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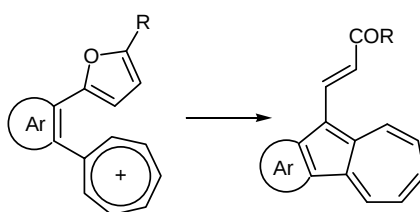
## SYNTHESIS OF 4-(AZULENO[*b*]INDOLYL)-3-BUTEN-2-ONES BY INTRAMOLECULAR TROPYLIUM ION-MEDIATED FURAN RING-UNRAVELLED REACTION

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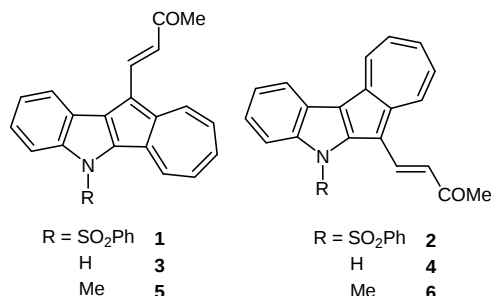
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**Abstract** – 4-(1-Benzenesulfonyl-6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (**1**) and 4-(1-benzenesulfonyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**2**) were synthesized from 1-benzenesulfonyl-3-(5-methylfuryl)-2-tropylioindole (**10**) and 1-benzenesulfonyl-2-(5-methylfuryl)-3-tropylioindole (**14**), respectively. The synthetic method is based on furan ring-unraveled reaction by the intramolecular electrophilic attack of the tropylium ion. 4-(6-Azuleno[1,2-*b*]indolyl)-3-buten-2-one (**3**) and 4-(11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**4**) could be easily obtained from **1** and **2**, respectively. Treatment of **3** and **4** with iodomethane gave *N*-methyl derivatives, 4-(1-methyl-6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (**5**) and 4-(1-methyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**6**), respectively, in moderated yield. The compounds, **1**, **2**, **3**, **4**, **5**, and **6**, which include the novel tetracyclic  $\pi$  conjugated azulene nuclei, are the azuleno[*b*]indole analogues of benzalacetone.

Azulene and its derivatives are of interest not only for their fundamental viewpoints,<sup>1</sup> but also their applied ones such as pharmaceutical, physiological activities and advanced materials.<sup>2</sup> Heteroaromatic fused ring systems containing azulene nuclei are also of interest and several kinds of such compounds have been reported.<sup>3</sup> We recently found a novel, efficient synthetic method of aromatic fused azulene derivatives having enone group from the corresponding aromatic compounds having a 2-furyl group and tropylium ion on their adjacent carbon atoms.<sup>4</sup>

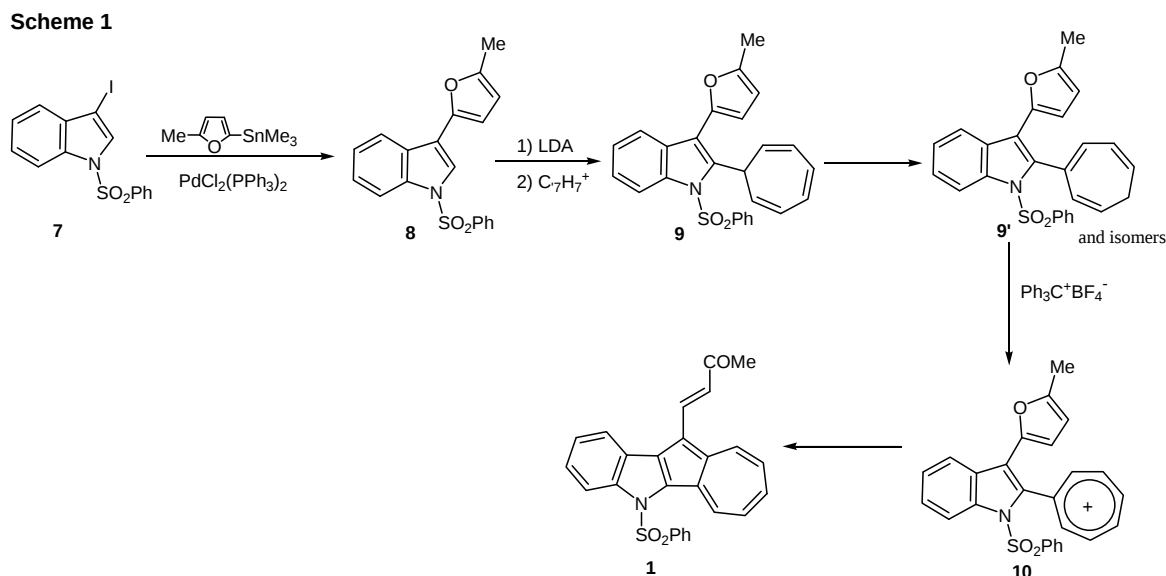


We wish to report on the synthesis of indole-fused azulenoind enones (**1**, **2**, **3**, **4**, **5**, and **6**), which are otherwise difficult to obtain, in order to see the scope and limitation of the reaction and to construct novel heteroaromatic-fused azulene nucleis.



### Synthesis of 4-(1-benzenesulfonyl-6-azuleno[1,2-b]indolyl)-3-buten-2-one (**1**)

The synthetic sequence leading to **1** from 3-iodo-1-benzenesulfonylindole (**7**)<sup>5</sup> is depicted in Scheme 1.



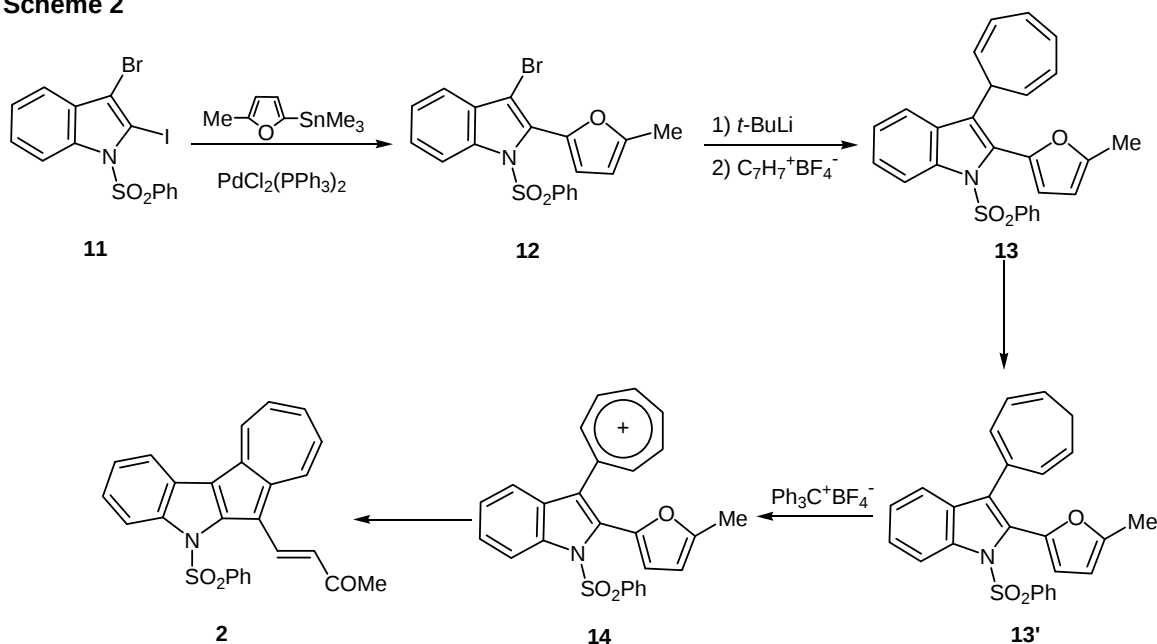
3-Iodo-1-benzenesulfonylindole (**7**) was treated with 5-methyl-2-trimethylstannylfuran<sup>6</sup> in the presence of bis(triphenylphosphine)palladium(II) dichloride to give 1-benzenesulfonyl-3-(5-methyl-2-furyl)indole (**8**) in 40% yield. Treatment of **8** with lithium diisopropylamide (LDA) at  $-78^\circ\text{C}$ , followed by addition of powdered tropylium tetrafluoroborate to give 1-benzenesulfonyl-2-cycloheptatrienyl-3-(5-methyl-2-furyl)indole (**9**) in 45% yield. In order to diminish the steric hindrance in the subsequent hydride-abstraction process, **9** was thermally isomerized by sigmatropic rearrangement to an isomeric mixture (**9'**).<sup>7</sup> The isomeric mixture (**9'**) was treated with an equimolar amount of triphenylmethyl tetrafluoroborate in dry dichloromethane at  $0^\circ\text{C}$  for 10 min, followed by addition of dry ether, to afford 1-benzenesulfonyl-3-(5-methyl-2-furyl)-2-tropylioidole (**10**) as black crystals in 60% yield. Refluxing

the acetonitrile solution ( $3.3 \times 10^{-3}$  M) of **10** for 1.5 h gave the desired 4-(1-benzenesulfonyl-6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (**1**), but the yield was only 27%. When 2,6-di-*t*-butylpyridine or methyltrimethoxysilane was used as an acid scavenger,<sup>8</sup> the yield of **1** markedly increased to 84% and 87%, respectively.

### Synthesis of 4-(1-benzenesulfonyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**2**)

4-(1-Benzenesulfonyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**2**), which is an isomer of **1**, could be successfully obtained from 1-benzenesulfonyl-2-(5-methyl-2-furyl)-3-tropylioindole (**14**) in a similar manner as described above. The synthetic sequence leading to **2** from 1-benzenesulfonyl-3-bromo-2-iodoindole (**11**)<sup>9</sup> is depicted in Scheme 2.

Scheme 2

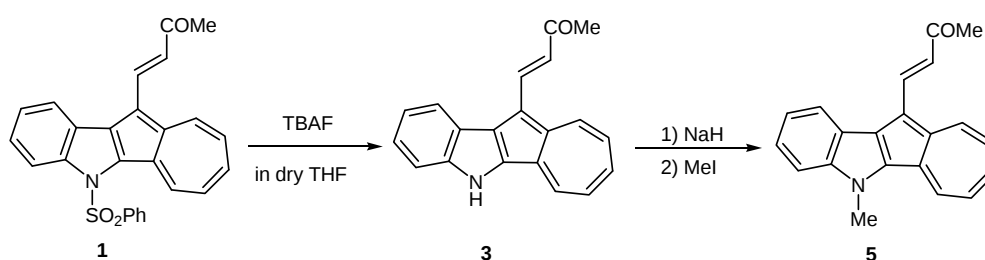


The palladium(II) catalyzed Stille reaction of **11** with 2-methyl-5-trimethylstannylfuran gave 1-benzenesulfonyl-3-bromo-2-(5-methyl-2-furyl)indole (**12**) in 50% yield. Then **12** was treated with *t*-butyllithium in dry cyclopentyl methyl ether at  $-78^\circ\text{C}$ , followed by addition of powdered tropylium tetrafluoroborate to give 1-benzenesulfonyl-3-cycloheptatrienyl-2-(5-methyl-2-furyl)indole (**13**), together with a small amount of by-products. Since the separating of the mixture of **13** and by-products was very difficult, the mixture was used for the next synthetic step without further purification. After thermal isomerization of **13** to **13'**, hydride abstraction using triphenylmethyl tetrafluoroborate gave 1-benzenesulfonyl-2-(5-methyl-2-furyl)-3-tropylioindole (**14**). When the acetonitrile solution of **14** was allowed to stand at ambient temperature in the presence of methyltrimethoxysilane gave the desired 4-(1-benzenesulfonyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**2**) in 67% yield.

**Synthesis of 4-(6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (3) and 4-(1-methyl-6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (5)**

Treatment of **1** with 1.1 molar equivalent of tetrabutylammonium fluoride<sup>10</sup> in dry THF under reflux for 2 h gave the debenzenesulfonated compound, 4-(6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (**3**) in 52% yield. *N*-Methyl derivative, 4-(1-methyl-6-azuleno[1,2-*b*]indolyl)-3-buten-2-one (**5**), was easily obtained from **3**. Thus, **3** was treated with sodium hydride in dry DMF, followed by addition of iodomethane, to afford **5** in 47% yield (Scheme 3).

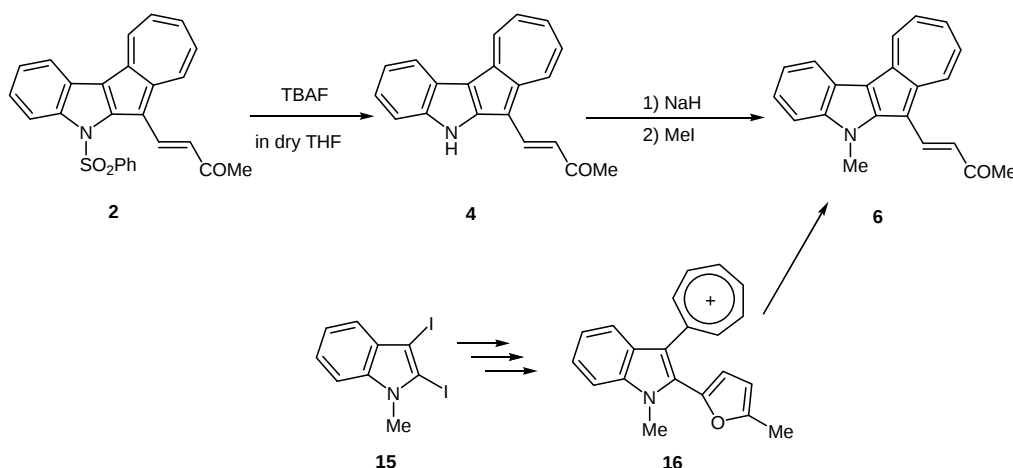
**Scheme 3**



**Synthesis 4-(11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (4) and 4-(1-methyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (6)**

In a similar manner as described above, 4-(11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**4**) and 4-(1-methyl-11-azuleno[2,1-*b*]indolyl)-3-buten-2-one (**6**) could be obtained from **2** and **4**, respectively. *N*-methyl derivative (**6**) was also obtained *via* 2-(5-methyl-2-furyl)-1-methyl-3-tropylioidole (**16**),<sup>10</sup> starting from 1-methyl-2,3-diiodoindole (**15**)<sup>11</sup> (Scheme 4).

**Scheme 4**



The structures of these azuleno[*b*]indole derivatives, **1**, **2**, **3**, **4**, **5**, and **6** were confirmed by their <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectra as well as an elemental analysis. Moreover, structure of **6** was established by X-ray crystallography.<sup>11</sup> The coupling constants between the olefinic protons on these azuleno[*b*]indole

derivatives are *ca.* 16 Hz, indicating that the carbonyl group and azuleno[*b*]indole ring are *trans* to each other. X-Ray crystallographical analysis of **6** also established to be *trans* configuration.<sup>11</sup>

Since the starting materials are readily available, the procedure is simple and easy, the yields are moderate, and, further, the formation of azuleno[*b*]indole nuclei is difficult by other synthetic methods, it is considered that this is a valuable synthetic methodology leading to azuleno[*b*]indolyl enones.

## EXPERIMENTAL

All melting points were determined with a Yanako MP-J3 melting point apparatuses and uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on Bruker Avance-500 spectrophotometer and chemical shift values are given in  $\delta$  (ppm) relative to internal tetramethylsilane. IR spectra were recorded on a Horiba FT-710 spectrophotometer.

### *Preparation of 1-benzenesulfonyl-3-(5-methyl-2-furyl)indole (8)*

A mixture of 3-iodo-1-benzenesulfonylindole (**7**) (6.0 g, 15.7 mmol), 2-methyl-5-trimethylstannylfuran (5.0 g, 20.3 mmol), bis(triphenylphosphine)palladium(II) (1.5 g, 2.14 mmol), and dry THF (40 mL) was refluxed for 20 h under a nitrogen atmosphere. The solvent was evaporated in vacuo and the residue was purified by column chromatography over alumina using hexane as eluent to give **8** in 40% yield (2.1 g); pale yellow prisms; mp 105-106 °C ;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 2.38 (3H, s, Me), 6.08 (1H, d, *J* = 2.5 Hz, furan ring), 6.54 (1H, d, *J* = 2.5 Hz, furan ring), 7.30- 7.36 (2H, m, indole ring), 7.41-7.50 (3H, m, benzene ring), 7.83-8.03 (5H, m, benzene and indole ring);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 13.6, 107.3, 107.4, 113.8, 114.9, 120.9, 121.2, 123.8, 125.1, 126.8, 127.5, 129.3, 133.9, 135.3, 138.1, 146.2, 151.5; IR (KBr, cm<sup>-1</sup>) 3171, 3055, 2916, 1449, 1359, 1339, 1305, 1182, 1165, 1113, 1089, 949. Anal. Calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>3</sub>S: C, 67.64; H, 4.48. Found: C, 67.54; H, 4.52.

### *Preparation of 1-benzenesulfonyl-3-bromo-2-(5-methyl-2-furyl)indole (12)*

A mixture of 1-benzenesulfonyl-3-bromo-2-iodoindole (**11**) (3.00 g, 6.49 mmol), 2-methyl-5-trimethylstannylfuran (2.07 g, 8.44 mmol), bis(triphenylphosphine)palladium(II) (1.37 g, 1.95 mmol), and dry toluene (55 mL) was refluxed for 20 h under a nitrogen atmosphere. The solvent was evaporated in vacuo and the residue was purified by column chromatography over silica gel using hexane as eluent to give **12** in 50% yield (1.35 g); colorless needles; mp 114-116 °C ;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 2.37 (3H, s, Me), 6.18 (1H, d, *J* = 3.1 Hz, furan ring), 6.61 (1H, d, *J* = 3.1 Hz, furan ring), 7.34-7.50 (6H, m, benzene and indole rings), 7.67 (2H, d, *J* = 7.4, benzene ring), 8.23 (1H, d, *J* = 8.4, indole ring);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 13.8, 105.3, 107.2, 115.6, 115.7, 120.3, 124.6, 126.7, 126.9, 128.3, 128.9, 129.2, 133.8, 136.4, 138.0, 140.3, 154.1; IR (KBr, cm<sup>-1</sup>) 3109, 2924, 1580, 1445, 1377, 1343, 1181, 1013. Anal. Calcd for C<sub>19</sub>H<sub>14</sub>NO<sub>3</sub>SBr: C,

54.82; H, 3.39. Found: C, 55.02; H, 3.34.

***Preparation of 1-benzenesulfonyl-2-cycloheptatrienyl-3-(5-methyl-2-furyl)indole (9)***

To a solution of **8** (4.50 g, 13.5 mmol) in dry THF (110 mL) was added slowly 10.2 mL of lithium diisopropylamide (2.0 M solution in heptane/THF/ethylbenzene, 20 mmol) under a nitrogen atmosphere at  $-78^{\circ}\text{C}$ . The reaction mixture was stirred for 2 h at  $-78^{\circ}\text{C}$ . Then, powdered tropylium tetrafluoroborate (3.56 g, 20.3 mmol) was added in limited amounts. The mixture was allowed to warm to rt and stirred overnight. The reaction mixture was poured into 100 mL of aqueous ammonia (3%). The organic layer was separated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated in vacuo and the residue was purified by column chromatography over alumina using hexane as eluent to give **9** in 45% yield (2.6 g); colorless prisms; mp  $118\text{--}121^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.30 (3H, s, Me), 3.99 (1H, t,  $J = 5.3$  Hz, seven-membered ring), 5.61 (2H, dd,  $J = 5.3, 8.7$  Hz, seven-membered ring), 6.05 (1H, d,  $J = 3.2$  Hz, furan ring), 6.09–6.14 (2H, m, seven-membered ring), 6.43 (1H, d,  $J = 3.2$  Hz, furan ring), 6.63 (2H, dd,  $J = 3.1, 3.2$  Hz, seven-membered ring), 7.30–7.41 (4H, m, indole and benzene rings), 7.50–7.68 (3H, m, benzene ring), 7.84 (1H, d,  $J = 7.5$  Hz, indole ring), 8.30 (1H, d,  $J = 8.3$  Hz, indole ring);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 13.6, 37.6, 107.1, 112.1, 114.7, 115.4, 120.5, 123.1, 123.9, 124.0, 125.1, 126.7, 128.9, 129.1, 130.4, 133.7, 136.6, 138.5, 138.9, 145.2, 152.0; IR (KBr,  $\text{cm}^{-1}$ ) 3025, 2919, 1581, 1446, 1370, 1185, 729. Anal. Calcd for  $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{S}$ : C, 73.04; H, 4.95. Found: C, 72.86; H, 4.98.

***Preparation of 1-benzenesulfonyl-3-cycloheptatrienyl-2-(5-methyl-2-furyl)indole (13)***

To a solution of **12** (3.00 g, 7.20 mmol) in dry THF (115 mL) was added slowly 5.96 mL of *t*-butyllithium (1.45 M solution in pentane, 8.64 mmol) under a nitrogen atmosphere at  $-78^{\circ}\text{C}$ . The reaction mixture was stirred for 2 h at  $-78^{\circ}\text{C}$ . Then, powdered tropylium tetrafluoroborate (1.92 g, 10.8 mmol) was added in limited amounts. The mixture was allowed to warm to rt and stirred overnight. The reaction mixture was poured into 40 mL of aqueous ammonia (6%). The organic layer was separated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated in vacuo and the residue was purified by column chromatography over alumina using hexane as eluent to give **13** in 35% yield (1.09 g); reddish yellow oil. This oil is not pure, but was used for the next synthetic step;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.15 (3H, s, Me), 3.07 (1H, t,  $J = 5.3$  Hz, seven-membered ring), 5.58 (2H, t,  $J = 5.4$  Hz, seven-membered ring), 5.74 (2H, m, seven-membered ring), 5.93 (1H, d,  $J = 3.0$  Hz, furan ring), 6.11 (1H, d,  $J = 3.0$  Hz, furan ring), 6.17 (3H, m, benzene ring), 6.61 (4H, m, benzene and seven-membered rings), 7.08 (1H, dd,  $J = 7.3, 7.7$  Hz, indole ring), 7.20 (1H, dd,  $J = 7.5, 7.8$  Hz, indole ring), 7.48 (1H, d,  $J = 8.3$  Hz), 7.70 (1H, d,  $J = 7.9$  Hz).

***Thermal isomerization of 9 and 13 to 9' and 13', respectively***

The xylene solution of **9** was refluxed for 5 h. The solvent was evaporated in *vacuo* and the residue was subjected to short-chromatography over alumina to give the isomeric mixture **9'** in almost quantitative yield. In a similar manner, **13** was thermally isomerized to the isomeric mixture **13'**.

**Preparation of 1-benzenesulfonyl-3-(5-methyl-2-furyl)-2-tropylioindole (10)**

A solution of **9'** (600 mg, 1.40 mmol) in 5 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of triphenylmethyl tetrafluoroborate (660 mg, 2.00 mmol) in 5 mL of dry CH<sub>2</sub>Cl<sub>2</sub> at 0 °C and was stirred for 10 min. Then 200 mL of dry Et<sub>2</sub>O was added and stirred for 10 min. 1-Benzensulfonyl-3-(5-methyl-2-furyl)-2-tropylioindole (**10**), which was separated out as black precipitates, was collected by filtration and washed with dry ether; Yield: 88% (0.52 g). mp > 200 °C.  $\delta_{\text{H}}$  (500 MHz, CD<sub>3</sub>CN) 2.13 (3H, s, Me), 6.21 (1H, d,  $J$  = 3.3 Hz, furan ring), 6.80 (1H, d,  $J$  = 3.3 Hz, furan ring), 7.47-7.56 (5H, m, benzene and indole rings), 7.63-7.69 (2H, m, benzene ring), 7.94 (1H, d,  $J$  = 8.2 Hz, indole ring), 8.33 (1H, d,  $J$  = 8.2 Hz, indole ring), 9.06-9.14 (4H, m, tropylium ring), 9.45 (2H, d,  $J$  = 9.9 Hz, tropylium ring);  $\delta_{\text{C}}$  (125 MHz, CD<sub>3</sub>CN) 12.0, 108.3, 114.0, 122.2, 123.9, 126.1, 126.6, 127.4, 127.6, 128.7, 129.3, 130.9, 134.5, 134.9, 138.7, 143.1, 151.2, 153.8, 154.8, 156.2, 159.1.

**Preparation of 1-benzenesulfonyl-2-(5-methyl-2-furyl)-3-tropylioindole (14)**

The procedure described above was used yielding **14** (47%). Reddish-brown powders, mp > 300 °C.  $\delta_{\text{H}}$  (500 MHz, CD<sub>3</sub>CN) 2.22 (3H, s, Me), 6.12 (1H, d,  $J$  = 3.2 Hz, furan ring), 6.49 (1H, d,  $J$  = 3.3 Hz, furan ring), 7.40 (1H, d,  $J$  = 7.5 Hz, benzene ring), 7.54-7.62 (2H, m, indole ring), 7.72 (3H, m, benzene and indole rings), 8.31 (1H, d,  $J$  = 8.6 Hz, indole ring), 8.76-8.85 (6H, m, tropylium ring);  $\delta_{\text{C}}$  (125 MHz, CD<sub>3</sub>CN) 12.5, 108.0, 115.6, 124.8, 125.4, 126.2, 126.5, 126.9, 127.4, 129.0, 129.4, 132.2, 134.7, 136.8, 137.1, 138.7, 152.1, 152.8, 154.4, 156.0, 162.1.

**Preparation of 4-(1-benzenesulfonyl-6-azuleno[1,2-b]indolyl)-3-buten-2-one (1)**

A solution of **10** (240 mg, 0.467 mmol) and methytrimethoxysilane (448 mg, 3.29 mmol) in 140 mL of dry acetonitrile was refluxed for 1.5 h. The solvent was evaporated in *vacuo* and the residue was purified by column chromatography over silica gel and recrystallization from toluene-CH<sub>2</sub>Cl<sub>2</sub>. Yield: 46% (92 mg). Dark green needles, mp 174 °C (decomp).  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 2.48 (3H, s, Me), 6.93 (1H, d,  $J$  = 16.2 Hz, olefine), 7.11 (2H, dd,  $J$  = 6.8, 7.3 Hz, benzene ring), 7.32-7.40 (4H, m, benzene and seven-membered rings), 7.43 (1H, dd,  $J$  = 7.5, 7.8 Hz, indole ring), 7.50 (1H, m, seven-membered ring), 7.57 (1H, dd,  $J$  = 7.5, 8.3 Hz, indole ring), 7.77 (1H, m, seven-membered ring), 8.14 (1H, d,  $J$  = 7.8 Hz, indole ring), 8.35 (1H, d,  $J$  = 16.0 Hz, olefine), 8.48 (1H, d,  $J$  = 8.3 Hz, indole), 8.69 (1H, d,  $J$  = 9.8 Hz, seven-membered ring), 9.57 (1H, d,  $J$  = 9.8 Hz, seven-membered ring);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 27.8, 114.0,

118.0, 123.0, 125.2, 125.3, 126.5, 127.2, 128.4, 132.1, 133.7, 135.0, 135.2, 135.8, 136.4, 139.0, 139.1, 142.0, 145.8, 198.0. IR(KBr,  $\text{cm}^{-1}$ ) 1645, 1601, 1569, 1365, 1254, 1181, 744, 724. Calcd for  $\text{C}_{26}\text{H}_{19}\text{NO}_3\text{S}$ : C, 73.39; H, 4.50. Found: C, 73.30; H, 4.48.

**Preparation of 4-(1-benzenesulfonyl-11-azuleno[2,1-b]indolyl)-3-buten-2-one (2)**

The procedure described above was used yielding **2** (67%). Green needles, mp 171 °C (decomp).  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.62 (3H, s, Me), 6.64 (1H, d,  $J = 16.6$  Hz, olefine), 6.93 (2H, dd,  $J = 4.4, 7.5$  Hz, benzene ring), 7.39 (1H, dd,  $J = 7.4, 7.5$  Hz, benzene ring), 7.43-7.49 (4H, m, indole and seven-membered rings), 7.63 (2H, d,  $J = 8.5$  Hz, benzene ring), 7.75 (1H, dd,  $J = 9.8, 9.9$  Hz, seven-membered ring), 8.02 (1H, d,  $J = 6.5$  Hz, indole ring), 8.42 (1H, d,  $J = 9.0$  Hz, indole ring), 8.71 (1H, d,  $J = 9.5$  Hz, seven-membered ring), 8.77 (1H, d,  $J = 16.6$  Hz, olefine), 8.83 (1H, d,  $J = 10.1$  Hz, seven-membered ring);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 26.0, 109.7, 116.7, 120.0, 120.4, 125.0, 125.1, 125.3, 126.3, 126.6, 126.7, 129.1, 130.5, 131.1, 133.6, 133.8, 136.1, 137.3, 137.7, 139.9, 142.4, 143.0, 147.9, 199.9. IR (KBr,  $\text{cm}^{-1}$ ) 1656, 1609, 1436, 1367, 1253, 1179, 758. Anal. Calcd for  $\text{C}_{26}\text{H}_{19}\text{NO}_3\text{S}$ : C, 73.39; H, 4.50. Found: C, 73.22; H, 4.61.

**Preparation of 4-(6-azuleno[1,2-b]indolyl)-3-buten-2-one (3)**

Tetra *n*-butylammonium fluoride (1.0 M THF solution, 0.52 ml, 0.52 mmol) was added to a solution of **1** (200 mg, 0.47 mmol) in 15 mL of dry THF under a nitrogen atmosphere. The mixture was refluxed for 1.5 h. Usual work-up afforded **3** as black needles. Yield: 52% (70 mg). Mp 253 °C (decomp).  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.55 (3H, s, Me), 7.20-7.24 (2H, m, indole ring), 7.30 (1H, d,  $J = 15.9$  Hz, olefin), 7.38 (1H, t,  $J = 7.6$  Hz, seven-membered ring), 7.55 (1H, dd,  $J = 7.2, 8.2$  Hz, seven-membered ring), 7.61-7.65 (2H, m, seven-membered ring), 8.36 (1H, d,  $J = 9.2$  Hz, indole ring), 8.46 (1H, d,  $J = 8.0$  Hz, seven-membered), 8.54 (1H, d,  $J = 15.8$  Hz, olefin), 8.66 (1H, br s, N-H), 8.70 (1H, d,  $J = 10.0$  Hz, indole ring). Anal. Calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}$ : C, 84.19; H, 5.30. Found: C, 84.20; H, 5.18.

**Preparation of 4-(11-azuleno[2,1-b]indolyl)-3-buten-2-one (4)**

The procedure described above was used yielding **4** (80%). Dark brown powders, mp 235-240 °C.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.53(3H, s, Me), 6.70 (1H, d,  $J = 15.8$  Hz, olefin), 7.39-7.58 (4H, m, indole and seven-membered ring), 7.63 (1H, d,  $J = 7.3$  Hz, indole ring), 7.70 (1H, d,  $J = 9.6, 9.7$  Hz, seven-membered ring), 8.23 (1H, d,  $J = 7.5$  Hz, indole ring), 8.38 (1H, d,  $J = 15.8$  Hz, olefin), 8.61 (1H, d,  $J = 10.0$  Hz, seven-membered ring), 8.75 (1H, d,  $J = 8.0$  Hz, seven-membered ring), 9.04 (1H, br s, N-H). Anal. Calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}$ : C, 84.19; H, 5.30. Found: C, 84.32; H, 5.22.

**Preparation of 4-(1-methyl-6-azuleno[1,2-b]indolyl)-3-buten-2-one (5)**

To a solution of **3** (17.0 mg, 0.06 mmol) in 5 mL of DMF, powdered NaH (50-72%, 3.50 mg) was added. The mixture was stirred at ambient temperature for 1 h and 12.0 mg (0.085 mmol) of iodomethane was added. The reaction mixture was allowed to stand at ca. 50 °C for 1 h. Usual work-up gave **5** as dark brown needles. Yield 47 % (8.4 mg). Mp 158-162 °C (decomp).  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.44 (3H, s, Me), 4.04 (3H, s, N-CH<sub>3</sub>), 7.03-7.07 (2H, m, seven-membered ring), 7.12 (1H, d,  $J$  = 15.6 Hz, olefin), 7.27 (2H, dd,  $J$  = 7.1, 7.9 Hz, seven-membered ring), 7.42-7.52 (3H, m, olefin and indole ring), 8.32-8.35 (2H, m, seven-membered ring), 8.38 (1H, d,  $J$  = 9.3 Hz, indole ring), 8.48 (1H, d,  $J$  = 10.2 Hz, indole ring);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 28.0, 31.8, 109.3, 115.8, 119.3, 119.4, 122.5, 123.4, 123.7, 124.8, 124.9, 126.2, 130.7, 131.0, 133.7, 134.9, 136.5, 137.3, 140.7, 146.1, 198.3. IR (KBr,  $\text{cm}^{-1}$ ) 2924, 16065, 1626, 1592, 1480, 1259, 1000, 942, 731. Anal. Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}$ : C, 84.25; H, 5.72. Found: C, 84.18; H5.80.

#### Preparation of 4-(1-methyl-11-azuleno[2,1-b]indolyl)-3-buten-2-one (**6**)

The procedure described above was used yielding **6** (66%). Dark brown powders, mp 132 °C.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 2.39 (3H, s, Me), 3.79 (3H, s, N-CH<sub>3</sub>), 6.64 (1H, d,  $J$  = 15.9 Hz, olefin), 7.29-7.40 (5H, m, indole and seven-membered ring), 7.52 (1H, dd,  $J$  = 9.7, 9.7 Hz, seven-membered ring), 7.99 (1H, d,  $J$  = 7.4 Hz, indole ring), 8.12 (1H, d,  $J$  = 15.9 Hz, olefin), 8.38 (1H, d,  $J$  = 10.0 Hz, seven-membered ring), 8.41 (1H, d,  $J$  = 9.5 Hz, seven-membered ring);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ) 27.9, 32.1, 105.5, 109.5, 118.0, 120.1, 120.9, 121.7, 123.7, 124.8, 126.3, 126.9, 129.8, 131.0, 133.3, 133.8, 135.0, 144.5, 145.4, 152.2, 197.6. IR (KBr,  $\text{cm}^{-1}$ ) 2919, 2359, 1630, 1524, 1250, 1169, 1142, 739, 697. Anal. Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}$ : C, 84.25; H, 5.72; N, 4.68. Found: C, 84.01; H, 5.72; N, 4.68.

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