

## **Supporting Information**

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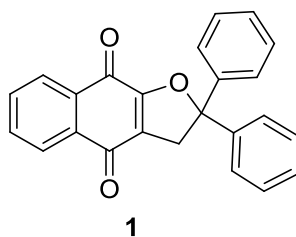
## 1. General information

TLC were performed on 5 cm × 10 cm aluminium plates coated with silica gel (layer 0.2 mm) 60F<sub>254</sub> (Merck) in an appropriate solvent. The following adsorbent was used for flash column chromatography: silica gel 60 (Merck, particle size 0.063-0.200 nm, 70-230 mesh ASTM). Melting points were determined through capillary tubes, with a B-540 Büchi melting point apparatus. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded in CDCl<sub>3</sub>, with tetramethylsilane (Me<sub>4</sub>Si) as an internal reference using a Bruker ARX 200 spectrometer operating at 200 MHz for <sup>1</sup>H-NMR and 50 MHz for <sup>13</sup>C-NMR; spectra were carried out at the Service Interuniversitaire de RMN de la Faculté de Pharmacie de Marseille. The <sup>1</sup>H chemical shifts are quoted in parts per million as  $\delta$  downfield from tetramethylsilane ( $\delta$  0.00) as an internal standard and the <sup>13</sup>C chemical shifts were referenced to the solvent peaks: CDCl<sub>3</sub> (76.9 ppm). Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet) and m (a more complex multiplet or overlapping multiplets). Mass spectra, run on an API-QqToF mass spectrometer, were carried out at the Spectropole de la Faculté des Sciences site Saint-Jérôme. X-ray analyses were performed on a Bruker-Nonius KappaCCD diffractometer with a graphite-monochromated Mo-K $\alpha$  radiation at 293 K. All commercial reagents were used without purification.

## 2. Experimental section

### - Typical procedure for the synthesis of **1**:

A solution of 2-hydroxy-1,4-naphthoquinone (1.06 mmol, 185 mg, 1 equiv.) in 25 mL of glacial acetic acid was stirred at 65°C in an open vessel. 1,1-Diphenylethylene (0.53 mmol, 95 mg, 0.5 equiv.) and manganese(III) acetate dihydrate (2.65 mmol, 710 mg, 2.5 equiv.) were added and the reaction was controlled by TLC until consumption of alkene. After 1 h, the reaction mixture was poured into 60 mL of cold water and extracted with dichloromethane (3 × 20 mL). The organic extracts were collected and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was evaporated under reduced pressure and crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 70/30), and the product obtained was recrystallized to afford product **1**.

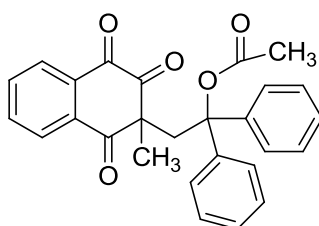


**1**<sup>1</sup>: Yield: 52%, Yellow solid, mp = 194-196°C <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.02-8.12 (m, 2H, Ar-H), 7.64-7.73 (m, 2H, Ar-H), 7.42-7.48 (m, 4H, Ar-H), 7.29-7.38 (m, 6H, Ar-H), 3.93 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta$  = 182.2, 177.6, 158.6, 143.5 (2C), 134.1, 133.0, 132.9, 131.6, 128.6 (4C), 128.1 (2C), 126.3, 126.0, 125.7 (4C), 123.7, 96.3, 41.6.

<sup>[1]</sup> M. Yilmaz, M. Yakut, A. T. Pekel *Synth. Commun.* **2008**, 38, 914-927.

- Typical procedure for the synthesis of **2**:

A solution of 2-hydroxy-3-methyl-1,4-naphthoquinone (1.06 mmol, 200 mg, 1 equiv.) in 25 mL of glacial acetic acid was stirred at 65°C in an open vessel. 1.1-Diphenylethylene (0.53 mmol, 95 mg, 0.5 equiv.) and manganese(III) acetate dihydrate (2.65 mmol, 710 mg, 2.5 equiv.) were added and the reaction was controlled by TLC until consumption of alkene. **After 1 h**, the reaction mixture was poured into 60 mL of cold water and extracted with dichloromethane (3 × 20 mL). The organic extracts were collected and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was evaporated under reduced pressure and crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 70/30), and the product obtained was recrystallized to afford product **2**.

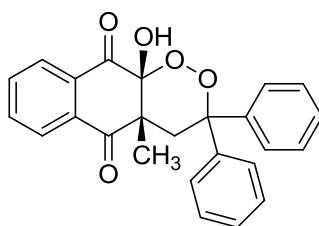


**2**

**2**: Yield: 63%, white solid, mp = 230°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 8.00-8.10 (m, 2H, Ar-H), 7.66-7.74 (m, 4H, Ar-H), 7.52-7.57 (m, 2H, Ar-H), 7.22-7.33 (m, 4H, Ar-H), 7.12-7.19 (m, 2H, Ar-H), 3.78 (d, J = 12.2 Hz, 1H, CH), 2.98 (d, J = 12.2 Hz, 1H, CH), 1.13 (s, 3H, CH<sub>3</sub>), 1.06 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.3, 187.8, 168.9, 148.0, 146.0, 135.3, 134.1, 134.0, 133.7, 128.5 (2C), 128.4 (2C), 127.9, 127.3, 126.9, 126.8, 124.6 (2C), 124.5 (2C), 107.6, 91.3, 61.4, 43.8, 20.3, 19.8. HRMS (ESI): m/z [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>27</sub>H<sub>22</sub>O<sub>5</sub> : 444.1805 ; found : 444.1808.

- Typical procedure for the synthesis of **3-27**:

A solution of 2-hydroxy-3-methyl-1,4-naphthoquinone (1.06 mmol, 200 mg, 1 equiv.) in 25 mL of glacial acetic acid was stirred at room temperature in an open vessel. Corresponding alkene (0.53 mmol, 0.5 equiv.) and manganese(III) acetate dihydrate (0.21 mmol, 57 mg, 0.2 equiv.) were added and the reaction was controlled by TLC until consumption of alkene. After 1 h, the reaction mixture was poured into 60 mL of cold water and extracted with dichloromethane (3 × 20 mL). The organic extracts were collected and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was evaporated under reduced pressure, crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 70/30), and the product obtained was recrystallized to afford products **3-27**, products **8'-20'** and products **19'', 21''-27''**.

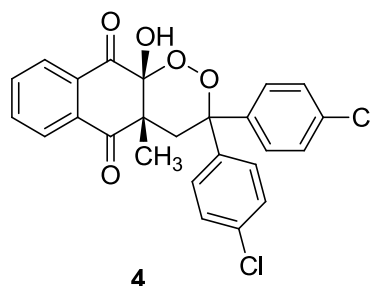


**3**

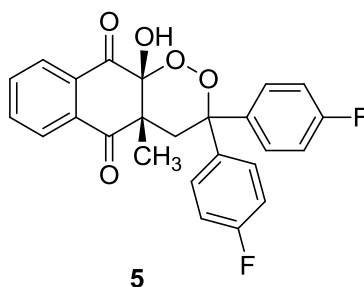
**3:** Yield: 95%, white solid, mp = 167-168°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.96-7.99 (m, 1H, Ar-H), 7.53-7.77 (m, 3H, Ar-H), 7.23-7.40 (m, 7H, Ar-H), 7.11-7.14 (m, 3H, Ar-H), 5.04 (s, 1H, OH), 3.68 (d, *J* = 13.6 Hz, 1H, CH), 2.88 (d, *J* = 13.6 Hz, 1H, CH), 1.25 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.5, 190.5, 142.8, 140.4, 135.6, 134.0, 133.9, 131.1, 128.4 (2C), 128.3, 127.7 (2C), 127.5 (2C), 127.4, 126.8, 126.7, 126.4 (2C), 98.8, 86.2, 49.0, 37.7, 23.8. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>20</sub>O<sub>5</sub> : 423.1203 ; found : 423.1204.

Crystal data for compound **3**: C<sub>25</sub>H<sub>20</sub>O<sub>5</sub>, (0.3x0.18x0.16 mm<sup>3</sup>), *M<sub>w</sub>* = 400.41, monoclinic, space group P2<sub>1/c</sub> (*T* = 293 K), *a* = 16.14371(17) Å, *b* = 7.60048(7) Å, *c* = 16.42538(17) Å, α = 90°, β = 99.4396(10)°, γ = 90°, *V* = 1988.10(4) Å<sup>3</sup>, *Z* = 4, *D<sub>calcd</sub>* = 1.338 g.cm<sup>-3</sup>, μ = 0.761 mm<sup>-1</sup>, *F*(000) = 840.0, index ranges -19 ≤ *h* ≤ 20, -9 ≤ *k* ≤ 9, -20 ≤ *l* ≤ 15, 2θ range = 10.92-148.566°, 273 variables and 0 restraint, were refined for 28457 reflections with *R* = 0.05, GoF = 1.039.

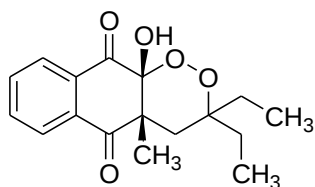
Crystallographic data for the structure **3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under number 1495135. Copie of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).



**4:** Yield: 86%, pink solid, mp = 152-153°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.99-8.04 (m, 1H, Ar-H), 7.65-7.74 (m, 3H, Ar-H), 7.26-7.33 (m, 6H, Ar-H), 7.14-7.18 (m, 2H, Ar-H), 5.26 (s, 1H, OH), 3.66 (d, *J* = 13.6 Hz, 1H, CH), 2.84 (d, *J* = 13.6 Hz, 1H, CH), 1.28 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.4, 190.1, 141.4, 138.8, 135.7, 134.6, 134.1, 133.9, 133.2, 131.4, 129.3 (2C), 128.6 (2C), 127.9 (2C), 127.8 (2C), 127.6, 126.7, 99.0, 85.6, 49.2, 37.7, 23.5. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>5</sub> : 491.0424; found : 491.0424.

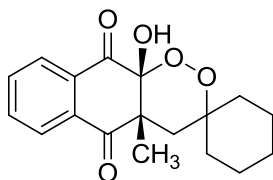


**5:** Yield: 79%, white solid, mp = 148°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.96-7.99 (m, 1H, Ar-H), 7.63-7.72 (m, 3H, Ar-H), 7.25-7.31 (m, 4H, Ar-H), 6.79-7.00 (m, 4H, Ar-H), 5.11 (s, 1H, OH), 3.61 (d, *J* = 13.6 Hz, 1H, CH), 2.83 (d, *J* = 13.6 Hz, 1H, CH), 1.24 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.6, 190.2, 162.5 (d, *J* = 248.6 Hz), 161.8 (d, *J* = 246.4), 138.5 (d, *J* = 3.2 Hz), 135.9, 135.8 (d, *J* = 3.2 Hz), 134.3, 133.7, 131.1, 129.7 (d, *J* = 8.3 Hz, 2C), 128.6 (d, *J* = 8.3 Hz, 2C), 127.5, 126.9, 115.4 (d, *J* = 21.6 Hz, 2C), 114.4 (d, *J* = 21.6 Hz, 2C), 98.8, 85.7, 49.1, 37.8, 23.8. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>25</sub>H<sub>18</sub>F<sub>2</sub>O<sub>5</sub> : 454.1461 ; found : 454.1460.



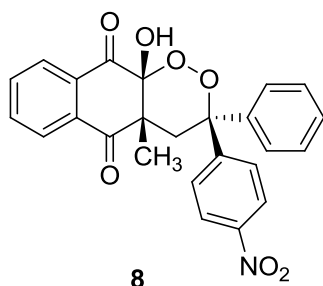
**6**

**6:** Yield: 54%, yellow solid, mp = 116°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.06-8.13 (m, 2H, Ar-H), 7.79-7.81 (m, 2H, Ar-H), 2.93 (d, *J* = 12.6 Hz, 1H, CH), 2.01 (d, *J* = 12.6 Hz, 1H, CH), 1.30-2.00 (m, 4H, 2CH<sub>2</sub>), 1.30 (s, 3H, CH<sub>3</sub>), 0.90 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>), 0.70 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 198.1, 194.2, 135.3, 134.7, 133.2, 132.9, 128.0, 127.4, 106.4, 91.7, 62.7, 44.9, 31.9, 29.5, 18.2, 8.6, 8.4. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>17</sub>H<sub>20</sub>O<sub>5</sub> : 322.1649 ; found : 322.1649.

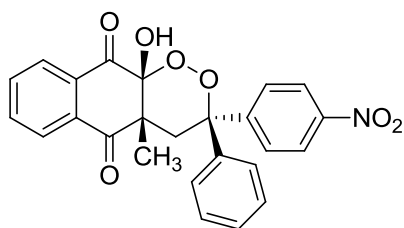


**7**

**7:** Yield: 40%, pink solid, mp = 147°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.14-8.18 (m, 2H, Ar-H), 7.77-7.86 (m, 2H, Ar-H), 4.63 (s, 1H, OH), 3.04 (d, *J* = 12.4 Hz, 1H, CH), 2.02 (d, *J* = 12.4 Hz, 1H, CH), 1.22-1.78 (m, 10H, CH<sub>2</sub>), 1.29 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 199.1, 192.4, 135.2, 134.4 (2C), 133.6, 128.0, 127.5, 100.4, 86.1, 61.4, 45.3, 41.1, 37.3, 25.2, 23.8, 23.7, 19.0. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>18</sub>H<sub>20</sub>O<sub>5</sub> : 334.1649 ; found : 334.1648.



**8**

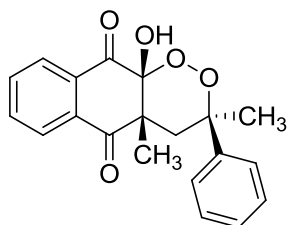


**8'**

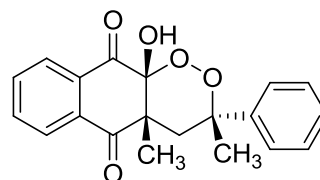
**8:** Yield: 62%, white solid, mp = 155°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 7.99-8.12 (m, 3H, Ar-H), 7.67-7.77 (m, 3H, Ar-H), 7.55-7.62 (m, 2H, Ar-H), 7.29-7.34 (m, 5H, Ar-H), 5.14 (s, 1H, OH), 3.72 (d, *J* = 14.2 Hz, 1H, CH), 2.93 (d, *J* = 14.2 Hz, 1H, CH), 1.26 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.3, 189.7, 148.6, 146.06, 141.6, 136.2, 134.5, 133.4, 131.0, 128.9, 128.8 (2C), 128.6, 127.5, 127.1, 126.1 (2C), 122.7 (2C), 98.8, 85.9, 49.4, 36.9, 23.6. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>7</sub> : 468.1054 ; found : 468.1052.

**8':** Yield: 21%, white solid, mp = 118°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.13 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.98-8.02 (m, 1H, Ar-H), 7.56-7.72 (m, 5H, Ar-H), 7.32-7.35 (m, 2H, Ar-

H), 7.15-7.19 (m, 3H, Ar-H), 5.15 (s, 1H, OH), 3.77 (d,  $J = 13.4$  Hz, 1H, CH), 2.80 (d,  $J = 13.4$  Hz, 1H, 1H), 1.25 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 194.9, 189.9, 150.2, 139.5, 135.6, 134.0$  (2C), 131.3, 127.9 (2C), 127.6, 127.4 (3C), 127.1 (2C), 126.8 (2C), 123.5 (2C), 99.2, 85.8, 49.2, 37.9, 23.3. HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>7</sub> : 468.1054 ; found : 468.1057.



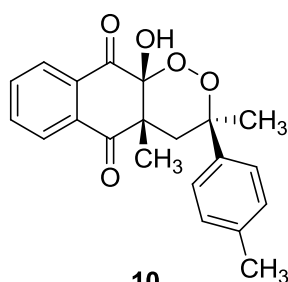
**9**



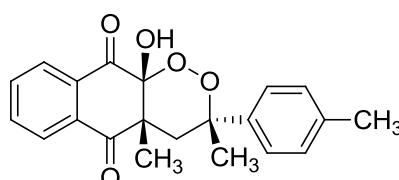
**9'**

**9**: Yield: 46%, white solid, mp = 132-133°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 8.37$  (dd,  $J = 7.6, 1.1$  Hz, 1H, Ar-H), 8.21 (dd,  $J = 7.4, 1.4$  Hz, 1H, Ar-H), 7.95 (td,  $J = 7.6, 1.6$  Hz, 1H, Ar-H), 7.88 (td,  $J = 7.4, 1.4$  Hz, 1H, Ar-H), 7.50-7.54 (m, 2H, Ar-H), 7.31-7.45 (m, 3H, Ar-H), 5.16 (s, 1H, OH), 3.14 (d,  $J = 13.6$  Hz, 1H, CH), 2.44 (d,  $J = 13.6$  Hz, 1H, CH), 1.56 (s, 3H, CH<sub>3</sub>), 1.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 196.8, 190.5, 145.2, 135.9, 134.5$  (2C), 133.9, 132.1, 128.4 (2C), 127.6, 127.4, 124.7 (2C), 99.5, 82.3, 50.1, 39.4, 26.4, 22.8. HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> : 361.1046 ; found : 361.1044.

**9'**: Yield: 37%, white solid, mp = 145-146°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 8.06$ -8.11 (m, 1H, Ar-H), 7.71-7.82 (m, 2H, Ar-H), 7.63-7.67 (m, 1H, Ar-H), 7.40-7.44 (m, 2H, Ar-H), 7.24-7.30 (m, 3H, Ar-H), 5.25 (s, 1H, OH), 3.47 (dd,  $J = 13.6$  Hz, 2.1 Hz, 1H, CH), 2.46 (dd,  $J = 13.6$  Hz 2.0 Hz, 1H, CH), 1.62 (s, 3H, CH<sub>3</sub>), 1.29 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 195.3, 190.5, 142.4, 135.4, 134.1, 133.8, 131.4, 127.5$  (2C), 127.4, 126.6, 126.5, 126.3 (2C), 98.8, 83.2, 48.9, 38.9, 30.6, 23.3. HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> : 361.1046 ; found : 361.1048.



**10**

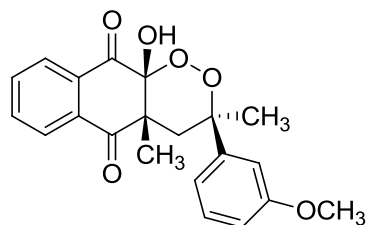


**10'**

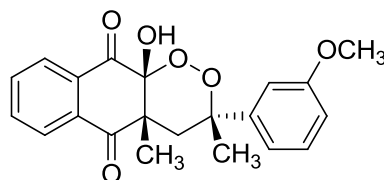
**10**: Yield: 49%, pink oil. <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 8.29$  (d,  $J = 7.7$  Hz, 1H, Ar-H), 8.14 (d,  $J = 7.2$  Hz, 1H, Ar-H), 7.78-7.92 (m, 2H, Ar-H), 7.35 (d,  $J = 8.1$  Hz, 2H, Ar-H), 7.16 (d,  $J = 8.1$  Hz, 2H, Ar-H), 5.07 (s, 1H, OH), 3.03 (d,  $J = 13.6$  Hz, 1H, CH), 2.37 (d,  $J = 13.6$  Hz, 1H, CH), 2.33 (s, 3H, CH<sub>3</sub>), 1.48 (s, 3H, CH<sub>3</sub>), 1.21 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 197.0, 190.5, 141.8, 137.5, 136.1, 134.7, 133.6, 131.9, 129.1$  (2C), 128.4, 127.5, 124.7 (2C), 99.3, 82.2, 50.1, 39.2, 26.2, 23.0, 21.1. HRMS (ESI):  $m/z$  [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>21</sub>H<sub>20</sub>O<sub>5</sub> : 370.1649 ; found : 370.1650.

**10'**: Yield: 33%, white solid, mp = 118°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 7.96$ -7.99 (m, 1H, Ar-H), 7.61-7.72 (m, 2H, Ar-H), 7.53-7.59 (m, 2H, Ar-H), 7.16 (d,  $J = 8.4$  Hz, 1H, Ar-H), 6.96 (d,  $J = 8.4$  Hz, 1H, Ar-H), 5.05 (s, 1H, OH), 3.33 (d,  $J = 13.6$  Hz, 1H, CH), 2.31 (d,  $J = 13.6$  Hz, 1H,

CH), 2.28 (s, 1H, CH), 2.26 (s, 3H, CH<sub>3</sub>), 1.48 (s, 3H, CH<sub>3</sub>), 1.16 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.5, 190.6, 139.2, 136.2, 135.6, 134.0 (2C), 131.1, 128.2 (2C), 127.4, 126.7, 126.2 (2C), 98.7, 83.2, 48.8, 38.9, 30.7, 23.5, 21.0. HRMS (ESI): m/z [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>21</sub>H<sub>20</sub>O<sub>5</sub> : 370.1650 ; found : 370.1649.



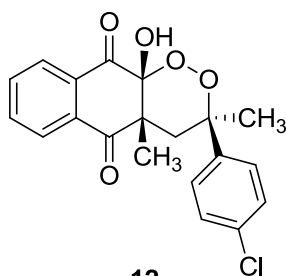
**11**



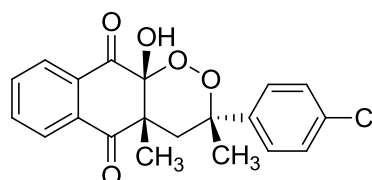
**11'**

**11**: Yield: 35%, yellow oil. <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.29 (d, *J* = 7.6 Hz, 1H, Ar-H), 8.15 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.77-7.92 (m, 2H, Ar-H), 7.24-7.30 (m, 1H, Ar-H), 6.99-7.03 (m, 2H, Ar-H), 6.79-6.84 (m, 1H, Ar-H), 5.07 (s, 1H, OH), 3.80 (s, 3H, CH<sub>3</sub>), 3.06 (d, *J* = 13.6 Hz, 1H, CH), 2.36 (d, *J* = 13.6 Hz, 1H, CH), 1.47 (s, 3H, CH<sub>3</sub>), 1.20 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 196.9, 190.4, 159.6, 146.5, 136.2, 134.7, 133.6, 131.9, 129.5, 128.4, 127.5, 116.9, 113.1, 110.6, 99.3, 82.3, 55.3, 50.0, 39.1, 29.7, 22.9. HRMS (ESI): m/z [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>21</sub>H<sub>20</sub>O<sub>6</sub> : 386.1598 ; found : 386.1596.

**11'**: Yield: 24%, yellow oil. <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 7.93-7.97 (m, 1H, Ar-H), 7.63-7.66 (m, 1H, Ar-H), 7.53-7.56 (m, 1H, Ar-H), 6.25 (d, *J* = 1.4 Hz, 1H, Ar-H), 7.05-7.12 (m, 1H, Ar-H), 6.83-6.86 (m, 2H, Ar-H), 6.65-6.68 (m, 1H, Ar-H), 5.04 (s, 1H, OH), 3.59 (s, 3H, CH<sub>3</sub>), 3.28 (d, *J* = 13.7 Hz, 1H, CH), 2.29 (d, *J* = 13.7 Hz, 1H, CH), 1.48 (s, 3H, CH<sub>3</sub>), 1.14 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.2, 190.5, 158.9, 143.9, 135.7, 134.0, 133.9, 131.1, 128.7, 127.4, 126.7, 118.9, 112.6, 112.9, 98.7, 83.2, 55.1, 48.8, 38.9, 30.4, 23.6. HRMS (ESI): m/z [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>20</sub>O<sub>6</sub> : 386.1598 ; found : 386.1595.



**12**

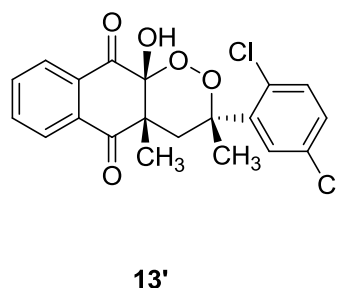
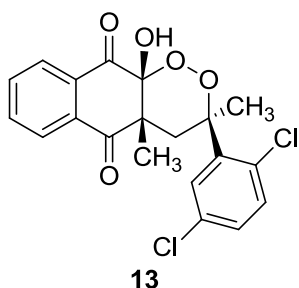


**12'**

**12**: Yield: 48%, white solid, mp = 97-98°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 7.23 (d, *J* = 7.6 Hz, 1H, Ar-H), 8.09 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.72-8.86 (m, 2H, Ar-H), 7.18-8.33 (m, 4H, Ar-H), 5.06 (s, 1H, OH), 2.98 (d, *J* = 13.4 Hz, 1H, CH), 2.25 (d, *J* = 13.4 Hz, 1H, CH), 1.39 (s, 3H, CH<sub>3</sub>), 1.13 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 196.5, 190.2, 143.8, 135.9, 134.5 (2C), 133.6, 132.0, 128.5 (2C), 128.3, 127.4, 126.2 (2C), 99.5, 82.1, 50.1, 39.2, 26.5, 22.6. HRMS (ESI): m/z [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>ClO<sub>5</sub> : 395.0657 ; found : 395.0659.

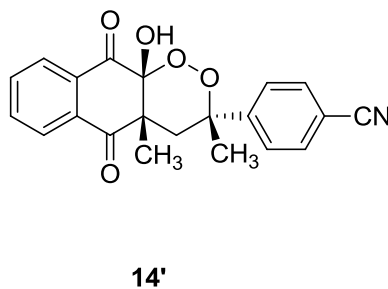
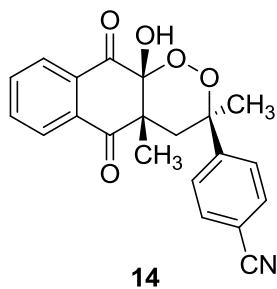
**12'**: Yield: 32%, white solid, mp = 137-138°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 7.95-7.98 (m, 1H, Ar-H), 7.65-7.69 (m, 2H, Ar-H), 7.57-7.62 (m, 1H, Ar-H), 7.20-7.25 (m, 2H, Ar-H), 7.08-7.12 (m, 2H, Ar-H), 5.11 (s, 1H, OH), 3.28 (d, *J* = 13.6 Hz, 1H, CH), 2.29 (d, *J* = 13.6 Hz, 1H, CH),

1.44 (s, 3H, CH<sub>3</sub>), 1.14 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.4, 190.2, 141.0, 135.6, 134.0 (2C), 132.6, 131.3, 127.8 (2C), 127.6 (2C), 127.5, 126.7, 98.8, 82.8, 49.0, 38.7, 30.5, 23.3. HRMS (ESI): m/z [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>ClO<sub>5</sub> : 395.0657 ; found : 395.0658.



**13**: Yield: 38%, white solid, mp = 149-150°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.31 (dd, *J* = 7.4 Hz, 1.6 Hz, 1H, Ar-H), 8.21 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H, Ar-H), 7.90 (td, *J* = 7.4 Hz, 1.6 Hz, 1H, Ar-H), 7.83 (dd, *J* = 7.4 Hz, 1.6 Hz, 1H, Ar-H), 7.53 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.28 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.15 (dd, *J* = 8.2 Hz, 2.4 Hz, 1H, Ar-H), 5.19 (s, 1H, OH), 3.48 (d, *J* = 13.7 Hz, 1H, CH), 2.50 (d, *J* = 13.7 Hz, 1H, CH), 1.50 (s, 3H, CH<sub>3</sub>), 1.22 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.4, 190.3, 144.7, 136.0, 134.5, 133.8, 132.9, 132.2, 131.4, 128.7, 128.5, 128.3, 127.8, 127.6, 101.0, 84.8, 50.1, 38.9, 25.3, 20.9. HRMS (ESI): m/z [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>5</sub> : 424.0713 ; found : 424.0714.

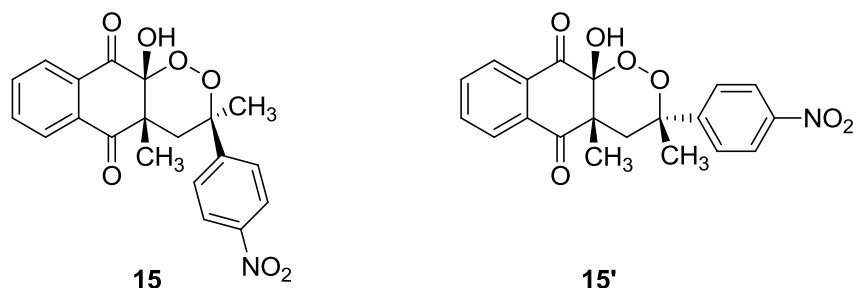
**13'**: Yield: 25%, white solid, mp = 136-137°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.09-8.13 (m, 1H, Ar-H), 7.79-7.82 (m, 2H, Ar-H), 7.66-7.70 (m, 1H, Ar-H), 7.48 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.38 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.17 (dd, *J* = 8.4 Hz, 2.5 Hz, 1H, Ar-H), 5.08 (s, 1H, OH), 4.08 (d, *J* = 13.9 Hz, 1H, CH), 2.27 (d, *J* = 13.9 Hz, 1H, CH), 1.76 (s, 3H, CH<sub>3</sub>), 1.22 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.3, 190.1, 141.4, 136.0, 134.3, 133.8, 132.4, 132.3, 131.1, 130.0, 128.8, 128.2, 127.3, 127.0, 99.02, 83.4, 49.1, 35.4, 26.0, 22.9. HRMS (ESI): m/z [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>5</sub> : 424.0713 ; found : 424.0713.



**14**: Yield: 42%, white solid, mp 135°C: <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 7.19-8.33 (m, 2H, Ar-H), 7.83-7.97 (m, 2H, Ar-H), 7.67 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.55 (d, *J* = 8.6 Hz, 2H, Ar-H), 5.11 (s, 1H, OH), 3.13 (d, *J* = 13.5 Hz, 1H, CH), 2.32 (d, *J* = 13.5 Hz, 1H, CH), 1.48 (s, 3H, CH<sub>3</sub>), 1.22 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 196.2, 189.9, 150.2, 136.2, 134.8, 133.4, 132.3 (2C), 131.6, 128.4, 127.6, 125.4 (2C), 118.6, 111.5, 99.5, 82.2, 49.9, 38.7, 26.7, 22.4. HRMS (ESI): m/z [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>5</sub> : 381.1445 ; found : 381.1448.

**14'**: Yield: 28%, white solid, mp 153°C: <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 7.99-8.03 (m, 1H, Ar-H), 7.70-7.74 (m, 2H, Ar-H), 7.57-7.61 (m, 1H, Ar-H), 7.42-7.50 (m, 4H, Ar-H), 5.12 (s, 1H, OH), 3.32 (d, *J* = 13.6

Hz, 1H, CH), 2.36 (d,  $J = 13.6$  Hz, 1H, CH), 1.49 (s, 3H, CH<sub>3</sub>), 1.16 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 195.2, 189.8, 147.9, 136.1, 134.4, 133.4, 131.4$  (2C), 131.1, 127.9, 127.1 (2C), 127.0, 118.9, 110.5, 98.6, 83.0, 49.1, 38.0, 30.2, 23.2. HRMS (ESI):  $m/z$  [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>5</sub> : 381.1445 ; found : 381.1447.



**15**: Yield: 45%, white solid, mp = 153°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 8.32-8.35$  (m, 4H, Ar-H), 7.84-7.98 (m, 2H, Ar-H), 7.60-7.64 (m, 2H, Ar-H), 5.12 (s, 1H, OH), 3.14 (d,  $J = 13.4$  Hz, 1H, CH), 2.33 (d,  $J = 13.4$  Hz, 1H, CH), 1.51 (s, 3H, CH<sub>3</sub>), 1.23 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 196.2, 189.9, 152.2, 147.1, 136.2, 134.8, 133.5, 131.6, 128.4, 127.6, 125.6$  (2C), 123.7 (2C), 99.6, 82.3, 50.0, 38.7, 26.9, 22.4. HRMS (ESI):  $m/z$  [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>7</sub> : 401.1343 ; found : 401.1344.

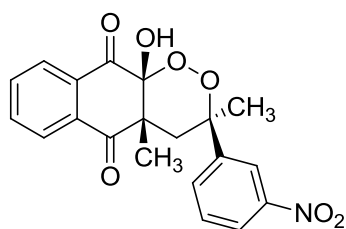
Crystal data for compound **15**: C<sub>20</sub>H<sub>17</sub>NO<sub>7</sub>, (0.4x0.16x0.1 mm<sup>3</sup>),  $M_w = 383.35$ , monoclinic, space group P2<sub>1/c</sub> ( $T = 293$  K),  $a = 7.6077(4)$  Å,  $b = 17.9285(7)$  Å,  $c = 13.5108(6)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 97.529(4)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1826.91(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}} = 1.394$  g.cm<sup>-3</sup>,  $\mu = 0.107$  mm<sup>-1</sup>,  $F(000) = 800.0$ , index ranges -9 ≤  $h$  ≤ 7, -23 ≤  $k$  ≤ 21, -17 ≤  $l$  ≤ 16,  $2\theta$  range = 6.922-56.33°, 256 variables and 0 restraint, were refined for 3863 reflections with  $I \geq 2\sigma_I$  to  $R = 0.05$ , GoF = 1.021.

Crystallographic data for the structure **15** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under number 1495137. Copie of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

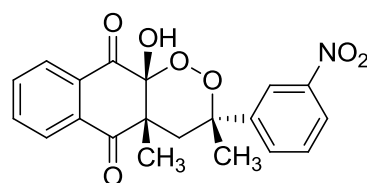
**15'**: Yield: 30%, white solid, mp = 156-157°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 8.01-8.06$  (m, 3H, Ar-H), 7.65-7.73 (m, 2H, Ar-H), 7.57-7.61 (m, 1H, Ar-H), 7.52 (d,  $J = 9.0$  Hz, 2H, Ar-H), 5.15 (s, 1H, OH), 3.36 (d,  $J = 13.9$  Hz, 1H, CH), 2.38 (d,  $J = 13.9$  Hz, 1H, CH), 1.51 (s, 3H, CH<sub>3</sub>), 1.17 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 195.2, 189.7, 150.1, 146.6, 136.2, 134.4, 133.3, 131.0, 127.5, 127.3$  (2C), 127.0, 122.8 (2C), 98.6, 83.0, 49.2, 37.9, 30.4, 23.2. HRMS (ESI):  $m/z$  [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>7</sub> : 401.1343 ; found : 401.1343.

Crystal data for compound **15'**: C<sub>20</sub>H<sub>17</sub>NO<sub>7</sub>, (0.34x0.18x0.07 mm<sup>3</sup>),  $M_w = 403.39$ , monoclinic, space group C2/c ( $T = 293$  K),  $a = 33.134(6)$  Å,  $b = 7.3925(3)$  Å,  $c = 23.922(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 135.55^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4103.4(19)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_{\text{calcd}} = 1.306$  g.cm<sup>-3</sup>,  $\mu = 0.099$  mm<sup>-1</sup>,  $F(000) = 1696.0$ , index ranges -38 ≤  $h$  ≤ 39, -9 ≤  $k$  ≤ 9, -26 ≤  $l$  ≤ 31,  $2\theta$  range = 6.702-56.292°, 289 variables and 0 restraint, were refined for 4391 reflections with  $I \geq 2\sigma_I$  to  $R = 0.05$ , GoF = 1.069.

Crystallographic data for the structure **15'** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under number 1495138. Copie of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).



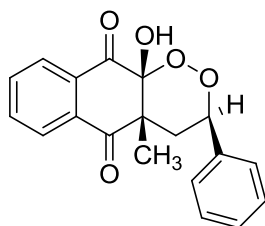
**16**



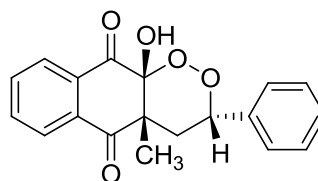
**16'**

**16:** Yield: 35%, yellow solid, mp = 149-150°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.13-8.19 (m, 2H, Ar-H), 8.30-8.33 (m, 2H, Ar-H), 7.77-7.94 (m, 3H, Ar-H), 7.51-7.57 (m, 1H, Ar-H), 5.13 (s, 1H, OH), 3.16 (d, *J* = 13.4 Hz, 1H, CH), 2.35 (d, *J* = 13.4 Hz, 1H, CH), 1.50 (s, 3H, CH<sub>3</sub>), 1.22 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 196.2, 189.9, 148.3, 147.2, 136.2, 134.8, 133.5, 131.6, 130.9 (2C), 129.5, 128.4 (2C), 127.6, 122.6, 120.0, 99.6, 82.0, 50.0, 38.7, 26.9, 22.4. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>7</sub>: 401.1343; found: 401.1346.

**16':** Yield: 23%, yellow solid, mp = 146-147°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.19 (s, 1H, Ar-H), 7.97-8.03 (m, 2H, Ar-H), 7.60-7.72 (m, 3H, Ar-H), 7.50-7.54 (m, 1H, Ar-H), 7.31-7.37 (m, 1H, Ar-H), 5.11 (s, 1H, OH), 3.35 (d, *J* = 13.9 Hz, 1H, CH), 2.36 (d, *J* = 13.9 Hz, 1H, CH), 1.51 (s, 3H, CH<sub>3</sub>), 1.15 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.5, 189.8, 147.8, 144.7, 136.0, 134.4, 133.4 (2C), 132.5, 131.0, 128.6 (2C), 127.3, 127.1, 121.8, 121.7, 98.7, 82.7, 49.2, 38.1, 29.7, 23.2. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>7</sub>: 401.1343; found: 401.1345.



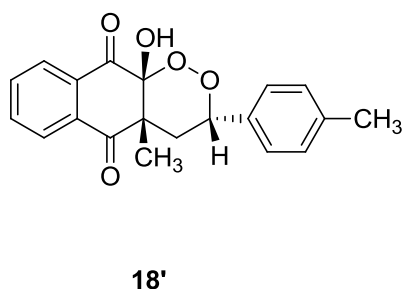
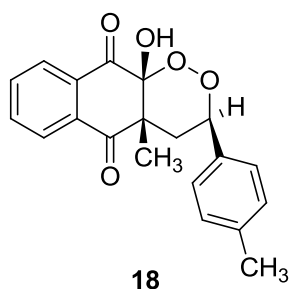
**17**



**17'**

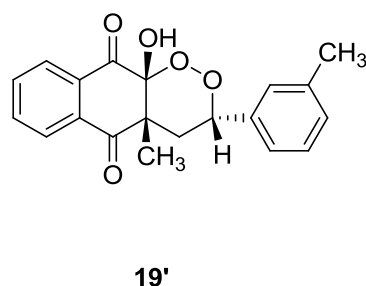
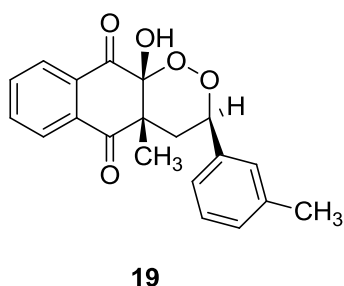
**17:** Yield: 44%, white solid, mp = 145°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.24 (d, *J* = 7.7 Hz, 1H, Ar-H), 8.12 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.75-7.90 (m, 2H, Ar-H), 7.33-7.43 (m, 5H, Ar-H), 5.20-5.27 (m, 2H, OH, CH), 2.32-2.82 (m, 2H, CH<sub>2</sub>), 1.23 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 197.0, 190.0, 137.6, 136.0, 134.4 (2C), 131.7, 129.0, 128.6 (2C), 128.2, 127.4, 127.3 (2C), 99.7, 81.4, 51.8, 34.3, 21.8. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>O<sub>5</sub>: 347.0890; found: 347.0890.

**17':** Yield: 44%, white solid, mp = 138°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.00-8.08 (m, 2H, Ar-H), 7.67-7.74 (m, 2H, Ar-H), 7.18-7.27 (m, 5H, Ar-H), 5.36-5.42 (m, 1H, CH), 5.18 (s, 1H, OH), 3.06 (m, 1H, CH), 2.32 (m, 1H, CH), 1.25 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.3, 190.1, 138.1, 135.5, 134.1, 133.7, 131.5, 128.4 (3C), 128.2, 127.5 (2C), 127.4, 100.9, 80.9, 50.1, 34.4, 20.2. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>O<sub>5</sub>: 347.0890; found: 347.0894.



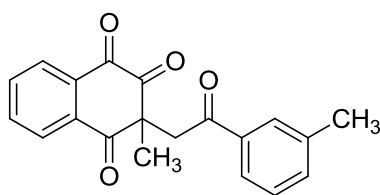
**18:** Yield: 48 %, white solid, mp = 118°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.14-8.28 (m, 2H, Ar-H), 7.82-7.74 (m, 2H, Ar-H), 7.33 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.19 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.16-5.21 (m, 1H, CH), 5.07 (s, 2H, OH), 2.73-2.81 (m, 1H, CH), 2.32-2.43 (m, 4H, CH, CH<sub>3</sub>), 1.25 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 197.1, 190.0, 139.1, 136.2, 134.5, 134.2, 134.1, 131.5, 129.3 (2C), 128.2, 127.5 (2C), 127.4, 99.5, 81.3, 51.8, 33.9, 21.9, 21.2. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> : 361.1046; found : 361.1047.

**18':** Yield: 32%, white solid, mp = 127°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.14-8.18 (m, 2H, Ar-H), 7.79-7.83 (m, 2H, Ar-H), 7.30 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.14 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.45 (dd, *J* = 7.6 Hz, 6.8 Hz, 1H, CH), 5.13 (s, 1H, OH), 3.19 (dd, *J* = 6.8 Hz, 13.6 Hz, 1H, CH), 2.38 (dd, *J* = 7.6 Hz, 13.6 Hz, 1H, CH), 2.34 (s, 3H, CH<sub>3</sub>), 1.33 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.4, 190.2, 138.5, 135.6, 134.6, 134.2, 133.4, 131.2, 129.2 (2C), 128.3, 127.2 (2C), 127.5, 100.8, 80.9, 50.2, 34.2, 21.2, 20.1. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> : 361.1046; found : 361.1048.



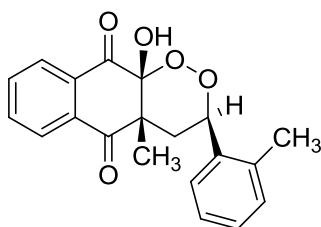
**19:** Yield: 35%, yellow oil. <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.25 (d, *J* = 7.6 Hz, 1H, Ar-H), 8.14 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.77-7.93 (m, 2H, Ar-H), 7.14-7.28 (m, 4H, Ar-H), 5.15-5.19 (m, 1H, CH), 5.07 (s, 1H, OH), 2.74-2.80 (m, 1H, 1CH), 2.35 (s, 3H, CH<sub>3</sub>), 2.30-2.43 (m, 1H, CH), 1.23 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 197.1, 190.0, 138.3, 137.0, 136.2, 134.5, 134.1, 131.4, 129.8, 128.5, 128.2, 128.0, 127.4, 124.5, 99.5, 81.5, 51.7, 34.1, 21.9, 21.3. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> : 356.1492; found: 356.1494.

**19':** Yield: 23%, yellow solid, mp = 128°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.10-8.16 (m, 2H, Ar-H), 7.76-7.81 (m, 2H, Ar-H), 7.08-7.22 (m, 4H, Ar-H), 5.40-5.46 (m, 1H, CH), 5.23 (s, 1H, OH), 3.10 (dd, *J* = 7.7 Hz, 13.4 Hz, 1H, 1CH), 2.30-2.36 (m, 4H, CH + CH<sub>3</sub>), 1.34 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.2, 190.2, 138.0, 138.1, 135.4, 134.0, 133.7, 131.5, 129.2, 128.3, 128.2 (2C), 127.3, 124.5, 100.9, 81.0, 50.1, 34.6, 21.2, 20.1. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub> : 356.1492; found: 356.1496.

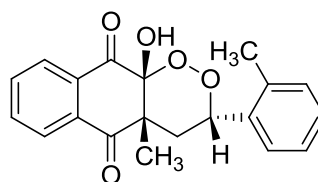


**19''**

**19''**: Yield: 31%, yellow oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.33-8.36 (m, 1H, Ar-H), 8.20-8.24 (m, 1H, Ar-H), 7.69-7.88 (m, 4H, Ar-H), 7.28-7.39 (m, 2H, Ar-H), 4.25 (d,  $J$  = 17.9 Hz, CH), 4.05 (d,  $J$  = 17.9 Hz, 1H, CH), 2.36 (s, 3H,  $\text{CH}_3$ ), 1.51 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.6, 195.7, 193.4, 179.1, 138.5, 135.7, 134.8 (3C), 134.1, 133.8, 129.0, 128.8, 128.5 (2C), 125.8, 59.8, 48.2, 22.2, 21.2. HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{16}\text{O}_4$  : 321.1121; found : 321.1128.



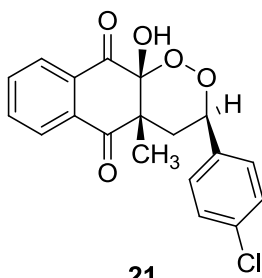
**20**



**20'**

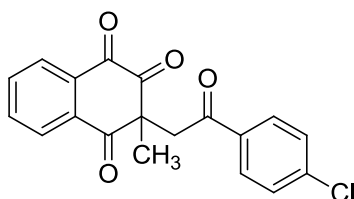
**20**: Yield: 34%, pink solid, mp = 153°C (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 9/1).  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.14-8.27 (m, 2H, Ar-H), 7.79-7.92 (m, 2H, Ar-H), 7.41-7.43 (m, 1H, Ar-H), 7.17-7.24 (m, 3H, Ar-H), 5.43 (dd,  $J$  = 2.2 Hz, 11.6 Hz, 1H, CH), 5.11 (s, 1H, OH), 2.74 (dd,  $J$  = 2.2 Hz, 13.4 Hz, 1H, CH), 2.41 (s, 3H,  $\text{CH}_3$ ), 2.34 (dd,  $J$  = 11.6 Hz, 13.4 Hz, 1H, CH), 1.24 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.4, 190.0, 136.5, 136.3, 135.7, 134.6, 134.2, 131.5, 130.6, 128.7, 128.3, 127.5, 126.2 (2C), 99.7, 78.4, 52.0, 33.7, 21.9, 19.1. HRMS (ESI):  $m/z$   $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_5$  : 356.1492 ; found : 356.1491.

**20'**: Yield: 18%, yellow solid, mp = 132-133°C (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 9/1).  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.17-8.22 (m, 2H, Ar-H), 7.76-7.87 (m, 2H, Ar-H), 7.17-7.19 (m, 3H, Ar-H), 7.32-7.35 (m, 1H, Ar-H), 5.64-5.70 (m, 1H, CH), 5.12 (s, 1H, OH), 3.09-3.18 (m, 1H, CH), 2.38 (s, 3H,  $\text{CH}_3$ ), 2.28-2.33 (m, 1H, CH), 1.35 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 195.3, 190.3, 136.3, 136.0, 135.7, 134.4, 133.4, 131.3, 130.5 (2C), 128.6, 126.5, 127.7, 126.6, 126.4 (2C), 101.2, 50.6, 33.9, 19.4. HRMS (ESI):  $m/z$   $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_5$  : 356.1492 ; found : 356.1488.



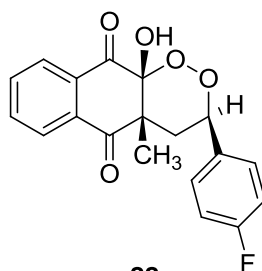
**21**

**21**: Yield: 28%, yellow oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12-8.25 (m, 2H, Ar-H), 7.77-7.92 (m, 2H, Ar-H), 7.33-7.35 (m, 4H, Ar-H), 5.14-5.20 (m, 1H, CH + OH), 2.73-2.79 (m, 1H, CH), 2.24-2.34 (m, 1H, CH), 1.23 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.0, 189.7, 136.3, 135.6, 134.9, 134.6, 134.0, 131.7, 128.8 (2C), 128.6 (2C), 128.7, 128.2, 127.5, 99.5, 80.6, 51.7, 41.0, 34.0, 21.8. HRMS (ESI):  $m/z$   $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_{19}\text{H}_{15}\text{ClO}_5$  : 376.0946 ; found : 376.0946.



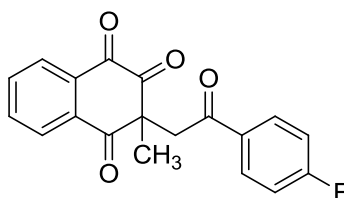
**21''**

**21''**: Yield: 40%, yellow oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.35-8.39 (m, 1H, Ar-H), 8.23-8.26 (m, 1H, Ar-H), 8.09-8.13 (m, 1H, Ar-H), 7.89-7.93 (m, 4H, Ar-H), 7.85 (d,  $J$  = 8.6 Hz, 2H, Ar-H), 7.43 (d,  $J$  = 8.6 Hz, 2H, Ar-H), 4.21 (d,  $J$  = 18.0 Hz, 1H, CH), 4.05 (d,  $J$  = 18.0 Hz, 1H, CH), 1.53 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.1, 195.4, 193.2, 190.1, 140.5, 135.5, 134.7, 133.7, 129.8 (2C), 129.7, 129.0 (2C), 128.9, 128.7, 128.5, 60.1, 47.6, 22.2. HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{13}\text{ClO}_4$  : 341.0575; found : 341.0580



**22**

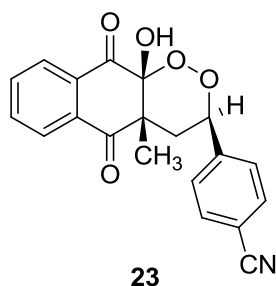
**22**: Yield: 23%, pink oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12-8.25 (m, 2H, Ar-H), 7.78-7.92 (m, 2H, Ar-H), 7.37-7.42 (m, 2H, Ar-H), 7.02-7.08 (m, 2H, Ar-H), 5.08-5.21 (m, 2H, CH + OH), 2.76 (dd,  $J$  = 11.2 Hz, 13.4 Hz, 1H, CH), 2.32 (dd,  $J$  = 11.8 Hz, 13.4 Hz, 1H, CH), 1.23 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.1, 189.9, 163.1 (d,  $J$  = 247.7 Hz), 136.3, 134.7, 134.1, 132.9 (d,  $J$  = 3.2 Hz), 131.5, 129.4 (d,  $J$  = 8.3 Hz, 2C), 128.3, 127.5, 115.5 (d,  $J$  = 21.6 Hz, 2C), 99.6, 80.7, 51.8, 34.0, 21.9. HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{15}\text{FO}_5$  : 365.0796 ; found : 365.0793.



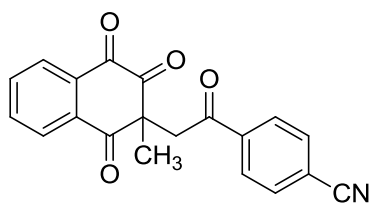
**22''**

**22''**: Yield: 34%, yellow oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.19-8.34 (m, 2H, Ar-H), 7.85-8.94 (m, 4H, Ar-H), 7.05-7.12 (m, 2H, Ar-H), 4.20 (d,  $J$  = 17.8 Hz, CH), 4.0 (d,  $J$  = 17.8 Hz, 1H, CH), 1.49 (s, 3H,  $\text{CH}_3$ ).

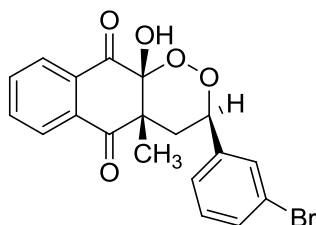
$^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 195.7, 195.5, 193.2, 179.2, 166.3 (d,  $J$  = 256.0 Hz), 135.4, 134.7, 134.4, 134.0, 131.8, 131.2 (d,  $J$  = 9.6 Hz, 2C), 128.7, 128.5, 115.8 (d,  $J$  = 22.1 Hz, 2C), 60.1, 47.7, 22.2. HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{13}\text{FO}_4$  : 325.0871; found : 325.0869.



**23**: Yield: 22%, yellow solid, mp = 142-143°C (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 9/1).  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.13-8.25 (m, 2H, Ar-H), 7.79-7.94 (m, 2H, Ar-H), 7.49-7.58 (m, 4H, Ar-H), 5.21-5.27 (s, 1H, CH), 5.10 (s, 1H, OH), 2.79 (dd,  $J$  = 2.2 Hz, 13.4 Hz, 1H, CH), 2.26 (dd,  $J$  = 11.7 Hz, 13.4 Hz, 2H, CH), 1.23 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.7, 189.4, 142.7, 136.2, 134.6, 134.3, 132.4 (2C), 131.6, 128.2, 127.6 (2C), 127.5, 118.2, 113.0, 99.7, 80.3, 51.6, 34.4, 21.7. HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}_5$  : 372.0842 ; found : 372.0842.

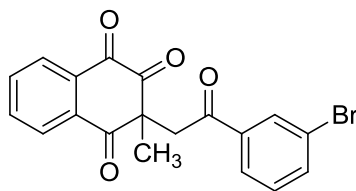


**23''**: Yield: 33%, yellow oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.32-8.35 (m, 1H, Ar-H), 8.23-8.35 (m, 1H, Ar-H), 7.95 (d,  $J$  = 8.3 Hz, 2H, Ar-H), 7.75 (d,  $J$  = 8.3 Hz, 2H, Ar-H), 4.19 (d,  $J$  = 18.2 Hz, CH), 4.02 (d,  $J$  = 18.2 Hz, 1H, CH), 1.51 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 195.1, 193.0, 179.3, 138.2, 135.7, 134.9, 134.2, 134.0, 132.5 (2C), 128.8 (3C), 128.6, 117.5, 117.3, 60.4, 47.0, 22.4. HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{13}\text{NO}_4$  : 332.0917 ; found : 332.0917.



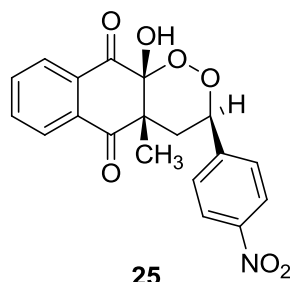
**24**: Yield: 25%, pink oil.  $^1\text{H}$  NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.25 (d,  $J$  = 7.7 Hz, 1H, Ar-H), 8.15 (d,  $J$  = 7.4 Hz, 1H, Ar-H), 7.91 (ddd,  $J$  = 7.6 Hz, 7.4 Hz, 1.6 Hz, 1H, Ar-H), 7.82 (ddd,  $J$  = 7.6 Hz, 7.4 Hz, 1.4 Hz, 1H, Ar-H), 7.58 (d,  $J$  = 1.3 Hz, 1H, Ar-H), 7.49 (dd,  $J$  = 7.7 Hz, 1.6 Hz, 1H, Ar-H), 7.34 (dd,  $J$  = 7.7 Hz, 1.1 Hz, 1H, Ar-H), 7.21-7.26 (m, 1H, Ar-H), 5.14-128 (m, 2H, CH, OH), 2.78 (d,  $J$  = 13.4 Hz, 1H, CH), 2.30 (dd,  $J$  = 13.4 Hz, 12.0 Hz, 1H, CH), 1.25 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.5MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.8, 189.7, 136.1, 134.4,

132.0 (2C), 130.2, 130.1, 128.2 (2C), 127.4 (2C), 125.7, 122.7, 99.7, 80.6, 51.8, 34.3, 21.7. HRMS (ESI):  $m/z$   $[M + NH_4]^+$  calcd for  $C_{19}H_{15}BrO_5$  : 420.0441 ; found : 420.0439.



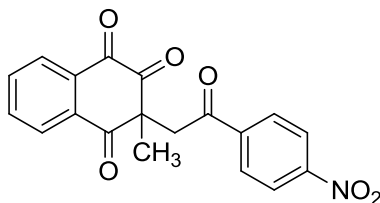
**24''**

**24''**: Yield: 37%, yellow oil.  $^1H$  NMR (250MHz,  $CDCl_3$ ):  $\delta$  = 8.31-8.35 (m, 1H, Ar-H), = 8.19-8.23 (m, 1H, Ar-H), 8.00-8.02 (m, 1H, Ar-H), 7.80-7.89 (m, 3H, Ar-H), 7.66-7.77 (m, 1H, Ar-H), 7.24-7.34 (m, 1H, Ar-H), 4.19 (d,  $J$  = 18.0 Hz, 1H, CH), 4.0 (d,  $J$  = 18.0 Hz, 1H, CH), 1.50 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR (62.5MHz,  $CDCl_3$ ):  $\delta$  = 196.0, 195.4, 193.1, 179.3, 137.1, 136.7, 135.6, 134.8, 134.3, 134.1, 131.5, 130.2, 128.7, 128.5, 126.9, 123.0, 60.2, 47.4, 22.3. HRMS (ESI):  $m/z$   $[M + H]^+$  calcd for  $C_{19}H_{13}BrO_4$  : 385.0070 ; found : 385.0071.



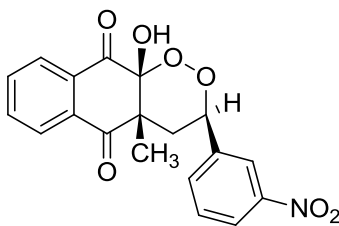
**25**

**25**: Yield: 29%, white solid, mp = 141-142°C (petroleum ether/ $CH_2Cl_2$ , 9/1).  $^1H$  NMR (250MHz,  $CDCl_3$ ):  $\delta$  = 8.16-8.28 (m, 4H, Ar-H), 7.82-7.96 (m, 2H, Ar-H), 7.58 (d,  $J$  = 8.0 Hz, 2H, Ar-H), 5.32 (dd,  $J$  = 12.0 Hz, 1.9 Hz, 1H, CH), 5.17 (s, 1H, OH), 2.84 (dd,  $J$  = 13.4 Hz, 1.9 Hz, 1H, CH), 2.28 (dd,  $J$  = 13.4 Hz, 12.0 Hz, 1H, CH), 1.25 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR (62.5MHz,  $CDCl_3$ ):  $\delta$  = 195.8, 188.5, 147.5, 143.7, 135.3, 133.7, 133.4, 130.7, 127.4, 127.8 (2C), 126.6, 122.9 (2C), 98.9, 79.22, 50.75, 33.64, 20.8. HRMS (ESI):  $m/z$   $[M + NH_4]^+$  calcd for  $C_{19}H_{15}NO_7$  : 387.1187 ; found : 387.1190.



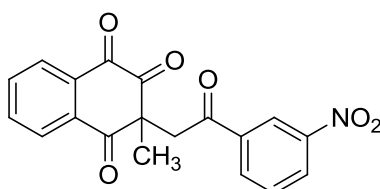
**25''**

**25''**: Yield: 43%, yellow solid, mp = 123°C (petroleum ether/ $CH_2Cl_2$ , 9/1).  $^1H$  NMR (250MHz,  $CDCl_3$ ):  $\delta$  = 8.21-8.37 (m, 4H, Ar-H), 8.05-8.09 (m, 2H, Ar-H), 7.88-7.92 (m, 2H, Ar-H), 4.21 (d,  $J$  = 18.1 Hz, 1H, CH), 4.05 (d,  $J$  = 18.1 Hz, 1H, CH), 1.53 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR (62.5MHz,  $CDCl_3$ ):  $\delta$  = 195.9, 195.1, 193.0, 179.4, 151.0, 139.8, 135.7, 134.9, 134.2, 134.0, 129.4 (2C), 128.8, 128.6, 123.8 (2C), 60.5, 47.1, 22.4. HRMS (ESI):  $m/z$   $[M + Na]^+$  calcd for  $C_{19}H_{13}NO_6$  : 374.0635 ; found : 374.0640.



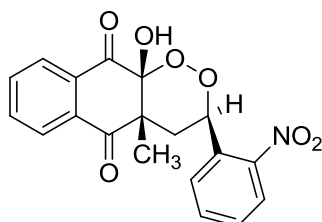
**26**

**26:** Yield: 24%, yellow solid, mp = 139°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.29 (dd, *J* = 4.9 Hz, 1.4 Hz, 1H, Ar-H), 8.25-8.26 (m, 1H, Ar-H), 8.22 (dd, *J* = 2.2 Hz, 1.1 Hz, 1H, Ar-H), 8.16-8.20 (m, 1H, Ar-H), 7.94 (td, *J* = 7.4 Hz, 1.4 Hz, 1H, Ar-H), 7.85 (td, *J* = 7.4 Hz, 1.4 Hz, 1H, Ar-H), 7.75-7.78 (m, 1H, Ar-H), 7.58 (t, *J* = 7.9 Hz, 1H, Ar-H), 5.32 (dd, *J* = 11.7 Hz, 2.3 Hz, 1H, CH), 5.15 (s, 1H, OH), 2.86 (dd, *J* = 13.3 Hz, 2.3 Hz, 1H, CH), 2.32 (dd, *J* = 13.3 Hz, 11.7 Hz, 1H, CH), 1.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 196.7, 189.3, 148.2, 139.1, 136.3, 134.6, 133.9, 133.2, 131.2, 129.6, 128.2, 127.4, 123.8, 122.1, 99.5, 79.9, 51.5, 33.8, 21.7. HRMS (ESI): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>7</sub> : 387.1187; found : 387.1182.



**26''**

**26'':** Yield: 35%, yellow solid, mp = 183°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.79 (dd, *J* = 1.9 Hz, 1.7 Hz, 1H, Ar-H), 8.45-8.49 (m, 1H, Ar-H), 8.36-8.40 (m, 1H, Ar-H), 8.22-8.27 (m, 1H, Ar-H), 7.91-7.95 (m, 2H, Ar-H), 7.69 (t, *J* = 7.9 Hz, 1H, Ar-H), 5.31 (s, 1H, CH), 4.27 (d, *J* = 18.0 Hz, 1H, CH), 4.09 (d, *J* = 18.0 Hz, 1H, CH), 1.57 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>): δ = 195.3, 192.9, 180.0, 136.6, 135.6, 134.9, 134.2, 134.0, 133.6, 129.9 (2C), 128.8, 128.6 (2C), 127.9, 123.3, 60.5, 46.8, 22.4. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>13</sub>NO<sub>6</sub> : 352.0816 ; found : 352.0818.



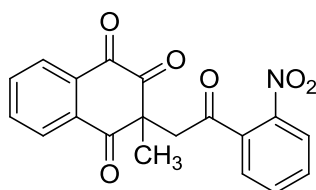
**27**

**27:** Yield: 22%, yellow solid, mp = 147°C (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>): δ = 8.29 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H, Ar-H), 8.13 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H, Ar-H), 7.87-7.94 (m, 2H, Ar-H), 7.85 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H, Ar-H), 7.74 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H, Ar-H), 7.65 (td, *J* = 7.9 Hz, 1.2 Hz, 1H, Ar-H), 7.48 (td, *J* = 7.4 Hz, 1.6 Hz, 1H, Ar-H), 5.73 (dd, *J* = 11.4 Hz, 2.2 Hz, 1H, CH), 5.16 (s, 1H,

OH), 3.11 (dd,  $J = 13.3$  Hz, 2.2 Hz, 1H, CH), 2.22 (dd,  $J = 13.3$  Hz, 11.4 Hz, 1H, CH), 1.22 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 195.9, 189.6, 148.2, 136.4, 134.5, 134.2, 133.4, 132.8, 131.2, 129.4, 128.5, 127.4, 124.4, 99.8, 51.7, 34.6, 21.7$ . HRMS (ESI):  $m/z$  [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>7</sub>: 387.1187; found: 387.1183.

Crystal data for compound **27**: C<sub>19</sub>H<sub>15</sub>NO<sub>7</sub>, (0.36x0.26x0.14 mm<sup>3</sup>),  $M_w = 351.30$ , monoclinic, space group P2<sub>1/n</sub> ( $T = 293$  K),  $a = 7.9834(3)$  Å,  $b = 17.6071(6)$  Å,  $c = 12.0243(5)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 102.179(4)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1652.17(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}} = 1.412$  g.cm<sup>-3</sup>,  $\mu = 0.107$  mm<sup>-1</sup>,  $F(000) = 728.0$ , index ranges  $-10 \leq h \leq 9$ ,  $-22 \leq k \leq 23$ ,  $-11 \leq l \leq 15$ ,  $2\theta$  range =  $6.85$ - $56.29^\circ$ , 236 variables and 0 restraint, were refined for 3434 reflections with  $I \geq 2\sigma_I$  to  $R = 0.05$ , GoF = 1.069.

Crystallographic data for the structure **27** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under number 1495140. Copie of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).



**27''**

**27''**: Yield: 32%, yellow solid, mp =  $152^\circ\text{C}$  (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 9/1). <sup>1</sup>H NMR (250MHz, CDCl<sub>3</sub>):  $\delta = 7.50$ - $8.65$  (m, 2H, Ar-H),  $7.69$ - $7.75$  (m, 1H, Ar-H),  $7.85$ - $8.90$  (m, 2H, Ar-H),  $8.05$ - $8.08$  (m, 1H, Ar-H),  $8.27$ - $8.33$  (m, 1H, Ar-H),  $4.05$  (d,  $J = 18.3$  Hz, CH),  $3.86$  (d,  $J = 18.3$  Hz, 1H, CH),  $1.47$  (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (62.5MHz, CDCl<sub>3</sub>):  $\delta = 199.2, 194.6, 193.0, 179.6, 145.7, 135.9, 135.5, 135.0, 134.8, 134.1, 132.9, 131.0, 128.8, 127.7, 126.0, 124.4, 60.8, 49.6, 22.5$ . HRMS (ESI):  $m/z$  [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>13</sub>NO<sub>6</sub>: 352.0816; found: 352.0818.

Crystal data for compound **27''**: C<sub>19</sub>H<sub>13</sub>NO<sub>6</sub>, (0.4x0.24x0.12 mm<sup>3</sup>),  $M_w = 338.64$ , triclinic, space group P-1 ( $T = 293$  K),  $a = 11.7759(4)$  Å,  $b = 12.0137(4)$  Å,  $c = 13.2565(5)$  Å,  $\alpha = 105.781(3)^\circ$ ,  $\beta = 107.535(3)^\circ$ ,  $\gamma = 92.139(3)^\circ$ ,  $V = 1706.28(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.438$  g.cm<sup>-3</sup>,  $\mu = 0.111$  mm<sup>-1</sup>,  $F(000) = 768.0$ , index ranges  $-15 \leq h \leq 15$ ,  $-14 \leq k \leq 15$ ,  $-15 \leq l \leq 17$ ,  $2\theta$  range =  $6.904$ - $56.07^\circ$ , 491 variables and 0 restraint, were refined for 7092 reflections with  $I \geq 2\sigma_I$  to  $R = 0.05$ , GoF = 1.038.

Crystallographic data for the structure **27''** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under number 1495141. Copie of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

