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Synthesis of 4-(3-Bromo-2-Hydroxy-5-Methylphenyl)-2-Dialkylamino-1,3-Dithiolium Chlorides

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Abstract: New water soluble 4-(3-bromo-2-hydroxy-5-methylphenyl)-2-dialkylamino-1,3-dithiolium chlorides have been synthesized from the corresponding mesoionic phenolates. The latter have been obtained by heterocyclocondensation of dithiocarbamates followed by basic hydrolysis.

Keywords: Dithiocarbamates; 1,3-Dithiolium salts; Mesoionic compounds.

Introduction

The remarkably fast development of the 1,3-dithiolium salts chemistry over the past decade has been prompted by several factors. These compounds are hetero analogs of tropylium cation. Secondly, the ability of *S*-containing heterocycles to give charge-transfer complexes with suitable acceptors has provided the additional stimulus for the study of such structure since the complexes obtained exhibit metal-like conductivity in quite a large number of cases.[1] On the other hand, solvatochromic dyes have

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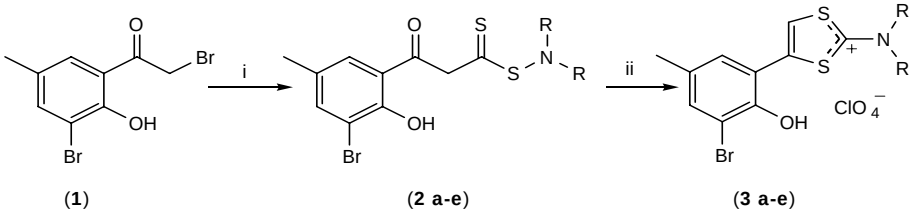
played an important role in the understanding of solvent polarity effects and are increasingly important as probes of complex biological systems.[2-4] The systems where a donor moiety is linked through a σ- or π-bonded bridge to the acceptor moiety received special interest.[5] A variety of acceptor units have been investigated with special attention paid to cationic systems, such as pyridinium and bipyridinium cations.[6-8]

In a previous paper we have investigated the solvatochromism of several mesoionic phenolates.[9] We have also detected an interesting equilibrium between the solutions of 1,3-dithiolium chlorides and of corresponding mesoionic phenolates.[10] In order to extend the investigation on the above equilibrium we wish to report the synthesis of a series of 4-(3-bromo-2-hydroxy-5-methylphenyl)-2-dialkylamino-1,3-dithiolium chlorides.

Results and Discussion

In order to extend our previuos investigations on the heterocyclocondensation of a series of 2-hydroxyacetophenones,[11, 12] we describe here the synthesis of some 4-(3-bromo-2-hydroxy-5-methylphenyl)-2-dialkylamino-1,3-dithiolium perchlorates (Scheme 1).

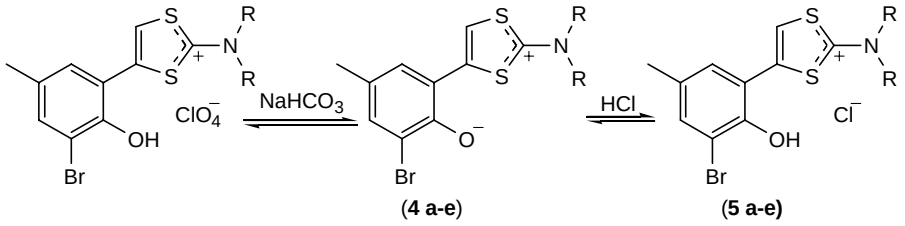


(**1**) (**2 a-e**) (**3 a-e**)

Scheme 1

(**2**), (**3**), (**4**), (**5**)	**R**	**R**
a	CH_3	CH_3
b	CH_2CH_3	CH_2CH_3
c	$(CH_2)_4$	
d	$(CH_2)_5$	
e	$(CH_2)_2$-O-$(CH_2)_2$	

Treatment of perchlorates (**3a-e)** under heterogeneous conditions, with saturated aqueous potassium hydrogencarbonate solution affords 6-bromo-4-methyl-2-(1,3-dithiol-2-ylium-4-yl)phenolates (**4a-e**), in quantitative yields. The molecular structure of the new compounds was proved by analytical and spectral data and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compounds (**4a-e**) with 70% perchloric acid regenerates the 1,3-dithiolium perchlorates in quantitative yields (Scheme 2). 6-Bromo-4-methyl-2-(1,3-dithiol-2-ylium-4-yl)phenolates were isolated as yellow crystalline products that present the features of mesoionic compounds.[13-15] The presence of a hydroxy substituent in an *ortho*-position induces an extended delocalization of the negative charge up to the C(4)-C(5) bond of the dithiolium ring.



Scheme 2

We have been able to isolate the 1,3-dithiolium chlorides (**5a-e**) using the interconversion possibilities between the mesoionic phenolates

and their salts. Thus, 4-(3-bromo-2-hydroxy-5-methylphenyl)-1,3-dithiolium chlorides have been isolated as a solid crystalline product by the treatment of an acetonic suspension of (**4**) with 37% hydrochloric acid (Scheme 2).

Conclusions

The synthesis of water soluble 4-(3-bromo-2-hydroxy-5-methylphenyl)-2-dialkylamino-1,3-dithiolium chlorides has been accomplished from the corresponding mesoionic compounds. The latter have been synthesized by heterocondensation of 1-(3-bromo-2-hydroxy-5-methylphenyl)-2-(*N*,*N*-dialkylaminocarboditioate)-1-ethanones, followed by base treatment of 1,3-dithiolium perchlorates.

Experimental

Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker DPX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N, S) were conducted using the CE440 Elemental Analyser; their results were found to be in good agreement (±0.25%) with the calculated values. Mass spectra were recorded on a Finnigan MAT 90X spectrometer.

1-(3-Bromo-2-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-pyrrolidine-1-carbodithioate (**2c**)*; General Procedure*

To a solution of 2-bromo-1-(3-bromo-2-hydroxy-5-methylphenyl)ethan-1-one (**1**, 3.08 g, 0.01 mol) in acetone (30 mL) a solution of pyrrolidinium pyrrolidine-1-carbodithioate (2.18 g, 0.01 mol) in acetone-water (1:1, 30 mL) was added. After 5 min under stirring at rt the

precipitate was filtered, washed with water and dried off. Recrystallization from dioxane (25 mL) gave colorless crystals; yield 3 g (80%).

Mp 171-172 °C. IR (ATR): 2868, 1633, 1434, 1321, 1236, 1150, 951, 854, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.99 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 2.22 (s, 3H, CH_3-5), 3.73 (t, ^3J = 7.5 Hz, 2H, CH_2), 3.89 (t, ^3J = 7.5 Hz, 2H, CH_2), 4.87 (s, 2H, CH_2), 7.44 (d, ^4J = 2.3 Hz, 1H, H-4), 7.93 (d, ^4J = 2.3 Hz, 1H, H-6), 12.04 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 22.1, 54.4, 62.2, 114.4, 125.9, 129.8, 132.7, 138.2, 157.5, 196.5, 204.9. MS (ESI): *m/z* = 374 (M^+).

2-(3-Bromo-2-hydroxy-5-methylphenyl)-2-oxoethyl-N,N-dimethyldithio-carbamate (**2a**):

Yield 73%. Mp 170-171 °C. IR (ATR): 2912, 1640, 1447, 1322, 1210, 1145, 975, 851, 771, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3-5), 3.46 (s, 3H, CH_3-N), 3.51 (s, 3H, CH_3-N), 4.84 (s, 2H, CH_2), 7.46 (d, ^4J = 2.4 Hz, 1H, H-3), 7.92 (d, ^4J = 2.3 Hz, 1H, H-6), 12.02 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 44.1, 62.1, 114.3, 125.7, 129.5, 132.8, 138.5, 157.4, 196.1, 204.4. MS (ESI): *m/z* = 348 (M^+).

2-(3-Bromo-2-hydroxy-5-methylphenyl)-2-oxoethyl-N,N-diethyldithio-carbamate (**2b**):

Yield 70%. Mp 132-133 °C. IR (ATR): 2977, 1633, 1413, 1352, 1236, 1202, 1151, 760, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, 3H, CH_3), 1.36 (t, 3H, CH_3), 2.23 (s, 3H, CH_3-5), 3.81 (q, 2H, CH_2), 4.00 (q, 2H, CH_2), 4.85 (s, 2H, CH_2), 7.45 (d, ^4J = 2.3 Hz, 1H, H-4), 7.94 (d, ^4J = 2.3 Hz, 1H, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ =

12.4, 19.1, 48.1, 62.3, 114.1, 126.2, 130.1, 132.9, 138.4, 157.6, 196.0, 204.1. MS (ESI): *m/z* = 360 (M^+).

1-(3-Bromo-2-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-piperidine-1-carbodithioate (**2d**):

Yield 85%. Mp 165-166 °C. IR (ATR): 2865, 1631, 1432, 1320, 1234, 1152, 948, 853, 684 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (m, 6H, $3CH_2$), 2.23 (s, 3H, CH_3-5), 3.95 (m, 2H, $2CH_2$), 4.24 (m, 2H, CH_2), 4.86 (s, 2H, CH_2), 7.44 (d, ^4J = 2.4 Hz, 1H, H-3), 7.93 (d, ^4J = 2.4 Hz, 1H, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.0, 24.1, 25.7, 54.3, 62.5, 114.7, 125.7, 129.5, 132.9, 138.5, 157.4, 196.4, 204.7. MS (ESI): *m/z* = 388 (M^+).

1-(3-Bromo-2-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-morpholine-1-carbodithioate (**2e**):

Yield 76%. Mp 180-181 °C. IR (ATR): 2899, 1649, 1419, 1326, 1227, 1113, 993, 681 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3-5), 3.80 (m, 4H, CH_2-O-CH_2), 4.05 (m, 2H, CH_2-N), 4.29 (m, 2H, N-CH_2), 4.89 (s, 2H, CH_2), 7.48 (d, ^4J = 2.3 Hz, 1H, H-3), 7.93 (d, ^4J = 2.3 Hz, 1H, H-6), 12.05 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5, 56.1, 62.3, 67.5, 114.1, 125.5, 129.4, 132.7, 138.8, 157.6, 196.1, 204.5. MS (ESI): *m/z* = 390 (M^+).

4-(3-Bromo-2-hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**3d**); *General Procedure*

To a mixture of conc sulfuric acid (1.9 mL) and glacial acetic acid (5.7 mL) 1-(3-bromo-2-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-

piperidine-1-carbodithioate (**2d**, 1.9 g, 4.89 mmol) was added in small portions. After 10 min at 80 °C perchloric acid (70%, 1 mL) was added and the reaction mixture was diluted with methyl acetate (15 mL). The precipitate was filtered, washed with water and dried off. Recrystallization from ethanol (50 mL) gave colorless crystals; yield 1.93 g (84%).

Mp 201-202 °C. IR (ATR): 3577, 3118, 1561, 1524, 1444, 1255, 1068, 619 cm^{-1}. ^1H NMR (300 MHz, DMSO- d_6): δ = 1.79 (m, 6H, $3CH_2$), 2.25 (s, 3H, CH_3-5), 3.86 (m, 4H, $2CH_2$), 7.34 (d, ^4J = 2.3 Hz, 1H, H-3), 7.57 (d, ^4J = 2.3 Hz, 1H, H-6), 8.05 (s, 1H, H-5), 10.36 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 21.1, 24.4, 55.9, 56.4, 112.3, 116.5, 117.9, 128.4, 129.8, 131.1, 132.5, 154.6, 187.3. MS (ESI): *m/z* = 371 (M^+- ClO_4).

2-(Dimethylamino)-4-(3-bromo-2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium perchlorate (**3a**):

Yield 81%. Mp 221-222 °C (dec). IR (ATR): 3573, 3126, 1575, 1526, 1411, 1260, 1073, 620 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3H, CH_3-5), 3.53 (s, 3H, CH_3), 3.56 (s, 3H, CH_3), 7.34 (d, ^4J = 2.4 Hz, 1H, H-3), 7.60 (d, ^4J = 2.4 Hz, 1H, H-6), 8.16 (s, 1H, H-5), 10.11 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 19.8, 46.7, 47.1, 112.5, 116.7, 117.4, 128.9, 129.2, 130.5, 132.7, 154.1, 187.1. MS (ESI): *m/z* = 331 (M^+-ClO_4).

2-(Diethylamino)-4-(3-bromo-2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium perchlorate (**3b**):

Yield 78%. Mp 196-197 °C. IR (ATR): 3064, 1555, 1518, 1446, 1245, 1095, 1025, 619 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.43 (t, 6H, $2CH_3$), 2.26 (s, 3H, CH_3-5), 3.84 (q, 2H, CH_2), 3.95 (q, 2H, CH_2), 7.25

(d, ^4J = 2.5 Hz, 1H, H-4), 7.47 (d, ^4J = 2.5 Hz, 1H, H-6), 8.03 (s, 1H, H-5), 10.17 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.7, 22.5, 23.0, 46.0, 47.1, 112.8, 116.9, 117.1, 128.7, 129.4, 130.7, 132.5, 154.8, 187.7. MS (ESI): *m/z* = 359 (M^+-ClO_4).

4-(3-Bromo-2-hydroxy-5-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**3c**):

Yield 92%. Mp 202-203 °C. IR (ATR): 3586, 3118, 1560, 1520, 1448, 1257, 1069, 620 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.24 (m, 7H, CH_3-5 + 2CH_2), 3.65 (t, 2H, CH_2), 3.67 (t, 2H, CH_2), 7.35 (d, ^4J = 2.4 Hz, 1H, H-4), 7.60 (d, ^4J = 2.4 Hz, 1H, H-6), 8.13 (s, 1H, H-5), 10.12 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.8, 22.4, 22.8, 56.5, 56.9, 112.7, 116.2, 117.0, 128.4, 129.1, 130.5, 132.7, 154.4, 187.1 . MS (ESI): *m/z* = 357 (M^+-ClO_4).

4-(3-Bromo-2-hydroxy-5-methylphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate (**3e**):

Yield 87%. Mp 205-206 °C. IR (ATR): 3600, 3116, 1555, 1430, 1259, 1077, 620 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.26 (s, 3H, CH_3-5), 3.97 (m, 8H, 4CH_2), 7.55 (d, ^4J = 2.3 Hz, 1H, H-4), 7.61 (d, ^4J = 2.3 Hz, 1H, H-6), 8.13 (s, 1H, H-5), 10.40 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 57.8, 58.4, 68.4, 112.5, 116.6, 117.8, 128.1, 129.5, 130.7, 132.3, 154.9, 187.7 . MS (ESI): *m/z* = 373 (M^+- ClO_4).

6-Bromo-4-methyl-2-[2-(piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4d**)*; General Procedure*

To a saturated sodium hydrogencarbonate solution (30 mL) perchlorate **3d** (1 g, 2.12 mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2 h under vigorous stirring at room temperature, the yellow solid was filtered off, washed with water, and dried. Recrystallization from DMF gave yellow crystals; yield 0.78 g (100%).
Mp 217-218 °C (dec). IR (ATR): 3005, 1563, 1462, 1220, 781 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 2.20 (s, 3H, CH_3-5), 2.25 (m, 4H, $2CH_2$), 3.64 (t, 2H, CH_2), 3.75 (t, 2H, CH_2), 7.33 (d, ^4J = 2.4 Hz, 1H, H-5), 7.60 (d, ^4J = 2.4 Hz, 1H, H-3), 8.06 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.8, 21.2, 24.4, 56.0, 56.4, 112.5, 116.9, 118.1, 128.5, 129.9, 131.4, 132.9, 154.8, 187.9. MS (ESI): *m/z* = 370.

6-Bromo-2-[2-(dimethylamino)-1,3-dithiol-2-ylium-4-yl]-4-methylphenolate (**4a**):

Yield 100%. Mp 225-226 °C (dec). IR (ATR): 2987, 1563, 1509, 1474, 1410, 1220, 860, 788 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 2.20 (s, 3H, CH_3-5), 3.53 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 7.30 (d, ^4J = 2.4 Hz, 1H, H-5), 7.62 (d, ^4J = 2.4 Hz, 1H, H-3), 8.10 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.8, 46.6, 47.0, 112.4, 116.7, 117.3, 128.7, 129.4, 130.4, 132.5, 154.4, 187.8 . MS (ESI): *m/z* = 330.

6-Bromo-2-[2-(diethylamino)-1,3-dithiol-2-ylium-4-yl]-4-methylphenolate (**4b**):

Yield 100%. Mp 226-227 °C (dec). IR (ATR): 1495, 1463, 1275, 852, 777, 620 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.42 (t, 6H, $2CH_3$),

2.22 (s, 3H, CH_3-5), 3.83 (q, 2H, CH_2), 3.94 (q, 2H, CH_2), 7.23 (d, ^4J = 2.4 Hz, 1H, H-5), 7.46 (d, ^4J = 2.4 Hz, 1H, H-3), 8.00 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.6, 22.4, 23.1, 46.5, 47.2, 112.9, 116.8, 117.6, 128.8, 129.3, 130.4, 132.7, 154.2, 187.5. MS (ESI): *m/z* = 358.

6-Bromo-4-methyl-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4c**):

Yield 100%. Mp 228-229 °C (dec). IR (ATR): 3007, 2974, 1550, 1497, 1473, 1450, 1346, 1228, 1197, 862, 789 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.20 (s, 3H, CH_3-5), 2.25 (m, 4H, 2CH_2), 3.64 (t, 2H, CH_2), 3.75 (t, 2H, CH_2), 7.33 (d, ^4J = 2.4 Hz, 1H, H-5), 7.60 (d, ^4J = 2.4 Hz, 1H, H-6), 8.06 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.8, 22.1, 22.7, 56.4, 56.7, 112.6, 116.1, 117.0, 128.5, 129.4, 130.3, 132.4, 154.3, 187.0 . MS (ESI): *m/z* = 356.

6-Bromo-4-Methyl-2-[2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4e**):

Yield 100%. Mp 195-196 °C (dec). IR (ATR): 2862, 1458, 1254, 892, 793 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.25 (s, 3H, CH_3-5), 3.98 (m, 8H, 4CH_2), 7.53 (d, ^4J = 2.4 Hz, 1H, H-5), 7.60 (d, ^4J = 2.3 Hz, 1H, H-3), 8.02 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.8, 57.7, 58.4, 68.4, 112.4, 116.5, 117.7, 128.3, 129.6, 130.8, 132.9, 154.6, 187.8 . MS (ESI): *m/z* = 372.

4-(3-Bromo-2-hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium chloride (**5d**); *General Procedure*

To a suspension of mesoionic phenolate **4d** (0.5 g, 1.35 mmol) in acetone (10 mL) a soln of HCl (37%, 0.57 mL, 6.7 mmol) was added. The reaction mixture was vigorously stirred at rt for 2 h, then filtered and washed with acetone. Recrystallization from ethanol gave colorless crystals; yield 0.52 g (95%).

Mp 197-198 °C (dec). IR (ATR): 3501, 3432, 2853, 1557, 1508, 1445, 1259, 879, 779 cm^{-1}. ^1H NMR (300 MHz, DMSO- d_6): δ = 1.65 (m, 6H, $3CH_2$), 2.24 (s, 3H, CH_3-5), 3.84 (m, 4H, $2CH_2$), 7.33 (d, ^4J = 2.5 Hz, 1H, H-4), 7.58 (d, ^4J = 2.3 Hz, 1H, H-6), 8.15 (s, 1H, H-5), 10.20 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 21.0, 24.5, 55.8, 56.3, 112.3, 116.4, 117.8, 128.3, 129.6, 131.0, 132.3, 154.4, 187.9.MS (ESI): *m/z* = 371 (M^+-Cl).

2-(Dimethylamino)-4-(3-bromo-2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium chloride (**5a**):

Yield 92%. Mp 195-196 °C (dec). IR (ATR): 3379, 3089, 1559, 1469, 1404, 1283, 1180, 864, 710 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 2.22 (s, 3H, CH_3-5), 3.55 (s, 3H, CH_3), 3.57 (s, 3H, CH_3), 7.32 (d, ^4J = 2.4 Hz, 1H, H-4), 7.58 (d, ^4J = 2.4 Hz, 1H, H-6), 8.12 (s, 1H, H-5), 10.22 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.7, 46.5, 47.01, 112.5, 116.1, 117.4, 128.5, 129.1, 130.1, 132.4, 154.8, 187.4. MS (ESI): *m/z* = 331 (M^+-Cl).

2-(Diethylamino)-4-(3-bromo-2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium chloride (**5b**):

Yield 91%. Mp 166-167 °C. IR (ATR): 2980, 1555, 1518, 1445, 1340, 1260, 779, 620 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.40 (t, 6H,

$2CH_3$), 2.23 (s, 3H, CH_3-5), 3.85 (q, 2H, CH_2), 3.93 (q, 2H, CH_2), 7.23 (d, ^4J = 2.4 Hz, 1H, H-4), 7.49 (d, ^4J = 2.4 Hz, 1H, H-6), 8.13 (s, 1H, H-5), 10.19 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 19.7, 22.8, 23.1, 46.2, 47.0, 112.5, 116.4, 117.0, 128.5, 129.7, 130.9, 132.4, 154.5, 187.1. MS (ESI): *m/z* = 259 (M^+-Cl).

4-(3-Bromo-2-hydroxy-5-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium chloride (**5c**):

Yield 97%. Mp 231-232 °C (dec). IR (ATR): 3300, 1556, 1514, 1451, 1337, 1245, 845 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.23 (s, 3H, CH_3-5), 2.29 (m, 4H, $2CH_2$), 3.69 (t, 2H, CH_2), 3.77 (t, 2H, CH_2), 7.35 (d, ^4J = 2.3 Hz, 1H, H-4), 7.61 (d, ^4J = 2.3 Hz, 1H, H-6), 8.11 (s, 1H, H-5), 10.22 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.7, 22.3, 22.8, 56.6, 56.9, 112.8, 116.1, 117.3, 128.5, 129.6, 130.4, 132.6, 154.8, 187.8 . MS (ESI): *m/z* = 255 (M^+- Cl).

4-(3-Bromo-2-hydroxy-5-methylphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium chloride (**5e**):

Yield 90%. Mp 107-108 °C. IR (ATR): 3304, 1549, 1504, 1214, 872, 754, 598 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.24 (s, 3H, CH_3-5), 3.96 (m, 8H, $4CH_2$), 7.53 (d, ^4J = 2.5 Hz, 1H, H-4), 7.53 (d, ^4J = 2.3 Hz, 1H, H-6), 8.18 (s, 1H, H-5), 10.23 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 19.9, 57.6, 58.1, 68.3, 112.4, 116.4, 117.3, 128.6, 129.9, 130.5, 132.4, 155.1, 187.5 . MS (ESI): *m/z* = 373 (M^+- Cl).

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