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Stereoselective synthesis of subincanadine alkaloids framework

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Starting from *N*-tosyltryptamine and (*S*)-acetoxysuccinic anhydride, a facile synthesis of (–)-indolizinoindolone has been demonstrated as a basic structural outline of bioactive subincanadine alkaloids. Regioselective Grignard reaction with (*S*)-acetoxysuccinimide, stereoselective intramolecular cyclization to form (–)-indolizinoindolone skeleton and $TiCl_4$ induced condensation with acetaldehyde for stereoselective generation of exocyclic carbon–carbon double bond are the key features.

Keywords: (*S*)-Acetoxysuccinimide, Grignard reaction, stereoselective Pictet–Spengler cyclization, alane reduction, PCC-oxidation, condensation, indolizinoindolone

The structurally interesting cytotoxic alkaloids subincanadines A–G were isolated in 2002 by Ohsaki and co-workers from the bark of the Brazilian medicinal plant *Aspidosperma subincanum* (Figure 1)[1,2]. A few new synthetic routes to these target compounds have been reported in the recent literature[3–12]. Retrosynthetically, the corresponding tryptamine derived (*S*)-acetoxysuccinimide would be a potential precursor for total synthesis of subincanadine alkaloids. In continuation of our past two decades' studies on total synthesis of bioactive natural products from the cyclic anhydride and derivatives[13–17]; we herein report the stereoselective synthesis of framework of these important alkaloids from readily available starting materials (Scheme I).

Reaction of *N*-tosyltryptamine **1**[18] and (*S*)-acetoxysuccinic anhydride **2**[19] in refluxing acetic acid–toluene mixture delivered the corresponding (*S*)-acetoxysuccinimide **3** in 75% yield. Regioselective nucleophilic ring opening of anhydride **2** to form the corresponding intermediate succinanilic acid and subsequent intramolecular dehydrative cyclization took place in one pot. In unsymmetrical imide **3**, the carbonyl group adjacent to an acetoxy group is more reactive due to the electron withdrawing inductive effect. As expected, Grignard reagent regioselectively attacked on the more reactive imide carbonyl to deliver intermediate lactamol **4**. Lactamol **4** was immediately used for the next step without any purification due to stability issues. Such types of lactamols display a ring–chain type tautomerism[17] and unfortunately, acid-catalyzed intramolecular dehydrative cyclization to directly obtain the product **7** was not completely diastereoselective (by TLC). Hydroxy-lactamol **4** on treatment with acetic anhydride/triethylamine selectively formed the corresponding acetoxy-lactamol intermediate **5**; which was also used for the next step without purification and characterization, again due to stability issues. Acid-catalyzed Pictet–Spengler cyclization[20] of acetoxy-lactamol **5** was diastereoselective and exclusively provided the desired product **6** in 66% yield over three steps (~100% *de*, by NMR). Acid-catalyzed intramolecular cyclization of intermediate **5** took place *via* the corresponding flat iminium ion intermediate and incoming nucleophile approached from the less hindered β-side to form product **6**. The compound **6** on de-acylation followed by alane reduction of lactam carbonyl delivered the expected amino alcohol **8** in 60% yield over two steps. Direct treatment of compound **6** with alane also resulted in alcohol **8** in much higher yield (95%) avoiding the separate deacylation step. Alcohol **8** on PCC-oxidation provided an anticipated ketone **9** in 92% yield. $TiCl_4$ mediated condensation of ketone **9** with acetaldehyde under the Li and co-workers conditions[6] delivered the thermodynamically stable α,β-unsaturated ketone **10** in 73% yield. As expected, the vinylic proton in compound **10** was more deshielded (6.39 ppm) due to the five membered *peri*-intraction with a ketone carbonyl[12]. Stereoselective synthesis of planned subincanadine carbon framework (–)-indolizinoindolone **10** was accomplished in eight steps with 20% overall yield.

Initial reaction of methylmagnesium bromide with α,β-unsaturated ketone **10** in absence of CuI, unexpectedly provided the 1,4-addition product **11** in 62% yield instead of desired 1,2-addition product. In the above specified reaction, Grignard reagent approached from the less hindered β-side and followed a diastereoselective Michael addition pathway plausibly for the steric congestion reasons (~100% *de*, by NMR).

In summary, we have described synthesis of (–)-indolizinoindolone as a possible precursor of subincanadine alkaloids and their unnatural congeners and derivatives. We feel that the direct or reductive introduction of suitably substituted carbon chain on the ketone carbonyl carbon under appropriate reaction conditions will provide a stereoselective pathway to the target compounds.

Experimental Section

Melting points are uncorrected. The ^{1}H NMR spectra were recorded on 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded on 200 (50 MHz) or 400 (100 MHz) NMR spectrometer. Mass spectra were recorded on MS-TOF mass spectrometer; ESI-HRMS were obtained on Orbitrap (quadrapole plus ion trap) and TOF mass analyzer. The IR spectra were recorded on an FT-IR spectrometer. Column chromatographic separations were carried out on silica gel (60–120 or 230–400 mesh). Commercially available L-malic acid, tryptamine, MeMgBr, TFA, $LiAlH_4$, PCC, $TiCl_4$ and CH_3CHO were used. The tosyl protected tryptamine and (*S*)-acetoxysuccinic anhydride were prepared by using known procedures[18,19].

(*S*)-2,5-Dioxo-1-(2-(1-tosyl-1*H*-indol-3-yl)ethyl) pyrrolidine-3-yl acetate [(–)-3]

(*S*)-Acetoxysuccinic anhydride (**2**, 1.55 g, 9.55 mmol) was added to a stirred suspension of tryptamine **1** (3.00 g, 9.55 mmol) in toluene (30 mL) and the reaction mixture was stirred for 10 min. AcOH (60 mL) was added to the above reaction mixture and it was refluxed for 36 h. The reaction mixture was allowed to reach 25°C and concentrated *in vacuo*. EtOAc (100 mL) was added to the obtained residue and the organic layer was washed with

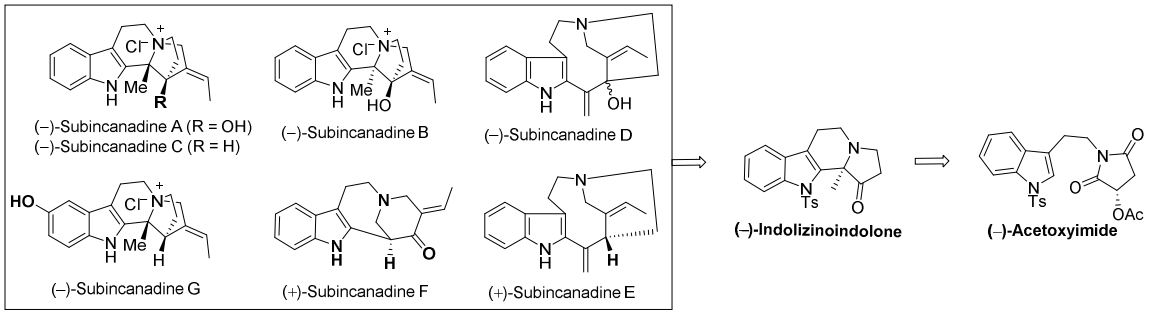
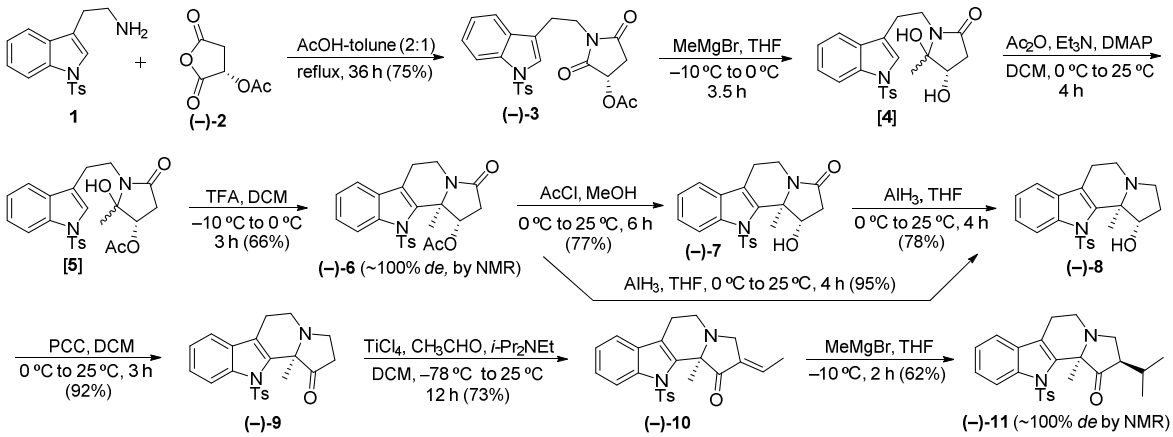


Figure 1 — Representative bioactive subincanadine alkaloids[1,2] and their concise retrosynthetic analysis



Scheme I — Stereoselective synthesis of basic skeleton of subincanadine alkaloids *via* Pictet–Spengler cyclization

saturated $NaHCO_3$ solution (3 × 25 mL), brine (50 mL), dried over anhyd. Na_2SO_4 and concentrated *in vacuo*. Purification of the obtained residue by column chromatography (silica gel, 60–120 mesh, PE–EtOAc, 70:30) yielded (*S*)-imide **3** as a faint yellow solid. Yield 3.20 g (75%). m.p.116–117°C. $[\alpha]_D^{25}$ –17.21° (*c* 0.6, $CHCl_3$); IR ($CHCl_3$): 1752, 1717, 1644, 1604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3 H), 2.33 (s, 3 H), 2.61 (dd, *J* = 20, 4 Hz, 1 H), 2.98 (t, *J* = 8 Hz, 2 H), 3.09 (dd, *J* = 20, 8 Hz, 1 H), 3.83 (t, *J* = 8 Hz, 2 H), 5.34 (dd, *J* = 8, 4 Hz, 1 H), 7.22 (d, *J* = 8 Hz, 2 H), 7.23 (t, *J* = 8 Hz, 1 H), 7.32 (t, *J* = 8 Hz, 1 H), 7.42 (s, 1 H), 7.57 (d, *J* = 8 Hz, 1 H), 7.75 (d, *J* = 8 Hz, 2 H), 7.96 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 21.5, 22.9, 35.6, 38.4, 67.4, 113.6, 118.3, 119.3, 123.2, 123.6, 124.8, 126.7, 129.8, 130.4, 135.0, 135.2, 144.9, 169.8, 173.0, 173.3; ESI-HRMS: *m/z* $[M + Na]^+$ Calcd for $C_{23}H_{22}N_2O_6SNa$: 477.1091. Found: 477.1083.

(1*S*, 11bR)-11b-Methyl-3-oxo-11-tosyl-2,3,5,6,11, 11b-hexahydro-1*H*-indolizino[8,7-*b*]indol-1-yl acetate [(–)-6]

To a stirred solution of (*S*)-acetoxysuccinimide **3** (2.00 g, 4.40 mmol) in THF (30 mL) under argon atmosphere was drop-wise added MeMgBr (11 mL, 22.02 mmol, 2 M solution in THF) at –10°C in 5 min. The reaction mixture was stirred at 0°C for 3.50 h and the reaction was quenched with saturated aq. NH_4Cl (25 mL). The aqueous layer was extracted with EtOAc (3 × 25 mL) and the combined organic layer was washed with brine (50 mL), dried over anhyd. Na_2SO_4 and concentrated *in vacuo* to afford diastereomeric mixture of lactamol **4** which was directly used for the next step. The above specified lactamol **4** was dissolved in CH_2Cl_2 (30 mL) and, Et_3N (1.63 mL, 11.68 mmol), Ac_2O (0.61 mL, 6.07 mmol) and DMAP (56 mg, 0.46 mmol) were slowly added at 0°C. The reaction mixture was stirred for 4 h allowing to reach 25°C. The reaction was quenched with water (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic layer was washed with brine (40 mL), dried over anhyd. Na_2SO_4 and concentrated *in vacuo*. The obtained diastereomeric mixture of lactamol acetate **5** was again directly used for next step. To a stirred solution of lactamol acetate **5** in CH_2Cl_2 (30 mL) was added TFA (1.50 mL, 13.2 mmol) at –10°C and the reaction mixture was stirred for 3 h allowing to reach 0°C. The reaction was quenched with saturated aq. $NaHCO_3$ (15 mL) at 0°C and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed with brine (40 mL) and dried over anhyd. Na_2SO_4. Concentration of the organic layer *in vacuo* followed by purification of the obtained residue by column chromatography (silica gel, 60–120 mesh, PE–EtOAc, 50:50) afforded single diastereomer **6** as a yellow solid. Yield 1.22 g, 66%. m.p.70–72°C. $[\alpha]_D^{25}$ –117.72° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$): 1742, 1694, 1599 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3 H), 2.16 (s, 3 H), 2.32 (s, 3 H), 2.39 (dd, *J* = 18, 4 Hz, 1 H), 2.66 (dd, *J* = 16, 4 Hz, 1 H), 2.72 (dd, *J* = 20, 8 Hz, 1 H), 2.99 (ddd, *J* = 16, 8, 4 Hz, 1 H), 3.25 (dt, *J* = 12, 4 Hz, 1 H), 4.45 (dd, *J* = 12, 8 Hz, 1 H), 6.02 (dd, *J* = 8, 2 Hz, 1 H), 7.17 (d *J* = 8 Hz, 2 H), 7.25 (dt, *J* = 8, 4 Hz, 1 H), 7.31 (dt, *J* = 8, 4 Hz, 1 H), 7.36 (dd, *J* = 8, 2 Hz, 1 H), 7.49 (d, *J* = 8 Hz, 2 H), 8.01 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.9, 21.1, 21.5, 22.8, 34.3, 38.3, 66.1, 71.3, 115.5, 118.8, 120.5, 124.0, 125.8, 126.2, 128.9, 129.8, 135.9, 137.2, 137.7, 144.9, 169.8, 172.7; ESI-HRMS: *m/z* $[M + H]^+$ Calcd for $C_{22}H_{25}N_2O_5S$: 453.1479. Found: 453.1475.

(1*S*,11b*R*)-1-Hydroxy-11b-methyl-11-tosyl-1,2,5,6, 11,11b-hexahydro-3*H*-indolizino[8,7-*b*]indol-3-one [(–)-7]

To a stirred solution of acetate **6** (1.00 g, 2.21 mmol) in MeOH (20 mL) was drop-wise added AcCl (1.20 g, 15.48 mmol) at 0°C. Ice bath was removed and the reaction mixture was stirred at 25°C for 6 h and concentrated *in vacuo* to afford alcohol **7**. Purification of the obtained residue by column chromatography (silica gel, 60–120 mesh, EtOAc–PE, 60:40) afforded pure alcohol **7** as a white solid. Yield 698 mg, 77%. m.p.105°C. $[\alpha]_D^{25}$–72.58° (*c* 0.3, $CHCl_3$); IR ($CHCl_3$): 3500, 1682, 1602 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.85 (s, 3 H), 2.35 (s, 3 H), 2.63 (dd, *J* = 16, 4 Hz, 1 H), 2.72 (dd, *J* = 16, 4 Hz, 1 H), 2.80– 2.92 (m, 2 H), 3.12 (dt, *J* = 12, 4, 1 H), 4.02 (s, 1 H), 4.53 (dd, *J* = 12, 4 Hz, 1 H), 4.84 (ddd, *J* = 8, 8, 4 Hz, 1 H), 7.20 (d, *J* = 8 Hz, 1H), 7.25–7.35 (m, 2 H), 7.39 (d, *J* = 8 Hz, 1 H), 7.47 (d, *J* = 8 Hz, 2 H), 8.02 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.2, 21.5, 21.7, 33.6, 38.7, 67.2, 70.8, 115.4, 118.9, 120.7, 124.3, 125.8, 126.0, 128.0, 129.0, 135.2, 137.0, 139.2, 145.3, 170.4; ESI-HRMS: *m/z* $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_4S$: 411.1373. Found: 411.1369.

(1*S*, 11b *R*)-11b-Methyl-11-tosyl-2, 3, 5, 6, 11, 11b-hexahydro-1*H*-indolizino[8,7-*b*]indol-1-ol [(–)-8]

To a stirred slurry of $AlCl_3$ (170 mg, 1.31 mmol) in THF (10 mL) was added suspension of LAH (162 mg,

4.38 mmol) in THF (20 mL) at 0°C under argon atmosphere. The reaction mixture was stirred for 10 min and solution of lactam **7** (600 mg, 2.19 mmol) in THF (10 mL) was added drop-wise. The reaction mixture was stirred for 4 h at 25°C, quenched with saturated aq. Na_2SO_4 (2 mL), filtered through Celite pad, dried over anhyd. Na_2SO_4 and concentrated *in vacuo*. Purification of the obtained residue by column chromatography (silica gel, 230–400 mesh, EtOAc–PE, 80:20) afforded aminol **8** as a yellow solid. Yield 452 mg, 78%. m.p.163–165°C. $[\alpha]_D^{25}$–88.90° (*c* 0.6, $CHCl_3$). The compound **6** on treatment with alane using above procedure also directly resulted in alcohol **8** in 95% yield. IR ($CHCl_3$): 3422, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 3 H), 1.80–1.93 (m, 1 H), 2.10–2.20 (m, 1 H), 2.33 (s, 3 H), 2.55 (dd, *J* = 12, 4 Hz, 1 H), 2.57–2.65 (m, 1 H), 2.82 (t, *J* = 8 Hz, 1 H), 2.96 (ddd, *J* = 16, 12, 8 Hz, 1 H), 3.25–3.45 (m, 3 H), 4.75 (t, *J* = 8 Hz, 1 H), 7.17 (d, *J* = 8 Hz, 2 H), 7.20–7.30 (m, 2 H), 7.37–7.42 (m, 1 H), 7.48 (d, *J* = 8 Hz, 2 H), 7.95–8.03 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.4, 21.5, 22.2, 32.0, 41.0, 46.1, 65.2, 77.4, 115.2, 118.1, 118.6, 123.7, 125.0, 126.0, 129.4, 129.8, 136.3, 136.8, 141.5, 144.6; ESI-HRMS: *m*/*z* $[M + H]^+$ Calcd for $C_{22}H_{25}N_2O_3S$: 397.1580. Found: 397.1580.

(*R*)-11b-Methyl-11-tosyl-2,3,5,6,11,11b-hexahydro-1*H*-indolizino[8,7-*b*]indol-1-one [(–)-9]

To a solution of compound **8** (450 mg, 1.13 mmol) in CH_2Cl_2 (15 mL) was added PCC (485 mg 2.26 mmol) over Celite (485 mg) at 0°C under argon atmosphere. The reaction mixture was stirred for 3 h allowing to reach 25°C. The reaction mixture was diluted with Et_2O (25 mL), vigorously stirred for 30 min and filtered through Celite pad. The filtrate was dried over anhyd. Na_2SO_4 and concentrated *in vacuo*. Purification of the obtained residue by column chromatography (silica gel, 60–120 mesh, EtOAc–PE, 60:40) afforded compound **9** as a yellow solid. Yield 412 mg, 92%. m.p.167–169°C. $[\alpha]_D^{25}$–98.57° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$): 1761, 1601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 3 H), 2.03 (ddd, *J* = 16, 8, 4 Hz, 1 H), 2.32 (s, 3 H), 2.39 (dd, *J* = 20, 8 Hz, 1 H), 2.63 (dd, *J* = 18, 8 Hz, 1 H), 2.91 (dd, *J* = 18, 12 Hz, 1 H), 2.98 (dt, *J* = 8, 2 Hz, 1 H), 3.12 (ddd, *J* = 16, 12, 8 Hz, 1 H), 3.23 (dd, *J* = 16, 8 Hz, 1 H), 3.41 (ddd, *J* = 12, 8, 2 Hz, 1 H), 7.15 (d, *J* = 8 Hz, 2 H), 7.27 (t, *J* = 8 Hz, 1 H), 7.34 (t, *J* = 8 Hz, 1 H), 7.42 (d, *J* = 8 Hz, 1 H), 7.51 (d, *J* = 8 Hz, 2 H), 8.18 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 17.4, 21.5, 22.6, 33.8, 40.3, 42.4, 65.2, 115.8, 118.4, 120.0, 123.6, 125.5, 126.5, 129.4, 129.5, 133.5, 135.9, 137.9, 144.4, 206.1; ESI-HRMS: *m*/*z* $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_3S$: 395.1424. Found: 395.1419.

(*R*,*E*)-2-Ethylidene-11b-methyl-11-tosyl-2,3,5,6,11,11b-hexahydro-1*H*-indolizino[8,7-*b*]indol-1-one [(–)-10]

Stirred solution of compound **9** (350 mg, 0.88 mmol) in anhydrous CH_2Cl_2 (10 mL) was cooled to –78°C and $TiCl_4$ (1.06 mL, 1.06 mmol, 1 M solution in CH_2Cl_2) was added drop-wise. The mixture was stirred at –78°C for 5 min and diisopropylethylamine (200 µL, 1.144 mmol) was added slowly. The reaction mixture was stirred at –78°C for an additional 30 min and anhydrous acetaldehyde (123 µL, 2.64 mmol) in CH_2Cl (5 mL) was added drop-wise. The resulting mixture was stirred at –78°C for 2 h and then at 25°C for 10 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhyd. Na_2SO_4 and concentrated *in vacuo*. The obtained product was purified by column chromatography (silica gel, 60–120 mesh, EtOAc–PE, 60:40) to give the pure product **10** as a yellow solid. Yield 272 mg, 73%. m.p.82–83°C. $[\alpha]_D^{25}$–131.56° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$): 1720, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.63 (d, *J* = 8 Hz, 3 H), 1.91 (s, 3 H), 2.30 (s, 3 H), 2.65 (dd, *J* = 16, 8 Hz, 1 H), 3.14 (ddd, *J* = 16, 12, 8 Hz, 1 H), 3.26 (dd, *J* = 16, 8 Hz, 1 H), 3.40 (d, *J* = 16 Hz, 1 H), 3.47 (ddd, *J* = 16, 8, 4 Hz, 1H), 3.57 (d, *J* = 8 Hz, 1 H), 6.39 (tq, *J* = 8, 4 Hz, 1H), 7.09 (d, *J* = 8 Hz, 2 H), 7.24 (t, *J* = 8 Hz, 1 H), 7.30 (t, *J* = 8 Hz, 1 H), 7.40 (d, *J* = 8 Hz, 1 H), 7.47 (d, *J* = 8 Hz, 2 H), 8.11 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 17.6, 21.4, 22.6, 40.2, 46.6, 66.9, 116.1, 118.3, 120.4, 123.5, 125.4, 126.6, 129.2, 129.6, 131.5, 133.99, 134.03, 136.0, 138.1, 144.0, 195.7; ESI-HRMS: *m*/*z* $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_3S$: 421.1580. Found: 421.1577.

(2*R*,11b*R*)-2-Isopropyl-11b-methyl-11-tosyl-2,3,5,6,11,11b-hexahydro-1*H*-indolizino[8,7-*b*]indol-1-one [(–)-11]

To a stirred solution of compound **10** (60 mg, 0.142 mmol) in THF (10 mL) was drop-wise added MeMgBr (357 µL, 0.357 mmol, 1 M solution in THF) at –10°C under argon atmosphere. The reaction mixture was allowed to stir at 0°C for 2 h and the reaction was quenched with saturated aq. NH_4Cl (5 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL) and the

combined organic layer was washed with brine (20 mL) and dried over anhyd. Na_2SO_4. Concentration of organic layer *in vacuo* followed by column chromatography (silica gel, 60–120 mesh, EtOAc–PE, 60:40) gave pure product **11** as a white solid. Yield 38 mg, 62%. m.p.140–142°C. $[\alpha]_D^{25}$ –250.66° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$): 1732, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.53 (d, *J* = 8 Hz, 3 H), 0.88 (d, *J* = 8 Hz, 3 H), 1.87 (s, 3 H), 1.25–1.35 (m, 1 H), 2.30 (s, 3 H), 2.25–2.38 (m, 1 H), 2.53–2.62 (m, 2 H), 3.02 (t, *J* = 8 Hz, 1 H), 3.11 (ddd, *J* = 16, 12, 8 Hz, 1 H), 3.26 (dd, *J* = 16, 8 Hz, 1 H), 3.48 (ddd, *J* = 16, 8, 4 Hz, 1 H), 7.10 (d, *J* = 8 Hz, 2 H), 7.22 (t, *J* = 8 Hz, 1 H), 7.29 (t, *J* = 8 Hz, 1 H), 7.37 (d, *J* = 8 Hz, 1 H), 7.52 (d, *J* = 8 Hz, 2 H), 8.07 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 19.6, 20.6, 21.5, 23.2, 29.0, 40.4, 47.1, 52.2, 66.1, 116.4, 118.3, 121.3, 123.7, 125.4, 126.7, 129.3, 130.0, 133.8, 135.6, 138.0, 144.1, 208.5; ESI-HRMS: *m/z* $[M + H]^+$ Calcd for $C_{25}H_{29}N_2O_3S$: 437.1893. Found: 437.1892.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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