

SYNTHESIS OF AN ANNULENOANNULENONE,  
3*H*-BENZO[*e*]CYCL[3.3.2]AZIN-3-ONE

Yoshiro Matsuda,\* Shinya Kohra, Keisuke Katou, Takashi Uemura,  
and Kouhei Yamashita

*Faculty of Environmental Studies, Nagasaki University, 1-14 Bunkyo-machi  
Nagasaki 852-8521, Japan*

**Abstract** - A new nitrogen-bridged annulenoannulene, 3*H*-benzo[*e*]cycl[3.3.2]-azin-3-one (**10a**) was synthesized from the starting phenylpyridine (**6**) via the reaction of the indolizine derivative (**9a**) with polyphosphoric acid (PPA) as the key step.

In view of the interest in heterocyclic annulene<sup>1-6</sup> we have previously reported a new nitrogen-bridged heterocyclic system, cyclazine (cycl[3.2.2]azines,<sup>7</sup> benzocycl[3.2.2]azine,<sup>8</sup> cycl[3.2.2]azinophanes,<sup>9</sup> cycl[3.3.2]azinones,<sup>10</sup> cycl[3.3.3]azines,<sup>5,6</sup> 3*H*-cycl[3.2.2]azinocycl[3.3.2]azinone,<sup>11, 12</sup> cycl[3.2.2]azino-cycl[3.2.2]azine<sup>13</sup>). However, there has been no report on the synthesis of the annulenoannulene, 3*H*-benzocycl[3.3.2]azin-3-one (**10a**). In this paper we wish to report a synthesis of the benzocyclazinones (**10a,b**) by the reaction of ethyl 2-phenylindolizine-3-carboxylate derivatives (**9a,b**) with PPA.

Our first attempt to synthesize **10a** from *o*-bromoacetophenone (**1**) as the starting compound was fruitless. *o*-Bromoacetophenone (**1**) was allowed to react with *N*-bromosuccinimide (NBS) in refluxing CHCl<sub>3</sub> for 6 h and then the crude dibromide was treated with pyridine, followed by the cyclization of the crude salt (**2**) with methyl acetylenecarboxylate (MAC) in DMSO with K<sub>2</sub>CO<sub>3</sub> to give methyl 2'-bromobenzoylindolizine-1-carboxylate (**3**) in the yield of 30 % based on **1**. Heck reaction<sup>14</sup> of **3** using Pd(OCOCH<sub>3</sub>)<sub>2</sub>, Ag<sub>2</sub>CO<sub>3</sub>, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, and tetrabutylammonium bromide in DMF for 20 h at 100°C under nitrogen atmosphere gave the undesired indenoindolizine derivative (**4**). Hydrolysis of **4** using 30 % NaOH in refluxing MeOH for 20 h followed by acidification with 10 % HCl gave the corresponding acid and then decarboxylation of the acid was conducted by Cu<sub>2</sub>O in boiling nitrobenzene for 30 h to afford indenoindolizin-10-one (**5**) in the yield of 18 % based on **4**.

Our further attempt to synthesize **10** from 2-phenylpyridine (**6**) as the starting compound was fruitful.

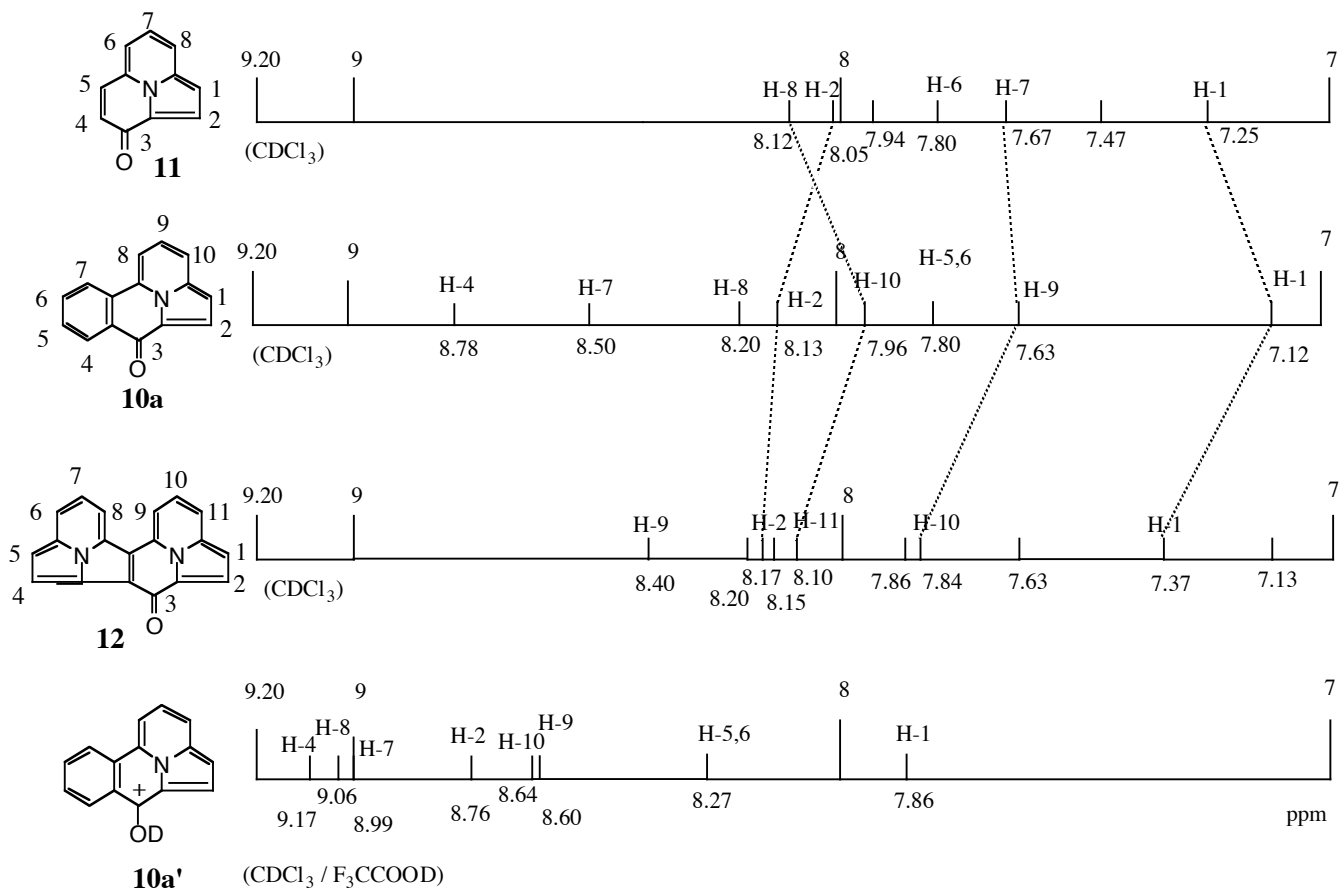
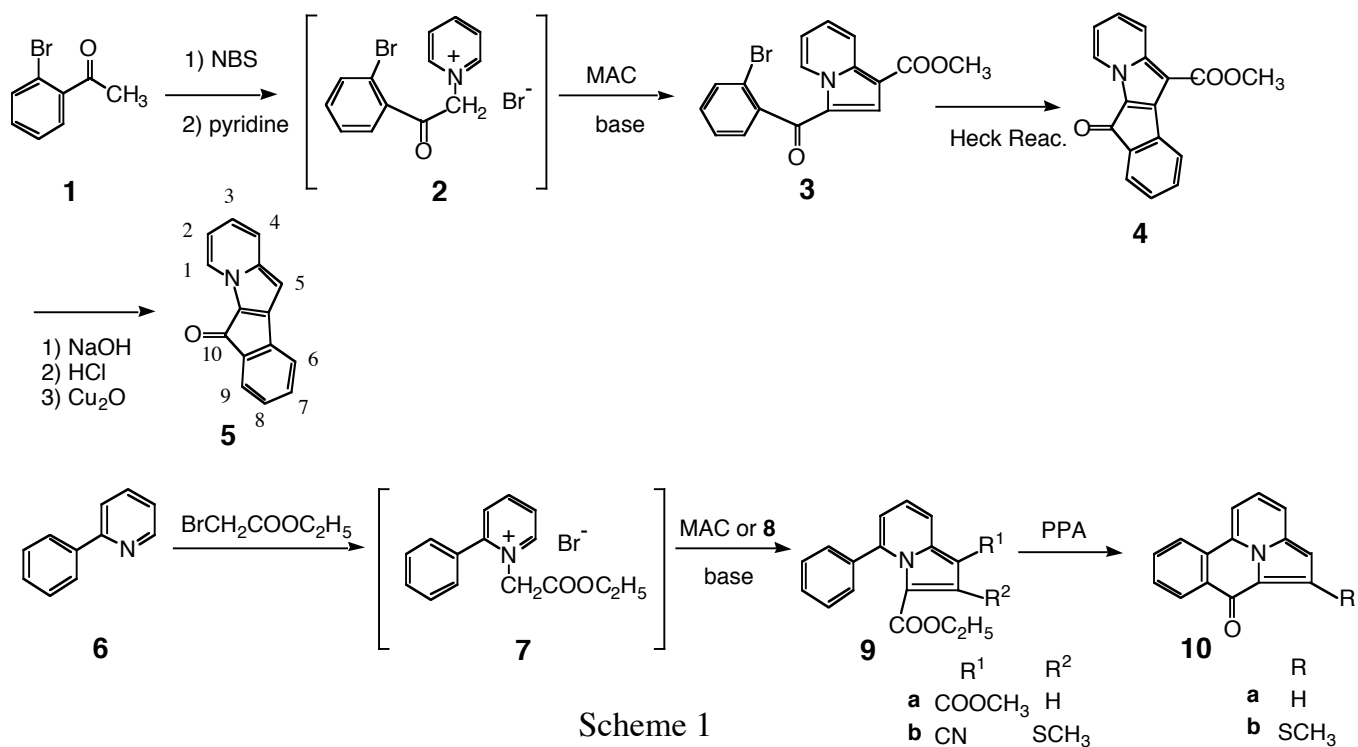
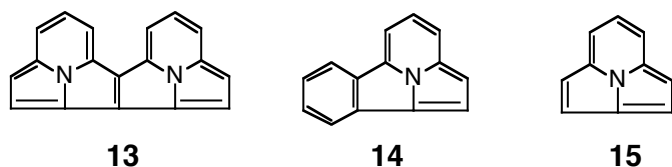


Figure 1 Chemical Shifts of **10a**, **10a'**, **11**, and **12**

2-Phenylpyridine (**6**) was reacted with ethyl bromoacetate for 5 h at 100°C, followed by the cyclization<sup>15</sup> of the crude product (**7**) with MAC and K<sub>2</sub>CO<sub>3</sub> in DMF at room temperature or **7** and 3,3-bis(methylthio)-2-benzenesulfonylacrylonitrile (**8**) with N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> in refluxing EtOH to give the corresponding indolizine derivatives (**9a,b**). The desired 3*H*-benzocyclazinones (**10a,b**) were obtained by the reaction of **9a,b** with PPA for 10 h at 140°C.

The structure of **10a** was supported by a satisfactory elemental analysis and the signals of six doublets (7.12: C<sub>1</sub>-H, d, *J* = 4.7 Hz; 7.96: C<sub>10</sub>-H, d, *J* = 8.5 Hz; 8.20: C<sub>8</sub>-H, d, *J* = 7.3 Hz; 8.13: C<sub>2</sub>-H, d, *J* = 4.7 Hz; 8.50: C<sub>7</sub>-H, d, *J* = 7.1 Hz; 8.78: C<sub>4</sub>-H, d, *J* = 7.8 Hz) in the <sup>1</sup>H-NMR spectrum. Benzocyclazinone (**10a**) is pale orange crystals and soluble in most of organic solvents giving pale orange solutions. It is stable to heat, light, and acids. The selected chemical shifts of cyclazinone (**11**),<sup>16</sup> benzocyclazinone (**10a**), and cyclazinocyclazinone (**12**)<sup>12</sup> are shown in Figure 1. The chemical shifts clearly show that there is the decreasing order of diatropicity of the cyclazinones (**12** > **11** > **10a**). Thus, the diatropicity of a cyclazinone ring is considerably decreased by fusion of a benzene ring and fusion of a second cyclazine increases the diamagnetic ring current of the cyclazinone ring. On the other hand we reported the synthesis of cycl[3.2.2]azinocycl[3.2.2]azine (**13**).<sup>13</sup>



Scheme 2

Then we pointed out that the diatropicity of a cycl[3.2.2]azine ring is considerably increased by fusion of a benzene ring; benzocycl[3.2.2]azine (**14**)<sup>8</sup> to a more extent than cycl[3.2.2]azine (**15**),<sup>17</sup> and fusion of a second cycl[3.2.2]azine; cycl[3.2.2]azinocycl[3.2.2]azine (**13**) also induces

the diamagnetic ring current of the cycl[3.2.2]azine ring, although to a more extent than benzene. Thus there is the decreasing order of diatropicity of the cycl[3.2.2]azines (**13** > **14** > **15**). The reasons for difference of the decreasing order of diatropicity between the cyclazines and the cyclazinones are unclear at present time. As pointed out in previous papers,<sup>10, 12, 18</sup> the diamagnetic ring current is increased when cyclazinones are protonated. Thus, when **10a** is dissolved in CDCl<sub>3</sub> with CF<sub>3</sub>COOD, the chemical shifts of **10a'** appear at a lower field as compared with **10a**. Furthermore, we are in the process of preparing other cyclazines with the hope of expanding understanding of these interesting compounds.

## EXPERIMENTAL

Melting points were determined with a Mitamura Mel-Temp and are uncorrected. IR spectra were recorded in KBr pellets on a FT/IR-430 (JASCO) spectrophotometer. UV spectra were recorded on a UV-310 (Shimadzu) spectrophotometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on a Gemini 300 (VARIAN) and a VARIAN UNITY plus 500 (VARIAN) spectrometers with tetramethylsilane as an

internal standard. Chemical shifts are reported in parts per million ( $\delta$ ). Elemental analyses (C,H,N) of all compounds described here were performed on a Yanagimoto MT-2 CHN recorder.

### **Methyl 3-(2-bromobenzoyl)indolizine-1-carboxylate (3)**

A mixture of 2-bromoacetophenone (1.00 g, 5 mmol) and NBS (0.89 g, 5 mmol) in  $\text{CHCl}_3$  (20 mL) was refluxed for 6 h. The reaction mixture was washed with 5% aq.  $\text{Na}_2\text{CO}_3$  (10 mL), dried ( $\text{Na}_2\text{SO}_4$ , 1 g), and evaporated under reduced pressure to give 2,2'-dibromoacetophenone. To a solution of crude 2,2'-dibromoacetophenone in acetone (5 mL) was added dropwise pyridine (0.4 g, 5 mmol) at 0 °C and the mixture was stirred for a day at rt. The resulting salt (**2**) was collected by filtration and washed with acetone. A mixture of the crude salt (**2**), MAC (0.40 g, 5 mmol), and  $\text{K}_2\text{CO}_3$  (0.69 g, 5 mmol) in DMSO (30 mL) was stirred for 3 days at rt. The mixture was poured into ice-water and the resulting precipitate was collected by filtration, washed with water, and dried to give **3**.

**3**: mp 147-149 °C (MeOH), yield 0.54 g, 30 % (based on **1**). IR (KBr) 1615 (CO), 1698 (CO)  $\text{cm}^{-1}$ ; UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 235 (4.26), 255 (4.07), 278 (4.23), 328 (3.90), 361 (4.17) nm;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 3.88 (3H, s,  $\text{CH}_3$ ), 7.17 (1H, t,  $J = 6$  Hz,  $\text{C}_6\text{-H}$ ), 7.35-7.55 (3H, m, Ar-H), 7.49 (1H, s,  $\text{C}_2\text{-H}$ ), 7.68 (1H, d,  $J = 8$  Hz,  $\text{C}_6\text{-H}$ ), 8.41 (1H, t,  $J = 9$  Hz,  $\text{C}_8\text{-H}$ ), 10.05 (1H, d,  $J = 7$  Hz,  $\text{C}_5\text{-H}$ ). *Anal.* Calcd for  $\text{C}_{17}\text{H}_{12}\text{NO}_3\text{Br}$ : C, 57.00; H, 3.38; N, 3.91. Found: C, 57.26; H, 3.64; N, 3.79.

### **Methyl indeno[1,2-*b*]indolizin-10-one-5-carboxylate (4)**

A mixture of **3** (1.07g, 3 mmol),  $\text{Pd}(\text{OCOCH}_3)_2$  (0.07 g, 0.6 mmol),  $\text{P}(\text{C}_6\text{H}_5)_3$  (0.31 g, 1.2 mmol),  $\text{Ag}_2\text{CO}_3$  (1.65 g, 6 mmol), and  $(\text{C}_4\text{H}_9)_4\text{NBr}$  (0.58 g, 1.8 mmol) in DMF (60 mL) under the nitrogen atmosphere was stirred for 20 h at 100 °C. After filtration, the mixture was evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a fraction of benzene:  $\text{CHCl}_3$  (1:1), **4** was obtained.

**4**: mp 201-202 °C (MeOH), yield 0.35 g, 43 %. IR (KBr) 1680 (CO), 1709 (CO)  $\text{cm}^{-1}$ ; UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 223 (4.00), 240 (3.97), 272 (4.08), 300 (3.99), 320 (3.85), 335 (3.89), 445 (3.07) nm;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 4.01 (3H, s,  $\text{CH}_3$ ), 6.98 (1H, t,  $J = 6.6$  Hz,  $\text{C}_2\text{-H}$ ), 7.20 (1H, t,  $J = 7.1$  Hz,  $\text{C}_7\text{-H}$ ), 7.27 (1H, dd,  $J = 6.6, 9.0$  Hz,  $\text{C}_3\text{-H}$ ), 7.33 (1H, t,  $J = 7.1$  Hz,  $\text{C}_8\text{-H}$ ), 7.43 (1H, d,  $J = 7.1$  Hz,  $\text{C}_6\text{-H}$ ), 7.85 (1H, d,  $J = 7.1$  Hz,  $\text{C}_9\text{-H}$ ), 8.23 (1H, d,  $J = 9.0$  Hz,  $\text{C}_4\text{-H}$ ), 8.59 (1H, d,  $J = 6.6$  Hz,  $\text{C}_1\text{-H}$ ). *Anal.* Calcd for  $\text{C}_{17}\text{H}_{11}\text{NO}_3$ : C, 73.64; H, 4.00; N, 5.05. Found: C, 73.48; H, 4.17; N, 5.02.

### **Indeno[1,2-*b*]indolizin-10-one (5)**

A mixture of **4** (0.83 g, 3 mmol) and 30 % aq. NaOH (17 mL) in MeOH (15 mL) was refluxed for 20 h. The mixture was poured into ice-water and acidified to litmus with 10 % HCl (20 mL). The resulting precipitate was collected by filtration, washed with water, and dried to give the acid. A mixture of the crude acid and  $\text{Cu}_2\text{O}$  (0.3 g) in nitrobenzene (60 mL) was refluxed for 30 h. The mixture was evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a

fraction of benzene: CHCl<sub>3</sub> (5 : 1), **5** was obtained in the yield of 18 % (0.12 g) based on **4**.

**5**: mp 185-187 °C (MeOH); IR (KBr) 1666 (CO) cm<sup>-1</sup>; UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 262 (4.61), 278 (4.38), 288 (4.42), 326 (4.09), 337 (4.06), 441 (3.93) nm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 6.34 (1H, s, C<sub>5</sub>-H), 6.77 (1H, t, *J* = 6.9 Hz, C<sub>2</sub>-H), 6.96 (1H, dd, *J* = 6.9, 8.9 Hz, C<sub>3</sub>-H), 7.12 (1H, t, *J* = 7.3 Hz, C<sub>8</sub>-H), 7.17 (1H, d, *J* = 7.3 Hz, C<sub>6</sub>-H), 7.23 (1H, t, *J* = 7.3 Hz, C<sub>7</sub>-H), 7.36 (1H, d, *J* = 8.9 Hz, C<sub>4</sub>-H), 7.39 (1H, d, *J* = 7.3 Hz, C<sub>9</sub>-H), 8.46 (1H, d, *J* = 6.9 Hz, C<sub>1</sub>-H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 96.1, 114.7, 119.9, 120.7, 123.0, 123.4, 127.0, 128.4, 132.2, 137.8, 141.0, 144.9, 171.6, 178.1. *Anal.* Calcd for C<sub>15</sub>H<sub>9</sub>NO: C, 82.18; H, 4.14; N, 6.39. Found: C, 81.93; H, 4.13; N, 6.37. MS *m/z* 219.

### **Ethyl 1-cyano-2-methylthio-4-phenylindolizine-3-carboxylate (9b)**

A mixture of 2-phenylpyridine (**6**) (15.5g, 0.1 mol) and ethyl bromoacetate (16.7 g, 0.1 mol) was heated for 5 h at 100 °C to give the salt (**7**). The mixture of the crude salt (**7**), **8** (28.5 g, 0.1 mol) and N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (20.2 g, 0.2 mol) in EtOH (200 mL) was refluxed for 10 h, after which the mixture was evaporated under reduced pressure and the residue was poured into ice-water. The mixture was extracted with CHCl<sub>3</sub> (3x100 mL) and the combined extracts were washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>, 10 g), and evaporated under reduced pressure. The residue was then submitted to column chromatography on silica gel. From a fraction of benzene-CHCl<sub>3</sub> (5 : 1), the product (**9b**) was obtained.

**9b**: mp 134-137 °C (EtOH), yield 5.7 g, 17 % based on **6**. IR (KBr) 1700 (CO), 2211 (CN) cm<sup>-1</sup>; UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 240 (4.35), 270 (4.39), 347 (3.94) nm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 1.04 (3H, t, *J* = 7.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.73 (3H, s, SCH<sub>3</sub>), 3.61 (2H, q, *J* = 7.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.83 (1H, d, *J* = 7.4 Hz, C<sub>8</sub>-H), 7.35 (1H, dd, *J* = 7.4, 8.8 Hz, C<sub>7</sub>-H), 7.42-7.51 (5H, m, Ar-H), 7.63 (1H, d, *J* = 8.8 Hz, C<sub>6</sub>-H). *Anal.* Calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S: C, 67.84; H, 4.79; N, 8.33. Found: C, 67.66; H, 4.87; N, 8.08.

### **3H-Benzo[e]cycl[3.3.2]azin-3-one (10a)**

A mixture of 2-phenylpyridine (**6**) (1.55 g, 10 mmol) and ethyl bromoacetate (1.67 g, 0.1 mol) was heated for 5 h at 100 °C to give the salt (**7**). A mixture of the crude salt (**7**), MAC (8.4 g, 10 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol) in DMSO (50 mL) was stirred for 3 days at rt. The mixture was poured into ice-water and extracted with CHCl<sub>3</sub> (3x100 mL). The extract was dried (Na<sub>2</sub>SO<sub>4</sub>, 10 g) and evaporated to give oily compound (**9a**). A mixture of the oily compound (**9a**) and PPA (100 mL) was heated for 10 h at 140°C. The mixture was poured into ice and made basic to litmus with K<sub>2</sub>CO<sub>3</sub>. The mixture was extracted with CHCl<sub>3</sub> (3x100 mL). The extract was dried (Na<sub>2</sub>SO<sub>4</sub>, 10 g) and evaporated. The residue was submitted to column chromatography on silica gel. From a fraction of benzene: CHCl<sub>3</sub> (6:1), **10a** was obtained in the yield of 12 % (0.26 g) based on **6**.

**10a**: mp 179-180 °C (MeOH); IR (KBr) 1618 (CO) cm<sup>-1</sup>; UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 235 (4.48), 259 (4.62), 273 (4.58), 313 (3.47), 365 (3.89), 405 (4.19), 426 (4.31) nm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 7.12 (1H, d, *J* = 4.7 Hz, C<sub>1</sub>-H), 7.63 (1H, dd, *J* = 7.3, 8.5 Hz, C<sub>9</sub>-H), 7.77-7.83 (2H, m, C<sub>5,6</sub>-H), 7.96 (1H, d, *J* = 8.5 Hz, C<sub>10</sub>-H),

8.13 (1H, d,  $J = 4.7$  Hz, C<sub>2</sub>-H), 8.20 (1H, d,  $J = 7.3$  Hz, C<sub>8</sub>-H), 8.50 (1H, d,  $J = 7.1$  Hz, C<sub>7</sub>-H), 8.78 (1H, d,  $J = 7.8$  Hz, C<sub>4</sub>-H); <sup>1</sup>H-NMR (F<sub>3</sub>CCOOD in CDCl<sub>3</sub>) 7.86 (1H, d,  $J = 5.8$  Hz, C<sub>1</sub>-H), 8.22-8.32 (2H, m, C<sub>5,6</sub>-H), 8.60 (1H, t,  $J = 8.3$  Hz, C<sub>9</sub>-H), 8.64 (1H, d,  $J = 8.3$  Hz, C<sub>10</sub>-H), 8.76 (1H, d,  $J = 5.8$  Hz, C<sub>2</sub>-H), 8.99 (1H, d,  $J = 7.7$  Hz, C<sub>7</sub>-H), 9.06 (1H, d,  $J = 8.3$  Hz, C<sub>8</sub>-H), 9.17 (1H, d,  $J = 7.1$  Hz, C<sub>4</sub>-H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 107.9, 112.2, 118.9, 120.5, 122.8, 123.3, 124.9, 126.8, 128.7, 128.9, 129.9, 131.1, 132.9, 136.6, 170.0. *Anal.* Calcd for C<sub>15</sub>H<sub>9</sub>NO: C, 82.18; H, 4.14; N, 6.39. Found: C, 82.26; H, 4.43; N, 6.43. MS  $m/z$  219.

### 2-Methylthio-3H-benzo[e]cycl[3.3.2]azin-3-one (10b)

A mixture of **9b** (0.34 g, 1 mmol) and PPA (10 mL) was heated for 10 h at 140°C. The mixture was poured into ice-water and alkalized to litmus with K<sub>2</sub>CO<sub>3</sub>. The mixture was extracted with CHCl<sub>3</sub> (3x20 mL). The extract was dried (Na<sub>2</sub>SO<sub>4</sub>, 1 g) and evaporated. The residue was submitted to column chromatography on silica gel. From a fraction of benzene: CHCl<sub>3</sub> (6:1), **10b** was obtained in the yield of 34 % (0.09 g).

**10b**: mp 215-217 °C (MeOH); IR (KBr) 1614 (CO) cm<sup>-1</sup>; UV (EtOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 217 (4.31), 247 (4.63), 272 (4.09), 315 (4.32), 394 (4.00), 415 (4.20) nm; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 2.68 (3H, s, SCH<sub>3</sub>), 6.88 (1H, s, C<sub>1</sub>-H), 7.67 (1H, t,  $J = 8$  Hz, C<sub>9</sub>-H), 7.82-7.90 (3H, m, C<sub>5,6,10</sub>-H), 8.17 (1H, d,  $J = 8$  Hz, C<sub>8</sub>-H), 8.57 (1H, d,  $J = 6.6$  Hz, C<sub>7</sub>-H), 8.83 (1H, d,  $J = 6.8$  Hz, C<sub>4</sub>-H). *Anal.* Calcd for C<sub>16</sub>H<sub>11</sub>NOS: C, 72.43; H, 4.18; N, 5.28. Found: C, 72.61; H, 4.05; N, 5.16

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