

## Synthesis of Benzo[5,6]cyclohepta[b]indol-6-one Derivatives

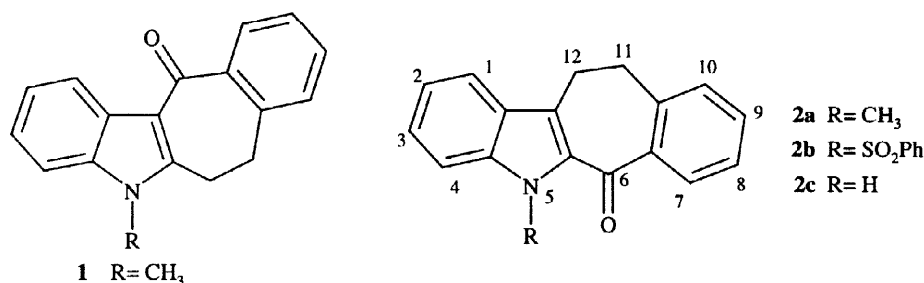
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**Abstract:** An effective synthesis of 5,6,11,12-tetrahydrobenzo[5,6]cyclohepta[b]indole-6-ones **2** was reported. Reactivity studies of the compound **2a** led us to the preparation of 11-substituted derivatives **9–13** via the palladium-mediated cross-coupling reactions or an elimination-addition reaction. © 1999 Elsevier Science Ltd. All rights reserved.

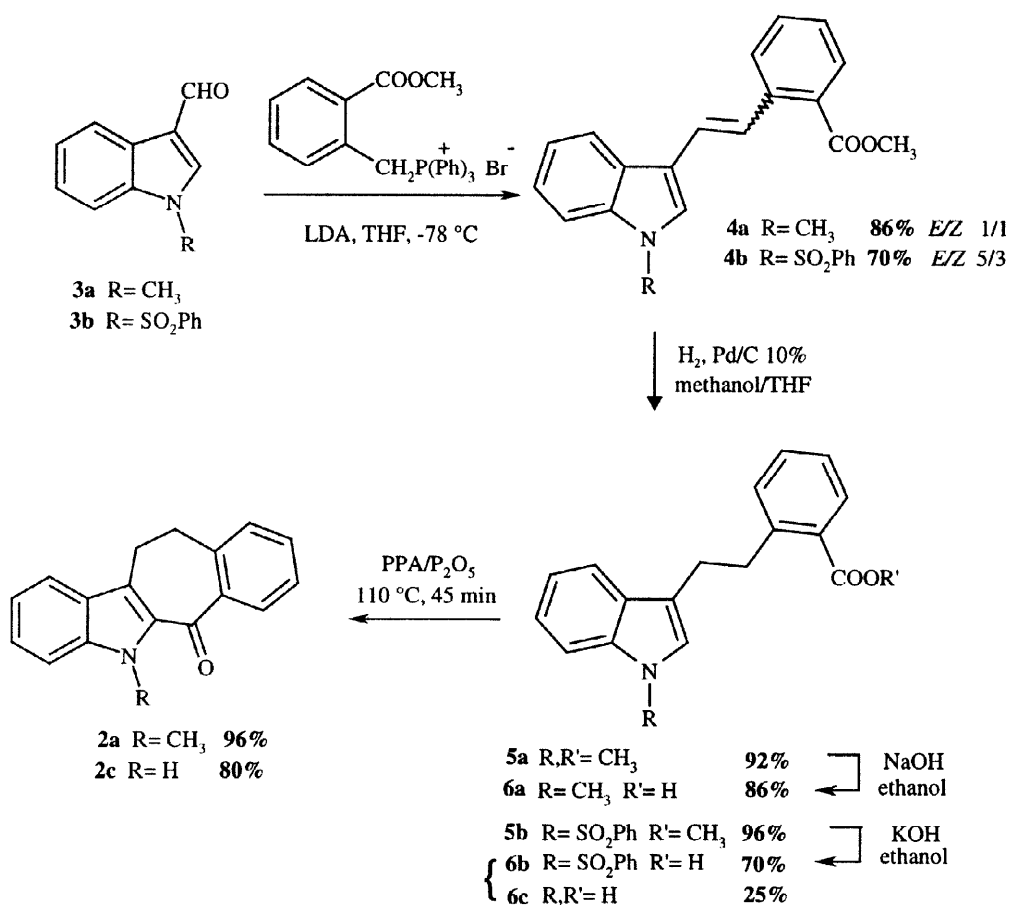
A large number of medicinal agents and molecules displaying potent biological properties (antitumoral, antihistaminic, antiinflammatory, antipsychotic) contain two aromatic rings (pyridine, benzene or pyrrole rings) fused to a central seven-membered ring.<sup>1</sup> Recently, we have described the syntheses of new potent antiinflammatory<sup>2</sup> and antitumor agents<sup>3</sup> having an indole and a phenyl rings around a central seven-membered ring. Antitumor derivatives were all prepared from 5-methyl-6,7-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole **1**.<sup>4</sup> Modest *in vitro* cytotoxicities were observed. Following these results, we became interested in the preparation of 5,6,11,12-tetrahydrobenzo[5,6]cyclohepta[b]indol-6-ones **2** to evaluate their antitumoral potential.



Only one publication on an analogous ring system has been found. Compound **2c** was prepared in 37% overall yield by K. Yamane *et al* from benzocycloheptene-5,6-dione through a Fischer indolization.<sup>5</sup> Herein, we report a new approach to the elaboration of this ring system. Also, transformations of **2** were investigated in order to obtain potent therapeutic derivatives. Considering our synthetic pathway toward **1**,<sup>3</sup> we have applied this strategy for the preparation of fused indole ring system **2** starting from 1-methyl- or 1-phenylsulfonylindole-3-carboxaldehyde **3a** or **3b**. The synthesis of **2** was carried out as shown in Scheme 1. The 3-formylindoles **3a**

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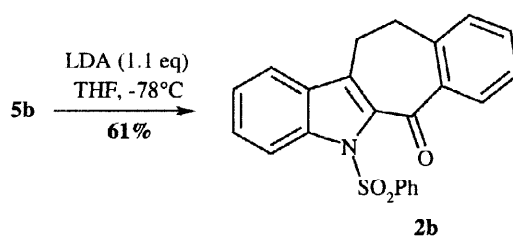
and **3b** were prepared according to literature methods.<sup>6,7</sup> A Wittig reaction of **3a** with the ylide prepared from (2-carbomethoxybenzyl)triphenylphosphonium bromide and lithium diisopropylamide gave an *E/Z* mixture (1:1)<sup>8</sup> of alkene **4a** in 86% yield. The same reaction with **3b** led to the compound **4b** in 70% yield (*E/Z* ratio 5:3). Both compounds **4a** and **4b** were hydrogenated over 10% Pd/C catalyst in dioxane at room temperature to afford **5a** and **5b** in 92% and 96% yield respectively. Saponification of ester **5a** gave the corresponding acid **6a** in good yield. The saponification of **5b** gave a mixture of acids **6b/6c** (ratio  $\approx$  7:3), which were separated by column chromatography. Longer reaction time increases the proportion of **6c**. Thus after 12 h, **6c** was isolated in 62% yield.



Scheme 1

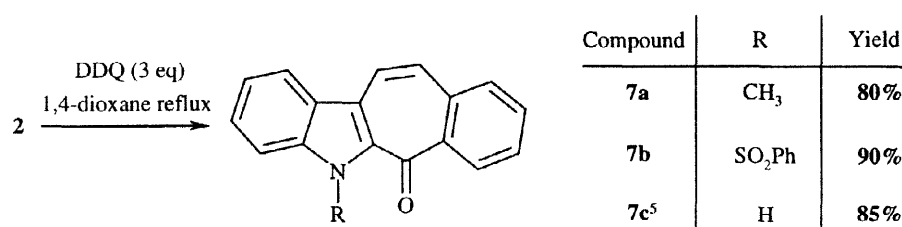
Target ketones **2a** and **2c**<sup>5</sup> were obtained by intramolecular cyclization<sup>9</sup> of acids **6a** and **6b** (or **6c**), using a large excess of polyphosphoric acid and phosphorus pentoxide (80–96% yield). No cyclization on position-4 of the indole ring was observed. Hydrolysis of the phenylsulfonyl group of **6b** occurred during the cyclization to give the unprotected ketone **2c**. The *N*-phenylsulfonyl ketone **2b** was prepared in 61% yield

through a lithiation in position-2<sup>10</sup> of **5b** with lithium diisopropylamide in tetrahydrofuran at -78 °C followed by a nucleophilic addition of the intermediate anion on the carboxyl group (Scheme 2).



**Scheme 2**

The generation of a double bond between carbons 11 and 12 was undertaken. Thus, the unsaturated ketones **7** were prepared in good yields by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of **2** in 1,4-dioxane (Scheme 3). *N*-Alkylation of compound **7c** with alkylamino halides is currently underway to obtain new indolic compounds for testing as potential anticancer agents.



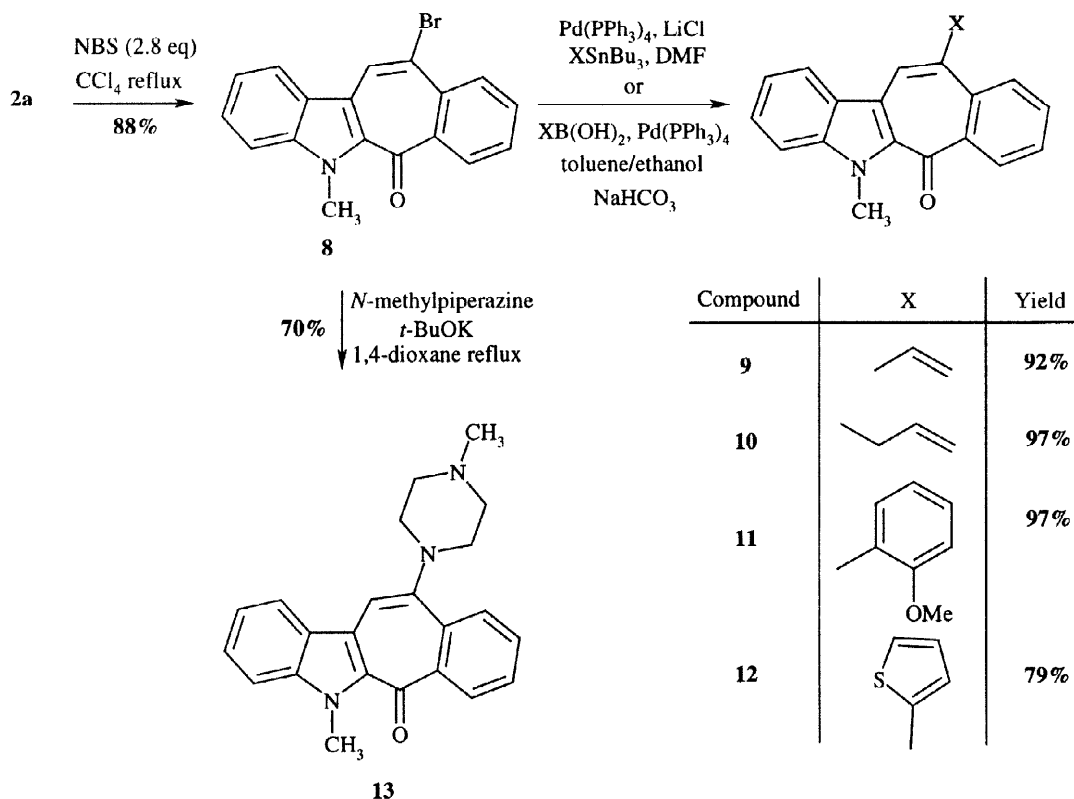
**Scheme 3**

Interestingly, attempts to transform compound **2a** into the desired compound **7a** with 1 eq. of *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride<sup>11</sup> yielded a mixture of **7a** and **8**. In our experiments, no bromination occurred on the indole ring. Increase of the amount of NBS (2.8 eq) gave the 11-bromo ketone **8** in 88% yield (Scheme 4). The structure of **8** was confirmed by NOESY experiments.

This key compound **8** opens the route to the preparation of a wide range of 11-substituted derivatives *via* the well-documented palladium-mediated cross-coupling reactions such as the Stille<sup>12</sup> or Suzuki reactions<sup>13</sup> or an elimination-addition reaction.<sup>11</sup> Stille coupling reactions were performed on compound **8** (Scheme 4). It was allowed to react with vinyltributyltin in the presence of lithium chloride and bis(triphenylphosphine)palladium chloride catalysts in *N,N*-dimethylformamide at 90 °C to produce **9** in 92% yield. Compound **10** was prepared in a similar way in good yield using allyltributyltin.

Aryl derivatives were elaborated through a modified Suzuki coupling reaction<sup>14</sup> between the compound **8** and selected arylboronic acids (2-methoxybenzene boronic acid and 2-thiophene boronic acid) in the

presence of freshly prepared tetrakis(triphenyl)palladium.<sup>15</sup> Compounds **11** and **12** were obtained in 97% and 79% yield respectively.



Scheme 4

Compound **13** was obtained in 70% yield by reacting **8** with *N*-methylpiperazine in refluxing 1,4-dioxane. The structure was again firmly established by a NOESY experiment.

In conclusion, we developed an alternative route to the preparation of 5,6,11,12-tetrahydrobenzo[5,6]cyclohepta[*b*]indol-6-ones **2**. The reactivity of the 11-bromo derivative **8** was investigated. This led to the synthesis of 11-substituted derivatives **9-13** in good yields *via* palladium-mediated cross-coupling reactions or an elimination-addition reaction.

## Experimental

*General:* Melting points were determined using a Büchi SMP-20 melting point apparatus and are uncorrected. The infrared spectra of compounds were recorded on a Perkin Elmer FTIR paragon 1000 spectrometer. NMR spectra were recorded at 300 °K in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> on a Bruker Avance DPX 250 (250.13 MHz for <sup>1</sup>H and 62.90 MHz for <sup>13</sup>C). Chemical shifts are expressed in parts per million and referenced to TMS. Mass spectra were recorded on Perkin-Elmer SCIEX API 300 using ionspray

methodology. Thin layer chromatography was performed on precoated plate of silica gel 60F<sub>254</sub> (Merck) and the spots visualised using an ultraviolet lamp. Column chromatography was performed with Merck silica gel 60 (0.040 mm–0.063 mm) as the stationary phase. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone before use. All air and moisture sensitive reactions were conducted under a prepurified argon atmosphere in flame-dried glassware.

#### 2-[2-(1-Methyl-1*H*-3-indolyl)-1-ethenyl]benzoic acid methyl ester (**4a**)

To a suspension of (2-carbomethoxybenzyl)triphenyl phosphonium bromide (9.26 g, 18.9 mmoles) in anhydrous THF (120 ml), 2*M* lithium diisopropylamide in heptane (9.45 ml, 18.9 mmoles) was added dropwise at -78 °C. After 30 min, a solution of **3a** (1.0 g, 6.3 mmoles) in THF (20 ml) was added dropwise with vigorous stirring at -78 °C. The mixture was stirred 1 h at -78 °C, then 1 h at room temperature and THF was distilled off at reduced pressure. The residue was partitioned between ethyl acetate (30 ml) and 10% hydrochloric acid (30 ml), the aqueous phase separated and extracted with ethyl acetate (2 x 30 ml). The organic layer was dried over MgSO<sub>4</sub> and evaporated *in vacuo*. The crude oil was purified by column chromatography using petroleum ether-dichloromethane 1:1 as the eluting solvent to afford **4a** (1.83 g, 86%) as a yellow oil (*E/Z* ratio 1:1); IR (film)  $\nu$  1722 (CO) cm<sup>-1</sup>; **Z isomer** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.60 (s, 3H, CH<sub>3</sub>), 3.87 (s, 3H, CH<sub>3</sub>), 6.54 (s, 1H, H<sub>Ar</sub>), 6.83 (d, 1H, *J* = 12.0 Hz, =CH), 6.92 (d, 1H, *J* = 12.0 Hz, =CH), 7.05–7.12 (m, 1H, H<sub>Ar</sub>), 7.20–7.38 (m, 4H, H<sub>Ar</sub>), 7.49–7.53 (m, 2H, H<sub>Ar</sub>), 8.02–8.04 (m, 1H, H<sub>Ar</sub>). **E isomer** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.76 (s, 3H, CH<sub>3</sub>), 3.96 (s, 3H, CH<sub>3</sub>), 7.18–7.36 (m, 6H, =CH + H<sub>Ar</sub>), 7.50 (t, 1H, *J* = 7.5 Hz, H<sub>Ar</sub>), 7.80 (broad d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 7.93 (dd, 1H, *J* = 1.3, 8.0 Hz, H<sub>Ar</sub>), 8.06 (d, 1H, *J* = 16.5 Hz, =CH), 8.06–8.09 (m, 1H, H<sub>Ar</sub>). **Z isomer** <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  32.8 (CH<sub>3</sub>), 51.9 (CH<sub>3</sub>) 109.1 (CH), 111.3 (C), 119.2 (CH), 119.4 (CH), 120.6 (CH), 121.7 (CH), 125.9 (CH), 126.7 (CH), 127.5 (C), 127.9 (CH), 129.2 (C), 130.5 (CH), 130.9 (CH), 131.9 (CH), 136.3 (C), 141.1 (C), 167.7 (CO). **E isomer** <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  32.8 (CH<sub>3</sub>), 52.0 (CH<sub>3</sub>), 109.5 (CH), 114.2 (C), 120.3 (2 CH), 122.2 (CH), 122.7 (CH), 124.3 (CH), 125.8 (CH), 125.9 (CH), 126.1 (C), 127.7 (C), 129.1 (CH), 130.7 (CH), 131.9 (CH), 137.7 (C), 140.2 (C), 168.2 (CO); Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub>: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.57; H, 6.04; N, 4.69; MS *m/z* 292 (M+1)<sup>+</sup>.

#### 2-[2-(1-Phenylsulfonyl-1*H*-3-indolyl)-1-ethenyl]benzoic acid methyl ester (**4b**)

With the same methodology but using **3b** as starting material, **4b** was isolated after column chromatography (eluent petroleum ether-dichloromethane 1:1) in 70% yield as a yellow oil (*E/Z* ratio 5:3); IR (film) 1718 (CO) cm<sup>-1</sup>; **Z isomer** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.84 (s, 3H, CH<sub>3</sub>), 6.66 (d, 1H, *J* = 12.0 Hz, =CH), 6.99 (s, 1H, H<sub>Ar</sub>), 7.16–7.52 (m, 10H, =CH + H<sub>Ar</sub>), 7.67–7.74 (m, 2H, H<sub>Ar</sub>), 7.93 (broad d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 8.04 (broad d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>); **E isomer** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.93 (s, 3H, CH<sub>3</sub>), 7.09 (d, 1H, *J* = 16.5 Hz, HC=), 7.15–8.09 (m, 14H, H<sub>Ar</sub>), 8.15 (d, 1H, *J* = 16.5 Hz, =CH); **Z isomer** <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  52.0 (CH<sub>3</sub>), 113.4 (CH), 118.6 (CH), 118.8 (C), 119.8 (CH), 123.3 (CH), 124.2 (CH), 124.8

(CH), 126.7 (2 CH), 127.5 (CH), 129.0 (C), 129.1 (2 CH), 130.2 (C), 130.4 (CH), 130.7 (CH), 132.0 (CH), 132.3 (CH), 133.7 (CH), 134.5 (C), 137.9 (C), 139.6 (C), 167.3 (CO); *E* isomer  $^{13}\text{C}$  NMR (62.90 MHz,  $\text{CDCl}_3$ )  $\delta$  52.0 ( $\text{CH}_3$ ), 113.6 (CH), 120.7 (CH), 121.0 (C), 121.9 (CH), 123.8 (CH), 124.7 (CH), 125.0 (CH), 126.4 (CH), 126.6 (2 CH), 127.1 (CH), 128.0 (C), 128.3 (CH), 128.8 (C), 129.2 (2 CH), 130.7 (CH), 132.1 (CH), 133.8 (CH), 135.5 (C), 137.7 (C), 139.1 (C), 167.6 (CO); Anal. Calcd. for  $\text{C}_{24}\text{H}_{19}\text{NO}_4\text{S}$ : C, 69.05; H, 4.59; N, 3.36. Found: C, 68.81; H, 4.73; N, 3.45; MS  $m/z$  418 ( $\text{M}+1$ ) $^+$ .

#### 2-[2-(1-Methyl-1*H*-3-indolyl)-1-ethyl]benzoic acid methyl ester (**5a**)

A mixture of **4a** (1.4 g, 4.8 mmol) and Pd/C 10% (152 mg) in methanol/THF (30 ml, 2/1 v/v) was shaken in a Parr apparatus under 40 psi of hydrogen at room temperature for 2 h. The catalyst was removed by filtration, and evaporation of the solvent. The crude was purified by column chromatography (eluent petroleum ether-dichloromethane 1:1) to give **5a** (1.3 g, 92%) as a colorless oil; IR (film)  $\nu$  1722 (CO)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  3.11 (t, 2H,  $J = 8.0$  Hz,  $\text{CH}_2$ ), 3.41 (t, 2H,  $J = 8.0$  Hz,  $\text{CH}_2$ ), 3.76 (s, 3H,  $\text{CH}_3$ ), 3.90 (s, 3H,  $\text{CH}_3$ ), 6.86 (s, 1H,  $\text{H}_{\text{Ar}}$ ), 7.18–7.53 (m, 6H,  $\text{H}_{\text{Ar}}$ ), 7.79 (broad d, 1H,  $J = 8.0$  Hz,  $\text{H}_{\text{Ar}}$ ), 7.93–7.94 (m, 1H,  $\text{H}_{\text{Ar}}$ ).  $^{13}\text{C}$  NMR (62.90 MHz,  $\text{CDCl}_3$ )  $\delta$  27.4 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_3$ ), 35.4 ( $\text{CH}_2$ ), 51.7 ( $\text{CH}_3$ ), 108.9 (CH), 114.5 (C), 118.4 (CH), 119.0 (CH), 120.8 (CH), 125.7 (CH), 126.2 (CH), 127.8 (C), 129.5 (C), 130.4 (CH), 131.4 (CH), 131.7 (CH), 136.9 (C), 143.9 (C), 167.9 (CO); Anal. Calcd. for  $\text{C}_{19}\text{H}_{19}\text{NO}_2$ : C, 77.79; H, 6.53; N, 4.77. Found: C, 78.04; H, 6.41; N, 4.88; MS  $m/z$  294 ( $\text{M}+1$ ) $^+$ .

#### 2-[2-(1-Phenylsulfonyl-1*H*-3-indolyl)-1-ethyl]benzoic acid methyl ester (**5b**)

Using the same procedure and the same eluent for the final purification, **5b** was prepared in 96% yield; m.p. 85–86 °C (methanol washing); IR (KBr) 1720 (CO)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  2.97 (t, 2H,  $J = 8.0$  Hz,  $\text{CH}_2$ ), 3.31 (t, 2H,  $J = 8.0$  Hz,  $\text{CH}_2$ ), 3.80 (s, 3H,  $\text{CH}_3$ ), 7.10–7.56 (m, 10H,  $\text{H}_{\text{Ar}}$ ), 7.80–7.99 (m, 4H,  $\text{H}_{\text{Ar}}$ );  $^{13}\text{C}$  NMR (62.90 MHz,  $\text{CDCl}_3$ )  $\delta$  26.9 ( $\text{CH}_2$ ), 34.0 ( $\text{CH}_2$ ), 51.8 ( $\text{CH}_3$ ), 113.5 (CH), 119.6 (CH), 122.7 (C), 122.8 (CH), 123.0 (CH), 124.5 (CH), 126.1 (CH), 126.5 (2 CH), 129.0 (2 CH), 129.3 (C), 130.6 (CH), 130.9 (C), 131.0 (CH), 131.9 (CH), 133.5 (CH), 135.1 (C), 138.1 (C), 143.0 (C), 167.6 (CO); Anal. Calcd. for  $\text{C}_{24}\text{H}_{21}\text{NO}_4\text{S}$ : C, 68.72; H, 5.05; N, 3.34. Found: C, 68.43; H, 5.21; N, 3.47; MS  $m/z$  420 ( $\text{M}+1$ ) $^+$ .

#### 2-[2-(1-Methyl-1*H*-3-indolyl)-1-ethyl]benzoic acid (**6a**)

A solution of ester **5a** (1.28 g, 4.4 mmol) in ethanol 95% (25 ml) and sodium hydroxide (698 mg, 17.4 mmol) was stirred at reflux for 16 h. The solvent was removed *in vacuo*, water (20 ml) was added to the residue and the pH was adjusted to 1 by careful addition of 10% hydrochloric acid. After extraction with dichloromethane (2 x 20 ml), the organic layer was dried over  $\text{MgSO}_4$  and evaporated. The residue was separated by column chromatography (dichloromethane-methanol 95:5) to give **6a** (1.05 g, 86%) as crystals; m.p. 147–148 °C (ether washing); IR (film)  $\nu$  3300–2400 (OH), 1686 (CO)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  3.12 (t, 2H,  $J = 8.0$  Hz,  $\text{CH}_2$ ), 3.47 (t, 2H,  $J = 8.0$  Hz,  $\text{CH}_2$ ), 3.70 (s, 3H,  $\text{CH}_3$ ), 6.82 (s, 1H,  $\text{H}_{\text{Ar}}$ ), 7.09–7.37 (m, 5H,  $\text{H}_{\text{Ar}}$ ), 7.50 (t, 1H,  $J = 6.9$  Hz,  $\text{H}_{\text{Ar}}$ ), 7.72 (d, 1H,  $J = 8.0$  Hz,  $\text{H}_{\text{Ar}}$ ), 8.12 (d, 1H,  $J = 8.0$  Hz,  $\text{H}_{\text{Ar}}$ );  $^{13}\text{C}$

NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  27.5 (CH<sub>3</sub>), 32.5 (CH<sub>2</sub>), 36.0 (CH<sub>2</sub>), 109.0 (CH), 114.7 (C), 118.6 (CH), 119.1 (CH), 121.4 (CH), 126.0 (CH), 126.4 (CH), 127.9 (C), 128.3 (C), 131.5 (CH), 131.6 (CH) 132.9 (CH), 137.0 (C), 145.2 (C), 173.3 (CO); Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.80; H, 6.02; N, 5.15; MS *m/z* 280 (M+1)<sup>+</sup>.

**2-[2-(1-Phenylsulfonyl-1*H*-3-indolyl)-1-ethyl]benzoic acid (6b) and 2-(1*H*-3-indolyl-1-ethyl)benzoic acid (6c)**

A solution of ester **5b** (500 mg, 1.2 mmol) in ethanol 95% (20 ml) and potassium hydroxide (375 mg, mmol) was stirred at reflux for 3 h. The solvent was removed *in vacuo*, water (20 ml) was added to the residue and the pH was adjusted to 1 by careful addition of 10% hydrochloric acid. After extraction with dichloromethane (2 x 20 ml), the organic layer was dried over MgSO<sub>4</sub> and evaporated. The residue was separated by column chromatography (dichloromethane) to give **6b** (338 mg, 70%) and **6c** (79 mg, 25%) as crystals; **6b**: m.p. 164-165 °C (methanol); IR (KBr)  $\nu$  3300-2400 (OH), 1714 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.00 (t, 2H, *J* = 8.0 Hz, CH<sub>2</sub>), 3.38 (t, 2H, *J* = 8.0 Hz, CH<sub>2</sub>), 7.13-7.58 (m, 10H, H<sub>Ar</sub>), 7.82 (d, 2H, *J* = 7.5 Hz, H<sub>Ar</sub>), 7.97 (d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 8.08 (d, 1H, *J* = 7.5 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  27.0 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 113.6 (CH), 119.6 (CH), 122.9 (CH), 122.9 (CH), 123.1 (CH), 124.6 (CH), 126.4 (CH), 126.6 (2 CH), 128.1 (C), 129.1 (2 CH), 131.0 (C), 131.4 (CH), 131.8 (C), 132.9 (CH), 133.5 (CH), 135.2 (C), 138.2 (C), 144.2 (C), 173.0 (CO); Anal. Calcd. for C<sub>23</sub>H<sub>19</sub>NO<sub>4</sub>S: C, 68.13; H, 4.72; N, 3.45. Found: C, 68.48; H, 4.85; N, 3.62; MS *m/z* 406 (M+1)<sup>+</sup>. **6c**: m.p. 160-161 °C (methanol); IR (KBr)  $\nu$  3402 (NH), 3300-2400 (OH), 1688 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>)  $\delta$  3.10 (t, 2H, *J* = 7.9 Hz, CH<sub>2</sub>), 3.45 (t, 2H, *J* = 7.9 Hz, CH<sub>2</sub>), 6.90-7.10 (m, 3H, H<sub>Ar</sub>), 7.30-7.49 (m, 4H, H<sub>Ar</sub>), 7.65 (d, 1H, *J* = 7.5 Hz, H<sub>Ar</sub>), 7.81 (dd, 1H, *J* = 1.0, 7.5 Hz, H<sub>Ar</sub>), 10.74 (broad s, 1H, NH); <sup>13</sup>C NMR (62,90 MHz, DMSO-d<sub>6</sub>)  $\delta$  28.0 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>), 111.8 (CH), 114.9 (C), 118.6 (CH), 119.0 (CH), 121.3 (CH), 122.7 (CH), 126.4 (CH), 127.6 (C), 130.6 (CH), 131.2 (C), 131.4 (CH), 132.0 (CH), 136.7 (C), 143.6 (C), 169.7 (CO); Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>: C, 76.96; H, 5.70; N, 5.28. Found: C, 79.62; H, 5.86; N, 5.39; MS *m/z* 266 (M+1)<sup>+</sup>.

**5-Methyl-5,6,11,12-tetrahydrobenzo[5,6]cyclohepta[b]indol-6-one (2a)**

Finely powdered **6a** (1.0 g, 3.6 mmol) was added to polyphosphoric acid (5.7 g) and phosphorus pentoxide (0.75 g) with stirring at 90 °C. After the addition was complete, the mixture was stirred at 110 °C for 1 h. After cooling, ice was added, then the mixture was neutralized with saturated sodium hydrogenocarbonate, and extracted with dichloromethane (2 x 15 ml). The combined organic layers were dried over MgSO<sub>4</sub> and evaporated. The crude residue was purified by column chromatography (eluent petroleum ether-dichloromethane 1:3) to afford **2a** (898 mg, 96%) as crystals; m.p. 103-104 °C (petroleum ether-ethyl acetate); IR (KBr)  $\nu$  1621 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  2.98-3.00 (m, 4H, CH<sub>2</sub>), 3.95 (s, 3H, CH<sub>3</sub>), 6.97-7.03 (m, 1H, H<sub>Ar</sub>), 7.09-7.32 (m, 5H, H<sub>Ar</sub>), 7.46 (broad d, 1H, *J* = 8.1 Hz, H<sub>Ar</sub>), 7.88 (dd, 1H, *J* = 1.5, 8.1 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  24.8 (CH<sub>2</sub>), 32.8 (CH<sub>3</sub>), 34.8 (CH<sub>2</sub>), 109.9 (CH), 119.7

(CH), 120.5 (CH), 125.5 (C), 126.1 (CH), 126.4 (CH + C), 128.7 (CH), 129.5 (CH), 131.3 (CH), 132.4 (C), 139.2 (C), 139.4 (C), 139.9 (C), 186.9 (CO); Anal. Calcd. for  $C_{18}H_{15}NO$ : C, 82.73; H, 5.79; N, 5.36. Found: C, 83.02; H, 5.61; N, 5.50; MS  $m/z$  262 (M+1)<sup>+</sup>.

#### 5-Phenylsulfonyl-5,6,11,12-tetrahydrobenzo[5,6]cyclohepta[b]indol-6-one (2b)

To a stirred solution of **5b** (200 mg, 0.48 mmol) in anhydrous THF (20 ml) at  $-78$  °C, 2M lithium diisopropylamide in heptane (0.36 ml, 0.72 mmoles) was added dropwise. The mixture was stirred 1 hour at  $-78$  °C, then 1 h at room temperature and THF was evaporated. The residue was partitioned between ethyl acetate (10 ml) and 10% hydrochloric acid (10 ml), the aqueous phase separated and extracted with dichloromethane (2 x 5 ml). The organic layer was dried over  $MgSO_4$  and evaporated *in vacuo*. The crude oil was purified by column chromatography (eluent petroleum ether-dichloromethane 1:1) to afford **2b** (120 mg, 61%); m.p. 137-138 °C (petroleum ether-dichloromethane); IR (KBr)  $\nu$  1658 (CO)  $cm^{-1}$ ;  $^1H$  NMR (250 MHz,  $CDCl_3$ )  $\delta$  3.17-3.24 (m, 4H,  $CH_2$ ), 7.29-7.69 (m, 9H,  $H_{Ar}$ ), 7.91 (dd, 1H,  $J = 1.5, 8.0$  Hz,  $H_{Ar}$ ), 8.20-8.27 (m, 3H,  $H_{Ar}$ );  $^{13}C$  NMR (62.90 MHz,  $CDCl_3$ )  $\delta$  24.3 ( $CH_2$ ), 33.8 ( $CH_2$ ), 116.1 (CH), 120.8 (CH), 123.7 (CH), 127.1 (3 CH), 128.3 (CH), 128.7 (2 CH), 129.1 (CH), 129.2 (CH), 131.8 (CH), 132.7 (C), 133.1 (CH), 135.8 (C), 138.2 (C), 139.3 (C), 139.5 (C), 140.8 (C), 186.2 (CO); Anal. Calcd. for  $C_{23}H_{17}NO_3S$ : C, 71.30; H, 4.42; N, 3.62. Found: C, 71.63; H, 4.57; N, 3.46; MS  $m/z$  388 (M+1)<sup>+</sup>.

#### 5,6,11,12-Tetrahydrobenzo[5,6]cyclohepta[b]indol-6-one (2c)

Following the procedure used for the preparation of **2a**, compound **2c** was obtained (column chromatography eluent: petroleum ether-ethyl acetate 9:1) in 80% yield as crystals; m.p. 181-182 °C (methanol washing) (Lit.<sup>5</sup> m.p. 185-186 °C); IR (KBr)  $\nu$  3307 (NH)  $cm^{-1}$ , 1618 (CO)  $cm^{-1}$ ;  $^1H$  NMR (250 MHz,  $CDCl_3$ )  $\delta$  3.20-3.30 (m, 4H,  $CH_2$ ), 7.14 (t, 1H,  $J = 8.0$  Hz,  $H_{Ar}$ ), 7.33-7.49 (m, 5H,  $H_{Ar}$ ), 7.66 (d, 1H,  $J = 8.0$  Hz,  $H_{Ar}$ ), 8.14 (dd, 1H,  $J = 1.6, 7.6$  Hz,  $H_{Ar}$ ), 9.49 (s, 1H, NH);  $^{13}C$  NMR (62.90 MHz,  $CDCl_3$ )  $\delta$  24.3 ( $CH_2$ ), 36.0 ( $CH_2$ ), 112.1 (CH), 120.2 (CH), 121.2 (CH), 126.2 (C), 126.8 (CH), 127.0 (CH), 127.2 (C), 130.2 (2 CH), 132.6 (CH), 133.2 (C), 136.8 (C), 137.3 (C), 141.1 (C), 184.3 (CO); Anal. Calcd. for  $C_{17}H_{13}NO$ : C, 82.57; H, 5.30; N, 5.66. Found: C, 82.83; H, 5.13; N, 5.81; MS  $m/z$  248 (M+1)<sup>+</sup>.

#### General procedure to prepare compounds 7

A solution of **2** (1 eq) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (3 eq) in dry 1,4-dioxane was stirred at reflux under argon for 12 h. After cooling, the solution was diluted with dichloromethane, then washed successively with aqueous 10% sodium hydroxide solution twice and water once. The organic layer was dried over  $MgSO_4$  and evaporated. The crude residue was purified by column chromatography (eluent: petroleum ether-dichloromethane 6:4 for **7a**, 4:6 for **7b** and dichloromethane for **7c**) to afford the desired compounds **7**.

#### 5-Methyl-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (7a)

Yield: 80%; m.p. 102-103 °C (dichloromethane-methanol); IR (KBr)  $\nu$  1605 (CO)  $cm^{-1}$ ;  $^1H$  NMR (250 MHz,  $CDCl_3$ )  $\delta$  4.32 (s, 3H,  $CH_3$ ), 7.25 (d, 1H,  $J = 11.5$  Hz, =CH), 7.32-7.37 (m, 1H,  $H_{Ar}$ ), 7.54-7.77 (m, 6H, =CH



+ H<sub>Ar</sub>), 8.07 (d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 8.71 (dd, 1H, *J* = 1.5, 8.0 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>) δ 33.2 (CH<sub>3</sub>), 110.3 (CH), 120.6 (CH), 121.0 (CH), 121.4 (CH), 121.6 (C), 124.6 (C), 127.0 (CH), 128.0 (CH), 128.7 (CH), 130.6 (CH), 131.3 (CH), 132.8 (CH), 136.0 (C), 136.4 (C), 137.3 (C), 140.0 (C), 181.2 (CO); Anal. Calcd. for C<sub>18</sub>H<sub>13</sub>NO: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.63; H, 5.14; N, 5.25; MS *m/z* 260 (M+1)<sup>+</sup>

#### 5-Phenylsulfonyl-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (7b)

Yield: 90%; m.p. 205–207 °C (dichloromethane-methanol); IR *v* 1617 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.25–7.66 (m, 10H, =CH + H<sub>Ar</sub>), 7.93 (d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 8.17–8.44 (m, 4H, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>) δ 115.9 (CH), 118.9 (CH), 120.8 (CH), 124.0 (CH), 126.3 (C), 126.8 (C), 127.1 (C), 127.3 (2 CH), 128.7 (CH), 128.8 (2 CH), 129.6 (CH), 130.3 (CH), 131.5 (CH), 132.1 (CH), 133.5 (CH), 133.7 (CH), 134.3 (C), 138.4 (C), 139.5 (C), 140.6 (C), 181.6 (CO); Anal. Calcd. for C<sub>23</sub>H<sub>15</sub>NO<sub>3</sub>S: C, 71.67; H, 3.92; N, 3.63. Found: C, 71.98; H, 4.03; N, 3.50. MS *m/z* 386 (M+1)<sup>+</sup>.

#### 5,6-Dihydrobenzo[5,6]cyclohepta[b]indol-6-one (7c)

Yield: 85%; m.p. 250 °C (methanol) (Lit.<sup>5</sup> m.p. > 270 °C); IR *v* 3243 (NH), 1581, 1560 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>) δ 7.32 (t, 1H, *J* = 7.5 Hz, H<sub>Ar</sub>), 7.49–8.07 (m, 7H, =CH + H<sub>Ar</sub>), 8.28 (d, 1H, *J* = 7.5 Hz, H<sub>Ar</sub>), 8.87 (dd, 1H, *J* = 1.3, 7.5 Hz, H<sub>Ar</sub>), 12.48 (s, 1H, NH); <sup>13</sup>C NMR (62.90 MHz, DMSO-d<sub>6</sub>) δ 112.8 (CH), 120.1 (CH), 120.9 (CH), 121.4 (CH), 122.6 (CH), 125.5 (CH), 127.2 (CH), 128.4 (C), 129.0 (C), 130.1 (CH), 132.2 (C), 134.1 (CH), 134.6 (C), 136.7 (CH), 137.0 (C), 137.8 (C), 177.2 (CO); Anal. Calcd. for C<sub>17</sub>H<sub>11</sub>NO: C, 83.25; H, 4.52; N, 5.71. Found: C, 83.23; H, 4.70; N, 5.88; MS *m/z* 246 (M+1)<sup>+</sup>.

#### 5-Methyl-11-bromo-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (8)

To a solution of **2a** (0.5 g, 1.9 mmoles) in dry CCl<sub>4</sub> (40 ml) under argon was added *N*-bromosuccinimide (1.1 g, 6.2 mmoles). The reaction was stirred at reflux for 2 h. The mixture was hydrolyzed with water (15 ml) and extracted with dichloromethane (3 x 15 ml). Organic layer was dried over MgSO<sub>4</sub> and evaporated. The crude oil was purified by column chromatography (eluent petroleum ether-dichloromethane 7:3) to afford **8** (565 mg, 88%) as crystals; m.p. 156–157 °C (methanol); IR (KBr) *v* 1615 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 4.17 (s, 3H, CH<sub>3</sub>), 7.29–7.35 (m, 1H, H<sub>Ar</sub>), 7.37–7.47 (m, 2H, H<sub>Ar</sub>), 7.56–7.70 (m, 2H, H<sub>Ar</sub>), 7.87 (d 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 8.21 (s, 1H, =CH), 8.41 (dd, 1H, *J* = 1.0, 8.4 Hz, H<sub>Ar</sub>), 8.47 (dd, 1H, *J* = 1.6, 5.1 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>) δ 32.5 (CH<sub>3</sub>), 110.4 (CH), 119.6 (C), 120.5 (CH), 121.5 (CH), 122.3 (C), 124.1 (C), 126.3 (CH), 127.2 (CH), 129.0 (CH), 130.6 (CH), 131.5 (CH), 132.5 (CH), 133.5 (C), 135.8 (C), 138.2 (C), 139.9 (C), 181.7 (CO); Anal. Calcd. for C<sub>18</sub>H<sub>12</sub>BrNO: C, 63.92; H, 3.58; N, 4.14. Found: C, 63.57; H, 3.69; N, 4.28; MS *m/z* 338 (M+1)<sup>+</sup>, 340 (M+3)<sup>+</sup>.

#### General procedure for the Stille reaction

To a suspension of freshly prepared tetrakis(triphenylphosphine)palladium (6 mol%) and LiCl (2.8 eq.) in anhydrous DMF was added a solution of **8** (1 eq) and stannane (1.5 eq) in anhydrous DMF under argon. The

solution was stirred at 90 °C for 1.5 h. After cooling, water and ethyl acetate were added to the mixture. After extraction, the organic layer was washed with water, then dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified by column chromatography (eluent petroleum ether-dichloromethane 7:3 for **9** and **10**) to give the desired compound.

**5-Methyl-11-vinyl-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (9)**

Yield: 92%; m.p. 228 °C (dichloromethane-methanol); IR (KBr)  $\nu$  1611 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  4.22 (s, 3H, CH<sub>3</sub>), 5.47 (dd, 1H, *J* = 1.5, 10.8 Hz, =CH<sub>2</sub>), 5.76 (dd, 1H, *J* = 1.5, 17.0 Hz, =CH<sub>2</sub>), 7.07 (dd, 1H, *J* = 10.8, 17.0 Hz, =CH), 7.29-7.36 (m, 1H, H<sub>Ar</sub>), 7.49-7.69 (m, 4H, H<sub>Ar</sub>), 7.84 (s, 1H, =CH), 8.00-8.08 (m, 2H, H<sub>Ar</sub>), 8.55 (dd, 1H, *J* = 2.5, 7.5 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  32.3 (CH<sub>3</sub>), 110.3 (CH), 116.8 (CH<sub>2</sub>), 120.6 (CH), 120.7 (CH), 120.9 (C), 121.0 (CH), 125.2 (C), 126.9 (CH), 128.1 (CH), 129.5 (CH), 130.4 (CH), 130.5 (CH), 134.8 (C), 136.1 (C), 136.2 (C), 139.4 (C), 140.1 (C), 140.6 (CH), 182.9 (CO); Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>NO: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.47; H, 5.39; N, 4.75; MS *m/z* 286 (M+1)<sup>+</sup>.

**5-Methyl-11-allyl-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (10)**

Yield: 97%; m.p. 101-103 °C (dichloromethane-methanol); IR (KBr)  $\nu$  1617 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.81 (broad d, 2H, *J* = 5.8 Hz, CH<sub>2</sub>), 4.21 (s, 3H, CH<sub>3</sub>), 5.15-5.29 (m, 2H, =CH<sub>2</sub>), 6.02-6.18 (m, 1H, =CH), 7.28-7.34 (m, 1H, H<sub>Ar</sub>), 7.49-7.71 (m, 5H, =CH + H<sub>Ar</sub>), 8.01 (t, 2H, *J* = 8.0 Hz, H<sub>Ar</sub>), 8.58 (dd, 1H, *J* = 1.8, 8.0 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  32.2 (CH<sub>3</sub>), 42.9 (CH<sub>2</sub>), 110.2 (CH), 116.7 (CH<sub>2</sub>), 120.6 (CH), 120.8 (CH), 121.1 (C), 122.4 (CH), 124.9 (C), 126.8 (CH), 127.8 (CH), 127.9 (CH), 130.8 (CH), 130.9 (CH), 134.0 (C), 135.7 (C), 135.9 (C), 137.0 (CH), 139.5 (C), 140.1 (C), 182.8 (CO); Anal. Calcd. for C<sub>21</sub>H<sub>17</sub>NO: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.02; H, 5.90; N, 4.84; MS *m/z* 300 (M+1)<sup>+</sup>.

**General procedure for the Suzuki reaction.**

To a solution of **8** (1 eq) in anhydrous toluene was added freshly prepared tetrakis(triphenylphosphine)-palladium (5 mol %). The resulting homogeneous solution was stirred for 30 min at room temperature. A boronic acid (1.5 eq.) diluted in absolute ethanol was added, followed immediately by saturated aqueous sodium hydrogenocarbonate. This biphasic solution was heated to reflux (1 to 3 h). After cooling, the reaction mixture was poured into brine solution. After separation, the aqueous phase was washed with toluene. The combined organic phases were dried over MgSO<sub>4</sub> and evaporated. The crude residue was purified by column chromatography (eluent petroleum ether-dichloromethane 6:4 for **11** and **12**).

**5-Methyl-11-(2-methoxyphenyl)-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (11)**

Yield: 97%; m.p. 195 °C (dichloromethane-methanol); IR (KBr)  $\nu$  1617 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  3.53 (s, 3H, CH<sub>3</sub>), 4.17 (s, 3H, CH<sub>3</sub>), 6.91 (d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 7.03 (t, 1H, *J* = 7.0 Hz, H<sub>Ar</sub>), 7.14-7.20 (m, 1H, H<sub>Ar</sub>), 7.32-7.50 (m, 7H, H<sub>Ar</sub>), 7.62 (s, 1H, =CH), 7.89 (d, 1H, *J* = 8.0 Hz, H<sub>Ar</sub>), 7.56 (d, 1H, *J* = 1.4, 8.0 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  32.6 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 110.3 (CH), 111.1 (CH),

120.8 (CH), 120.9 (CH), 121.0 (CH), 121.1 (C), 123.4 (CH), 125.2 (C), 126.9 (CH), 127.8 (CH), 129.1 (CH), 130.4 (CH), 130.5 (CH), 130.6 (CH), 131.4 (CH), 133.7 (C), 136.0 (C), 136.3 (C), 136.4 (C), 138.7 (C), 140.2 (C), 157.2 (C), 182.8 (CO); Anal. Calcd. for C<sub>25</sub>H<sub>19</sub>NO<sub>2</sub>: C, 82.17; H, 5.24; N, 3.83. Found: C, 82.03; H, 5.33; N, 3.66; MS m/z 366 (M+1)<sup>+</sup>.

#### 5-Methyl-11-(2-thienyl)-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (12)

Yield: 79%; m.p. 176-177 °C (dichloromethane-methanol); IR (KBr)  $\nu$  1610 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  4.22 (s, 3H, CH<sub>3</sub>), 7.12-7.15 (m, 2H, H<sub>Ar</sub>), 7.28-7.34 (m, 1H, H<sub>Ar</sub>), 7.40 (dd, 1H, *J* = 2.0, 4.0 Hz, H<sub>Ar</sub>), 7.50-7.65 (m, 4H, H<sub>Ar</sub>), 7.84 (dd, 1H, *J* = 1.6, 8.0 Hz, H<sub>Ar</sub>), 7.91 (s, 1H, =CH), 8.01 (d, 1H, *J* = 7.7 Hz, H<sub>Ar</sub>), 8.54 (dd, 1H, *J* = 1.6, 7.7 Hz, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  32.3 (CH<sub>3</sub>), 110.4 (CH), 120.3 (C), 120.7 (CH), 121.3 (CH), 123.9 (CH), 125.1 (C), 125.4 (CH), 127.0 (CH), 127.2 (CH), 127.6 (CH), 128.4 (CH), 130.0 (CH), 130.4 (CH), 131.2 (CH), 131.6 (C), 136.1 (C), 136.2 (C), 139.6 (C), 140.1 (C), 146.9 (C), 182.9 (CO); Anal. Calcd. for C<sub>22</sub>H<sub>15</sub>NOS: C, 77.39; H, 4.43; N, 4.10. Found: C, 77.02; H, 4.58; N, 4.23; MS m/z 342 (M+1)<sup>+</sup>.

#### 5-Methyl-11-(4-methylpiperazino)-5,6-dihydrobenzo[5,6]cyclohepta[b]indol-6-one (13)

To a solution of **8** (100 mg, 0.29 mmol) in anhydrous 1,4-dioxane (5 ml) was added potassium *t*-butoxide (49 mg, 0.44 mmol) and *N*-methylpiperazine (0.1 ml, 0.90 mmoles) under argon. The solution was stirred at reflux until disappearance of the starting material. After cooling, the solvent was evaporated. The crude product was purified by column chromatography (eluent dichloromethane-methanol 95:5) to give **13** (72 mg, 70%) as an oil; IR (film)  $\nu$  1617 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  2.41 (s, 3H, CH<sub>3</sub>), 2.60-2.75 (m, 4H, CH<sub>2</sub>), 3.00-3.10 (m, 4H, CH<sub>2</sub>), 4.14 (s, 3H, CH<sub>3</sub>), 7.10 (s, 1H, =CH), 7.22-7.29 (m, 1H, H<sub>Ar</sub>), 7.41-7.52 (m, 2H, H<sub>Ar</sub>), 7.57-7.70 (m, 2H, H<sub>Ar</sub>), 7.97 (broad d, 1H, *J* = 10.0 Hz, H<sub>Ar</sub>), 8.43-8.48 (m, 2H, H<sub>Ar</sub>); <sup>13</sup>C NMR (62.90 MHz, CDCl<sub>3</sub>)  $\delta$  31.9 (CH<sub>3</sub>), 46.1 (CH<sub>3</sub>), 51.8 (2 CH<sub>2</sub>), 55.5 (2 CH<sub>2</sub>), 106.4 (CH), 110.2 (CH), 120.5 (CH), 120.8 (CH), 121.3 (C), 125.2 (C), 126.8 (CH), 128.5 (CH), 128.7 (CH), 130.2 (CH), 130.8 (CH), 133.7 (C), 134.7 (C), 140.1 (C), 140.2 (C), 147.5 (C), 182.7 (CO); Anal. Calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O: C, 77.28; H, 6.49; N, 11.76. Found: C, 77.50; H, 6.32; N, 11.83; MS m/z 358 (M+1)<sup>+</sup>.

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