



# Three-component synthesis of new unsymmetrical oxindoles via Friedel–Crafts type reaction

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## ABSTRACT

The synthesis of 2-(3-(4-(dimethylamino)phenyl)-2-oxoindolin-3-yl)-1*H*-indene-1,3(2*H*)-diones as new unsymmetrical oxindoles via a Friedel–Crafts type three-component reaction of 1,3-indandion, *N,N*-dimethylaniline and isatins in ethanol in the presence of  $\text{LiClO}_4$  is reported.

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## 1. Introduction

Multi-component reactions (MCRs) have offered many fascinating and challenging transformations in organic synthesis.<sup>1</sup> The atom-economy, convergent character, operational simplicity, structural diversity, and complexity of the molecules are the major advantages associated with multi-component reactions. Besides this multi-component reactions are emerging as a powerful tool in the synthesis of biologically important compounds.<sup>2</sup>

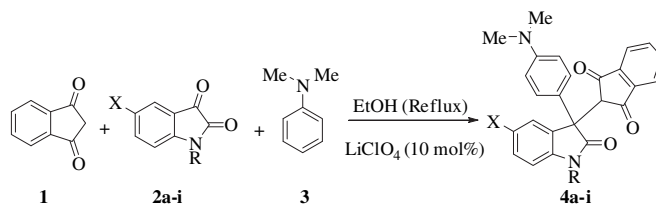
Friedel–Crafts reaction<sup>3</sup> is one of the oldest carbon–carbon bond forming processes, and is still an attractive method to introduce substituents on aromatic rings. Initial works concerned Friedel–Crafts acylation from acyl chlorides or alkylation from alkyl halides. To perform acylations, Lewis acids are needed. More than stoichiometric amounts of  $\text{AlCl}_3$  or  $\text{BF}_3$  are required, whereas catalytic amounts of rare-earth triflates,<sup>4</sup> more specially scandium triflate,<sup>5</sup> perfluorinated rare-earth metals,<sup>6</sup> gallium triflate<sup>7</sup> or bismuth triflate,<sup>8</sup> allow the formation of the expected products.

Isatin is a privileged lead molecule for designing potential bio-active agents, and its derivatives have been shown to possess a broad spectrum of bioactivity as many of which were assessed anti-HIV,<sup>9</sup> antiviral,<sup>10</sup> anti-tumor,<sup>11</sup> antifungal,<sup>12</sup> anti-angiogenic,<sup>13</sup> anticonvulsants,<sup>14</sup> anti-Parkinson's disease therapeutic,<sup>15</sup> and effective SARS coronavirus 3CL protease inhibitor.<sup>16</sup> These interesting properties prompted many efforts toward the synthesis and pharmacological screening of isatin derivatives. During these investigations, the

indolin-2-one (oxindole) moiety has been recognized as a biologically active framework.<sup>17</sup> Oxindole is an integral constituent of many natural products.<sup>18</sup> Thus, it is not surprising that access to several members of this class may be the goal of many research laboratories.

Recently,  $\text{LiClO}_4$  has emerged as a powerful promoter in many chemical processes and in different organic media.<sup>19</sup> The development of method, which allows the reaction under essentially mild and neutral conditions should heighten the synthetic potential of the reaction. The  $\text{LiClO}_4$  medium provides a convenient procedure to carry out reactions under simple and neutral conditions.

Although several isatin-based reactions have been reported by our<sup>20</sup> or other research groups<sup>21</sup> for the synthesis of new oxindoles, the synthesis of 2-(3-(4-(dimethylamino)phenyl)-2-oxoindolin-3-yl)-indene-diones **4** has not been reported yet. In this paper, for the first time we report an efficient synthesis of new unsymmetrical oxindoles **4** based on a Friedel–Crafts type three-component reaction of 1,3-indandione **1**, isatins **2** and *N,N*-dimethylaniline **3** in the presence of  $\text{LiClO}_4$  as an inexpensive and available catalyst (Scheme 1).



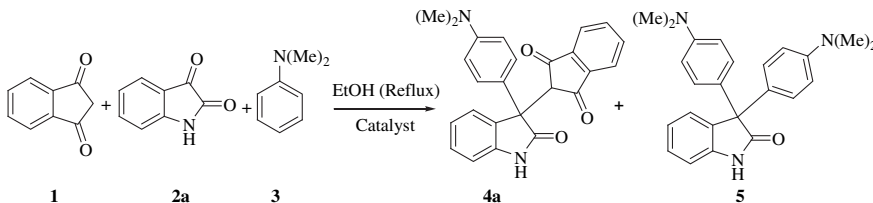
Scheme 1. Synthesis of unsymmetrical oxindoles **4**.

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## 2. Results and discussion

Our initial experiments were focused on the three-component reaction of 1,3-indandione **1** (1 mmol), isatin **2a** (1 mmol), and *N,N*-dimethylaniline **3** (1 mmol) as a simple model substrate using different catalysts in refluxing EtOH, and the results are listed in Table 1.

**Table 1**  
Screening of catalysts



| Entry | Catalyst (mol %)        | Time (h) | Yields <b>4a</b> (%) | Yields <b>5a</b> (%) |
|-------|-------------------------|----------|----------------------|----------------------|
| 1     | LiClO <sub>4</sub> (5)  | 3        | 80                   | <10                  |
| 2     | LiClO <sub>4</sub> (10) | 3        | 95                   | Trace                |
| 3     | LiClO <sub>4</sub> (15) | 3        | 96                   | Trace                |
| 4     | <i>p</i> -TSA (10)      | 3        | 30                   | 35                   |
| 5     | HOAc (10)               | 3        | 25                   | 43                   |
| 6     | AlCl <sub>3</sub> (10)  | 3        | 55                   | 27                   |
| 7     | ZnCl <sub>2</sub> (10)  | 3        | 37                   | 46                   |
| 8     | CAN (10)                | 3        | 32                   | 37                   |
| 9     | InCl <sub>3</sub>       | 3        | 35                   | 49                   |
| 10    | None                    | 7        | Trace                | Trace                |

<sup>a</sup> Isolated yield based on precipitation.

It was observed that when HOAc, *p*-TSA, ZnCl<sub>2</sub>, CAN, and InCl<sub>3</sub> were used, it led to the formation of **5** as major product and desired product **4a** as a minor product in a low yield (Table 1). AlCl<sub>3</sub> showed better selectivity for **4a** in comparison to **5**. LiClO<sub>4</sub> was found to be the best catalyst for the synthesis of unsymmetrical oxindole **4a**. As can be seen from Table 1, when the amount of the LiClO<sub>4</sub> increased from 5 to 10, and 15 mol %, the yields increased from 80 to 95 and 96%, respectively. It was found that 10 mol % LiClO<sub>4</sub> in EtOH is sufficient to push this reaction forward (Table 1, entry 2). More amounts of the LiClO<sub>4</sub> (15 mol %) did not improve the yields and decreasing the amount of LiClO<sub>4</sub> (5 mol %) resulted in a decrease in the yield of **4a** and increase in the yield of **5**. When this reaction was carried out without LiClO<sub>4</sub> the yield of the product was Trace even after 7 h (entry 10).

Then, we examined the solvent effect on the LiClO<sub>4</sub>-catalyzed model reaction. The results of Table 2 demonstrate that solvent affected the efficiency of the reaction and EtOH was the best choice of solvent (Table 2). In other solvents, such as CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, THF, H<sub>2</sub>O, and CHCl<sub>3</sub>, low yield of **4a** was obtained with significant formation of **5**. Therefore, the use of the commercially available, inexpensive, and easily handled LiClO<sub>4</sub> in EtOH provides a convenient procedure for the synthesis of unsymmetrical oxindole **4a** under neutral and simple conditions.

**Table 2**  
Solvent effect on the reaction<sup>a</sup>

| Entry | Solvent (Reflux)                | Yield <b>4a</b> (%) | Yield <b>5b</b> (%) |
|-------|---------------------------------|---------------------|---------------------|
| 1     | CH <sub>3</sub> CN              | 33                  | 52                  |
| 2     | CH <sub>2</sub> Cl <sub>2</sub> | Trace               | 37                  |
| 3     | THF                             | <20                 | 63                  |
| 4     | H <sub>2</sub> O                | Trace               | 52                  |
| 5     | EtOH                            | 95                  | Trace               |
| 6     | CHCl <sub>3</sub>               | <20                 | 49                  |

<sup>a</sup> Reaction time=3 h, LiClO<sub>4</sub> (10 mol %).

<sup>b</sup> Isolated yield.

To study the generality of this protocol, a library of nine substituted 2-(3-(4-(dimethylamino)phenyl)-2-oxoindolin-3-yl)-1*H*-indene-1,3(2*H*)-diones **4a–i** were built using 1,3-indandione **1**, isatins **2a–i**, and *N,N*-dimethylaniline **3** (Table 3). All compounds are stable solids whose structures were established by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and elemental analysis.

**Table 3**  
Synthesis of unsymmetrical oxindoles **4**

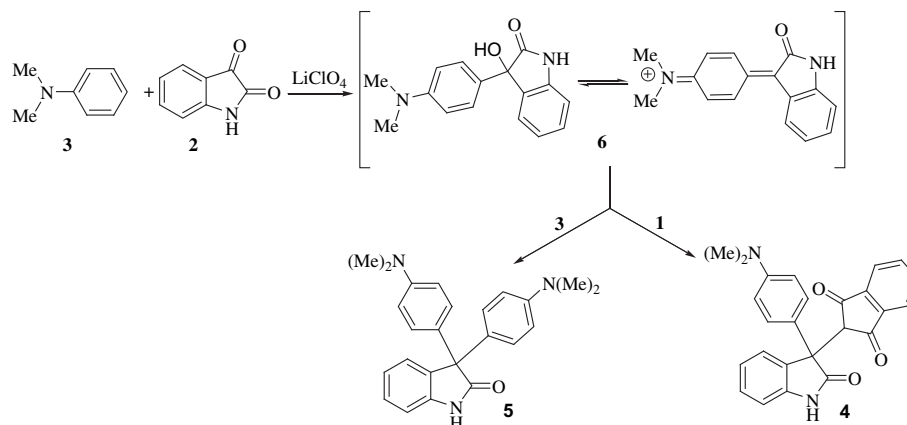
| Product <b>4</b> | R  | X               | Yields (%) | Time <sup>a</sup> (h) |
|------------------|----|-----------------|------------|-----------------------|
| <b>a</b>         | H  | H               | 95         | 3                     |
| <b>b</b>         | Me | H               | 90         | 4.5                   |
| <b>c</b>         | Et | H               | 87         | 6                     |
| <b>d</b>         | H  | Br              | 90         | 4                     |
| <b>e</b>         | H  | NO <sub>2</sub> | 91         | 3.5                   |
| <b>f</b>         | H  | Me              | 94         | 4                     |
| <b>g</b>         | H  | F               | 98         | 4                     |
| <b>h</b>         | Me | Br              | 90         | 6                     |
| <b>i</b>         | Et | NO <sub>2</sub> | 85         | 7                     |

<sup>a</sup> Isolated yields.

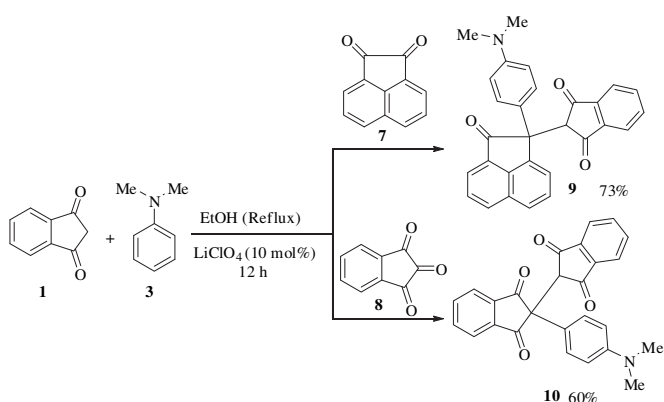
The plausible mechanism of this Friedel–Crafts type reaction is given in Scheme 2. Aromatic amine **3** reacts with isatin **2** to generate an intermediate **6**, followed by a nucleophilic addition with 1,3-indandione **1** to afford unsymmetrical oxindole **4**. Compound **5** was also formed by the attack of another molecule of **3** on intermediate **6**.

To further explore the potential of the reaction, we investigated the reaction of acenaphthylene-1,2-dione **7** and ninhydrin **8** instead of isatin **2** and obtained 2-(1-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydroacenaphthylene-1-yl)-1*H*-indene-1,3(2*H*)-dione **9** and 2-(4-(dimethylamino)phenyl)-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetraone **10** in 73% and 60% yield, respectively (Scheme 3).

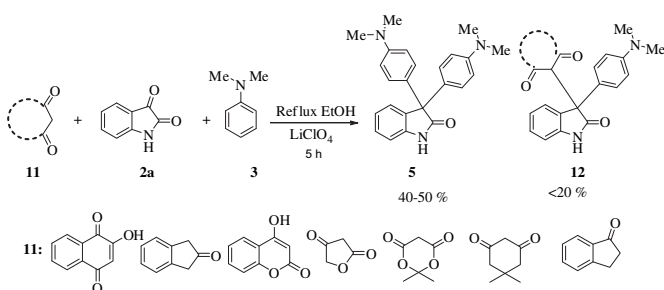
It is notable, when we carried out the reaction with another cyclic 1,3-dicarbonyl compounds **11**, the TLC and <sup>1</sup>H NMR spectra of the reaction mixture showed a combination of starting materials and numerous products; low yields of desired products **12** were obtained and compound **5** was produced as a major product (Scheme 4).



Scheme 2. Proposed mechanism of the reaction.



Scheme 3. Examining acenaphthylene-1,2-dione and ninhydrin instead of isatin.



Scheme 4. Examining different CH-acids instead of 1,3-indandione.

### 3. Conclusion

In conclusion, we have developed an efficient three-component reaction of 1,3-indandione, isatins, and *N,N*-dimethylaniline using  $\text{LiClO}_4$  as a catalyst. The reaction is operationally simple and offers high yields of the new unsymmetrical oxindole derivatives. Prominent among the advantages of this new method are novelty, operational simplicity and easy work-up procedures employed.

### 4. Experimental

#### 4.1. General

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13

and 75.47 MHz, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on solutions in  $\text{DMSO}-d_6$ . IR spectra were recorded using an FTIR apparatus. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer.

The chemicals used in this work were obtained from Fluka and Merck and were used without purification.

**4.1.1. 2-(3-(4-(Dimethylamino)phenyl)-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (4a).** A mixture of 1,3-indandione (1 mmol), isatin (1 mmol), *N,N*-dimethylaniline (1 mmol), and  $\text{LiClO}_4$  (10 mol %) in refluxing ethanol (5 mL) was stirred for 3 h (the progress of the reaction was monitored by TLC). After completion, the reaction mixture was filtered and the precipitate washed with diethyl ether (10 mL) to afford the pure product **4a** as greenish powder (0.396 g, 95%); mp 240 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3357, 3080, 1737, 1706.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{H}}$ =2.86 (6H, s,  $2\text{CH}_3$ ), 4.71 (1H, s, CH), 6.64–7.89 (12H, m, H-Ar), 10.47 (1H, s, NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{C}}$ =40.6, 55.5, 57.2, 110.3, 112.5, 121.6, 123.0, 124.8, 128.1, 129.1, 129.5, 136.5, 143.3, 144.2, 149.2, 178.0, 179.4, 197.7, 198.0. MS (EI, 70 eV)  $m/z$ : 396 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_3$ : C, 75.74; H, 5.08; N, 7.07. Found: C, 75.65; H, 5.03; N, 7.01%.

**4.1.2. 2-(3-(4-(Dimethylamino)phenyl)-1-methyl-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (4b).** Yellow powder (0.41 g, 90%); mp 230 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3425, 3043, 1742, 1706.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{H}}$ =3.00 (6H, s,  $\text{CH}_3$ ), 3.13 (3H, s,  $\text{CH}_3$ ), 4.78 (1H, s, CH), 6.62–7.90 (12H, m, H-Ar).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{C}}$ =26.8, 40.5, 54.8, 57.5, 109.4, 112.4, 122.3, 123.1, 124.5, 128.2, 128.6, 129.3, 136.4, 136.6, 141.7, 142.4, 143.0, 144.8, 176.5, 197.5, 197.6, 197.8. MS (EI, 70 eV)  $m/z$ : 410 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_3$ : C, 76.08; H, 5.40; N, 6.82. Found: C, 75.97; H, 5.47; N, 6.74%.

**4.1.3. 2-(3-(4-(Dimethylamino)phenyl)-1-ethyl-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (4c).** Yellow powder (0.42 g, 87%); mp 243 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3415, 3045, 1718, 1605.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{H}}$ =1.17 (3H, t,  $J$ =5.7 Hz,  $\text{CH}_3$ ), 2.86 (6H, s,  $\text{CH}_3$ ), 3.58–3.76 (2H, m,  $\text{CH}_2$ ), 4.80 (1H, s, CH), 6.46–7.91 (12H, m, H-Ar).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{C}}$ =12.4, 34.7, 40.5, 54.8, 57.5, 109.4, 112.4, 122.1, 123.0, 123.1, 124.7, 125.0, 128.1, 129.0, 129.3, 136.4, 136.6, 141.7, 143.0, 143.8, 149.9, 176.1, 197.5, 197.8. MS (EI, 70 eV)  $m/z$ : 424 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_3$ : C, 76.39; H, 5.70; N, 6.60. Found: C, 76.45; H, 5.66; N, 6.69%.

**4.1.4. 2-(5-Bromo-3-(4-(dimethylamino)phenyl)-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (4d).** Cream powder (0.474 g, 90%); mp 250 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3190, 3111, 1711, 1617.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta_{\text{H}}$ =2.87 (6H, s,  $2\text{CH}_3$ ), 4.83 (1H, s, CH),

6.66–7.92 (11H, m, H–Ar), 10.66 (1H, s, NH).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =40.4, 55.9, 57.0, 112.3, 112.5, 113.1, 123.0, 124.8, 127.4, 127.9, 131.8, 136.6, 141.9, 142.5, 142.7, 149.9, 177.6, 197.2, 197.9. MS (EI, 70 eV)  $m/z$ : 476 ( $\text{M}^+$ ), 474 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{BrN}_2\text{O}_3$ : C, 63.17; H, 4.03; N, 5.89. Found: C, 63.10; H, 4.11; N, 5.98%.

**4.1.5.** 2-(3-(4-(Dimethylamino)phenyl)-5-nitro-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (**4e**). Cream powder (0.44 g, 91%); mp 215 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3451, 3184, 1742, 1706, 1612.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =2.88 (6H, s, 2CH<sub>3</sub>), 5.00 (1H, s, CH), 6.66–8.15 (11H, m, H–Ar), 11.29 (1H, s, NH).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =40.5, 56.4, 57.3, 110.5, 112.6, 120.3, 123.2, 124.3, 126.6, 127.9, 131.3, 136.8, 141.7, 142.1, 142.7, 149.7, 150.0, 178.4, 197.1, 197.6. MS (EI, 70 eV)  $m/z$ : 441 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}_5$ : C, 68.02; H, 4.34; N, 9.52. Found: C, 67.91; H, 4.28; N, 9.43%.

**4.1.6.** 2-(3-(4-(Dimethylamino)phenyl)-5-methyl-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (**4f**). Cream powder (0.41 g, 94%); mp 239 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3362, 3190, 1742, 1721, 1690.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =1.96 (3H, s, CH<sub>3</sub>), 2.87 (6H, s, 2CH<sub>3</sub>), 4.69 (1H, s, CH), 6.47–7.90 (11H, m, H–Ar), 10.36 (1H, s, NH).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =21.0, 40.5, 55.6, 57.2, 110.0, 112.4, 122.9, 125.5, 128.1, 129.3, 129.7, 130.2, 136.3, 136.4, 140.8, 141.9, 149.8, 178.0, 198.0. MS (EI, 70 eV)  $m/z$ : 410 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_3$ : C, 76.08, H, 5.40; N, 6.82. Found: C, 75.99; H, 5.46; N, 6.77%.

**4.1.7.** 2-(3-(4-(Dimethylamino)phenyl)-5-fluoro-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (**4g**). Cream powder (0.41 g, 98%); mp 252 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3398, 1737, 1711, 1705.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =2.87 (6H, s, 2CH<sub>3</sub>), 4.78 (1H, s, CH), 6.53–7.91 (11H, m, H–Ar), 10.54 (1H, s, NH).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =40.5, 56.2, 56.9, 111.1, 112.1, 112.5, 115.3, 123.1, 124.8, 128.0, 136.6, 139.4, 141.9, 142.8, 149.9, 177.9, 197.3, 197.8. MS (EI, 70 eV)  $m/z$ : 414 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{FN}_2\text{O}_3$ : C, 72.45, H, 4.62; N, 6.76. Found: C, 72.55; H, 4.68; N, 6.69%.

**4.1.8.** 2-(5-Bromo-3-(4-(dimethylamino)phenyl)-1-methyl-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (**4h**). Cream powder (0.49 g, 90%); mp 220 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3420, 1742, 1715, 1701.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =2.50 (6H, s, 2CH<sub>3</sub>), 3.12 (3H, s, CH<sub>3</sub>), 4.91 (1H, s, CH), 6.65–8.31 (11H, m, H–Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =26.9, 40.4, 55.1, 57.5, 111.4, 112.5, 113.9, 123.1, 123.2, 127.1, 128.0, 131.7, 132.0, 136.7, 141.7, 142.7, 150.6, 176.0, 197.2, 197.7. MS (EI, 70 eV)  $m/z$ : 490 ( $\text{M}^+$ ), 488 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{21}\text{BrN}_2\text{O}_3$ : C, 63.81, H, 4.33; N, 5.72. Found: C, 63.70; H, 4.25; N, 5.61%.

**4.1.9.** 2-(3-(4-(Dimethylamino)phenyl)-1-ethyl-5-nitro-2-oxoindolin-3-yl)-1H-indene-1,3(2H)-dione (**4i**). Yellow powder (0.47 g, 85%); mp 220 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3085, 1748, 1732, 1711.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =1.19 (3H, t,  $J$ =6.8 Hz, CH<sub>3</sub>), 2.87 (6H, s, 2CH<sub>3</sub>), 3.77–3.81 (2H, m, CH<sub>2</sub>), 5.09 (1H, s, CH), 6.65–8.23 (11H, m, H–Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =12.3, 35.4, 40.4, 54.6, 57.7, 109.7, 112.6, 120.0, 123.3, 123.6, 126.6, 127.9, 130.6, 136.8, 141.6, 142.4, 142.7, 149.8, 150.1, 176.6, 197.0, 197.4. MS (EI, 70 eV)  $m/z$ : 469 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_5$ : C, 69.07, H, 4.94; N, 8.95. Found: C, 69.13; H, 4.99; N, 8.87.

**4.1.10.** 2-(1-(4-(Dimethylamino)phenyl)-2-oxo-1,2-dihydroacenaphthylene-1-yl)-1H-indene-1,3(2H)-dione (**9**). Yellow powder (0.43 g, 73%); mp 284 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3278, 3075, 1717, 1654.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =2.81 (6H, s, 2CH<sub>3</sub>), 5.19 (1H, s, CH), 6.58–8.21 (14H, m, H–Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =40.4, 58.3, 60.0, 112.4, 121.9, 122.9, 123.1, 125.3, 125.5, 128.3, 128.9, 129.4, 130.6, 131.9, 132.2, 136.4, 136.7, 138.9, 141.2, 141.6,

143.2, 149.8, 198.2, 201.0. MS (EI, 70 eV)  $m/z$ : 431 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{29}\text{H}_{21}\text{NO}_3$ : C, 80.72, H, 4.91; N, 3.25. Found: C, 80.65; H, 4.99; N, 3.32%.

**4.1.11.** 2-(4-(Dimethylamino)phenyl)-1H,1'H-2,2'-biindene-1,1',3,3'(2H,2'H)-tetraone (**10**). Yellow powder (0.41 g, 60%); mp 291 °C dec; IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3243, 3078, 1716, 1702.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$ =2.86 (6H, s, 2CH<sub>3</sub>), 4.76 (1H, s, CH), 6.64–7.99 (12H, m, H–Ar).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$ =40.4, 57.7, 109.7, 112.6, 120.0, 123.3, 123.8, 126.6, 127.9, 130.6, 135.8, 136.8, 141.6, 142.4, 142.7, 149.8, 150.1, 197.0, 197.4, 198.3, 199.9. MS (EI, 70 eV)  $m/z$ : 409 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{19}\text{NO}_4$ : C, 76.27, H, 4.68; N, 3.42. Found: C, 76.16; H, 4.60; N, 3.51%.

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## Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.02.054.

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