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Synthesis and Nucleophilic Substitution Reaction of 1-Halo-9*H*-thioxanthen-9-one

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This paper is dedicated to professor Habib Firouzabadi on the occasion of his honorable retirement and for his continues, past and future devotions and endeavors to the field of organic chemistry.

Treatment of thiosalicylic acids with *p*-halotoluene in concentrated sulfuric acid gave 1-halo-9H-thioxanthen-one **3** and its isomer **4** in high yields. Aromatic nucleophilic substitutions of the resulted 1-halo-9*H*-thioxanthen-9-ones with O-, N- and S-nucleophiles are studied in a comparative manner, and various new O-, N- and S-substituted 9*H*-thioxanthen-9-ones are obtained.

Keywords: Thioxanthen-9-one, Thiosalicylic acid, Nucleophile, Substitution reaction.

INTRODUCTION

9*H*-Thioxanthen-9-ones are an important class of compounds and are a common heterocyclic scaffold in biologically active and medicinally significant compounds. The 9*H*-thioxanthen-9-one ring is the core structure of a wide variety of naturally occurring and synthetic compounds that exhibit extraordinary anti-tumor,[1-3,6,9] anti-parasitic, [4,5] and anti-cancer activity [6,7,10]. 9*H*-Thioxanthen-9-one derivatives are potential anti-cancer drugs and some 9*H*-thioxanthen-9-ones containing plant extract are directly used in traditional medicines [5-7].

Beside a wide variety of chemical and industrial applications, synthetic derivatives of 9*H*-thioxanthen-9-ones as well as naturally occurring derivatives have been used for medical purposes. The biological and photochemical behavior [11-14] of this family of 9*H*-thioxanthen-9-one derivatives made these substances attractive for synthetic studies.

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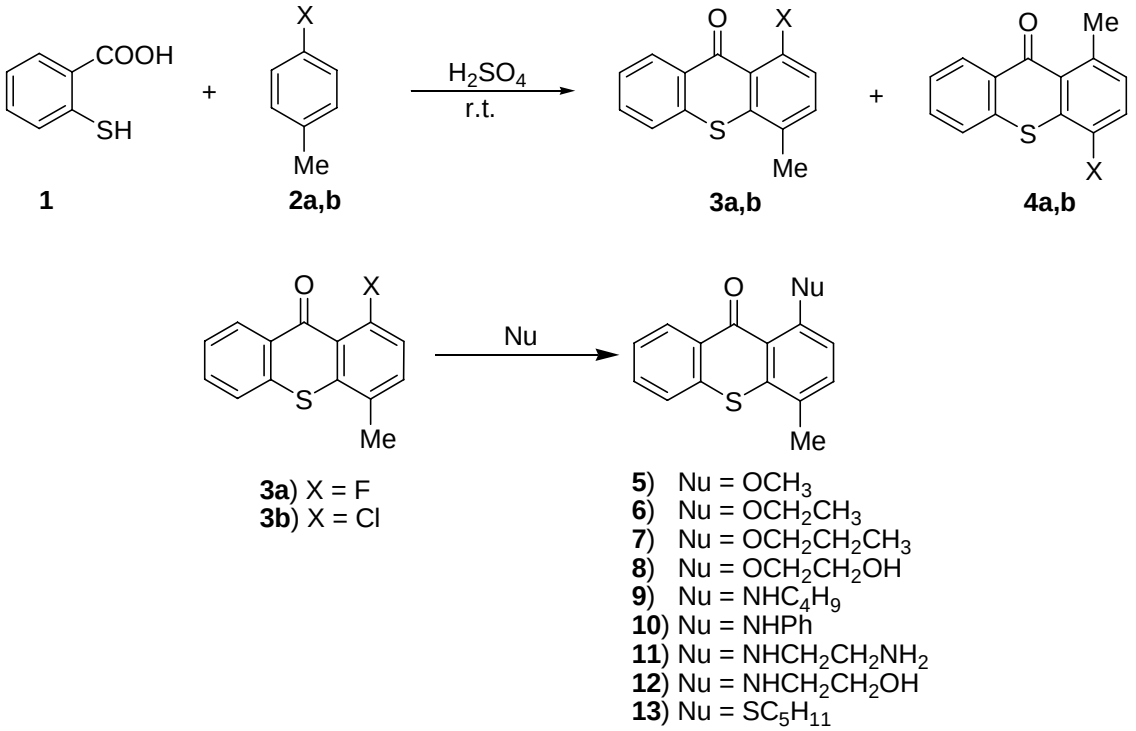
Nucleophilic substitution of aromatic halo groups S_NAr has attracted increasing attention in recent years for both theoretical [15] and synthetic reasons [16-20]. Possibility to run such reactions in dipolar media in high concentrations with short reaction times and excellent yields has prompted their introduction into industrial processes [21]. However, the functions are displaced by nucleophiles in dipolar aprotic solvents [16-20]. The S_NAr reaction proceeds with decreasing facility in the series of F, NO_2>>Cl>Br>I, so that for practical purposes, bromine and iodine displacement are lacking in synthetic utility [22-26]. In this paper we report our preliminary results concerning the nucleophilic aromatic substitution on two new chloro and fluoro substituted 9*H*-thioxanthen-9-ones **3a** and **3b** in a comparative manner (Scheme 1).

Reaction of thiosalicylic acid **1** with *p*-fluorotoluene **2a** was carried out in sulfuric acid and 1-fluoro-4-methyl-9*H*-thioxanthen-9-one **3a** and 4-fluoro-1-methyl-9*H*-thioxanthen-9-one **4a** were obtained in 40% and 37% yields respectively. Similar reaction of thiosalicylic acid **1** with *p*-chlorotoluene **2b**



Scheme 1

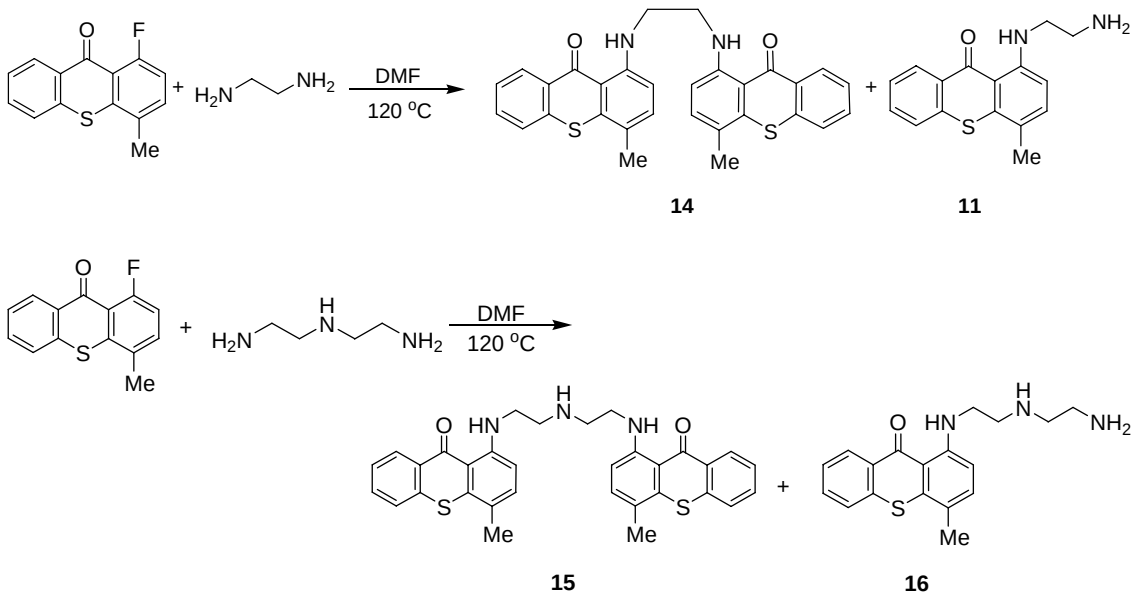
in concentrated sulfuric acid produced 1-chloro-9*H*-thioxanthen-9-one **3b** and its isomer **4b** in 36% and 38% yields respectively.

Generally, in direct nucleophilic aromatic substitution, fluorides are shows to be the most reactive halide, and substitution of the chloro group usually requires more vigorous conditions [16,17,27-29]. However, reaction of 1-fluoro-4-methyl-9*H*-thioxanthen-9-one **3a** (X=F) with sodium methoxide in methanol produced the new 1-methoxy-4-methyl-9*H*-thioxanthen-9-one **5** in 84% yield, whereas the chloro substituted 9*H*-thioxanthen-9-one **3b** (X=Cl) gave the same product in 38% yield. When the latter reaction was carried out in DMF, the yield was increased to 56%.

The use of acetonitrile and dimethyl sulfoxide (DMSO) were not found to be superior solvents than DMF, though the reaction of 9*H*-thioxanthen-9-one **3b** (X=Cl) with sodium methoxide in acetonitrile or DMSO, afforded compound **5** in 52% and 47% yields respectively. Similarly, the reaction of 9*H*-thioxanthen-9-one **3a** (X=F) with sodium in ethanol and propanol afforded 9*H*-thioxanthen-9-ones **6** and **7** in 98 and 85% yields respectively, while 9*H*-thioxanthen-9-one **3b** (X=Cl) reacted with sodium ethoxide and propanolate in DMF to produced compounds **6** and **7** in 52 and 44% yields respectively.

Subsequently, the reaction of 9*H*-thioxanthen-9-one **3a** with sodium and diethylene glycol in DMF afforded the new 9*H*-thioxanthen-9-one **8** with an ethylenoxy side chain in 81% yield, while the reaction of 1-chloro-9*H*-thioxanthen-9-one **3b** under similar conditions produced 9*H*-thioxanthen-9-one **8** in 56% yield, and an enhancement of the yield was observed for nucleophilic substitution of the chloro group by diethylene glycol. Similar to l-chloroanthraquinone [13,16,30,31] the chloro group of 9*H*-thioxanthen-9-one **3b** is more readily substituted by diethylene glycol than the simple aliphatic alcohols. This enhancement in the rate of substitution reaction of **3b** may result from the nucleophilicity enhancement of diethylene glycol by either complexation of the cation with nucleophile, or a self-solvation process which deaggregates the alkoxide [17, 31].

Reaction of 9*H*-thioxanthen-9-ones **3a** and **3b** with *n*-buthylamine in DMF in two separated reactions afforded 9*H*-thioxanthen-9-one **9** in 85% and 54% yields respectively.



Scheme 2

However the reaction of 9*H*-thioxanthen-9-one **3a** with ethylenediamine in DMF at 120 °C afforded two substituted 9*H*-thioxanthen-9-one **11** and **14** in 24% and 53% yields respectively while this reaction at 100 °C, in DMF, using excess amount of ethylenediamine, produced 9*H*-thioxanthen-9-one **11** in 66% yield. Compound **11** was also obtained from 9*H*-thioxanthen-9-one **3b** under the above mentioned conditions in 48% yield, but heating of compound **3a** and diethylenetriamine in DMF, produced 9*H*-thioxanthen-9-one **15** in 57% yield together with 9*H*-thioxanthen-9-one **16** in 15% yield. However the reaction of 9*H*-thioxanthen-9-one **3b** with diethylenetriamine in DMF at 130 °C afforded only 9*H*-thioxanthen-9-one **16** in 56% yield as the sole product (Scheme 2).

Subsequently, the reaction of 9*H*-thioxanthen-9-one **3a** with an aromatic amine like aniline in DMF at 120 °C doesn't produce any product. However the reaction of **3a** with aminoethanol in DMF produced 1-[(2-hydroxyethyl)amino]-4-methyl-9*H*-thioxanthen-9-one **12** in excellent yield. Reaction of 9*H*-thioxanthen-9-one **3a** with sodium 1-pentanethiolate in 1-pentanethiol produced the new 9*H*-thioxanthen-9-one **13** in 86% yield, whereas the chloro substituted 9*H*-thioxanthen-9-one **3b** under the above mentioned conditions gave the same product in 40% yield.

In conclusion, we have found that the use of sulfuric acid offers a convenient method for the synthesis of halo substituted 9*H*-thioxanthen-9-one. Nucleophilic aromatic substitution of these 1-halo-9*H*-thioxanthen-9-ones affords a range of new substituted heterocyclic compounds in high yield and purity which are not available through other synthetic methods. In addition, the simplicity and convenience of this procedure make this method a highly useful technique in organic synthesis.

EXPERIMENTAL

Instrumentation, Analyses and Starting Materials:

NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H-NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instruments at 70 or 20 ev. Melting points were determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. Column chromatography was carried out on columns of silica gel 60 (70-230 mesh) in glass columns (2-3 cm

diameter) using 15-30 gram of silica gel per one gram of crude mixture. Chemicals Material were either prepared in our laboratories or were purchased from Fluka, Aldrich and Merck Chemical Companies

General procedure for synthesis of 1-halo-9*H*-thioxanthen-9-one derivatives:

Thiosalicylic acid (1.6 g, 0.01 mol) was slowly added to 15 ml of cold concentrated sulfuric acid (98%) and the mixture was stirred for 5 min to insure thorough mixing. *p*-Halotoluene (0.027 mol) was then added slowly to the stirred mixture over the period of 30 min. After the addition, the reaction mixture was stirred at room temperature for 18 h. The reaction mixture was changed from red to dark red on heating. It was then cooled to room temperature and poured slowly into 300 ml of ice-water. The resulting yellow precipitate was filtered and washed with water (3×50 ml). The yellow solid was washed with saturated aqueous sodium hydrogen carbonate and washed with water again to remove alkali and dried at room temperature over night.

1-Fluoro-4-methyl-9*H*-thioxanthen-9-one (3a):

mp=128-130 °C; IR (KBr) υ cm^{-1}: 1643 (s), 1589 (s), 1446 (s), 1307 (s), 894 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ(ppm) 8.35 (1H, d, *J*=7.9), 7.52-7.32 (3H, m), 7.23 (1H, dd, $^3J_{HH}$=8.2, $^4J_{FH}$=4.9), 6.87 (1H, dd, $^3J_{HH}$ =8.1, $^3J_{FH}$ =8.2), 2.28 (3H, s,); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ(ppm) 179.5, 164.2, 159.9, 138.1, 135.3, 134.1, 133.9, 132.1, 130.3, 129.6, 129.5, 129.3, 125.7, 113.5, 113.1, 19.2; MS: m/z (%) =244 (100, M^+), 245 (38.3), 215 (55.4), 149 (40.9). Anal. calc. for $C_{14}H_9FOS$ (244.28): C, 68.84; H, 3.71. found: C, 68.73; H, 3.68.

1-Chloro-4-methyl-9*H*-thioxanthen-9-one (3b):

mp=137-139 °C; IR (KBr, cm^{-1}): 1640 (s), 1581 (s), 1447 (s), 1302 (s), 897 (s); ^{1}H NMR (DMSO-d_6, 250 MHz) δ 8.35 (1H, d, *J*=7.9), 7.52-7.39 (3H, m), 7.30 (1H, d, *J*=8.0), 7.20 (1H, d, *J*=7.9), 2.38 (3H, s); ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 183.6, 138.8, 134.6, 133.7, 132.9, 132.6, 131.9, 130.9, 129.4, 129.2, 126.6, 126.2, 125.4, 19.6; MS: m/z (%) 261 (16, M+1), 260 (56.2, M^+), 161 (16), 197 (17.2), 167 (20.7), 149 (100). Anal. calc. for $C_{14}H_9ClOS$ (260.74): C, 64.49; H, 3.48. found: C, 64.42; H, 3.46.

Nucleophilic Substitution of 1-Halo-9Hthioxanthen-9-ones 3a and 3b:

Preparation of Alkoxyxanthones (5-8):

General Procedure A: By F-displacement. To a well stirring solution of sodium (100 mg, 4 mmol) in alcohol (10 ml) was added 9*H*-thioxanthen-9-one **3a** and heated at refluxing temperature. The cold reaction mixture was poured onto crushed ice (100 g) and extracted with chloroform (3×50 ml). The organic layer was washed with water (2×50 ml) and brine (50 ml), dried over Na_2SO_4 and evaporated to give the corresponding alkoxysubstituted 9*H*-thioxanthen-9-ones **5-8** in good yields.

General Procedure B: By Cl-displacement. A mixture of 9*H*-thioxanthen-9-one **3b** (0.001 mol) and sodium alkoxide (0.01 mol) in dry DMF (10 ml) was refluxed. Then the reaction mixture was added to crushed ice (100 g) and the product was isolated as was mentioned above. (Scheme I).

General procedure for the Nucleophilic Substitution on 1-Halo-9*H*-thioxanthen-9-one by Amines:

The reaction includes addition of an excess amount of amine (3 mmol) to a solution of 1-fluoro-9*H*-thioxanthen-9-one (1 mmol) in DMF and then heating in an oil bath at 120 °C for 10 hours. The color of the reaction mixture changed from yellow to red on heating. The reaction progress was monitored by TLC. After cooling the red solution, a yellow suspension was formed which was then diluted with cooled water. The solid was filtered and washed with water and then dried at room temperature.

1-Methoxy-4-methyl-9*H*-thioxanthen-9-one (5):

mp=127-129 °C; IR (KBr, cm^{-1}): 1630 (s), 1583 (s), 1442 (s), 1263 (s), 1018 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.38 (1H, d, *J*=7.9), 7.47 (1H, s), 7.28-7.39 (3H, m), 6.80 (1H, d, *J*=8.4), 3.89 (3H, s), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 181.0, 160.3, 135.0, 134.9, 131.6, 130.1, 127.8, 127.5, 126.5, 124.9, 123.9, 119.4, 109.6, 55.4, 20.1; MS: m/z (%) 256 (35.6, M^+), 135 (34.3), 122 (69.6), 107 (100 base peak), 77 (49.6). Anal. calc. for $C_{15}H_{12}O_2S$ (256.32): C, 70.29; H, 4.72. found: C, 70.33; H, 4.69.

1-Ethoxy-4-methyl-9*H*-thioxanthen-9-one (6):

mp=115-117 °C; IR (KBr, cm^{-1}): 1635 (s), 1578 (s), 1440 (s), 1262 (s), 1025 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.35 (1H, d, *J*=7.7), 7.42 (1H, s), 7.32-7.28 (2H, m), 7.20 (1H, d, *J*=8.3), 6.73 (1H, d, *J*=8.3), 4.07 (2H, q, *J*=6.9), 2.29 (3H, s), 1.46 (3H, t, *J*=6.9), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 181.0, 159.7,138.3, 134.9, 133.7, 131.8, 131.4, 129.3, 126.2, 125.3, 119.9, 110.1, 65.1, 19.2, 14.8. Anal. calc. for $C_{16}H_{14}O_2S$ (270.34): C, 71.09; H, 5.22. found: C, 71.12; H, 5.18.

4-Methyl-1-propoxy-9*H*-thioxanthen-9-one (7):

mp=77-79 °C; IR (KBr, cm^{-1}): 1637 (s), 1581 (s), 1442 (s), 1267 (s), 1022 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.40 (1H, d, *J*=7.8), 7.45 (1H, s), 7.42-7.31 (2H, m), 7.24 (1H, d, *J*=8.4), 6.78 (1H, d, *J*=8.4), 4.01 (2H, t, *J*=6.6), 2.34 (3H, s), 2.00-1.86 (2H, m), 1.12 (3H, t, *J*=7.3); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 180.9, 159.9, 138.2, 134.9, 133.7, 131.1, 131.3, 129.3, 126.2, 125.3, 125.1, 119.9, 109.9, 71.0, 22.6, 19.2, 10.6; MS: m/z (%) =284 (21.3, M^+), 255 (100), 241 (56.8), 213 (24.6), 184 (29.3,), 152 (18.4). Anal. calc. for $C_{17}H_{16}O_2S$ (284.37): C, 71.80; H, 5.67. found: C, 71.76; H, 5.65.

1-(2-Hydroxyethoxy)-4-methyl-9*H*-thioxanthen-9-one (8):

mp=121-123 °C; IR (KBr, cm^{-1}): 3510 (b), 1637 (s), 1580 (s), 1434 (s), 1269 (s), 1047 (s), 933 (s), 748 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.38 (1H, d, *J*=7.7), 7.50-7.37 (3H, m), 7.27 (1H, d, *J*=8.3), 6.82 (1H, d, *J*=8.3), 4.26 (2H, t, *J*=4.6), 3.96 (2H, t, *J*=4.6), 2.34 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 181.7, 159.8, 138.4, 135.2, 133.9, 131.7, 129.4, 129.1, 126.5, 126.1, 125.4, 120.2, 112.2, 72.7, 60.8, 19.2; MS: m/z (%) 286 (19.3, M^+), 268 (13.1), 240 (86.9), 213 (28.0), 184 (29.0), 149 (25.2). Anal. calc. for $C_{16}H_{14}O_3S$ (286.35): C, 67.11; H, 4.93. found: C, 67.14; H, 4.95.

1-(Butylamino)-4-methyl-9*H*-thioxanthen-9-one (9):

mp=100-102 °C; IR (KBr, cm^{-1}): 3230 (w), 2922 (w), 2850 (w), 1612 (s), 1554 (s), 1516 (s), 1228 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 10.15 (1H, s), 8.50 (1H, d, *J*=7.7), 7.48-7.35 (3H, m), 7.18 (1H, d, *J*=8.5), 6.48 (1H, d, *J*=8.5),3.20 (2H, t, *J*=6.7), 2.27 (3H, s), 1.78-1.72 (2H, m), 1.57-1.48 (2H, m), 1.04-1.00 (2H, m), 0.92 (3H, m); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 183.1, 152.4, 136.1, 135.5,131.3, 130.3, 129.0, 128.1, 127.7, 125.8, 125.3, 117.6, 106.8, 42.8, 31.0, 20.5, 19.0, 13.9, MS: m/z (%) 297 (6.3, M^+), 254 (30.4), 149 (21.9). Anal. calc. for $C_{18}H_{19}NOS$ (297.42): C, 72.69; H, 6.44. found: C, 72.57; H, 6.40.

1-[(2-Aminoethyl)amino]-4-methyl-9*H*-thioxanthen-9-one (11):

mp=176-178 °C; IR (KBr, cm^{-1}): 3327 (s), 2860 (w), 1660 (s), 1614 (s), 1516 (s), 1438 (s), 1388 (s), 1259 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 10.28 (1H, s), 8.44 (1H, d, *J*=7.3), 7.53-7.49 (1H, m), 7.42-7.36 (2H, m), 7.24 (1H, d, *J*=8.5), 6.57 (1H, d, *J*=8.5), 3.66-3.59 (2H, m), 3.55-3.45 (2H, m), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 161.5, 135.6, 131.7, 129.1, 126.1, 125.5, 107.0, 42.3, 37.3, 19.1; MS: m/z (%) 272 (0.5), 254 (38.3) 152 (10.4). Anal. calc. for $C_{16}H_{16}N_2OS$ (284.38): C, 67.58; H, 5.67. found: C, 67.56; H, 5.65.

1-[(2-Hydroxyethyl)amino]-4-methyl-9*H*-thioxanthen-9-one (12):

mp=179-181 °C; IR (KBr, cm^{-1}): 3458 (b), 1600 (s), 1510 (s), 1271 (s), 1226 (s), 1068 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 10.46 (1H, s), 8.43 (1H, d, *J*=7.9), 7.47-7.43 (1H, m), 7.37-7.31 (2H, m), 7.18 (1H, d, *J*=8.5), 6.56 (1H, d, *J*=8.5), 3.90 (2H, t, *J*=5.4), 3.41 (2H, t, *J*=5.4), 2.35 (3H, s); ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 181.9, 152.0, 136.4, 135.9, 135.0, 132.1, 129.4, 128.5, 126.4, 125.7, 117.3, 111.6, 107.3 59.1, 44.8, 18.4; MS: m/z (%) 285 (20.6, M^+), 254 (100), 226 (11.9), 149 (14.6). Anal. calc. for $C_{16}H_{15}NO_2S$ (258.36): C, 67.34; H, 5.30. found: C, 67.38; H, 5.33.

4-Methyl-1-(pentylsulfanyl)-9*H*-thioxanthen-9-one (13):

IR (KBr, cm^{-1}): 1610 (s), 1550 (s), 1512 (s), 1225 (s); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.29 (1H, d, *J*=8.2), 7.49-7.49 (1H, m), 7.36-7.30 (2H, m), 7.09 (1H, d, *J*=7.8), 2.84-2.79 (2H, m), 2.77 (3H, s), 1.55-1.49 (2H, m), 1.32-1.19 (4H, m), 0.81-0.76 (3H, m); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 180.1, 149.4, 136.1, 135.5, 131.3, 130.3, 129.0, 128.1, 127.7, 125.8, 125.3, 117.6, 106.8, 41.8, 31.0, 21.5, 20.0, 13.2, MS: m/z (%) 328 (60.2, M^+), 262 (92.8), 187 (19.9), 129 (15). Anal. calc. for $C_{19}H_{20}OS_2$ (328.49): C, 69.47; H, 6.14. found: C, 69.44; H, 6.11.

4-Methyl-1-({2-[(4-methyl-9-oxo-9*H*-thioxanthen-1-yl) amino]ethyl}amino)-9*H*-thioxanthen-9-one (14):

mp=88-90 °C; IR (KBr, cm^{-1}): 2348 (w), 1614 (s), 1552 (s), 1420 (s), 1269 (s), 1210 (s), 937 (s), 812 (s); ^{1}H NMR

($CDCl_3$, 250 MHz) δ 8.33 (2H, d, *J*=7.8), 7.52-7.50 (2H, m), 7.41-7.32 (4H, m), 7.23 (2H, d, *J*=8.4), 6.84 (2H, d, *J*=8.4), 3.89 (4H, s), 2.83 (6H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 182.0, 152.6, 137.4, 135.0, 133.3, 132.7, 131.2, 128.9, 125.9, 125.2, 122.1, 117.9, 112.6, 43.8, 18.9; MS: m/z (%) 451 (2.8) 368 (4.4), 313 (5.5), 236 (13.3), 171 (12.1). Anal. calc. for $C_{30}H_{24}N_2O_2S_2$ (508.66): C, 70.84; H, 4.76. found: C, 70.80; H, 4.74.

4-Methyl-1-{[2-({2-[(4-methyl-9-oxo-9*H*-thioxanthen-1-yl) amino]ethyl}amino)ethyl]amino}-9*H*-thioxanthen-9-one (15):

IR (KBr, cm^{-1}): 2358 (w), 1610 (s), 1554 (s), 1421 (s), 1269 (s), 1211 (s), 934 (s), 802 (s), 744 (s); ^1H NMR ($CDCl_3$, 250 MHz) δ 10.23 (2H, s), 8.38 (2H, d, *J*=7.6), 7.50-7.45 (2H, m), 7.35-7.26 (4H, m), 7.15 (2H, d, *J*=8.5), 6.56 (2H, d, *J*=8.5), 3.49 (4H, t, *J*=6.0), 3.15 (4H, t, *J*=6.0), 2.25 (6H, s), 1.25 (1H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 150.5, 135.4, 131.3, 129.1, 125.8, 125.2, 106.9, 47.9, 42.4, 19.0. Anal. calc. for $C_{32}H_{29}N_3O_2S_2$ (551.72): C, 69.66; H, 5.30. found: C, 69.70; H, 5.33.

1-({2-[(2-Aminoethyl)amino]ethyl}amino)-4-methyl-9*H*-thioxanthen-9-one (16):

IR (KBr, cm^{-1}): 3325 (w), 1662 (s), 1611 (s), 1518 (s), 1436 (s), 1385 (s), 1260 (s); ^1H NMR ($CDCl_3$, 250 MHz) δ 10.24 (1H, s), 8.11 (1H, d, 7.7), 7.59-7.45 (1H, m), 7.37-7.26 (2H, m), 7.24 (1H, d, 8.5), 6.55 (1H, d, *J*=8.5), 3.62-3.38 (4H, m), 3.47-3.35 (4H, m), 2.25 (3H, s), 1.28 (2H, s), ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 150.5, 135.4, 131.3, 129.1, 125.8, 125.2, 106.9, 50.7, 48.2, 43.2, 40.9, 19.6. Anal. calc. for $C_{18}H_{21}N_3OS$ (327.44): C, 66.02; H, 6.46. found: C, 66.06; H, 6.49

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