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# Transition-Metal-Free Stereospecific Oxidative Annulative Coupling of Indolines with Aziridines

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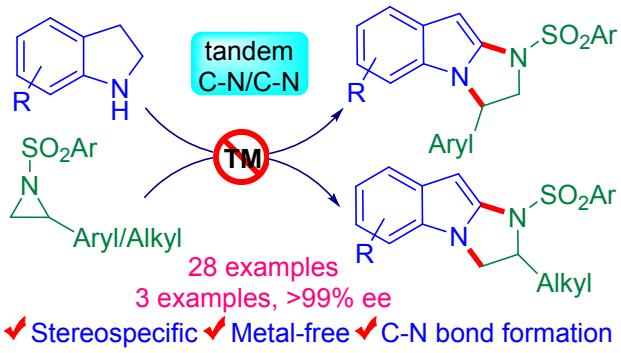
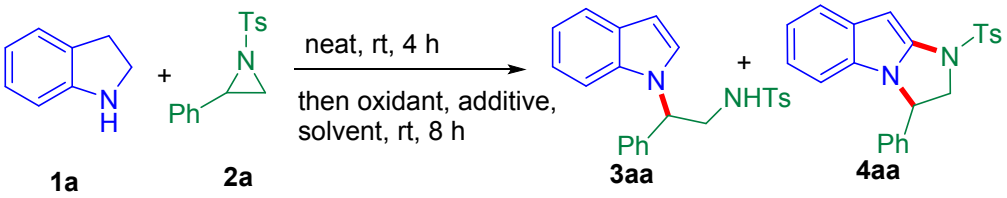



**ABSTRACT**: Tandem C-N bond formation for the oxidative annulation of indolines with aziridines is accomplished employing the combination of DDQ and NaOCl at ambient conditions. Optically active aziridine can be coupled with high enantiomeric purity (>99% *ee*). The substrate scope, stereocontrol with the enantioenriched substrate and scale up are the important practical advantages.

C-N bond formation[1] has attracted considerable attention due to the ubiquity of the aza-heterocycles in a broad spectrum of pharmaceuticals, functional materials and natural products.[2] In this realm, C-H functionalization of indoles[3] has witnessed impeccable growth, owing to the profuse prominence of the indole frameworks in myriads of bio-active molecules. Among them, imidazoindolines represent privileged structures due to their interesting biological properties.[4] Stereospecific syntheses of these fused structural frameworks in an atom and step-economical approach[5] would thus be valuable. While small ring heterocycles, due to their staple architecture and intrinsic ring strain, have propensity to undergo easy ring scissoring, and are thereby useful for the construction of diverse heterocycles.[6] Contextually,

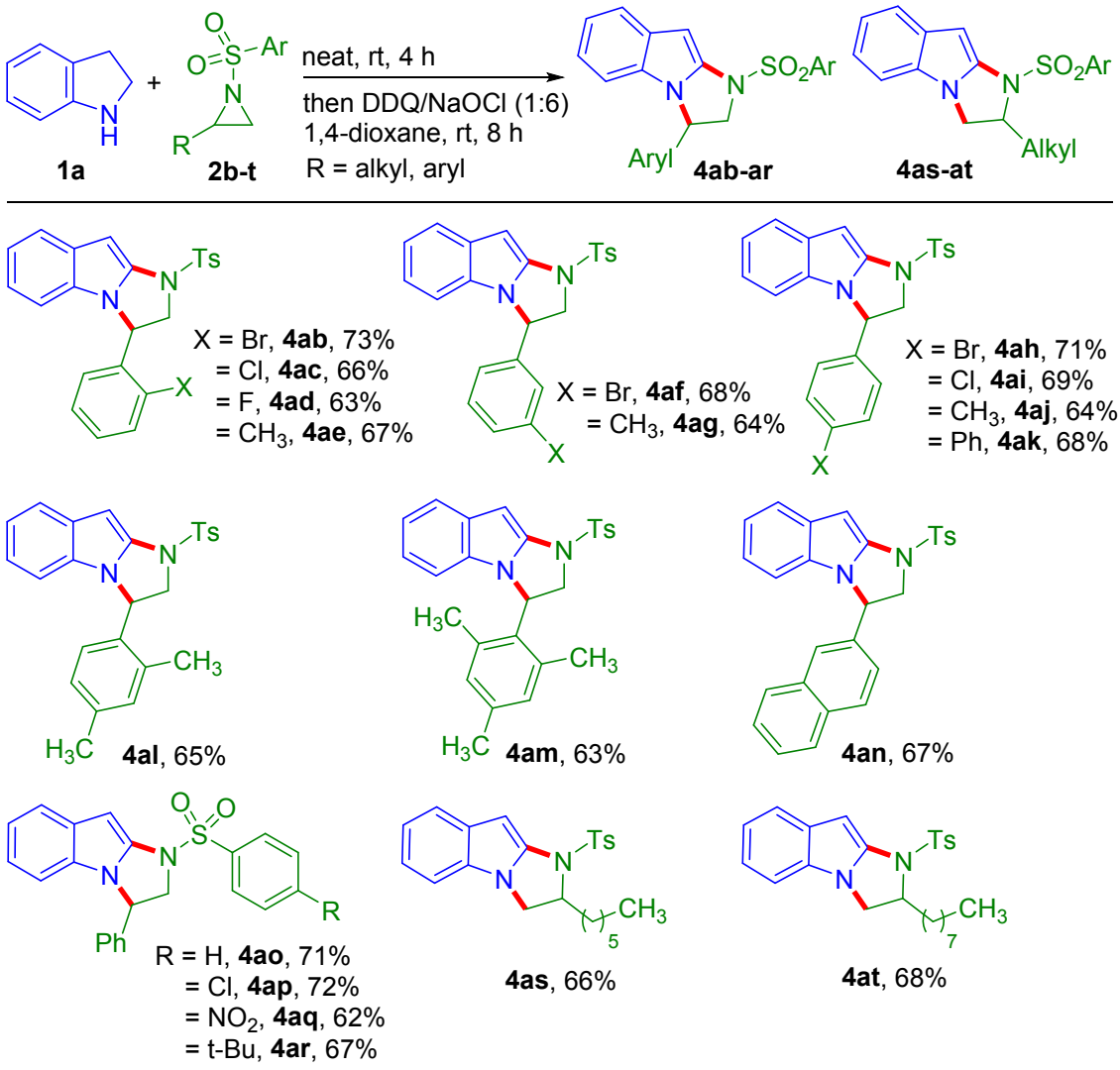
aziridines are versatile building blocks for the contemporary synthesis of *N*-heterocycles *via* a tandem C-N bond formation.[7,8] Consequently, development of synthetic strategies with these two heterocyclic units can lead a potential route to access fused structural scaffolds. Recently, NaOCl has been explored as an effective reagent for the oxidation for organic substrates,[9a] amidation of amines[9b] and C-N coupling of 3-alkylindoles with amino esters.[9c-d] Herein we report a stereospecific oxidative annulative coupling of indoles with N-sulfonyl aziridines using the combination of DDQ and NaOCl to furnish imidazoindoles at ambient conditions via a tandem C-N bond formation. The substrate scope, selectivity and transition-metal-free C-N bond formation[10] are the important features.

**Scheme 1. Optimization of the Reaction Conditions**




We began our optimization studies employing indoline **1a** and 2-phenyl-1-tosylaziridine **2a** as the test substrates using a series of oxidants, additives and solvents (see Scheme 1 and Table S1 in the SI). The heterocycle **4aa** was formed in 10% along with the ring opening **3aa** in 62%, when the neat substrates were stirred for 4 h at ambient conditions, and then 8 h with $PhI(OAc)_2$ as an oxidant and aqueous NaOCl solution as an additive in 1,4-dioxane. Subsequent screening of the oxidants led to an increase in the yield of **4aa** to 75% using DDQ, whereas *p*-benzoquinone produced inferior results. In contrast, $O_2$, TBHP and DTBP were not effective. In a set of additives studied, aqueous NaOCl, *t*-BuOCl and iodine, the former produced the best results. 1,4-Dioxane was found to be the solvent of choice, whereas THF, DMF, MeOH, 1,2-dichloroethane, toluene and $CH_3CN$ produced <57% yield. Control experiments confirmed that the combination of DDQ and NaOCl is essential to furnish the annulated **4aa**. Recrystallization of **4aa** gave single crystal, whose structure was determined using X-ray analysis (see SI).

**Scheme 2. Substrate Scope of Aziridines**[a-c]

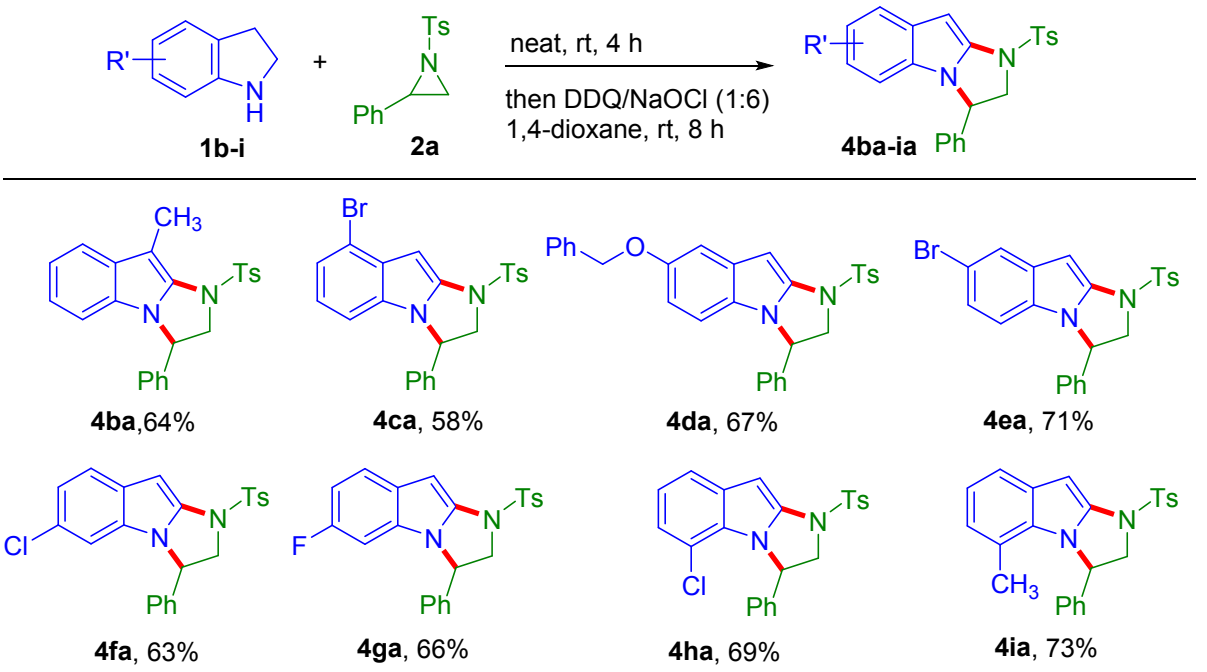



[a]Reaction conditions: **1a** (0.2 mmol), **2b-t** (0.24 mmol), neat, room temperature, 4 h; then DDQ (0.2 mmol), aq. NaOCl (4.2%, 2.1 mL), 1,4-dioxane (2 mL), room temperature, 8 h. [b]Isolated yield. [c]Accompanied a trace amount of **3** (see scheme 5 for a structure).

Having the optimized reaction conditions, we investigated the scope of the procedure for a series of aziridines **2b-t** with indoline **1a** as a standard substrate (Scheme 2). Aziridines having substitution at the 2-position of the aryl ring with bromo **2b**, chloro **2c**, fluoro **2d** and methyl **2e** groups gave the target heterocycles **4ab-ae** in 63-73% yields. Similar results observed with

aziridines bearing substitution at the 3-position of the aryl ring with bromo **2f** and methyl **2g** functionalities, giving **4af** and **4ag** in 68 and 64% yields, respectively. The reaction of aziridines containing substituents at the 4-position of the aryl ring with bromo **2h**, chloro **2i**, methyl **2j** and phenyl **2k** groups produced **4ah-ak** in 64-71% yields. Furthermore, di- and trimethyl substituted aziridines **2l-m** in the aryl ring participated to deliver **4al** and **4am** in 65 and 63% yields, respectively. In addition, 2-naphthyl aziridine **2n** was amenable to furnish **4an** in 67% yield. The reaction condition was extended to the coupling of aziridines bearing a varied *N*-sulfonyl aryl substituent. Aziridine having *N*-sulfonylphenyl **2o** produced **4ao** in 71% yield, whereas the reaction of aziridines having substitution at the 4-position of the *N*-sulfonyl aryl

**Scheme 3. Substrate Scope of Indolines**[a-c]

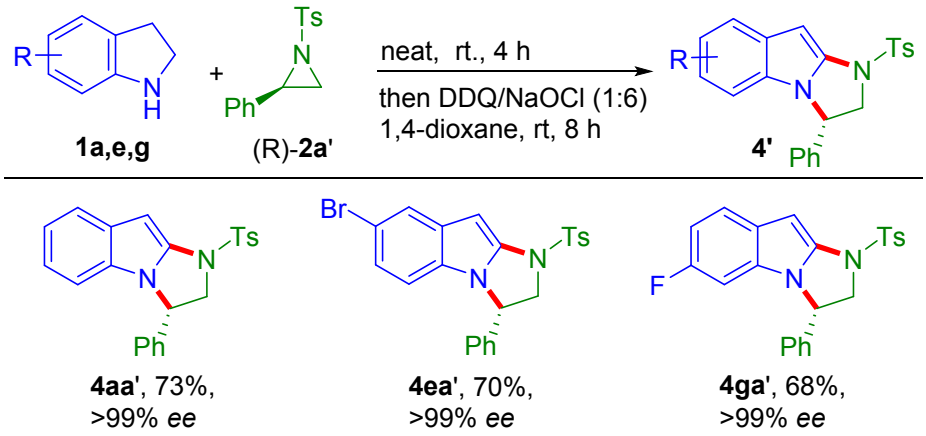



[a]Reaction conditions: **1b-i** (0.2 mmol), **2a** (0.24 mmol), neat, room temperature, 4 h; then DDQ (0.2 mmol), aq. NaOCl (4.2%, 2.1 mL), 1,4-dioxane (2 mL), room temperature, 8 h. [b]Isolated yield. [c]Accompanied a trace amount of **3** (see scheme 5 for a structure).

ring with chloro **2p**, nitro **2q** and *tert*-butyl **2r** functionalities, afforded **4ap-ar** in 62-72% yields. In addition, the reaction of 2-alkyl aziridines could be pursued and the ring opening occurred at the sterically less hindered C-3 position.[11] For examples, aziridines with hexyl **2s** and octyl **2t** substituents participated to produce **4as** and **4at** in 66 and 68% yields, respectively.

The scope of the procedure was further extended to the annulation of a series of substituted indolines **1b-i** with aziridine **2a** as a standard substrate (Scheme 3). The substrates bearing 3-methyl **1b**, 4-bromo **1c**, 5-benzyloxy **1d** and 5-bromo **1e** substituents delivered the target heterocycles **4ba-ea** in 58-71% yields, whereas the reaction of the substrates bearing 6-chloro **1f**, 6-fluoro **1g**, 7-chloro **1h** and 7-methyl **1i** functionalities afforded **4fa-ia** in 63-73% yields. These results suggest that the procedure can be employed for the annulative coupling of the broad range of indolines and aziridines.

**Scheme 4. Enantiospecific Synthesis**[a-c]

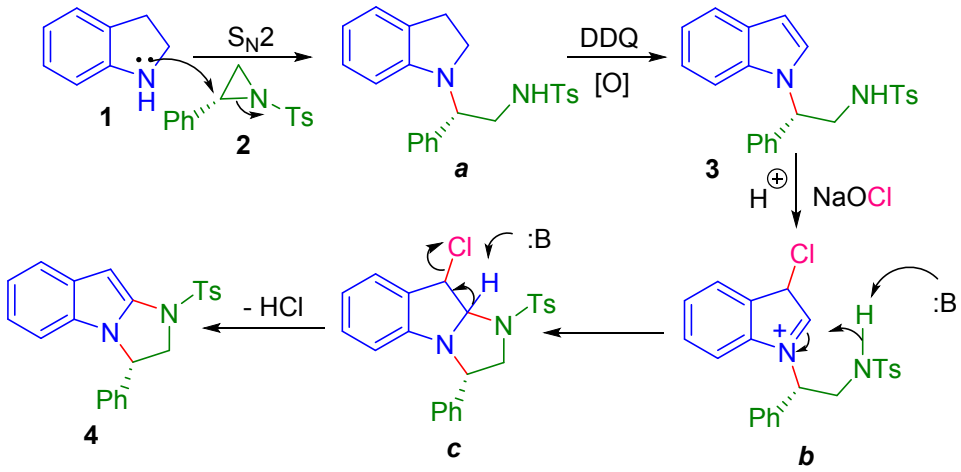



[a]Reaction conditions: **1a**,**e,g** (0.2 mmol), (R)-**2a′** (0.24 mmol), neat, room temperature, 4 h; then DDQ (0.2 mmol), aq. NaOCl (4.2%, 2.1 mL), 1,4-dioxane (2 mL), room temperature, 6 h. [b]Isolated yield. [c]Accompanied a trace amount of **3** (see scheme 5 for a structure).

To understand the stereochemical aspects, the reaction of **1a**, **1e** and **1g** studied using (*R*)-2-phenyl-1-tosylaziridine **2a′** as the representative substrates (Scheme 4). The reaction occurred

with high enantiomeric purity (>99% *ee*). For examples, the reaction of **1a** furnished **4aa′** in 73% yield and 99% *ee*. Similar enantiomeric purity (>99% *ee*) observed with indolines having 5-bromo **1e** and 6-fluoro **1g** substituents, providing **4ea′** and **4ga′** in 70% and 68% yields, respectively. The absolute configuration of **4aa′** was determined using a single crystal X-ray analysis (see SI). These results suggest that the ring opening of aziridine is stereospecific ($S_N2$) and the annulation can be realized in high enantiomeric purity.

**Scheme 5. Plausible Reaction Pathway**




To get insight into the reaction pathway, the coupling of **1a** with **2a** was performed as the representative substrates in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as well as 2,6-di-*tert*-butyl-4-methylphenol (BHT) (see Scheme S1a). As above, the reaction occurred, which suggests that a radical pathway is not likely. In addition, **1a** with **2a** under neat conditions for 4 h, followed by treatment with DDQ for 2 h in 1,4-dioxane, produced **3aa** in 81% yield (see Scheme S1b). The latter with NaOCl underwent annulation to produce **4aa** in 77% yield. These experimental results suggest that the stereospecific ring opening ($S_N2$) of aziridines with indolines can deliver ***a*** (Scheme 5).[12] The latter can oxidize using DDQ to furnish **3**, which can undergo an electrophilic chlorination using NaOCl[9] to give the iminium ion ***b*** that can lead to an intramolecular cyclization to furnish ***c***. Base promoted

dehydrochlorination of ***c*** can furnish the target heterocycle **4**, which can be reduced using $NaBH_3CN$ to yield imidazoindolines that are privileged structural scaffold with broad bio-active spectrum.[4] Scheme S2a presents some post synthetic applications for C-C coupling of **4** with organoboranes. The Pd-catalyzed Suzuki-coupling of **4ea** with 1-pyreneboronic acid produced **5** in 85% yield, while the borylation employing $B_2pin_2$ gave **6** in 73% yield. In addition, to reveal the scale up synthesis (3 mmol), the coupling of **1a** and **2a** was examined as the representative substrates. The reaction was effective to furnish the annulated target product in 66% yield (see Scheme S2b).

In conclusion, the stereospecific oxidative annulative coupling of indolines with aziridines is described employing DDQ as the oxidant and NaOCl as the electrophilic chlorinating reagent at ambient conditions. Enantiomeric purity, transition-metal-free tandem C-N bond formation and substrate scope are the important practical features.

## EXPERIMENTAL SECTION

**General Information**. Alkenes, (*R*)-(-)-2-phenylglycinol (99%), DDQ (98%), $Pd(dppf)Cl_2•CH_2Cl_2$ (>99%) and $Pd(PPh_3)_4$ (99%) of Aldrich, and NaOCl (4.2% w/v available chlorine) and chloramine-T hydrate (95%) of Merck were used as received. Indolines[13] and aziridines[14] were prepared according to reported procedure. SRL silica gel G/GF 254 plates were used for analytical TLC and SRL silica gel (60-120 mesh) was used for column chromatography. NMR spectra were recorded with Bruker Avance III 600 MHz and Ascend 400 MHz spectrometers using $CDCl_3$ as solvent and $Me_4Si$ as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in ppm and in Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra were collected on Perkin Elmer IR spectrometer. Q-Tof ESI-MS instrument (model HAB 273) was used for recording mass spectra. Optical rotations were

determined by using Rudolph autopol I automatic polarimeter. HPLC analysis was carried out using Waters-2489 with Daicel Chiralcel OD-H column using *iso*-propanol and hexane as an eluent. Single crystal X-ray data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation and the structure was solved by direct method using *SHELXL-16* (Göttingen, Germany).

**General Procedure for the Preparation of Indolines.**[13] To a solution of indole (3.0 mmol) in AcOH (15 mL) at 0 °C was added $NaBH_3CN$ (756 mg, 12.0 mmol) in portion-wise. The reaction was allowed to stir at room temperature for 8 h. After completion, aqueous NaOH (250 μL) was added slowly to the mixture at 0 °C and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed successively with brine (10 mL) and water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent produced a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent.

Indolines **1a-b**,[13a] **1c**,[13b] **1d**,[13a] **1e**,[13b] **1f -g**,[13c] **1h**[13d] and **1i**[13e] are known compounds and were synthesized according to the reported procedure. To show the purity, $^1$H NMR spectra are provided.

**4-Bromoindoline 1c**.[13b] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.49; purification on silica gel column chromatography using 1:19 ethyl acetate/hexane as eluent; thick liquid; yield 81% (478 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.88-6.79 (m, 2H), 6.53 (d, $J$ = 7.6 Hz, 1H), 3.88 (s, 1H), 3.59 (t, $J$ = 8.4 Hz, 2H), 3.05 (t, $J$ = 8.4 Hz, 2H).

**6-Chloroindoline 1f**.[13c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.51; purification on silica gel column chromatography using 1:19 ethyl acetate/hexane as eluent; thick liquid; yield 76% (348 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.10 (dd, $J$ = 8.4 Hz, 2.0 Hz, 1H), 6.50 (d, $J$ = 8.0 Hz, 1H), 3.75 (s, 1H), 3.55 (t, $J$ = 8.0 Hz, 2H), 3.01 (t, $J$ = 8.4 Hz, 2H).

**6-Fluoroindoline 1g**.[13c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.48; purification on silica gel column chromatography using 1:16 ethyl acetate/hexane as eluent; thick liquid; yield 73% (301 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.98 (t, *J* = 6.8 Hz, 1H), 6.37-6.30 (m, 2H), 3.82 (s, 1H), 3.59 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H).

**7-Chloroindoline 1h**.[13d] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.49; purification on silica gel column chromatography using 1:16 ethyl acetate/hexane as eluent; thick liquid; yield 84% (385 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.6 Hz, 1H), 3.97 (s, 1H), 3.62 (t, *J* = 8.4 Hz, 2H), 3.11 (t, *J* = 8.4 Hz, 2H).

**7-Methylindoline 1i**.[13e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.52; purification on silica gel column chromatography using 1:19 ethyl acetate/hexane as eluent; thick liquid; yield 79% (315 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 3.57 (t, *J* = 8.4 Hz, 2H), 3.06 (t, *J* = 8.4 Hz, 2H), 2.14 (s, 3H).

**General Procedure for Preparation of Aziridines.**[14] To a stirred solution of alkene (1.0 mmol) and benzyltriethylammonium chloride (0.05 mmol, 11.4 mg) in $CH_2Cl_2/H_2O$ (2:1, 15 mL) were added chloramine-T (1.1 mmol, 250.8 mg) and iodine (0.1 mmol, 25.4 mg) at room temperature. The stirring was continued for 24 h, and then treated with a saturated $Na_2S_2O_3$ (5 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent.

Aziridines **2a-b**,[14e] **2c**,[14c] **2d**,[14e] **2e**,[14c] **2f**,[14e] **2g**,[14b] **2h**,[14a] **2i-j**,[14b] **2k**,[14d] **2l**,[14c] **2m-n**,[14e] **2o-r**,[14a] and **2s-t**[14c] are known compounds and were synthesized according to the reported procedure. To show the purity, $^1$H NMR spectra are provided.

**2-Phenyl-1-tosylaziridine 2a**.[14e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.41; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as

eluent; colorless solid; yield 73% (199 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.30-7.27 (m, 3H), 7.22-7.20 (m, 2H), 3.79-3.76 (m, 1H), 2.99 (d, $J$ = 7.2 Hz, 1H), 2.43 (s, 3H), 2.39 (d, $J$ = 4.4 Hz, 1H).

**2-(2-Bromophenyl)-1-tosylaziridine 2b**.[14e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.38; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 65% (227 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J$ = 8.0 Hz, 2H), 7.52 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.36 (d, $J$ = 8.0 Hz, 2H), 7.23-7.11 (m, 3H), 4.00-3.97 (m, 1H), 3.04 (d, $J$ = 7.2 Hz, 1H), 2.45 (s, 3H), 2.27 (d, $J$ = 4.4 Hz, 1H).

**2-(2-Chlorophenyl)-1-tosylaziridine 2c**.[14c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.39; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 68% (208 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, $J$ = 8.0 Hz, 2H), 7.36-7.31 (m, 3H), 7.23-7.16 (m, 3H), 4.05-4.02 (m, 1H), 3.04 (d, $J$ = 7.6 Hz, 1H), 2.44 (s, 3H), 2.29 (d, $J$ = 4.4 Hz, 1H).

**2-(2-Fluorophenyl)-1-tosylaziridine 2d**.[14e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.36; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 63% (183 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J$ = 8.4 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.25-7.21 (m, 1H), 7.15-7.11 (m, 1H), 7.07-6.98 (m, 2H), 3.98-3.96 (m, 1H), 3.01 (d, $J$ = 7.2 Hz, 1H), 2.44 (s, 3H), 2.40 (d, $J$ = 4.4 Hz, 1H).

**2-(o-Tolyl)-1-tosylaziridine 2e**.[14c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 71% (203 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J$ = 8.4 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.19-7.09 (m, 4H), 3.88-3.85 (m, 1H), 2.99 (d, $J$ = 7.2 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.32 (d, $J$ = 4.4 Hz, 1H).

**2-(3-Bromophenyl)-1-tosylaziridine 2f**.[14e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.35; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 61% (213 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.41-7.38 (m, 1H), 7.35-7.33 (m, 3H), 7.16-7.15 (m, 2H), 3.73-3.70 (m, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.34 (d, *J* = 4.4 Hz, 1H).

**2-(m-Tolyl)-1-tosylaziridine 2g**.[14b] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.40; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 69% (198 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.02-7.00 (m, 2H), 3.75-3.72 (m, 1H), 2.96 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.38 (d, *J* = 4.8 Hz, 1H), 2.30 (s, 3H).

**2-(4-Bromophenyl)-1-tosylaziridine 2h**.[14a] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.38; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 72% (252 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.73-3.70 (m, 1H), 2.98 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.34 (d, *J* = 4.4 Hz, 1H).

**2-(4-Chlorophenyl)-1-tosylaziridine 2i**.[14b] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.37; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 65% (199 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27-7.26 (m, 1H), 7.25-7.24 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.74-3.71 (m, 1H), 2.98 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.34 (d, *J* = 4.4 Hz, 1H).

**2-(*p*-Tolyl)-1-tosylaziridine 2j**.[14b] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.41; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 74% (212 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz,

2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 3H), 3.75-3.72 (m, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 2.38 (d, J = 4.4 Hz, 1H), 2.30 (s, 3H).

**2-([1,1'-Biphenyl]-4-yl)-1-tosylaziridine 2k**.[14d] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.38; purification on silica gel column chromatography using 1:9 ethyl acetate/hexane as eluent; colorless solid; yield 59% (205 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.55-7.50 (m, 4H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.36-7.33 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.83-3.80 (m, 1H), 3.02 (d, *J* = 7.2 Hz, 1H), 2.44-2.42 (m, 4H).

**2-(2,4-Dimethylphenyl)-1-tosylaziridine 2l**.[14c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.35; purification on silica gel column chromatography using 1:9 ethyl acetate/hexane as eluent; colorless solid; yield 64% (192 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.98-6.95 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.84-3.81 (m, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 2.31 (d, *J* = 4.4 Hz, 1H), 2.27 (s, 3H).

**2-Mesityl-1-tosylaziridine 2m**.[14e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.32; purification on silica gel column chromatography using 1:9 ethyl acetate/hexane as eluent; colorless solid; yield 67% (211 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 2H), 3.87-3.84 (m, 1H), 2.94 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.30 (s, 6H), 2.23 (s, 3H), 2.17 (d, *J* = 4.8 Hz, 1H).

**2-(Naphthalen-2-yl)-1-tosylaziridine 2n**.[14e] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.37; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; colorless solid; yield 61% (197 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.80-7.72 (m, 4H), 7.48-7.45 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 3.94-3.91 (m, 1H), 3.07 (d, *J* = 7.2 Hz, 1H), 2.50 (d, *J* = 4.4 Hz, 1H), 2.42 (s, 3H).

**2-Phenyl-1-(phenylsulfonyl)aziridine 2o**.[14a] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.36; purification on silica gel column chromatography using 1:12 ethyl acetate and hexane as eluent; colorless solid; yield 63% (163 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.66-7.61 (m, 1H), 7.56-7.52 (m, 2H), 7.30-7.27 (m, 3H), 7.22-7.20 (m, 2H), 3.82-3.79 (m, 1H), 3.02 (d, *J* = 7.2 Hz, 1H), 2.42 (d, *J* = 4.4 Hz, 1H).

**1-((4-Nitrophenyl)sulfonyl)-2-phenylaziridine 2q**.[14a] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.29; purification on silica gel column chromatography using 1:9 ethyl acetate/hexane as eluent; orange solid; yield 51% (155 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 9.2 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.32-7.30 (m, 3H), 7.22-7.20 (m, 2H), 3.90-3.88 (m, 1H), 3.12 (d, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 4.8 Hz, 1H).

**1-((4-tert-Butyl)phenyl)sulfonyl)-2-phenylaziridine 2r**.[14a] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.32; purification on silica gel column chromatography using 1:9 ethyl acetate/hexane as eluent; colorless solid; yield 56% (176 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.30-7.27 (m, 3H), 7.23-7.22 (m, 2H), 3.81-3.79 (m, 1H), 2.99 (d, *J* = 7.2 Hz, 1H), 2.40 (d, *J* = 4.8 Hz, 1H), 1.34 (s, 9H).

**2-Hexyl-1-tosylaziridine 2s**.[14c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.36; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; thick liquid; yield 62% (174 mg); $^1$H NMR (400 MHz, $CDCl_3$), δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.74-2.68 (m, 1H), 2.64 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.06 (d, *J* = 4.8 Hz, 1H), 1.55-1.50 (m, 1H), 1.34-1.30 (m, 1H), 1.24-1.17 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H).

**2-Octyl-1-tosylaziridine 2t**.[14c] Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.36; purification on silica gel column chromatography using 1:12 ethyl acetate/hexane as eluent; thick liquid; yield 59% (182 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz,

2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.74-2.68 (m, 1H), 2.64 (d, *J* = 6.8 Hz, 1H), 2.44 (s, 3H), 2.06 (d, *J* = 4.8 Hz, 1H), 1.57-1.50 (m, 2H), 1.34-1.20 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H).

**Procedure for the Preparation of Chiral Aziridine**.[14e] To a stirred solution of (*R*)-(-)-2-phenylglycinol (1.0 mmol, 137 mg), TsCl (2.2 mmol, 420 mg) and DMAP (0.05 mmol, 6 mg) in dry $CH_2Cl_2$ (25 mL) at 0 °C was added $Et_3N$ (3.0 mmol). The resultant mixture was allowed to warm to room temperature and the stirring was continued for 24 h. The mixture was then treated with a saturated $NH_4Cl$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate (9:1) as the eluent.

**General Procedure for the Coupling of Indolines with Aziridines**. A mixture of indoline **1** (0.2 mmol) and aziridine **2** (0.24 mmol) was stirred for 4 h at room temperature. The resultant mixture was treated with 1,4-dioxane (2.0 mL), DDQ (45 mg, 0.2 mmol) and aq. NaOCl (4.2%, 2.1 mL, 1.2 mmol), and the stirring was continued for an additional 8 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (2 ×10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent.

**General Procedure for the Enantiospecific Annulative Coupling**. Indoline **1** (0.2 mmol) and (*R*)-2-phenyl-1-tosylaziridine **2a′** (0.24 mmol) were subjected to the above described reaction conditions. The enantiomeric purity was determined using chiral HPLC analysis.

**Scale-up Synthesis of 4aa**: Indoline **1a** (357 mg, 3 mmol) and 2-phenyl-1-tosylaziridine **2a** (983 mg, 3.6 mmol) were subjected to the reaction condition described in the general procedure to produce **4aa** in 66% yield (768 mg).

***N*-(2-(1H-Indol-1-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 3aa**. Analytical TLC on silica gel, 1:6 ethyl acetate/hexane; $R_f$ = 0.49; purification on silica gel column chromatography

using 1:9 ethyl acetate/hexane as eluent; colorless solid; mp 127-128 $^{o}$C; yield 81% (63 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J$ = 8.4 Hz, 2H), 7.63-7.61 (m, 1H), 7.30-7.26 (m, 5H), 7.13-7.06 (m, 6H), 6.57 (d, $J$ = 3.2 Hz, 1H), 5.59-5.56 (m, 1H), 4.49-4.45 (m, 1H), 3.89-3.83 (m, 1H), 3.76-3.69 (m, 1H), 2.44 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 143.9, 137.6, 136.7, 136.3, 130.0, 129.1, 128.8, 128.5, 127.1, 126.6, 124.5, 122.2, 121.2, 120.2, 109.9, 103.2, 59.0, 46.3, 21.7; FT-IR (KBr) 3283, 2922, 1598, 1493, 1458, 1326, 1308, 1158, 1092 cm$^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2S$: 391.1475, found: 391.1486.

**3-Phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4aa′.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.45; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 169-170 $^{o}$C; yield 73% (56 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, $J$ = 8.0 Hz, 2H), 7.45 (d, $J$ = 8.0 Hz, 1H), 7.22-7.18 (m, 1H), 7.15-7.11 (m, 4H), 6.98-6.94 (m, 1H), 6.82-6.78 (m, 3H), 6.50 (d, $J$ = 8.0 Hz, 1H), 6.23 (s, 1H), 5.25-5.21 (m, 1H), 4.57-4.52 (m, 1H), 3.93-3.88 (m, 1H), 2.31 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) δ 145.0, 141.8, 137.8, 133.3, 132.6, 130.5, 130.0, 129.2, 128.8, 127.8, 126.3, 120.56, 120.52, 109.5, 83.4, 61.2, 58.2, 21.7; FT-IR (KBr) 3053, 2918, 1616, 1597, 1566, 1493, 1454, 1422, 1361, 1306, 1168, 1106 cm$^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_2S$: 389.1318, found: 389.1318; $[\alpha]_D^{27}$ = +54.00 (c= 0.01, $CHCl_3$); HPLC: >99% ee [CHIRALCEL OD-H, hexane/$^{i}$PrOH = 90:10, flow rate: 1 mL /min, λ = 254 nm, $t_R$ = 23.67 min (minor), 31.97 min (major)].

**3-(2-Bromophenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ab**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 175-176 $^{o}$C; yield 73% (68 mg); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, $J$ = 8.4 Hz, 2H), 7.57-7.53 (m, 2H), 7.15-7.06 (m, 4H), 6.97-6.93 (m, 1H), 6.88 (t, $J$ = 7.2 Hz, 1H), 6.70 (d, $J$ = 8.0 Hz, 1H), 6.34 (s, 1H), 6.11-6.03

(m, 1H), 5.72-5.69 (m, 1H), 4.73-4.68 (m, 1H), 4.10-4.06 (m, 1H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 144.9, 141.8, 137.2, 133.1, 132.6, 130.3, 129.9, 129.7, 128.1, 127.7, 126.8, 122.6, 121.6, 120.8, 120.72, 120.70, 109.7, 83.8, 60.2, 57.2, 21.7; FT-IR (KBr) 3054, 2918, 1617, 1567, 1477, 1455, 1421, 1362, 1306, 1167, 1106 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}BrN_2O_2S$: 467.0423, found: 467.0426.

**3-(2-Chlorophenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ac**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane, $R_f$ = 0.43; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 172-173 °C; yield 66% (55 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 9.2 Hz, 1H), 7.19-7.12 (m, 3H), 7.08(t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.34 (s, 1H), 6.13 (d, *J* = 6.8 Hz, 1H), 5.76-5.73 (m, 1H), 4.72-4.67 (m, 1H), 4.11-4.08 (m, 1H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 141.8, 135.7, 133.1, 132.6, 131.8, 130.3, 129.9, 129.8, 129.4, 127.7, 127.4, 126.6, 120.8, 120.7, 120.6, 109.6, 83.8, 60.1, 54.9, 21.7; FT-IR (KBr) 3054, 2917, 1617, 1595, 1566, 1476, 1455, 1421, 1361, 1305, 1166, 1106 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}ClN_2O_2S$: 423.0929, found: 423.0929.

**3-(2-Fluorophenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ad**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.41; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; colorless solid; mp 176-177 °C; yield 63% (51 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09-7.04 (m, 2H), 6.96-6.91 (m, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.34-6.30 (m, 2H), 5.69-5.65 (m, 1H), 4.66-4.61(m, 1H), 4.13-4.09 (m, 1H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0 ($J_{C\text{-}F}$ = 245.3 Hz), 144.9, 141.7, 133.3, 132.7, 130.4, 130.1 ($J_{C\text{-}F}$ = 8.2 Hz), 129.9, 127.8, 127.0 ($J_{C\text{-}F}$ = 3.4 Hz), 125.4

($J_{C\text{-}F}$ = 12.8 Hz), 124.8 ($J_{C\text{-}F}$ = 3.6 Hz), 120.76, 120.71, 120.6, 115.8 ($J_{C\text{-}F}$ = 20.8 Hz), 109.4, 83.7, 60.2, 51.6 ($J_{C\text{-}F}$ = 4.8 Hz), 21.7; FT-IR (KBr) 3052, 2924, 1616, 1567, 1490, 1455, 1422, 1362, 1306, 1168, 1108 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}FN_2O_2S$: 407.1224, found: 407.1226.

**3-(*o*-Tolyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ae**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.45; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 176-177 $^oC$; yield 67% (53 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 4H), 7.07-7.03 (m, 1H), 6.91-6.87 (m, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.329-6.327 (m, 2H), 5.54-5.51 (m, 1H), 4.68-4.63 (m, 1H), 3.93-3.89 (m, 1H), 2.37 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 141.9, 135.5, 134.7, 133.3, 132.6, 131.0, 130.9, 130.6, 129.9, 128.3, 127.8, 126.8, 125.6, 120.58, 120.54, 120.50, 109.6, 83.5, 60.1, 55.1, 21.7, 19.2; FT-IR (KBr) 3052, 2921, 1616, 1597, 1566, 1477, 1455, 1425, 1361, 1306, 1168, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2S$: 403.1475, found: 403.1479.

**3-(3-Bromophenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4af**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.43; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 95-96 $^oC$; yield 68% (63 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.09-7.00 (m, 3H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.28-5.24 (m, 1H), 4.65-4.61 (m, 1H), 3.99-3.95 (m, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.2, 141.8, 140.3, 133.4, 132.5, 132.0, 130.8, 130.4, 130.0, 129.3, 127.8, 124.9, 123.3, 120.78, 120.71, 109.4, 83.8, 61.0, 57.5, 21.8; FT-IR (KBr) 3052, 2918, 1616, 1596, 1568, 1476, 1455, 1420, 1362, 1306, 1185,

1167, 1107, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}BrN_2O_2S$: 467.0423, found: 467.0423.

**3-(*m*-Tolyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ag**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.44; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 143-144 $^oC$; yield 64% (51 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.12-7.09 (m, 2H), 7.05-7.01 (m, 1H), 6.89-6.85 (m, 1H), 6.70-6.68 (m, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.30 (s, 1H), 5.27-5.23 (m, 1H), 4.63-4.59 (m, 1H), 3.99-3.94 (m, 1H), 2.39 (s, 3H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 141.9, 139.0, 137.7, 133.3, 132.5, 130.6, 129.9, 129.6, 129.0, 127.94, 126.96, 123.5, 120.49, 120.45, 109.6, 83.3, 61.2, 58.2, 21.7, 21.4; FT-IR (KBr) 3051, 2921, 1615, 1596, 1566, 1477, 1456, 1421, 1362, 1306, 1185, 1168, 1107, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2S$: 403.1475, found: 403.1478.

**3-(4-Bromophenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ah**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 171-172 $^oC$; yield 71% (66 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.31-7.29 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 6.93-6.89 (m, 1H), 6.68-6.66 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.30-5.27 (m, 1H), 4.65-5.61 (m, 1H), 3.98-3.94 (m, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 141.6, 137.0, 133.3, 132.6, 132.3, 130.4, 129.9, 127.9, 127.8, 127.7, 122.7, 120.74, 120.71, 109.4, 83.7, 61.0, 57.5, 21.7; FT-IR (KBr) 3051, 2922, 1617, 1596, 1566, 1477, 1455, 1421, 1361, 1306, 1185, 1166, 1071 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}BrN_2O_2S$: 467.0423, found: 467.0423.

**3-(4-Chlorophenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ai**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.41; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 142-143 °C; yield 69% (58 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.17-7.14 (m, 2H), 7.07-7.03 (m, 1H), 6.92-6.88 (m, 1H), 6.75-6.73 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.32-5.28 (m, 1H), 4.65-4.60 (m, 1H), 3.98-3.94 (m, 1H), 2.39 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 145.1, 141.7, 136.5, 134.6, 133.3, 132.7, 130.4, 129.9, 129.4, 128.6, 127.8, 127.5, 126.8, 120.75, 120.73, 109.4, 83.7, 61.1, 57.5, 21.7; FT-IR (KBr) 3063, 2922, 1708, 1567, 1492, 1456, 1362, 1306, 1168, 1090 cm$^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}ClN_2O_2S$: 423.0929, found: 423.0927.

**3-(*p*-Tolyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4aj**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.44; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 135-136 °C; yield 64% (51 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.04-7.01 (m, 3H), 6.89-6.85 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.29 (s, 1H), 5.28-5.25 (m, 1H), 4.62-4.57 (m, 1H), 3.97-3.93 (m, 1H), 2.39 (s, 3H), 2.31 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 144.9, 141.8, 138.7, 134.7, 133.3, 132.7, 130.6, 129.9, 129.86, 129.81, 127.8, 126.3, 120.5, 120.4, 109.6, 83.3, 61.2, 58.1, 21.7, 21.2; FT-IR (KBr) 3051, 2922, 1693, 1597, 1566, 1477, 1455, 1360, 1306, 1185, 1168, 1105 cm$^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2S$: 403.1475, found: 403.1480.

**3-([1,1'-Biphenyl]-4-yl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ak.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.46; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 198-199 °C; yield 68% (63 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.54-7.51 (m, 3H),

7.45-7.42 (m, 4H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.94-6.88 (m, 3H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.33(s, 1H), 5.38-5.34 (m, 1H), 4.68-4.63 (m, 1H), 4.05-4.00 (m, 1H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 145.0, 141.8, 141.7, 140.2, 136.7, 133.3, 132.6, 130.5, 129.9, 129.0, 127.9, 127.89, 127.81, 127.1, 126.7, 120.59, 120.56, 109.6, 83.4, 61.2, 58.0, 21.7; FT-IR (KBr) 3030, 2925, 1616, 1597, 1566, 1487, 1456, 1362, 1306, 1260, 1168, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{25}N_2O_2S$: 465.1631, found: 465.1631.

**3-(2,4-Dimethylphenyl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4al.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.44; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 146-147 °C; yield 65% (54 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.06-7.02 (m, 1H), 6.98 (s, 1H), 6.91-6.86 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.31(s, 1H), 6.27 (s, 1H), 5.51-5.47 (m, 1H), 4.65-4.60 (m, 1H), 3.89-3.85 (m, 1H), 2.37 (s, 3H), 2.26-2.22 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 141.9, 138.1, 134.5, 133.2, 132.6, 132.4, 131.8, 130.6, 129.9, 127.8, 127.5, 120.5, 120.47, 120.44, 109.7, 83.4, 60.2, 55.3, 21.7, 21.1, 19.0; FT-IR (KBr) 3052, 2922, 1615, 1596, 1565, 1477, 1455, 1361, 1306, 1185, 1168, 1103, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_2S$: 417.1631, found: 417.1632.

**3-Mesityl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4am**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.43; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 196-197 °C; yield 63% (54 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.27-7.25 (m, 2H), 7.02-6.98 (m, 1H), 6.90 (s, 1H), 6.84-6.80 (m, 1H), 6.67 (s, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 5.80 (t, *J* = 9.2 Hz, 1H), 4.58-4.53 (m, 1H), 4.01-3.96 (m, 1H), 2.39 (d, *J* = 2.4

Hz, 6H), 2.24 (s, 3H), 1.22 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 141.4, 138.5, 137.3, 136.7, 132.9, 132.7, 131.9, 130.6, 129.9, 127.9, 120.4, 120.3, 108.6, 83.1, 57.3, 53.8, 21.7, 20.9, 20.8, 18.2; FT-IR (KBr) 2922, 1615, 1457, 1425, 1363, 1306, 1170, 1090 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_2S$: 431.1788, found: 431.1790.

**3-(Naphthalen-2-yl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4an**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.47; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 183-184 °C; yield 67% (58 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 3H), 7.68-7.64 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.49-7.47 (m, 2H), 7.39 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.89-6.81 (m, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 5.50-5.46 (m, 1H), 4.74-4.69 (m, 1H), 4.09-4.05 (m, 1H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 141.9, 135.2, 133.3, 133.1, 132.6, 130.6, 129.9, 129.4, 128.1, 127.8, 126.8, 126.7, 125.8, 123.2, 120.6, 120.58, 120.56, 109.6, 83.6, 61.1, 58.4, 21.7; FT-IR (KBr) 3053, 2923, 1616, 1597, 1566, 1477, 1456, 1361, 1306, 1185, 1168, 1106, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{23}N_2O_2S$: 439.1475, found: 439.1478.

**3-Phenyl-1-(phenylsulfonyl)-2,3-dihydro-1H-imidazo[1,2-a]indole 4ao.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.44; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 174-175 °C; yield 71% (53 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.62-7.58 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.47-7.43 (m, 2H), 7.29-7.19 (m, 3H), 7.06-7.02 (m, 1H), 6.90-6.85 (m, 3H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H), 5.33-5.29 (m, 1H), 4.66-4.61 (m, 1H), 4.00-3.96 (m, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 141.7, 137.6, 135.5, 134.0, 133.3, 130.5, 129.4, 129.2, 128.9, 127.8, 126.3, 120.58, 120.56, 109.6, 83.4, 61.2, 58.2; FT-IR (KBr) 3060, 2924, 1616, 1566, 1477,

1454, 1362, 1307, 1220, 1171, 1090 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{18}N_2O_2S$: 375.1162, found: 375.1166.

**1-((4-Chlorophenyl)sulfonyl)-3-phenyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ap.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; colorless solid; mp 192-193 $^oC$; yield 72% (58 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.38-7.36 (m, 2H), 7.31-7.27 (m, 1H), 7.23-7.19 (m, 2H), 7.08-7.04 (m, 1H), 6.93-6.89 (m, 1H), 6.81-6.79 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.32 (s, 1H), 5.37-5.33 (m, 1H), 4.69-4.64 (m, 1H), 4.02-3.97 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 141.2, 140.7, 137.7, 134.0, 133.1, 130.5, 129.6, 129.3, 129.1, 128.8, 126.0, 120.8, 120.6, 109.7, 83.6, 61.3, 58.1; FT-IR (KBr) 3060, 2925, 1616, 1573, 1475, 1454, 1366, 1307, 1281, 1171, 1092 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{17}ClN_2O_2S$: 409.0772, found: 409.0777.

**1-((4-Nitrophenyl)sulfonyl)-3-phenyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4aq.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.40; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; orange solid; mp 194-195 $^oC$; yield 62% (51 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.96-6.92 (m, 1H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 5.40-5.37 (m, 1H), 4.75-4.70 (m, 1H), 4.09-4.05 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 150.8, 141.2, 140.4, 137.6, 132.8, 130.7, 129.2, 128.9, 128.8, 125.8, 124.4, 121.2, 120.9, 120.8, 109.8, 83.9, 61.5, 58.0; FT-IR (KBr) 3104, 2924, 1606, 1595, 1567, 1477, 1454, 1370, 1309, 1256, 1173, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{18}N_3O_4S$: 420.1013, found: 420.1012.

**1-((4-(*tert*-Butyl)phenyl)sulfonyl)-3-phenyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ar**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.44; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 193-194 $^oC$; yield 67% (57 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.89-6.86 (m, 3H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.32 (s, 1H), 5.35-5.31 (m, 1H), 4.65-4.60 (m, 1H), 3.99-3.95 (m, 1H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 141.9, 137.8, 133.4, 132.4, 130.5, 129.2, 128.9, 127.8, 126.39, 126.38, 120.52, 120.52, 120.4, 109.5, 83.2, 61.1, 58.2, 35.4, 31.1; FT-IR (KBr) 3057, 2963, 1617, 1593, 1566, 1476, 1455, 1361, 1307, 1266, 1131, 1085 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_2S$: 431.1788, found: 431.1791.

**2-Hexyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4as**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.43; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 113-114 $^oC$; yield 66% (52 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.53-7.50 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.08-7.05 (m, 2H), 7.01-6.99 (m, 1H), 6.27 (s, 1H), 4.50-4.44 (m, 1H), 3.81-3.77 (m, 1H), 3.70-3.67 (m, 1H), 2.34 (s, 3H), 2.06-1.98 (m, 1H), 1.90-1.81 (m, 1H), 1.44-1.25 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.7, 141.3, 133.9, 132.8, 130.8, 129.9, 127.5, 120.6, 120.5, 120.1, 108.7, 84.8, 66.2, 46.5, 35.8, 31.80, 29.1, 24.8, 22.7, 21.7, 14.2; FT-IR (KBr) 2922, 2859, 1562, 1457, 1428, 1306, 1185, 1167, 1090, 1008 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{29}N_2O_2S$: 397.1944, found: 397.1951.

**2-Octyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4at**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; colorless solid; mp 90-91 $^oC$; yield 68% (57 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.53-7.50 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09-7.04

(m, 2H), 7.02-6.99 (m, 1H), 6.27 (s, 1H), 4.50-4.44 (m, 1H), 3.81-3.77 (m, 1H), 3.70-3.67 (m, 1H), 2.34 (s, 3H), 2.06 – 1.98 (m, 1H), 1.90-1.81 (m, 1H), 1.45-1.27 (m, 12H), 0.88 (t, $J$ = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.7, 141.3, 134.0, 132.8, 130.8, 129.9, 127.5, 120.6, 120.5, 120.1, 108.7, 84.8, 66.2, 46.5, 35.8, 31.9, 29.57, 29.51, 29.3, 24.9, 22.7, 21.7, 14.2; FT-IR (KBr) 3051, 2924, 1618, 1597, 1562, 1478, 1457, 1361, 1306, 1276, 1167, 1089 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{25}H_{33}N_2O_2S$: 425.2257, found: 425.2260.

**9-Methyl-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ba**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.51; purification on silica gel column chromatography using 1:16 ethyl acetate/hexane as eluent; colorless solid; mp 130-131 $^{o}$C; yield 64% (53 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.54 (d, $J$ = 8.4 Hz, 3H), 7.279-7.277 (m, 1H), 7.18 (t, $J$ = 7.6 Hz, 2H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.09-7.05 (m, 1H), 6.93-6.89 (m, 1H), 6.80 (d, $J$ = 7.2 Hz, 2H), 6.45 (d, $J$ = 8.0 Hz, 1H), 4.87 (t, $J$ = 7.6 Hz, 1H), 4.78-4.73 (m, 1H), 4.15-4.10 (m, 1H), 2.55 (s, 3H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.6, 137.8, 137.2, 133.8, 133.3, 130.4, 130.0, 129.0, 128.4, 127.8, 126.3, 121.2, 119.8, 119.1, 109.6, 96.2, 63.3, 57.2, 21.7, 8.9; FT-IR (KBr) 2922, 1596, 1457, 1361, 1275, 1168, 1090, 1006 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2S$: 403.1475, found: 403.1477.

**8-Bromo-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ca**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.46; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; solid; colorless solid; mp 192-193 $^{o}$C; yield 58% (54 mg); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.73 (d, $J$ = 8.4 Hz, 2H), 7.24-7.16 (m, 4H), 7.15-7.11 (m, 2H), 6.77 (d, $J$ = 7.2 Hz 2H), 6.66 (t, $J$ = 8 Hz, 1H), 6.44 (d, $J$ = 8.4 Hz, 1H), 6.31 (s, 1H), 5.28-5.25 (m, 1H), 4.58-4.53 (m, 1H), 3.94-3.90 (m, 1H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.2, 142.2, 137.4, 133.7, 132.5, 130.6, 130.1, 129.3, 129.0, 127.8, 126.2, 123.5, 121.4, 113.8, 108.5, 83.6, 61.0, 58.4, 21.7; FT-IR (KBr) 3066, 2923, 1611, 1597, 1566,

1493, 1456, 1428, 1363, 1167 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}BrN_2O_2S$: 467.0423, found: 467.0426.

**7-(Benzyloxy)-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4da**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; colorless solid; mp 150-151 $^oC$; yield 67% (66 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 7.17-7.12 (m, 4H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.80-6.78 (m, 2H), 6.54 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.39 (d, *J* = 8.8 Hz, 1H), 6.17 (s, 1H), 5.20-5.17 (m, 1H), 4.98 (s, 2H), 4.55-4.50 (m, 1H), 3.89-3.85 (m, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 154.0, 145.0, 142.5, 137.76, 137.72, 134.0, 132.5, 130.0, 129.2, 128.8, 128.6, 127.9, 127.8, 127.6, 126.3, 125.8, 110.4, 110.2, 104.8, 83.5, 70.8, 61.1, 58.4, 21.7; FT-IR (KBr) 3063, 2921, 1621, 1576, 1494, 1478, 1451, 1363, 1289, 1168 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{27}N_2O_3S$: 495.1737, found: 495.1737.

**7-Bromo-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ea′**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.45; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 186-187 $^oC$; 70% (65 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.23-7.12 (m, 5H), 6.89 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.75-6.73 (m, 2H), 6.35 (d, *J* = 8.4 Hz, 1H), 6.17 (s, 1H), 5.24-5.21 (m, 1H), 4.58-4.53 (m, 1H), 3.93-3.88 (m, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.2, 142.8, 137.3, 134.9, 132.5, 130.0, 129.2, 129.1, 128.9, 127.8, 126.2, 123.2, 122.9, 113.8, 110.8, 82.8, 61.1, 58.3, 21.7; FT-IR (KBr) 3063, 2923, 1612, 1595, 1565, 1459, 1364, 1275, 1168 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}BrN_2O_2S$: 467.0423, found: 467.0427; $[\alpha]_D^{26}$ = +24.00 (c= 0.01, $CHCl_3$); HPLC: >99% *ee* [CHIRALCEL OD-H, hexane/$^i$PrOH = 90:10, flow rate: 1 mL /min, λ = 254 nm, $t_R$ = 18.56 min (minor), 25.91 min (major)].

**6-Chloro-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4fa**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.44; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp >200 $^oC$; yield 63% (53 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.32-7.28 (m, 1H), 7.25-7.21 (m, 4H), 7.01 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.84-6.82 (m, 2H), 6.54 (d, *J* = 2.0 Hz, 1H), 6.27 (s, 1H), 5.29-5.25 (m, 1H), 4.64-4.59 (m, 1H), 3.99-3.95 (m, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.2, 142.3, 137.3, 132.5, 131.8, 130.8, 130.0, 129.3, 129.0, 127.8, 126.1, 121.2, 121.1, 109.5, 83.3, 61.1, 58.3, 21.7; FT-IR (KBr) 3063, 2923, 1611, 1597, 1572, 1493, 1456, 1419, 1363, 1279, 1167 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}ClN_2O_2S$: 423.0929, found: 423.0928.

**6-Fluoro-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ga′**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.42; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; colorless solid; mp 188-189 $^oC$; yield 68% (55 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.41-7.38 (m, 1H), 7.32-7.27 (m, 1H), 7.24-7.21 (m, 4H), 6.85- 6.83 (m, 2H), 6.81-6.76 (m, 1H), 6.27 (s, 1H), 6.26-6.23 (m, 1H), 5.27-5.23 (m, 1H), 4.64-4.59 (m, 1H), 3.99-3.95 (m, 1H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 159.4 ($J_{C-F}$ = 235.65 Hz), 145.1, 142.05 ($J_{C-F}$ = 3.15 Hz), 137.2, 132.5, 130.3 ($J_{C-F}$ = 12.45 Hz), 130.0, 129.5, 129.3, 129.0, 127.8, 126.2, 121.0 ($J_{C-F}$ = 9.75 Hz), 108.7 ($J_{C-F}$ = 24 Hz), 96.6 ($J_{C-F}$ = 2.67 Hz), 83.2, 61.1, 58.2, 21.7; FT-IR (KBr) 3063, 2923, 1622, 1575, 1484, 1421, 1358, 1279 1167 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}FN_2O_2S$: 407.1224, found: 407.1228; $[\alpha]_D^{27}$ = +22.00 (c= 0.01, $CHCl_3$); HPLC: >99% *ee* [CHIRALCEL OD-H, hexane/$^i$PrOH = 90:10, flow rate: 1 mL /min, λ = 254 nm, $t_R$ = 17.63 min (minor), 28.30 min (major)].

**5-Chloro-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ha**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.43; purification on silica gel column chromatography using 1:11 ethyl acetate/hexane as eluent; colorless solid; mp 164-165 $^oC$; yield 69% (58 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.18-7.14 (m, 3H), 7.09-7.05 (m, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 2H), 6.33 (s, 1H), 5.87-5.85 (m, 1H), 4.50-4.46 (m, 1H), 4.18-4.15 (m, 1H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 142.7, 141.0, 135.3, 132.5, 130.0, 128.9, 128.0, 127.7, 127.4, 124.6, 121.5, 121.1, 118.9, 116.1, 83.2, 60.8, 59.4, 21.7; FT-IR (KBr) 3063, 2924, 1616, 1597, 1575, 1485, 1455, 1429, 1362, 1276, 1167 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{20}ClN_2O_2S$: 423.0929, found: 423.0931.

**5-Methyl-3-phenyl-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 4ia**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.46; purification on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent; colorless solid; mp 174-175 $^oC$; yield 73% (58 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.17-7.13 (m, 3H), 7.09-7.05 (m, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.53-6.50 (m, 2H), 6.32 (s, 1H), 5.67-5.64 (m, 1H), 4.53-4.49 (m, 1H), 4.16-4.13 (m, 1H), 2.36 (s, 3H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.8, 141.8, 141.3, 133.4, 132.6, 129.9, 129.8, 129.1, 128.0, 127.7, 124.6, 122.4, 120.9, 120.3, 118.2, 83.1, 60.9, 59.5, 21.7, 17.7; FT-IR (KBr) 3049, 2925, 1607, 1597, 1572, 1492, 1455, 1416, 1358, 1263, 1165, 1090 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2S$: 403.1475, found: 403.1477.

**3-Phenyl-7-(pyren-2-yl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 5**. Compound **4ea** (46 mg, 0.1 mmol), boronic acid (25 mg, 0.1 mmol), $Pd(PPh_3)_4$ (2.3 mg, 0.002 mmol), $Na_2CO_3$ (22 mg, 0.2 mmol) and $H_2O$ (50 mL) were stirred in toluene: EtOH (1:1, 2 mL) at 100 $^oC$ in an oil bath for 12 h under nitrogen atmosphere. After completion, the reaction mixture was cooled

to room temperature and passed through a short pad of celite using $CH_2Cl_2$ (10 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent to give **5.** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; $R_f$ = 0.46; grey solid; mp 151-152 $^oC$; yield 85% (50 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.23-8.17 (m, 3H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.10-8.05 (m, 2H), 8.01-7.97 (m, 3H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.76-7.75(m 1H), 7.36-7.29 (m, 5H), 7.16 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.01 (d, *J* = 6.8 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.40 (s, 1H), 5.43-5.39 (m, 1H), 4.71-4.67 (m, 1H), 4.07-4.03 (m, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 142.4, 138.9, 137.7, 133.6, 133.5, 132.6, 131.6, 131.1, 130.3, 130.1, 129.9, 129.3, 128.9, 128.8, 128.2, 127.9, 127.5, 127.25, 127.23, 126.4, 126.0, 125.9, 125.1, 125.0, 124.7, 124.6, 123.5, 122.5, 109.2, 83.5, 61.2, 58.4, 21.8; FT-IR (KBr) 2977, 2926, 1613, 1567, 1435, 1351, 1168, 1143, 1074 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{39}H_{29}N_2O_2S$: 589.1944, found: 589.1946.

**3-Phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-2,3-dihydro-1H-imidazo[1,2-a]indole 6**. Compound **4ea** (46 mg, 0.1 mmol), diboron (25 mg, 0.1 mmol), KOAc (20 mg, 0.2 mmol) and $Pd(dppf)Cl_2 \bullet CH_2Cl_2$(4 mg, 0.005 mmol) were stirred in THF (2 mL) at 100 $^oC$ in an oil bath for 12 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and passed through a short pad of celite using $CH_2Cl_2$ (15 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using 1:14 ethyl acetate/hexane as eluent to give **6**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane, $R_f$ = 0.48; colorless solid; mp 95-96 $^oC$; yield 73% (37 mg); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.24 (t, *J* = 1.6 Hz, 1H), 7.19-7.16 (m, 4H), 6.80 – 6.78 (m, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.35-5.31 (m, 1H), 4.65-4.61 (m, 1H), 4.02-3.98 (m, 1H), 2.37 (s, 3H), 1.32 (s, 12H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 145.0, 141.7, 137.8, 132.9, 132.4, 131.2, 129.9, 129.2, 128.7, 128.0, 127.8, 126.9, 126.1,

109.0, 83.7, 83.6, 61.3, 58.0, 25.0, 24.9, 21.7; FT-IR (KBr) 3039, 2924, 1739, 1573, 1470, 1456, 1432, 1364, 1311, 1168, 1090 $cm^{-1}$; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{32}BN_2O_4S$: 515.2170, found: 515.2184.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information having Table S1, Scheme S1-S2, crystallographic data for **4aa-4aa′**, HPLC chromatograms and NMR spectra of the starting materials and products are available free of charge on the ACS Publications website at DOI:

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### Notes

The author declares no competing financial interest.

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