

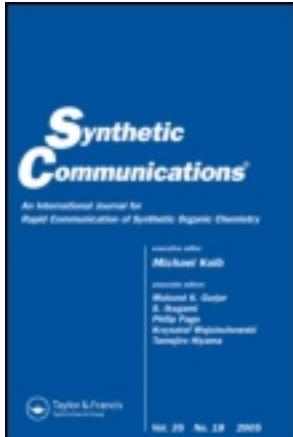
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## Synthesis of Mixed Aryl 2,3-Diarylsulphanyl-1,4-naphthoquinones

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**Abstract:** The reaction of 2-arylsulphanyl-1,4-naphthoquinone with aromatic thiols and sodium dithionite leads to bis-2,3-(arylsulphanyl)naphthalene-1,4-diols in high yield. Corresponding oxidized products, namely 2,3-diarylsulphanyl-1,4-naphthoquinones, are prepared in near quantitative yield by a copper(II)-catalyzed aerial oxidation reaction of bis-2,3-(arylsulphanyl)naphthalene-1,4-diols under mild condition.

**Keywords:** Bis-2,3-(arylsulphanyl)naphthalene-1,4-diols, C–S bond formation, 2,3-diarylsulphanyl-1,4-naphthoquinone, oxidation reactions

### INTRODUCTION

2-Arylsulphanyl-1,4-naphthoquinones are used as medicine.<sup>[1–6]</sup> They can be prepared by reactions of thiols on 1,4-naphthoquinone.<sup>[7–17]</sup> Depending on the stoichiometry of reactants, disubstituted derivatives of naphthoquinone are prepared.<sup>[18,19]</sup> The reaction of thiols with 1,4-naphthoquinone by potassium fluoride (KF)/Celite<sup>[7]</sup> and PdCl<sub>2</sub><sup>[18]</sup> and without a reagent<sup>[19]</sup> in refluxing ethanol leads to 2,3-diarylsulfanyl-1,4-naphthoquinones or 2-arylsulphanyl-1,4-naphthoquinone. A recent report suggests the utility of mixed 2,3-diarylsulphanyl naphthalene-1,4-diols as antifungal agents, but the synthetic procedures of the compounds are not disclosed.<sup>[20]</sup> Moreover, most of the literature reports on the simple 2,3-diarylsulphanyl-naphthalene-1,4-diols lack spectroscopic or other related data.<sup>[18,19]</sup> It may

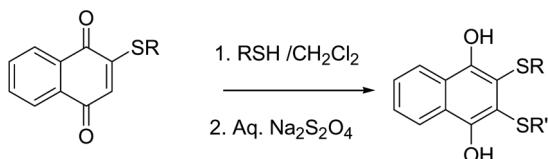
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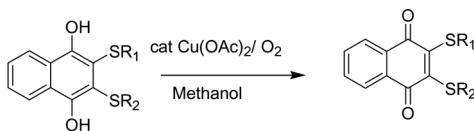
be mentioned that the introduction of two different thiol substituents on the ring of 1,4-naphthoquinone would lead to a new class of quinone compounds. We describe here the synthesis of different 2,3-diarylsulphanyl-1,4-naphthoquinones via 2,3-diarylsulphanyl naphthalene-1,4-diols that are prepared from the reaction of aromatic thiols on 2-arylsulphanyl-1,4-naphthoquinones. The 2,3-diarylsulphanyl naphthalene-1,4-diols are also oxidized by copper(II) acetate monohydrate-catalyzed aerial oxidation reactions.

## RESULTS AND DISCUSSION

The reaction of 2-arylsulphanyl-1,4-naphthoquinones with various aromatic thiols followed by reaction with sodium dithionite gave the corresponding 2,3-diarylsulphanyl naphthalene-1,4-diols in high yield. The method is also useful for synthesis of symmetric as well as unsymmetrical 2,3-diarylsulfanyl naphthalene-1,4-diols (Scheme 1). Although compound **1** is reported in literature, the detailed synthesis of it is not available.<sup>[20]</sup> The reaction of 1,4-naphthoquinone with thiophenol by potassium fluoride and Celite was reported earlier,<sup>[7]</sup> which gives 2,3-diarylsulphanyl-1,4-naphthoquinones in low yields along with mono-substituted derivative. However, we have observed that our reaction depicted in Scheme 1 gives exclusively bis-2,3-arylsulfanyl naphthalene-1,4-diols. The use of sodium dithionite in the reaction acts as a reducing agent of the carbonyl groups that may be formed through ariel oxidation of the products and provides a good method to isolate the diol products. The sodium metabisulphite,<sup>[21,22]</sup> and sodium dithionite<sup>[23,24]</sup> are often used for reduction of aromatic quinonic compounds to diols. The bis-2,3-arylsulphanyl naphthalene-1,4-diols can be prepared directly by stirring a methanol solution of aromatic thiol with 1,4-naphthoquinone for few hours; however, in such reactions the product undergoes slow oxidation to corresponding quinonic derivative and requires purification. The other important aspect of these reactions is the ease at which the



**Scheme 1.** R = C<sub>6</sub>H<sub>5</sub>-, R' = C<sub>6</sub>H<sub>5</sub>- (**1**); R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-, R' = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>- (**2**); R = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-, R' = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>- (**3**); R = 4-BrC<sub>6</sub>H<sub>4</sub>-, R' = 4-BrC<sub>6</sub>H<sub>4</sub>; (**4**); R = C<sub>6</sub>H<sub>5</sub>-, R' = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>- (**5**); R = C<sub>6</sub>H<sub>5</sub>-, R' = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>- (**6**); R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-, R' = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>- (**7**); R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-, R' = 4-BrC<sub>6</sub>H<sub>4</sub>- (**8**).



**Scheme 2.** R = C<sub>6</sub>H<sub>5</sub>-, R' = C<sub>6</sub>H<sub>5</sub>- (**9**); R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-, R' = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>- (**10**); R = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-, R' = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>- (**11**); R = 4-BrC<sub>6</sub>H<sub>4</sub>-, R' = 4-BrC<sub>6</sub>H<sub>4</sub> (**12**); R = C<sub>6</sub>H<sub>5</sub>-, R' = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>- (**13**); R = C<sub>6</sub>H<sub>5</sub>-, R' = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>- (**14**); R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-, R' = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>- (**15**); R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-, R' = 4-BrC<sub>6</sub>H<sub>4</sub>- (**16**).

2-arylsulphanyl-1,4-naphthoquinones can be prepared from 1,4-naphthoquinone,<sup>[18]</sup> which are used as starting materials in these reactions.

The bis-2,3-arylsulphanyl naphthalene-1,4-diols can be easily oxidized by warming their methanol solutions (Scheme 2) with a catalytic amount of copper(II) acetate monohydrate (10 mol%) under aerobic conditions. Several bis-2,3-arylsulphanyl-naphthalene-1,4-diols were oxidized by applying this oxidation procedure (Scheme 2).

The copper(II) complexes are known to oxidize hydroquinones.<sup>[25,26]</sup> Among these, CuSO<sub>4</sub> with alumina as a catalyst was used for oxidation of hydroquinone in air.<sup>[26]</sup> Our compounds (**1–4**) also can be oxidized by CuSO<sub>4</sub> along with alumina as catalyst. The advantages of the oxidation by copper(II) acetate as a catalyst for oxidation of these substrates are the mild reaction conditions and the formation of near quantitative yield without use of a solid support. The yields and the spectroscopic details of the products are listed in the experimental section. The oxidation reactions reported here do not lead to the C-S bond cleavage or over-oxidation to form corresponding sulphoxide derivatives, and the workup procedures for these reactions are also very simple.

In conclusion, we have developed the existing C-S bond formation reactions on 1,4-naphthoquinones to a convenient method for synthesis of bis-2,3-arylsulphanyl naphthalene-1,4-diols and their oxidation to 2-arylsulphanyl-1,4-naphthoquinones.

## EXPERIMENTAL

The 2-arylsulphanyl-1,4-naphthoquinones were synthesized by a reported procedure.<sup>[21,22]</sup>

### Synthesis of 2,3-Diarylsulphanyl naphthalene-1,4-diols from 2-Arylsulphanyl-1,4-naphthoquinones

A solution of arylthiol and 2-arylsulphanyl-1,4-naphthoquinone (1 mmol each) in dichloromethane (20 ml) was stirred at room temperature for 4 h.

The solution was evaporated under reduced pressure. A solution of sodium dithionite (2 mmol) in water (20 ml) was added, followed by ethylacetate (10 ml), to the crude product. The mixture was stirred for 2 h. The organic layer was separated and washed several times with water (10 ml each), and the products were obtained from the organic layer by crystallization.

### Spectroscopic Data for Mixed 2,3-Diarylsulphanyl-1,4-naphthalenediols

#### 2,3-Diphenylsulphanyl-1,4-naphthalenediol (**1**)

Yield 91%; mp 149 °C. Elemental anal. calcd. for  $C_{23}H_{18}O_2S_2$ : C, 70.74; H, 4.65. Found: C, 70.73; H, 4.63.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.31 (m, 2H), 7.65 (m, 2H), 7.19 (s, 1H), 7.17 (s, 1H), 7.09 (m, 4H), 6.99 (m, 2H), 6.93 (m, 3H), 2.23 (s, 3H). IR (KBr,  $cm^{-1}$ ): 3406 (bs), 3053 (w), 2919 (w), 1629 (w), 1573 (s), 1486 (w), 1434 (w), 1399 (s), 1260 (s), 1158 (w), 1081 (w), 1020 (w), 892 (s), 805 (w), 769 (w), 738 (w), 692 (w), 656 (w), 559 (w), 497 (w), 431 (s). UV-vis ( $\lambda$  max,  $CH_3CN$ ) 341, 357 nm ( $1.23 \times 10^4$  and  $1.31 \times 10^4$   $mol^{-1} dm^3 cm^{-1}$ ).

#### 2,3-Di-(4-methylphenyl)sulphanyl-1,4-naphthalenediol (**2**)

Yield 90%; mp 82°C. Elemental anal. calcd. for  $C_{23}H_{18}O_3S_2$ : C, 67.96; H, 4.46. Found: C, 67.95; H, 4.48.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.30 (m, 2H), 7.64 (m, 2H), 7.30 (s, 1H), 7.26 (s, 1H), 7.10 (m, 2H), 7.05 (d,  $J = 8.4$  Hz, 2H), 7.00 (m, 3H), 6.65 (d,  $J = 8.4$  Hz, 2H), 3.71 (s, 3H). IR (KBr,  $cm^{-1}$ ): 3394 (bs), 2938 (w), 2833 (w), 1592 (w), 1568 (s), 1494 (s), 1428 (w), 1398 (s), 1245 (s), 1026 (w), 885 (w), 769 (w), 659 (w). UV-vis ( $\lambda$  max,  $CH_3CN$ ) 341, 357 nm ( $1.33 \times 10^4$  and  $1.16 \times 10^4$   $mol^{-1} dm^3 cm^{-1}$ ).

#### 2,3-Di-(4-methoxyphenyl)sulphanyl-1,4-naphthalenediol (**3**)

Yield 94%; mp 132°C. Elemental anal. calcd. for  $C_{24}H_{20}O_3S_2$ : C, 68.54; H, 4.79. Found: C, 68.56; H, 4.82.  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.29 (m, 2H), 7.63 (m, 2H), 7.17 (s, 1H), 7.14 (s, 1H), 7.01 (m, 2H), 6.92 (m, 4H), 6.64 (m, 2H), 3.70 (s, 3H), 2.23 (s, 3H). IR (KBr,  $cm^{-1}$ ): 3400 (bs), 2922 (w), 2918 (w), 1578 (s), 1491 (s), 1435 (w), 1395 (w), 1247 (s), 1168 (w), 1082 (w), 1030 (w), 886 (s), 810 (w), 656 (w). UV-vis ( $\lambda$  max,  $CH_3CN$ ) 341, 357 nm ( $1.28 \times 10^4$  and  $1.37 \times 10^4$   $mol^{-1} dm^3 cm^{-1}$ ).

### 2,3-Di-(4-bromophenyl)sulphanyl-1,4-naphthalenediol (**4**)

Yield 96%; mp 192°C. Elemental anal. calcd. for C<sub>23</sub>H<sub>17</sub>O<sub>2</sub>S<sub>2</sub>Br: C, 58.85; H, 3.65. Found: C, 58.83; H, 3.66. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.32 (dd, *J* = 9.6, 3.2 Hz, 2H), 7.67 (dd, *J* = 9.6, 3.2 Hz, 2H), 7.18 (m, 2H), 7.07 (s, 1H), 7.05 (s, 1H), 6.89 (m, 4H), 6.82 (m, 2H), 2.24 (s, 3H). IR (KBr, cm<sup>-1</sup>): 3397 (bs), 2918 (w), 1568 (s), 1472 (w), 1397 (s), 1268 (s), 1246 (s), 1080 (s), 1005 (w), 885 (s), 805 (s), 772 (w), 658 (s), 556 (w). UV-vis ( $\lambda$  max, CH<sub>3</sub>CN) 341, 357 nm (1.76  $\times$  10<sup>4</sup> and 1.86  $\times$  10<sup>4</sup> mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

### 2-(Phenyl)-3-(4-methylphenyl)sulphanyl-1,4-naphthalenediol (**5**)

Yield 90%; mp 184°C. Elemental anal. calcd. for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>: C, 70.18; H, 4.28. Found: C, 70.20; H, 4.30. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.32 (dd, *J* = 9.6, 3.2 Hz, 2H), 7.66 (dd, *J* = 9.6, 3.2 Hz, 2H), 7.12 (s, 2H), 7.08 (m, 6H), 7.01 (m, 4H). IR (KBr, cm<sup>-1</sup>): 3401 (bs), 3360 (w), 3068 (w), 2366 (w), 1629 (w), 1573 (s), 1475 (w), 1431 (s), 1399 (s), 1255 (s), 1153 (w), 1081 (w), 1015 (w), 886 (s), 738 (s), 692 (w), 656 (w), 559 (w). UV-vis ( $\lambda$  max, CH<sub>3</sub>CN) 341, 357 nm (1.06  $\times$  10<sup>4</sup> and 1.12  $\times$  10<sup>4</sup> mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

### 2-(Phenyl)-3-(4-methoxyphenyl)sulphanyl-1,4-naphthalenediol (**6**)

Yield 92%; mp 158°C. Elemental anal. calcd. for C<sub>24</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub>: C, 71.25; H, 4.98. Found: C, 71.21; H, 4.94. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.30 (dd, *J* = 9.6, 3.6 Hz, 2H), 7.64 (dd, *J* = 9.6, 3.6 Hz, 2H), 7.16 (s, 2H), 6.92 (s, 8H), 2.23 (s, 6H). IR (KBr, cm<sup>-1</sup>): 3401 (bs), 3345 (w), 2919 (w), 2858 (w), 1573 (s), 1496 (s), 1434 (w), 1399 (s), 1255 (s), 1163 (w), 1086 (w), 1020 (w), 886 (s), 799 (s), 769 (w), 661 (w), 564 (w), 477 (w). UV-vis ( $\lambda$  max, CH<sub>3</sub>CN) 341, 357 nm (1.74  $\times$  10<sup>4</sup> and 1.84  $\times$  10<sup>4</sup> mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

### 2-(4-Methylphenyl)-3-(4-methoxyphenyl)sulphanyl-1,4-naphthalenediol (**7**)

Yield 89 %; mp 156°C. Elemental anal. calcd for C<sub>24</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub>: C, 66.03; H, 4.62. Found: C, 66.04; H, 4.66. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.28: (dd, *J* = 9.6, 3.2 Hz; 2H) 7.63 (dd, *J* = 9.6, 3.2 Hz, 2H), 7.26 (s, 2H), 7.00 (dd, *J* = 8.8, 2.4 Hz, 4H), 6.65 (dd, *J* = 8.8, 2.4 Hz, 4H), 3.71 (s, 6H). IR (KBr, cm<sup>-1</sup>): 3393 (bs), 2962 (w), 2833 (w), 1593 (w), 1569 (s), 1494 (s), 1463 (w), 1398 (w), 1245 (s), 1180 (w), 1033 (s), 885 (w), 821 (w), 659 (w). UV-vis ( $\lambda$  max, CH<sub>3</sub>CN) 342, 358 nm (0.73  $\times$  10<sup>4</sup> and 0.76  $\times$  10<sup>4</sup> mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

**2-(4-Methylphenyl)-3-(4-bromophenyl)sulphanyl-1,4-naphthalenediol (**8**)**

Yield 95%; mp 210°C. Elemental anal. calcd. for C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>Br<sub>2</sub>: C, 49.46; H, 2.64. Found: C, 49.48; H, 2.63. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 8.32: (dd, *J* = 8.8, 3.2 Hz, 2H), 7.69 (dd, *J* = 8.8, 3.2 Hz, 2H), 7.21 (dd, *J* = 7.6, 2 Hz, 4H), 7.075 (s, 2H), 6.82 (dd, *J* = 8.4, 2 Hz, 4H). IR (KBr, cm<sup>-1</sup>): 3398 (bs), 1569 (s), 1472 (s), 1402 (s), 1268 (w), 1251 (s), 1165 (s), 1080 (w), 1070 (w), 1008 (s), 885 (s), 806 (s), 657 (w), 557 (w). UV-vis ( $\lambda$  max, CH<sub>3</sub>CN) 341, 357 nm ( $1.71 \times 10^4$  and  $1.80 \times 10^4$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

**General Procedure for Oxidation of Bis-2,3-arylsulphanyl naphthalene-1,4-diol**

Copper(II) acetate monohydrate (0.017 g, 0.1 mmol) was added to a solution of bis-2,3-arylsulphanyl naphthalenediol (1 mmol) in methanol (10 ml). The mixture was refluxed at 60°C for 1 h and further stirred for 4 h at room temperature. Progress of the reaction was monitored by thin-layer chromatography (TLC) using ethyl acetate-hexane (1:5) as eluent. Once the reaction was completed, the solvent was removed, and the crude residue was dissolved in 30 ml methanol and filtered. The filtrate was recrystallized to obtain the corresponding bis-2,3-arylsulphanyl naphthoquinone.

**Spectroscopic Data**

**Bis-2,3-phenylsulphanyl-1,4-naphthalenedione (**9**)**

Yield 96%; mp 140°C (reported 136°C).<sup>[12]</sup> Elemental anal. calcd. for C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 70.56; H, 3.77. Found: C, 71.19; H, 3.75. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.98 (dd, *J* = 6, 2.8 Hz, 2H), 7.68 (dd, *J* = 5.6, 2.4 Hz, 2H), 7.37 (m, 4H), 7.29 (m, 6H). IR (KBr, cm<sup>-1</sup>): 3407 (bs), 1668 (s), 1579 (w), 1498 (w), 1475 (w), 1267 (s), 1138 (w), 1081 (w), 748 (s), 706 (w), 698 (w). UV-vis ( $\lambda$  max, CH<sub>3</sub>CN) 458 nm ( $3.85 \times 10^3$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

**Bis-2,3-(4-methoxyphenyl)sulphanyl-1,4-naphthalenedione (**10**)**

Yield 97%; mp 91°C (reported 108°C).<sup>[22]</sup> Elemental anal. calcd. for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>: C, 66.34; H, 4.18. Found: C, 66.33; H, 4.20. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.95 (dd, *J* = 5.6, 2.4 Hz, 2H), 7.64 (dd, *J* = 5.6, 2.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 3.81

(s, 6H). IR (KBr,  $\text{cm}^{-1}$ ): 3428 (bs), 2928 (w), 1659 (s), 1590 (s), 1492 (w), 1465 (w), 1289 (w), 1271 (s), 1245 (s), 1139 (s), 1029 (w), 838 (w), 700 (w) 531 (w). LC-MS (m/e) 435, 327. UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 458 nm ( $3.76 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

### Bis-2,3-(4-methylphenyl)sulphanyl-1,4-naphthalenedione (11)

Yield 98%; mp 160°C (reported 169°C).<sup>[12]</sup> Elemental anal. calcd. for  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{S}_2$ : C, 71.61; H, 4.51. Found: C, 71.63, H, 4.50.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.98 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.66 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.29 (d,  $J = 8 \text{ Hz}$ , 4H), 7.11 (d,  $J = 8 \text{ Hz}$ , 4H), 2.34 (s, 6H). IR (KBr,  $\text{cm}^{-1}$ ): 3433 (bw), 2921 (w), 1650 (s), 1664 (s), 1590 (w), 1492 (w), 1273 (s), 1134 (s), 1086 (w), 815 (s), 700 (w), 490 (w). UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 473 nm ( $3.83 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

### Bis-2,3-(4-bromophenyl)sulphanyl-1,4-naphthalenedione (12)

Yield 96%; mp 207°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.91 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.62 (dd,  $J = 5.6 \text{ Hz}, 2.4 \text{ Hz}$ , 2H), 7.36 (d,  $J = 8.4 \text{ Hz}$ , 4H), 7.17 (d,  $J = 8.4 \text{ Hz}$ , 4H). IR (KBr,  $\text{cm}^{-1}$ ): 3435 (bw), 1666 (s), 1654 (s), 1590 (w), 1504 (w), 1471 (w), 1270 (s), 1135 (s), 1080 (w), 1006 (w), 816 (s), 708 (w), 478 (w). LC-MS (m/e) 533. UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 457 nm ( $3.09 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

### Bis-2-(4-phenyl)-3-(4-bromophenyl)sulphanyl-1,4-naphthalenedione (13)

Yield 87%; mp 93°C. Elemental anal. calcd. for  $\text{C}_{23}\text{H}_{16}\text{O}_3\text{S}_2$ : C, 68.29; H, 3.99. Found: C, 68.31; H, 4.09.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.87 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.57 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.31 (d,  $J = 9.2 \text{ Hz}$ , 4H), 6.77 (d,  $J = 8.8 \text{ Hz}$ , 5H), 3.73 (s, 3H). IR (KBr,  $\text{cm}^{-1}$ ): 3433 (bs), 2926 (w), 1659 (s), 1590 (s), 1492 (w), 1464 (w), 1270 (s), 1245 (s), 1138 (s), 1025 (w), 809 (w), 700 (w), 530 (w). UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 457 nm ( $5.16 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

### Bis-2-(4-phenyl)-3-(4-methylphenyl)sulphanyl-1,4-naphthalenedione (14)

Yield 96%; mp 121°C. Elemental anal. calcd. for  $\text{C}_{23}\text{H}_{16}\text{O}_2\text{S}_2$ : C, 71.10; H, 4.15. Found: C, 71.22; H, 4.18.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.08 (dd,  $J = 8.8, 5.6 \text{ Hz}$ , 2H), 7.77 (dd,  $J = 9.2, 5.2 \text{ Hz}$ , 2H), 7.49 (d,  $J = 8 \text{ Hz}$ , 2H), 7.40 (m, 5H), 7.22 (d,  $J = 8 \text{ Hz}$ , 2H), 2.45 (s, 3H). IR

(KBr,  $\text{cm}^{-1}$ ): 3436 (bs), 2924 (w), 1664 (s), 1590 (w), 1497 (w), 1475 (w), 1264 (s), 1136 (s), 1082 (w), 812 (w), 706 (s), 503 (w). UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 460 nm ( $4.96 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

### Bis-2-(4-methylphenyl)-3-(4-methoxyphenyl)sulphanyl-1,4-naphthalenedione (**15**)

Yield 88%; mp 138°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.89 (dd,  $J = 5.6, 2.8 \text{ Hz}$ , 2H), 7.58 (dd,  $J = 6, 3.2 \text{ Hz}$ , 2H), 7.30 (d,  $J = 8.8 \text{ Hz}$ , 2H), 7.21 (d,  $J = 8.4 \text{ Hz}$ , 2H), 7.03 (d,  $J = 8.4 \text{ Hz}$ , 2H), 6.77 (d,  $J = 7.6 \text{ Hz}$ , 2H), 3.73 (s, 3H), 2.26 (s, 3H). IR (KBr,  $\text{cm}^{-1}$ ): 3436 (bs), 2927 (w), 1664 (s), 1590 (w), 1492 (s), 1267 (s), 1138 (s), 1033 (w), 814 (w), 700 (w). LC-MS (m/e) 420. UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 469 nm ( $5.17 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

### Bis-2-(4-methylphenyl)-3-(4-bromophenyl)sulphanyl-1,4-naphthalenedione (**16**)

Yield 92%; mp 178°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.98 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.69 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 2H), 7.42 (d,  $J = 8.8 \text{ Hz}$ , 2H), 7.26 (m, 4H), 7.12 (d,  $J = 8.8 \text{ Hz}$ ), 2.35 (s, 3H). IR (KBr,  $\text{cm}^{-1}$ ): 3435 (bs), 2922 (w), 1667 (s), 1654 (s), 1590 (w), 1503 (w), 1471 (w), 1270 (s), 1135 (s), 1080 (w), 1006 (w), 813 (w), 708 (w), 479 (w). LC-MS (m/e) 469. UV-vis ( $\lambda$  max,  $\text{CH}_3\text{CN}$ ) 458 nm ( $3.84 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

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### REFERENCES

1. Elslager, E. F.; Werbel, M. L.; Worth, D. F.; Donald, F. Synthetic schistosomicides, XIV: 1,4-Naphthoquinone mono(O-acyloximes), 4-amino-1,2-naphthoquinones, 2-amino-3-chloro-1,4-naphthoquinones, and other naphthoquinones. *J. Med. Chem.* **1970**, *13*, 104–109.
2. Kallmayer, H. J.; Tappe, C. The 4-amino-1,2-naphthoquinone derivatives of some psychotropic drugs of the desipramine type: Quinone-amine reactions. *Pharm. Acta Helv.* **1987**, *62*, 2–6.
3. Bullock, F. J.; Tweedie, J. F.; McRitchie, D. D.; Aurther, D. 2-Amino-1,4-naphthoquinone imines. *J. Chem. Soc. C* **1969**, 1799–1803.

4. Ryu, C. K.; Jeong, H. J.; Lee, S. K.; You, H. J.; Choi, K. U.; Shim, J. Y.; Heo, Y. H.; Lee, C. O. Effects of 6-arylamino-5,8-quinolinediones and 6-chloro-7-arylamino-5,8-isoquinolinediones on NAD(P)H: Quinone oxidoreductase (NQO1) activity and their cytotoxic potential. *Arch. Pharm. Res.* **2001**, *24*, 390–396.
5. Ryu, C. K.; Choi, J. A.; Kim, S. H. Synthesis and antifungal evaluation of 6-(N-arylamino)-7-methylthio-5,8-quinolinediones. *Arch. Pharma. Res.* **1998**, *21*, 440–444.
6. Fieser, L. F.; Berliner, E.; Bondhus, F. J.; Chang, F. C.; Dauben, W. G.; Ettlinger, M. G.; Fawaz, G.; Fields, M. H.; Charles, H.; Hans, V.; Wyman, R.; Wilson, A. G.; Wilson, E.; Wu, M.-I.; Leffler, M. T.; Hamlin, K. E.; Matson, E. J.; Moore, E. E.; Moore, M. B.; Zaugg, H. E. Naphthoquinone antimalarials XI: Related compounds. *J. Am. Chem. Soc.* **1948**, *70*, 3212–3215.
7. Errante, G.; Motta, G. L.; Lagana, C.; Wittebolle, V.; Sarciron, M.-É.; Barret, R. Synthesis and evaluation of antifungal activity of naphthoquinone derivatives. *Eur. J. Med. Chem.* **2006**, *41*, 773–778.
8. Gabbutt, C. D.; Hepworth, J. D.; Heron, B. M. Synthesis and reactivity of some thiochroman-3,4-diones. *Tetrahedron* **1994**, *50*, 7865–7878.
9. Asenjo, P.; Farina, F.; Martin, M. V.; Paredes, M. C.; Soto, J. J. Synthesis of 2-sulfur-substituted 1,4-anthraquinones: Application to the synthesis of anthracyclinone precursors. *Tetrahedron Lett.* **1995**, *36*, 319–832.
10. Yadav, J. S.; Reddy, B. V. S.; Swamy, T.; Ramireddy, N. Ionic liquids-promoted addition of arylsulfonic acids to p-quinones: A green synthesis of diaryl sulfones. *Synthesis* **2004**, 1849–1853.
11. Polonik, S. G.; Dmitrenok, P. S.; Makhan'kov, V. V.; Anufriev, V. F.; Vorozhtsov, N. Reductive heterocyclization of 2,3-dichloro-1,4-naphthoquinone into naphtho[2,3-f][1,2,3,4,5]pentathiepine-6,11-diol under the action of sodium hydrosulfide in DMF. *Russ. J. Org. Chem.* **2006**, *42*, 302–303.
12. Tandon, V.; Chhor, R. B.; Singh, R. V.; Rai, S.; Yadav, D. B. Design, synthesis, and biological evaluation of 1,2,3-disubstituted-1,4-dihydrobenzo [g] quinaxoline-5-10-diones and related compounds as antibacterial agent. *Bioorg. Med. Chem. Lett.* **2006**, *14*, 6120–6126.
13. Dimroth, O.; Kraft, L.; Aichinger, K. Action of thiophenol on quinone. *Justus Liebigs Ann. Chem.* **1940**, *545*, 124–139.
14. Fieser, L. F.; Brown, R. H. Synthesis of naphthoquinones for studies of the inhibition of enzyme systems. *J. Am. Chem. Soc.* **1949**, *71*, 3609–3614.
15. Iwao, M.; Kuraishi, T. A novel naphthoquinone synthesis via tandem directed lithiations. *Tetrahedron Lett.* **1985**, *26*, 6213–6216.
16. Villalba, M. M.; Litchfield, V. J.; Smith, R. B.; Franklin, A. M.; Livingstone, C.; Davis, J. J. A chromatographic tool for preparing combinatorial quinone-thiol conjugate libraries. *Biochem. Biophys. Methods* **2007**, *70*, 797–802.
17. Couladouros, E. A.; Strongilos, A. T. Product class 3: Naphtho-1,4-quinones. *Sci. Synth.* **2006**, *28*, 217–322.
18. Singh, W. M.; Karmakar, A.; Barooah, N.; Baruah, J. B. Variations in product in reactions of naphthoquinone with primary amines. *Beil. J. Org. Chem.* **2007**, *3*, 10.

19. Stasevych, M. V.; Plotnikov, M. Y.; Platonov, M. O.; Sabat, S. I.; Musyanovych, R. Y.; Novikov, V. P. Sulfur-containing derivatives of 1,4-naphthoquinone, part 2: Sulphenyl derivative synthesis. *Heteroatom Chem.* **2005**, *16*, 587–598.
20. Wittebolle, V.; Lemriss, S.; Morella, G. L.; Errante, J.; Boiron, P.; Barret, R.; Sarciron, M. E. Antifungal effects of aminosulphonide and disulphide derivatives. *Mycoses* **2006**, *49*, 169–175.
21. Miyaki, K.; Ikeda, N.; Mizuno, D. Antibacterial properties of 2 and 2,3-disubstituted 1,4-naphthoquinones. *Yakugaku Zasshi* **1953**, *73*, 961–964.
22. Ryu, C. K.; Choi, I. H.; Lee, J. Y.; Jung, S. H. Synthesis of benzo[b] naphtha[2,3-d]thiophen-6,11-diones via palladium(II) acetate mediated cyclisation of 3-arylthio-1,4-naphthoquinone. *Heterocycle* **2005**, *65*, 1205–1214.
23. Kostikov, A. P.; Popik, V. V. 2,5-Dihydroxbenzyl and (1,4-dihydroxy-2-naphthyl) methyl, novel reductivity and photo-cleavages for the hydroxyl moiety. *J. Org. Chem.* **2007**, *72*, 9190–9194.
24. Nguyen, V. T.; Claessens, S.; Habonimana, P.; Tehrani, K. A.; Van P. L.; DeKimpe, N. Synthesis of harounnoside, a naturally occurring pentalongin hydroquinone bis glucoside. *Synlett* **2006**, 2469–2471.
25. Puzari, A.; Baruah, J. B. Organic oxidative reactions mediated by copper. *J. Mol. Catal. A: Chem.* **2002**, *187*, 149–162.
26. Sakamoto, T.; Yonehara, H.; Pac, C. Catalytic activities of CuSO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> in dehydrogenation of arene by dioxygen. *J. Org. Chem.* **1997**, *62*, 3194–3196.