isomers differing at C-5 position of the 1,3-oxathiane ring were produced.

Repeated recrystallizations were required to obtain the purified trans isomers. As trans and cis isomers



R: *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_7H_{15}, *n*-C_8H_{17}.

R': OCH_3, OC_2H_5, $OC_3H_7^n$, $OC_4H_9^n$, $OC_5H_{11}^n$, CN.

Fig. 1.

exhibit C-2 proton signals of the 1,3-oxathiane ring in ^{1}H-NMR at δ 5.75 and 5.80 (R'=CN), respectively, the contamination of cis isomer can be detected by the examination of proton signals at δ 5.80.

The presence of 1,3-dithianes and 1,3-dioxanes can also be detected by the examination of C-2 proton signals at δ 5.10, and 5.30, respectively.

Absorptions of C2, C4, and C6 carbons of the 1,3-oxathiane ring in ^{13}C-NMR spectra, as determined by ^{1}H-complete decoupling (COM), ^{1}H-off resonance decoupling (OFR), and ^{1}H-selective decoupling (SEL) procedures, are located at δ 83.22, 34.84, and 75.55, respectively (R=C_8H_{17}, R'=CN). In ^{1}H-NMR, C4 proton signals are located at δ 3.4 (t), and 4.3 (m). The attribution of these two proton signals to the two protons attaching to C4 carbon of the 1,3-oxathiane ring derives from the fact that, in ^{1}H-selective decoupling of ^{13}C-NMR spectra, the peak of C2 carbon becomes more intense with irradiation of δ (3.4+4.3)/2, but indicates little change in both cases of irradiation of δ 3.4 and 4.3.

Measurements of mesomorphic ranges and assignments of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers. Mesomorphic ranges of the synthesized 2-(*p*-substituted phenyl)-5-alkyl-1,3 oxathianes and the corresponding 1,3-dithianes and 1,3-dioxanes are given in Table 1.

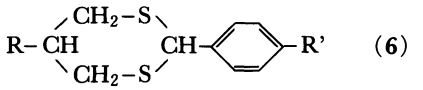
Transition temperatures of isotropic to nematic (T_{N-I}) for 2-(*p*-cyanophenyl)-5-alkyl-1,3-oxathianes were lower than those for the corresponding 1,3-dioxanes by about 20 °C. It is known generally that the larger the molecular width, the lower the T_{N-I} is.[6] The width of 2-(*p*-cyanophenyl)-5-alkyl- 1,3-oxathianes is larger than that of the corresponding 1,3-dioxanes because of the presence of a large sulfur atom.

2-(*p*-Cyanophenyl)-5-alkyl-1,3-dithianes did not exhibit any liquid crystal phases. As molecular width of 2-(*p*-cyanophenyl)-5-alkyl-1,3-dithianes having two sulfur atoms are larger than those of 1,3-dioxane and 1,3-oxathiane compounds, they seem to be unable to exhibit a nematic phase.

As regards compounds having 2-(*p*-alkoxyphenyl)

TABLE 1. TRANSITION TEMPERATURE OF COMPOUNDS 5 AND THE CORRESPONDING 1,3-DITHIANES AND 1,3-DIOXANES

	R	R'	Transition Temp/°C[a]
5-1	n-C_3H_7	OCH_3	C 55 I; 30
5-2	n-C_3H_7	OC_2H_5	C 54 I; 25
5-3	n-C_3H_7	n-OC_4H_9	C 57 I; 13 N 17
5-4	n-C_4H_9	OC_2H_5	C 76 I; 34
5-5	n-C_4H_9	n-OC_3H_7	C 54 I; 20
5-6	n-C_5H_{11}	OCH_3	C 75 I; 19
5-7	n-C_5H_{11}	OC_2H_5	C 85 I; 53
5-8	n-C_5H_{11}	n-OC_3H_7	C 66 I; 40
5-9	n-C_6H_{13}	OC_2H_5	C 58 I; 29 N 32
5-10	n-C_6H_{13}	n-OC_3H_7	C 58 I; 35
5-11	n-C_6H_{13}	n-OC_4H_9	C 55 I; 33
5-12	n-C_6H_{13}	n-OC_5H_{11}	C 56 I; 28 N 32
5-13	n-C_7H_{15}	OC_2H_5	C 67 I; 37 N 43
5-14	n-C_7H_{15}	n-OC_3H_7	C 64 I; 46
5-15	n-C_7H_{15}	n-OC_4H_9	C 70 I; 55 N 56
5-16	n-C_7H_{15}	n-OC_5H_{11}	C 66 I; 32 N 33
5-17	n-C_8H_{17}	OCH_3	C 54 I; 28
5-18	n-C_8H_{17}	OC_2H_5	C 68 I; 55
5-19	n-C_8H_{17}	n-OC_3H_7	C 60 I; 33 N 35
5-20	n-C_8H_{17}	n-OC_4H_9	C 61 I; 42 N 45
5-21	n-C_3H_7	CN	C 97 I; 21
5-22	n-C_4H_9	CN	C 92 I; 12
5-23	n-C_5H_{11}	CN	C 74 I; 11 N 19
5-24	n-C_6H_{13}	CN	C 73 I; 6 N 17
5-25	n-C_7H_{15}	CN	C 78 I; 15 N 30
5-26	n-C_8H_{17}	CN	C 70 I; 15 N 26



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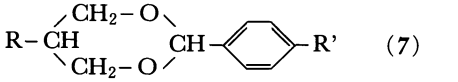
6-1	n-C_3H_7	OCH_3	C 97 I; 34
6-2	n-C_3H_7	n-OC_4H_9	C 46 I; 25
6-3	n-C_4H_9	OC_2H_5	C 75 I; 35
6-4	n-C_4H_9	n-OC_3H_7	C 65 I; 32
6-5	n-C_5H_{11}	OC_2H_5	C 57 I; 35
6-6	n-C_5H_{11}	n-OC_3H_7	C 55 I; 40
6-7	n-C_6H_{13}	OC_2H_5	C 61 I; 32 N 43
6-8	n-C_6H_{13}	n-OC_3H_7	C 75 I; 38
6-9	n-C_6H_{13}	n-OC_4H_9	C 55 I; 34 N 44
6-10	n-C_6H_{13}	n-OC_5H_{11}	C 60 I; 38 N 47
6-11	n-C_7H_{15}	OC_2H_5	C 70 I; 48 N 57
6-12	n-C_7H_{15}	n-OC_3H_7	C 60 I; 35 N 50
6-13	n-C_7H_{15}	n-OC_4H_9	C 59 I; 42 N 56
6-14	n-C_7H_{15}	n-OC_5H_{11}	C 67 I; 52 N 58
6-15	n-C_8H_{17}	n-OC_3H_7	C 56 I; 31 S_A 56
6-16	n-C_8H_{17}	n-OC_4H_9	C 57 I; 26 S_A 57
6-17	n-C_3H_7	CN	C 133 I; 78
6-18	n-C_4H_9	CN	C 88 I; 30
6-19	n-C_5H_{11}	CN	C 98 I; 28
6-20	n-C_6H_{13}	CN	C 90 I; 36
6-21	n-C_7H_{15}	CN	C 98 I; 43
6-22	n-C_8H_{17}	CN	C 93 I; 39



(7)

7-1	n-C_4H_9	n-OC_3H_7	C 43 I; N 25

Table 1. Continued

	R	R'	Transition Temp/°C[a]		R	R'	Transition Temp/°C[a]
7-2	*n*-C_6H_{13}	*n*-OC_4H_9	C $\xrightarrow{35.5}$ S_A $\xrightarrow{44}$ N $\xrightarrow{50}$ I	**7-6**	*n*-C_6H_{13}	CN	C $\xrightarrow{47}$ I; N $\xrightarrow{40.5}$ I
7-3	*n*-C_7H_{15}	*n*-OC_4H_9	C $\xrightarrow{49}$ S_A $\xrightarrow{59.5}$ I	**7-7**	*n*-C_7H_{15}	CN	C $\xrightarrow{54}$ I; N $\xrightarrow{52}$ I
7-4	*n*-C_4H_9	CN	C $\xrightarrow{42}$ I; N $\xrightarrow{35.5}$ I	**7-8**	*n*-C_8H_{17}	CN	C $\xrightarrow{60}$ I; N $\xrightarrow{51}$ I
7-5	*n*-C_5H_{11}	CN	C $\xrightarrow{55}$ I; N $\xrightarrow{48}$ I				

a) C=crystal; N=nematic; I=isotropic. b) Cited from Ref. 2. c) Cited from Ref. 7.

group, compounds **5** seem hardly to exhibit liquid-crystal phases. Namely, the nematic phase is too unstable to exist over a wide range of temperature. Even with a long alkyl chain (R=C_8H_{17}), they did not exhibit smectic phase. The molecular widths in hetero rings increase in the order: 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane. Therefore, lateral molecular interactions of 1,3-oxathianes are larger than those of 1,3-dithianes from this point of view. 1,3-Oxathiane compounds, however, are bent at the 1,3-oxathiane ring due to the difference of atomic size between sulfur and oxygen.

2-(*p*-Cyanophenyl)-5-alkyl-1,3-oxathianes having an alkyl chain with odd carbon numbers tend to have somewhat higher values of T_{N-I} (R=C_5H_{11}, 19°C; R=C_7H_{15}, 30°C), whereas those having an alkyl chain of even carbon numbers tend to have somewhat lower values (R=C_6H_{13}, 17°C; R=C_8H_{17}, 26°C).

The principal features of the mesomorphic behavior of compounds **5** are (1), in *p*-cyanophenyl compounds, monotropic nematic liquid crystal phase is exhibited around ordinary room temperature, and (2), in *p*-alkoxyphenyl compounds, mesomorphic phases are hardly recognized, and even for the compounds having a long alkyl chain (C_8H_{17}), any smectic phases could not be observed.

Experimental

IR, ^{1}H-NHR, ^{13}C-NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a JNM-FX 90 Q FT-NMR spectrometer, and a Hitachi RMU-6MG spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Mesomorphic phases and the transition temperatures were determined by means of both a Mitamura Riken micro melting-point apparatus equipped with polarizers and a Rigaku Denki D.S.C. CN8059L1, CN8208A2. The rate of cooling was fixed to 1°C/min.

2-Alkyl-3-bromo-1-propanol (2). To a solution of 48% HBr (50 g) and concd H_2SO_4 (15 g) cooled in an ice bath were added successively compound **1** (0.1 mol) and concd H_2SO_4 (25 g). The solution was kept at 70—75°C, for 18 h. The reaction mixture was then poured into ice water (200 g). The mixture was stirred and extracted twice with ether (each 400 ml). The extract was washed with cold 10% aq $NaHCO_3$ (100 ml), dried over anhyd. Na_2SO_4, and concentrated on a rotary evaporator at 30°C. The residue was distilled *in vacuo* to afford transparent liquid in a 40—50% yields.

Bp: 71—74°C/1—2 mmHg† (R=C_3H_7), 85—88°C/1—2 mmHg (R=C_4H_9), 93—95°C/1—2 mmHg (R=C_5H_{11}), 118—122°C/3—5 mmHg (R=C_6H_{13}), 104—107°C/1—2 mmHg (R=C_7H_{15}), 111—113°C/1—2 mmHg (R=C_8H_{17}). IR ($CHCl_3$) 3600 (OH), 2800—3000 (Alkyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ= 0.6—2.1 (m, R-CH), 2.3 (s, 1H, OH), 3.4—3.8 (m, 4H, CH_2-Br, CH_2-O).

2-Alkyl-3-mercapto-1-propanol (3). To a solution of thiourea (0.064 mol, 4.9 g) in triethylene glycol (8 ml) kept at 75°C was added compound **2** (0.016 mol) in a nitrogen atmosphere, followed by stirring at 75°C for 18 h. Tetraethylenepentamine (0.016 mol, 3.03 g) was then added, and the mixture was stirred at 75°C for 2 h under a nitrogen atomosphere. The reaction mixture was distilled *in vacuo* to afford transparent liquid in a 60—70% yields.

Bp: 90—92°C/1—2 mmHg (R=C_3H_7), 105—108°C/1—2 mmHg (R=C_4H_9), 128—135°C/1—2 mmHg (R=C_5H_{11}), 136—138°C/1—2 mmHg (R=C_6H_{13}), 138—140°C/1—2 mmHg (R=C_7H_{15}), 142—146°C/1—2 mmHg (R=C_8H_{17}). IR ($CHCl_3$) 3600 (OH), 2800—3000 (Alkyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ= 0.6—2.0 (m, R-CH, 2SH), 2.5—2.8 (m, 2H, -CH_2S), 3.3—3.9 (m, 3H, CH_2-OH).

2-(p-Substituted phenyl)-5-alkyl-1,3-oxathiane (5). To a solution of compound **3** (0.004 mol) and *p*-substituted benzaldehyde **4** (0.004 mol) in anhyd. $CHCl_3$ (200 ml) cooled in an ice bath were added $BF_3 \rightarrow (C_2HH_5)_2O$ (0.5 g) and molecular sieves (3A, 1/15; 3 g). The mixture was stirred at 0—5°C for 8 h and then at 20—25°C for 18 h. The solution was washed with 10% aq $NaHCO_3$ (400 ml), dried over anhyd. Na_2SO_4, and evaporated *in vacuo* at 40°C. The crude product was purified by recrystallizations from hexane, then if necessary, by centrifugal liquid chromatography.

2-(p-Alkoxyphenyl)-5-alkyl-1,3-oxathianes. IR ($CHCl_3$) 2800—3000 (Alkyl), 1600 (Ar), 1300 (Ether) cm^{-1}.

^{1}H-NMR ($CDCl_3$) Compounds **5-1**, **5-6**, and **5-17**: δ= 0.7—2.1 (m, R-CH), 2.7—3.0 (d, 2H, CH_2S), 3.4, 4.3 (t; 3.4, m; 4.3, 2H, CH_2O), 3.8 (s, 3H, OCH_3), 5.7 (s, 1H, $\overset{S}{\underset{O}{\diagdown}}$CH), 6.8—7.6 (q, 4H, ArH). Compounds **5-2**, **5-4**, **5-7**, **5-9**, **5-13**, and **5-18**: δ=0.7—2.1 (m, R-CH, O-CH_2-CH_3), 2.7—3.0 (d, 2H, CH_2-S), 3.4, 4.3 (t; 3.4, m; 4.3, 2H, CH_2-O), 4.05 (q, 2H, O-CH_2-CH_3), 5.7 (s, 1H, $\overset{S}{\underset{O}{\diagdown}}$CH), 6.7—7.6 (q, 4H, ArH). Others: δ=0.7—2.1 (m, R-CH, OCH_2-C_nH_{2n+1}), 2.7—3.0 (d, 2H, CH_2-S), 3.4, 4.3 (t; 3.4, m; 4.3, 2H, CH_2-O) 3.95 (t, 2H, -O-CH_2-C_nH_{2n+1}), 5.7 (s, 1H, $\overset{S}{\underset{O}{\diagdown}}$CH-). 6.8—7.6 (q, 4H,

†1 mmHg=133.322 Pa.

ArH).

5-1: Yield, 60%. Found: C, 66.51; H, 8.00. Calcd for $C_{14}H_{20}O_2S_1$: C, 66.63; H, 7.99. MS (*m/z*) 252 (M^+).

5-2: Yield, 56%. Found: C, 67.69; H, 8.35. Calcd for $C_{15}H_{22}O_2S_1$: C, 67.69; H, 8.35. MS (*m/z*) 266 (M^+).

5-3: Yield, 53%. Found: C, 69.41; H, 8.97. Calcd for $C_{17}H_{26}O_2S_1$: C, 69.34; H, 8.97. MS(*m/z*) 294 (M^+).

5-4: Yield, 45%. Found: C, 68.54; H, 8.61. Calcd for $C_{16}H_{24}O_2S_1$: C, 68.53; H, 8.63. MS (*m/z*) 280 (M^+).

5-5: Yield, 55%. Found: C, 69.31; H, 8.99. Calcd for $C_{17}H_{26}O_2S_1$: C, 69.34; H, 8.90. MS (*m/z*) 294 (M^+).

5-6: Yield, 45%. Found: C, 68.27; H, 8.65. Calcd for $C_{16}H_{24}O_2S_1$: C, 68.53; H, 8.63. MS (*m/z*) 280 (M^+).

5-7: Yield, 55%. Found: C, 69.34; H, 8.80. Calcd for $C_{17}H_{26}O_2S_1$: C, 69.34; H, 8.80. MS (*m/z*) 294 (M^+).

5-8: Yield, 59%. Found: C, 70.20; H, 9.12. Calcd for $C_{18}H_{28}O_2S_1$: C, 70.08; H, 9.15. MS (*m/z*) 308 (M^+).

5-9: Yield, 56%. Found: C, 70.14; H, 9.14. Calcd for $C_{18}H_{28}O_2S_1$: C, 70.08; H, 9.15. MS (*m/z*) 308 (M^+).

5-10: Yield, 64%. Found: C, 70.44, H, 9.42. Calcd for $C_{19}H_{30}O_2S_1$: C, 70.76; H, 9.38. MS (*m/z*) 322 (M^+).

5-11: Yield, 63%. Found: C, 71.42; H, 9.59. Calcd for $C_{20}H_{32}O_2S_1$: C, 71.38; H, 9.59. MS (*m/z*) 336 (M^+).

5-12: Yield, 68%. Found: C, 71.59; H, 9.82. Calcd for $C_{21}H_{34}O_2S_1$: C, 71.95; H, 9.78. MS (*m/z*) 350 (M^+).

5-13: Yield, 63%. Found: C, 70.72; H, 9.39. Calcd for $C_{19}H_{30}O_2S_1$: C, 70.76; H, 9.38. MS (*m/z*) 322 (M^+).

5-14: Yield, 59%. Found: C, 71.53; H, 9.57. Calcd for $C_{20}H_{32}O_2S_1$: C, 71.38; H, 9.59. MS (*m/z*) 336 (M^+).

5-15: Yield, 62%. Found: C, 72.15; H, 9.75. Calcd for $C_{21}H_{34}O_2S_1$: C, 71.95; H, 9.78. MS (*m/z*) 350 (M^+).

5-16: Yield, 66%. Found: C, 72.49; H, 9.95. Calcd for $C_{22}H_{36}O_2S_1$: C, 72.47; H, 9.95. MS (*m/z*) 364 (M^+).

5-17: Yield, 40%. Found: C, 71.01; H, 9.38. Calcd for $C_{19}H_{30}O_2S_1$: C, 70.76; H, 9.38. MS(*m/z*) 322 (M^+).

5-18: Yield, 44%. Found: C, 71.28; H, 9.60. Calcd for $C_{20}H_{32}O_2S_1$: C, 71.38; H, 9.59. MS(*m/z*) 336 (M^+).

5-19: Yield, 54%. Found: C, 71.90; H, 9.79. Calcd for $C_{21}H_{34}O_2S_1$: C, 71.95; H, 9.78. MS (*m/z*) 350 (M^+).

5-20: Yield, 51%. Found: C, 72.22; H, 10.01. Calcd for $C_{22}H_{36}O_2S_1$: C, 72.22; H, 9.95. MS (*m/z*) 364 (M^+).

2-(p-Cyanophenyl)-5-alkyl-1,3-oxathianes. IR ($CHCl_3$) 2800—3000 (Alkyl), 2230 (CN), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=0.7—2.1 (m, R-CH), 2.7—3.0 (d, 2H, CH_2-S), 3.4, 4.3 (t; 3.4, m; 4.3, 2H, CH_2O), 5.8 (s, 1H, $\overset{S}{O}$>CH), 7.65 (s, 4H, ArH).

5-21: Yield, 52% Found: C, 68.08; H, 6.92; N, 5.66. Calcd for $C_{14}H_{17}N_1O_1S_1$: C, 67.98; H, 6.93; N, 5.66. MS (*m/z*) 247 (M^+). ^{13}C-NMR ($CDCl_3$) δ=83.11 (C2 of the 1,3-oxathiane ring), 34.62 (C4), 75.42 (C6).

5-22: Yield, 36%. Found: C, 68.79; H, 7.33; N, 5.37. Calcd for $C_{15}H_{19}N_1O_1S_1$: C, 68.93; H, 7.33; N, 5.36. MS (*m/z*) 261 (M^+). ^{13}C-NMR ($CDCl_3$) δ=83.22 (C2), 34.84 (C4), 75.53 (C6).

5-23: Yield, 36%. Found: C, 69.45; H, 7.55; N, 4.99. Calcd for $C_{16}H_{21}N_1O_1S_1$: C, 69.78; H, 7.69; N, 5.09. MS (*m/z*) 275 (M^+). ^{13}C-NMR ($CDCl_3$) δ=83.11 (C2), 34.78 (C4), 75.47 (C6).

5-24: Yield, 41%. Fond: C, 70.76; H, 8.03; N, 4.81. Calcd for $C_{17}H_{23}N_1O_1S_1$: C, 70.54; H, 8.01; N, 4.84. MS (*m/z*) 289 (M^+). ^{13}C-NMR ($CDCl_3$) δ=83.22 (C2), 34.78 (C4), 75.58 (C6).

5-25: Yield, 45%. Found: C, 71.34; H, 8.31; N, 4.61. Calcd for $C_{18}H_{25}N_1O_1S_1$: C, 71.24; H, 8.30; N, 4.62. MS (*m/z*) 303 (M^+). ^{13}C-NMR ($CDCl_3$) δ=83.22 (C2), 34.78 (C4), 75.53 (C6).

5-26: Yield, 55%. Found: C, 71.76; H, 8.65; N, 4.13. Calcd for $C_{19}H_{27}N_1O_1S_1$: C, 71.88; H, 8.57; N, 4.41. MS (*m/z*) 317 (M^+). ^{13}C-NMR ($CDCl_3$) δ=83.22 (C2), 34.84 (C4), 75.55 (C6).

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