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A number of 3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole derivatives have been synthesized starting with methyl indole-4-carboxylate functionalized at the 3 position.

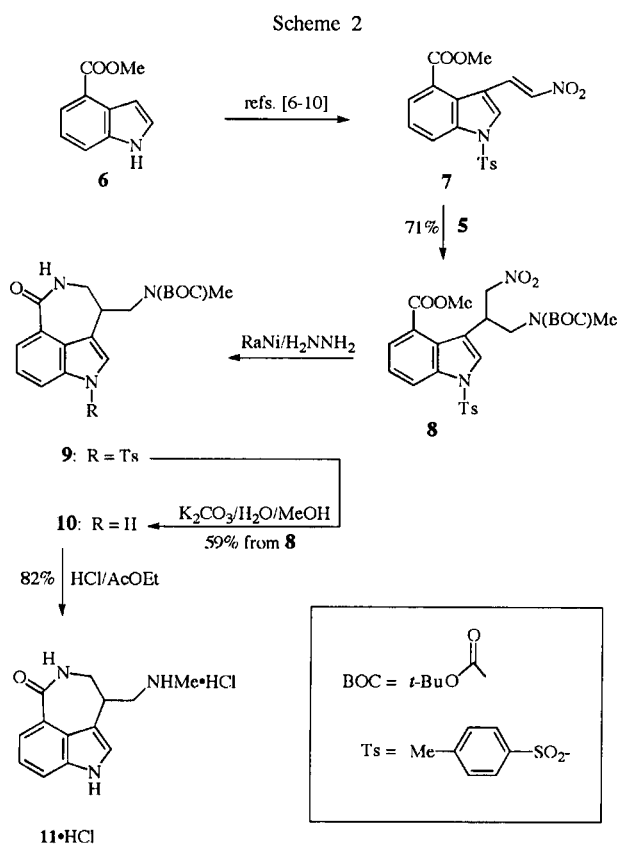
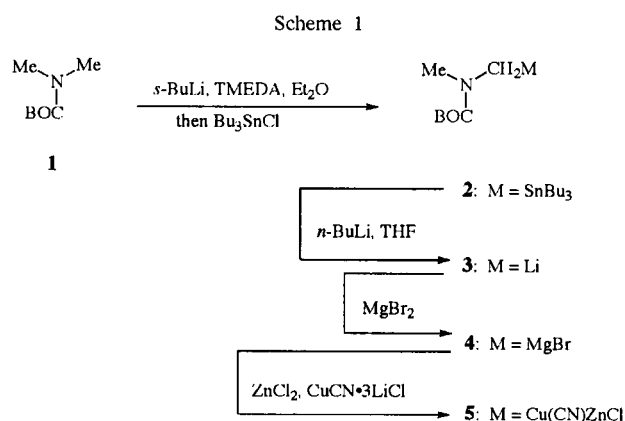
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The ergot alkaloids contain an indole unit that is bridged at positions 3 and 4 to form an additional ring system. Many compounds of this class exhibit powerful biological properties, and the hallucinogenic activity of lysergic acid diethylamide (LSD) serves as a well known example [1]. Several ergot types of drugs are currently being used in clinical practice. These include ergonovine and methylergonovine for treatment of postpartum hemorrhage, the antihypertension agent nicergoline, bromocriptine for treatment of prolactin disorders, and the antimigraine drug methylsergide. Recent studies have also shown that a large number of synthetic azepino-fused indoles exhibit potent activity on the central nervous system (CNS). Of these, compound **11** (Scheme 2) shows promise for development as a drug against migraine attacks [2].

Recently, we published a brief account of a novel synthesis of racemic compound **11** [3], and full experimental details are presented in this paper. We also describe synthesis of several analogs of this potent CNS agent.

The key features in the novel approach to **11** are a conjugate addition reaction of the apparent organometallic reagent **5** (Scheme 1) with the indole derivative **7** and a subsequent reductive cyclization at the resultant adduct **8** (Scheme 2). More specifically, the conjugate addition reaction provides a means for the introduction of the methylaminomethyl function at the azepine moiety of the final product **11**. The *tert*-butoxycarbonyl (BOC) derivative of dimethylamine (**1**) for generation of the apparent organometallic reagent **5** is readily available. Compound **1** can be efficiently prepared by the reaction of di-*tert*-butyl dicarbonate with dimethylamine or dimethylammonium chloride in the presence of triethylamine [4]. We found that the latter method is experimentally simpler and produces the desired product **1** in a greater yield. Other, less convenient synthetic routes to **1** involve reactions of commercially available dimethylcarbamoyl chloride [5] or phenyl chloroformate [4].

The nitrovinyl-substituted indole derivative **7** can be prepared by treatment of methyl indole-4-carboxylate (**6**) with 1-dimethylamino-2-nitroethylene [6] followed by tosylation [7]. However, the preparation of the reagent to add the 2-nitroethenyl group is difficult [8] and the commercially available reagent (Lancaster) is quite expensive.



A useful alternative to the synthesis of **7** involves formylation of **6** [9] followed by condensation of the resultant aldehyde with nitromethane in the presence of ammonium acetate [10], and then tosylation of the product. In this work the two approaches to **7** were examined and found to give similar results.

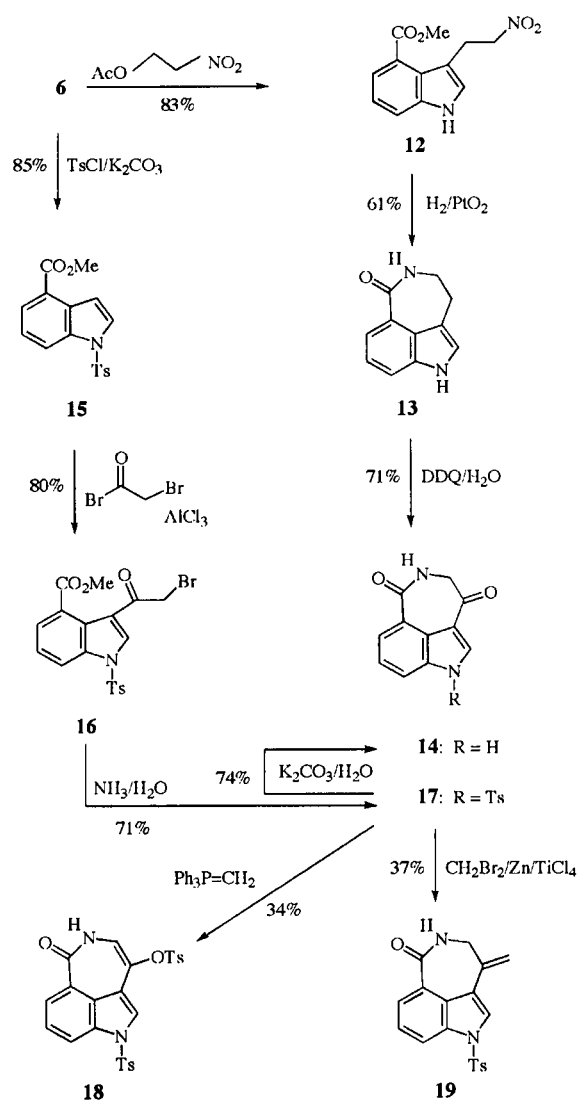
Initially, compound **1** was lithiated directly by the reaction with *s*-BuLi [11] and the resultant reagent **3** (Scheme 1) was allowed to react with the nitrovinyl derivative **7**. At  $-100^{\circ}$  this reaction gave the conjugate addition product **8** in a low yield, and the efficiency was even lower at  $-78^{\circ}$ . An indirect generation of the lithium reagent **3** [12], as shown in Scheme 1, by a sequence of the lithiation of **1**, preparation and purification of a tin derivative **2**, transmetallation of **2**, followed by the conjugate addition reaction of the resultant lithium reagent **3** with **7** at  $-100^{\circ}$  gave the adduct **8** in a 60% yield. Again, increasing the temperature to  $-78^{\circ}$  resulted in a sharp decrease of the efficiency of the last addition step. Because of the inconvenience of working at temperatures below  $-78^{\circ}$  the addition reactions of two other organometallic reagents derived from **3** were examined. These were a Grignard reagent **4** generated from **3** and  $\text{MgBr}_2$  and a copper-zinc reagent **5** generated from **3** in the presence of  $\text{ZnCl}_2$  and  $\text{CuCN}$  [13-16]. The starting lithium derivative **3** was derived from **2** as discussed above. In comparison to the addition reaction of the lithium reagent **3** with **7**, the reactions of either **4** or **5** were more efficient and could be conducted at temperatures above  $-78^{\circ}$ . The subsequent optimization studies showed that the best yield at 71% for the adduct **8** is obtained by using the copper-zinc reagent **5**.

Our synthetic approach to the final desired compound **11** involved reductive cyclization of **8** to the azepine derivative **9** followed by removal of the tosyl and *tert*-butoxycarbonyl groups. Many methods for reduction of nitroalkanes to alkylamines are known [17], and some of them have been successfully used in reductive cyclizations [2,18-20] that are similar to the desired conversion of **8** into **9**. On the other hand, the high sensitivity of the BOC group to hydrolysis limited the choice of reducing agents to those that work under neutral or mildly basic conditions. Hydrogenation of **8** in the presence of  $\text{PtO}_2$  [19,21] was slow at  $23^{\circ}$  under an atmospheric pressure of hydrogen and always gave **9** in a mixture with the starting material **8**. An attempted reduction of **8** with  $\text{NaBH}_4$  in the presence of 10%  $\text{Pd/C}$  as a catalyst [22] was unsuccessful. Finally, it was found that the treatment of **8** with hydrazine hydrate in the presence of Raney nickel [2,23] is a practical way to accomplish the reductive cyclization. This reaction was accompanied by partial detosylation to give a mixture of **9** and **10**. Without separation, the mixture was then subjected to a classical detosylation of indole derivatives under basic conditions [24,25] followed

by removal of the BOC group from the resultant pure product **10** by treatment with hydrogen chloride [26]. The overall yield of the hydrochloride of **11** thus obtained was 21%, which is a three-fold improvement over the previously reported preparation that started with the same substrate **6** [2]. The  $^1\text{H}$  NMR and IR spectra of **11**•HCl and the spectra of the authentic sample obtained from Solvay, Inc. were virtually identical. Following a single crystallization the purity of **11** was found to be greater than 99.9% by using a HPLC analysis on a C-18 column with various solvent systems.

In summary, we described a new, relatively efficient synthetic route to the CNS agent **11**. As noted previously, only the 3*R*(+)-enantiomer of **11** exhibits high biological activity [2]. Also as noted in the same report the active enantiomer can be obtained by crystallization of diastomeric salts.

Scheme 3



Due to the biological activity of **11** it was of interest to synthesize several analogs that comprise the same azepinoindole system but contain different substituents at position 3 of the azepine moiety. This is presented in Scheme 3. Following the reported nitroethylation of **6** [27] the resultant product **12** was subjected to reductive cyclization under modified conditions to give an azepinoindole **13** [27]. Oxidation of **13** by treatment with DDQ gave a new compound **14**. A different synthetic route to **14** is also presented in Scheme 3. This involves tosylation of **6** to give **15**, bromoacetylation of **15** followed by aminative cyclization of the resultant product **16** to yield **17**, and then removal of the tosyl group. Surprisingly, the reaction of methylenetriphenylphosphorane with **17** furnished the enol tosylate **18** as the major, low molecular weight product but not the expected methylene derivative **19**. On the other hand, the Wittig product **19** was obtained upon treatment of **17** with dibromomethane in the presence of zinc and titanium tetrachloride as a catalyst [28]. Studies of binding **13**, **14**, and **17-19** to various HT receptors are in progress, and the results will be reported in due course.

## EXPERIMENTAL

All reagents were obtained from Aldrich and/or Lancaster and used as supplied. Ether and tetrahydrofuran were distilled from sodium benzophenone ketyl immediately before use. Flash chromatography was conducted on silica gel as adsorbent. Unless stated otherwise,  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded in deuteriochloroform solutions with tetramethylsilane as internal reference. Melting points (Pyrex capillary) are not corrected.

*N*-(*t*-Butoxycarbonyl)-*N*-[(tributylstannyl)methyl]methylamine (**2**).

A solution of *N*-(*t*-Butoxycarbonyl)dimethylamine (**1**, 3.2 mL, 20 mmol) in ether (40 mL) was cooled to  $-70^\circ$  and treated with *N,N,N'*-tetramethylethylenediamine (3.6 mL, 24 mmol) and *s*-butyllithium (1.3 M in cyclohexane, 18.5 mL, 24 mmol) under a nitrogen atmosphere. The mixture was stirred at  $-70^\circ$  for 2 hours, treated with tributyltin chloride (6 mL, 22 mmol), allowed to reach  $20^\circ$  within 1 hour, quenched with a saturated aqueous solution of potassium fluoride (5 mL), and then extracted with ether (3 x 50 mL). The extract was washed with a saturated solution of sodium chloride (3 x 10 mL), dried over potassium carbonate, and concentrated on a rotary evaporator. Flash chromatography (hexanes, then hexanes/ethyl acetate, 98:2) furnished 6.4 g (74%) of **2** as a colorless oil;  $^1\text{H}$  NMR (deuteriobromoform,  $100^\circ$ ):  $\delta$  0.84 (m, 6H), 0.88 (t,  $J = 7$  Hz, 9H), 1.28 (m, 6H), 1.42 (s, 9H), 1.47 (m, 6H), 2.82 (s, 3H), 2.91 (m, 2H);  $^{13}\text{C}$  NMR (deuteriobromoform,  $100^\circ$ ):  $\delta$  9.9, 13.2, 26.5, 28.2, 28.3, 35.2, 37.0, 78.1, 154.5.

Anal. Calcd. for  $\text{C}_{19}\text{H}_{41}\text{NO}_2\text{Sn}$ : C, 52.55; H, 9.52; N, 3.23. Found: C, 52.39; H, 9.50; N, 3.20.

Methyl 3-[2-[*N*-(*t*-Butoxycarbonyl)methylamino]-1-(nitromethyl)ethyl]-1-(4-toluenesulfonyl)indole-4-carboxylate (**8**).

A solution of **2** (7.3 mL, 18.4 mmol) in tetrahydrofuran (80 mL) was cooled to  $-70^\circ$  and treated dropwise with *n*-butyllithium (2.5 M in hexanes, 7 mL, 17.5 mmol) under a nitrogen atmosphere. After stirring at  $-70^\circ$  for 1 hour the mixture was treated with zinc chloride (0.5 M in tetrahydrofuran, 3.5 mL, 17.5 mmol) and then with a solution of cuprous cyanide (1.65 g, 18.4 mmol) and lithium chloride (1.57 g, 36.8 mmol) in tetrahydrofuran (50 mL). The temperature was increased to  $0^\circ$ , and the mixture was stirred for 10 minutes to ensure the formation of the copper-zinc reagent **5** (see Scheme 1). The solution of **5** was cooled to  $-70^\circ$  and treated with a solution of nitroalkene **7** (5 g, 12.5 mmol) in tetrahydrofuran (50 mL), and the resultant mixture was stirred at  $0^\circ$  for 12 hours. After quenching with a solution of acetic acid (2.5 mL) in tetrahydrofuran (5 mL) the mixture was poured into a saturated aqueous solution of ammonium acetate (250 mL) and extracted with ether (3 x 100 mL). The extract was washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, and then concentrated on a rotary evaporator. Flash chromatography of the residue (hexanes/ethyl acetate, 7:3) furnished 4.9 g (71%) of compound **8** as colorless crystals; mp  $61-64^\circ$ ;  $^1\text{H}$  NMR ( $45^\circ$ ):  $\delta$  1.47 (s, 9H), 2.32 (s, 3H), 2.86 (s, 3H), 3.70 (m, 2H), 3.94 (s, 3H), 4.70 (m, 3H), 7.22 (d,  $J = 8$  Hz, 2H), 7.32 (t,  $J = 8$  Hz, 1H), 7.70 (m, 4H), 8.18 (d,  $J = 8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $45^\circ$ ):  $\delta$  21.5, 28.4, 34.7, 34.9, 51.5, 52.5, 77.7, 80.2, 117.7, 119.4, 124.2, 125.0, 126.4, 126.7, 126.9, 127.7, 130.1, 134.7, 136.1, 145.5, 156.3, 167.9.

Anal. Calcd. for  $\text{C}_{26}\text{H}_{31}\text{N}_3\text{O}_8\text{S}$ : C, 57.24; H, 5.73; N, 7.70. Found: C, 57.29; H, 5.86; N, 7.59.

3-[[*N*-(*t*-Butoxycarbonyl)methylamino]methyl]-6-oxo-3,4,5,6-tetrahydro-1*H*-azepino[5,4,3-*cd*]indole (**10**).

A mixture of compound **8** (4.85 g, 8.9 mmol), methanol (50 mL), Raney nickel (50% slurry in water, 5 g), and hydrazine hydrate (6.9 mL, 223 mmol) was stirred at  $23^\circ$  for 10 hours. Then the temperature was increased to  $50^\circ$ , four additional portions of hydrazine hydrate (1.4 mL each) were added in 1.5 hour intervals, and the mixture was stirred at  $50^\circ$  for 2 hours after the addition of the last portion. Filtration through Celite followed by concentration on a rotary evaporator gave an oily residue consisting of product **10** and its tosyl derivative **9**. Methanol (100 mL), water (10 mL), and potassium carbonate (3 g, 22 mmol) were added to this residue and the resultant mixture was heated under reflux and nitrogen atmosphere for 2 hours. Then the mixture was concentrated on a rotary evaporator, treated with water (25 mL), and extracted with dichloromethane (4 x 50 mL). The extract was washed with a saturated solution of sodium chloride, dried over magnesium sulfate, and concentrated. Flash chromatography (dichloromethane, then ethyl acetate) gave 1.75 g (59%) of product **10** as colorless crystals; mp  $139-142^\circ$ ;  $^1\text{H}$  NMR ( $45^\circ$ ):  $\delta$  1.32 (s, 9H), 2.86 (s, 3H), 3.2-3.9 (m, 5H), 6.82 (br s, exchangeable with deuterium oxide, 1H), 7.08 (s, 1H), 7.25 (t,  $J = 8$  Hz, 1H), 7.55 (d,  $J = 8$  Hz, 1H), 8.02 (d,  $J = 8$  Hz, 1H), 9.44 (br s, exchangeable with deuterium oxide, 1H);  $^{13}\text{C}$  NMR ( $45^\circ$ ):  $\delta$  28.4, 30.8, 36.8, 44.9, 52.0, 79.7, 115.7, 116.5, 121.8, 123.1, 123.6, 123.8, 124.8, 136.8, 156.2, 171.8.

Anal. Calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_3\text{O}_3 \cdot 1/2 \text{H}_2\text{O}$ : C, 63.89; H, 7.15; N, 12.42. Found: C, 64.04; H, 7.09; N, 12.47.

3-[(Methylamino)methyl]-6-oxo-3,4,5,6-tetrahydro-1H-azepino[5,4,3-*cd*]indole Hydrochloride (**11**•HCl).

A solution of compound **10** (1 g, 3 mmoles) in anhydrous ethyl acetate (15 mL) was treated with a solution of hydrogen chloride in ethyl acetate (3 M, 30 mL, 90 mmoles) and the resultant mixture was stirred at 23° for 10 hours. Then the colorless precipitate of **11**•HCl was filtered and washed with a small amount of absolute ethanol to give 0.6 g (73%). The ethanolic filtrate was concentrated and the resultant solid was crystallized from ethanol/methanol (1:1) to furnish an additional amount of **11**•HCl (75 mg, 9%); mp >300°. Product **11** was spectroscopically identical to the original sample obtained from Solvay Pharmaceuticals, Inc.

6-Oxo-3,4,5,6-tetrahydro-1H-azepino[5,4,3-*cd*]indole (**13**).

Treatment of methyl 1H-indole-4-carboxylate (**6**) with 2-nitroethyl acetate under the reported conditions [27] gave methyl 3-(2-nitroethyl)-1H-indole-4-carboxylate (**12**): yield 83%, mp 103-105° (lit. [27] yield 84%, mp 102-105°). Then a mixture of **12** (5.0 g, 20 mmoles), platinum dioxide (0.11 g, 0.5 mmole) in ethanol (95%, 60 mL) was stirred under an atmospheric pressure of hydrogen for 12 hours. Filtration followed by concentration of the solution and then crystallization of the residue from methanol gave compound **13**; yield 2.3 g (61%); mp 239-241° (lit. [27] yield 48%, mp 232-234°).

3,6-Dioxo-3,4,5,6-tetrahydro-1H-azepino[5,4,3-*cd*]indole (**14**).

A mixture of compound **13** (0.3 g, 1.6 mmoles), 2,3-dichloro-5,6-dicyanobenzoquinone (0.69 g, 3 mmoles), and tetrahydrofuran/water (9:1, 25 mL) was stirred under a nitrogen atmosphere at 23° for 24 hours. Then the mixture was treated with aqueous sodium hydrogen carbonate (10%, 200 mL) and extracted with ethyl acetate (5 x 25 mL). The extract was washed with solutions of sodium hydrogen carbonate and sodium chloride, dried over sodium sulfate, and concentrated. Silica gel chromatography (ethyl acetate/hexanes, 1:1; then ethyl acetate) gave compound **14** as colorless crystals; yield 0.23 g (71%); mp >300° (decomp.); <sup>1</sup>H NMR (dimethyl sulfoxide-*d*<sub>6</sub>): δ 3.93 (d, J = 4 Hz, 2H), 7.38 (t, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 1H), 7.93 (d, J = 8 Hz, 1H), 8.05 (bt, J = 4 Hz, 1H, exchangeable with deuterium oxide), 8.23 (s, 1H), 12.5 (bs, 1H, exchangeable with deuterium oxide); <sup>13</sup>C NMR (dimethyl sulfoxide-*d*<sub>6</sub>): δ 52.1, 116.0, 116.4, 122.6, 124.5, 124.7, 124.9, 132.0, 136.3, 169.0, 189.3.

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 66.00; H, 4.03; N, 13.99. Found: C, 65.93; H, 4.05; N, 13.90.

Methyl 1-Tosyl-1H-indole-4-carboxylate (**15**).

This compound was obtained by tosylation of **6** by using the procedure reported previously [29]. The crude product was triturated with ether/hexanes (2:3) and filtered to give colorless crystals; yield 85%; mp 133-135° (lit. [29] mp 133-134°).

Methyl 3-Bromoacetyl-1-tosyl-1H-indole-4-carboxylate (**16**).

A solution of compound **15** (2.4 g, 7.2 mmoles) in bromoacetyl bromide (8 mL, 92 mmoles) was cooled to 0° and treated slowly with aluminum chloride (2.9 g, 22 mmoles). The mixture was stirred at 23° for 2 hours and then poured onto ice. The resultant precipitate of **16** was filtered, washed with hydrochloric acid (5%) and water, and crystallized from 95% ethanol; yield 2.7 g (83%); mp 144-146°; <sup>1</sup>H NMR: δ 2.34 (s, 3H), 3.89 (s, 3H), 4.33 (s, 2H), 7.26 (d, J = 8 Hz, 2H), 7.42 (t, J =

8 Hz, 1H), 7.68 (d, J = 8 Hz, 1H), 7.81 (d, J = 8 Hz, 2H), 8.12 (d, J = 8 Hz, 1H), 8.24 (s, 1H); <sup>13</sup>C NMR: δ 21.6, 33.3, 52.3, 116.5, 119.8, 124.5, 125.5, 125.6, 126.5, 127.2, 130.4, 131.8, 134.0, 135.3, 146.4, 167.9, 187.8.

*Anal.* Calcd. for C<sub>19</sub>H<sub>16</sub>BrNO<sub>5</sub>S: C, 50.68; H, 3.58; N, 3.11. Found: C, 50.30; H, 3.57; N, 3.02.

3,6-Dioxo-1-tosyl-3,4,5,6-tetrahydro-1H-azepino[5,4,3-*cd*]indole (**17**).

A solution of compound **16** (2.4 g, 5.3 mmoles) in tetrahydrofuran (100 mL) was treated at 0° with aqueous ammonia (30%, 6 mL, 95 mmoles). The mixture was stirred at 23° for 1.5 hours and then concentrated on a rotary evaporator. Chromatography of the residue (ethyl acetate/hexanes) gave product **17**; yield 1.3 g (71%); mp 243-245° (decomp.); <sup>1</sup>H NMR: δ 2.39 (s, 3H), 4.09 (d, J = 6 Hz, 2H), 6.70 (bs, 1H, exchangeable with deuterium oxide), 7.32 (d, J = 8 Hz, 2H), 7.55 (t, J = 8 Hz, 1H), 7.86 (d, J = 8 Hz, 2H), 8.20-8.30 (m, 2H), 8.38 (s, 1H); <sup>13</sup>C NMR: δ 21.7, 52.6, 117.9, 120.4, 125.4, 126.0, 126.3, 127.3, 128.2, 130.5, 131.3, 134.1, 134.6, 146.6, 169.2, 188.5.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>S: C, 61.01; H, 3.98; N, 7.91. Found: C, 60.82; H, 3.99; N, 7.82.

Detosylation of **17** to **14**.

A mixture of compound **17** (0.06 g, 0.17 mmoles), potassium carbonate (0.06 g, 0.43 mmole), water (0.7 mL), and methanol (6 mL) was stirred at 23° for 30 minutes, and then poured into water (25 mL). Extraction with ethyl acetate (4 x 10 mL) was followed by workup and chromatography, as described above for **14**; yield 0.026 g (74%).

6-Oxo-3-tosyloxy-5,6-dihydro-1H-azepino[5,4,3-*cd*]indole (**18**).

Compound **17** (0.11 g, 0.32 mmole) was treated with a Wittig reagent derived from methyltriphenylphosphonium iodide (0.13 g, 0.32 mmole) under general conditions for the Wittig methylenation of ketones [30]. Standard workup followed by chromatography (ethyl acetate/hexanes, 1:1) gave 0.028 g (34%) of **18**; mp 180-185° (decomp.); <sup>1</sup>H NMR: δ 2.36 (s, 3H), 2.47 (s, 3H), 5.82 (d, J = 8 Hz, 1H), 7.00 (bd, J = 8 Hz, 1H, exchangeable with deuterium oxide), 7.21 (s, 1H), 7.26 (d, J = 8 Hz, 2H), 7.34 (t, J = 8 Hz, 1H), 7.38 (d, J = 8 Hz, 2H), 7.72 (d, J = 8 Hz, 2H), 7.90 (d, J = 8 Hz, 2H), 8.00 (d, J = 8 Hz, 1H), 8.02 (d, J = 8 Hz, 1H); hrms: (FAB, thioglycerol) calcd. for C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>H<sup>+</sup>: m/z 509.0841; observed m/z 509.0829.

3-Methylene-6-oxo-1-tosyl-3,4,5,6-tetrahydro-1H-azepino[5,4,3-*cd*]indole (**19**).

A methylenation reagent, prepared from zinc powder (0.6 g, 9.2 mmoles), dibromomethane (0.2 mL, 2.9 mmoles), and titanium tetrachloride (0.23 mL, 2.1 mmoles), in tetrahydrofuran (5 mL) by using a general procedure [28], was diluted with dichloromethane (1 mL), and the solution was added dropwise to a stirred solution of **17** (0.35 g, 1 mmole) in dichloromethane (30 mL) at 0° under a nitrogen atmosphere. The mixture was stirred at 23° for 3 hours and then quenched with aqueous sodium hydrogen carbonate (5%, 5 mL). Extraction with dichloromethane (4 x 25 mL) followed by drying of the extract over magnesium sulfate, concentration, and chromatography (ethyl acetate/hexanes, 1:4) gave 0.13 g (37%) of **19** as colorless crystals; mp 223-225° (decomp.); <sup>1</sup>H NMR: δ 2.34 (s, 3H), 3.97 (d, J = 6 Hz, 2H), 5.13 (s, 1H), 5.51 (s, 1H), 7.24 (d, J = 8 Hz, 2H), 7.44 (t, J = 8 Hz,

1H), 7.53 (br s, 1H, exchangeable with deuterium oxide), 7.76 (s, 1H), 7.78 (d, J = 8 Hz, 2H), 8.10 (d, J = 8 Hz, 1H), 8.15 (d, J = 8 Hz, 1H); <sup>13</sup>C NMR: δ 21.6, 48.0, 111.8, 117.2, 122.7, 122.9, 125.1, 125.9, 126.9, 127.1, 127.2, 130.1, 134.8, 134.9, 136.5, 145.6, 169.6.

Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S: C, 64.75; H, 4.58; N, 7.95. Found: C, 64.47; H, 4.69; N, 7.78.

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