Note

Site-Selective Rh-Catalyzed C-7 and C-6 Dual C-H Functionalization of Indolines: Synthesis of Functionalized Pyrrolocarbazoles

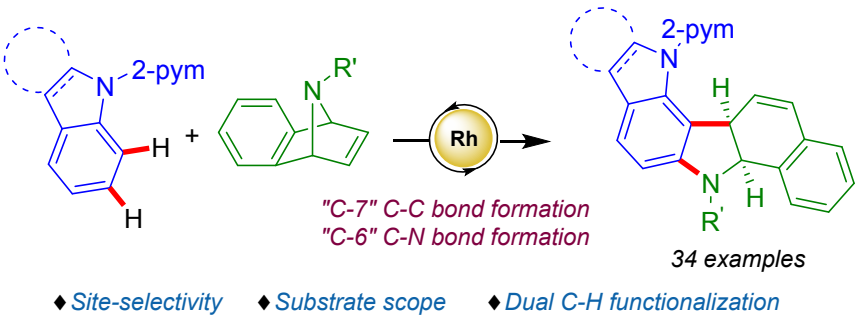
Sonbidya Banerjee, SUNDARAVEL VIVEK KUMAR, and Tharmalingam Punniyamurthy

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b03180 • Publication Date (Web): 09 Jan 2020

Site-Selective Rh-Catalyzed C-7 and C-6 Dual C-H Functionalization of Indolines: Synthesis of Functionalized Pyrrolocarbazoles

Sonbidya Banerjee, Sundaravel Vivek Kumar and Tharmalingam Punniyamurthy*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

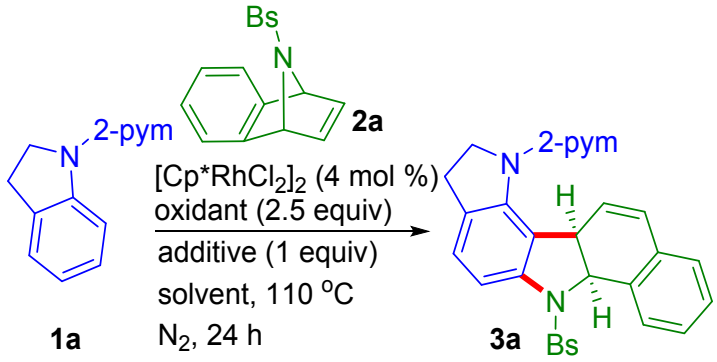


ABSTRACT: A site-selective dual C-7 and C-6 C-H functionalization of indolines with azabenzonorbornadienes has been accomplished using Rh-catalysis. The reaction affords a potential route towards pyrrolocarbazoles with broad scope and functional group tolerance.

Transition-metal-catalyzed direct C-H functionalization revolutionizes the transformation of simple substrates into complex molecules with structural diversity and atom economy.[1,2] Indole and its analogue are ubiquitous in natural products and pharmaceuticals.[3] Particularly, pyrrolo-/indolocarbazoles represents an appealing class of structural motifs[4] that exhibit interesting medicinal[5] and material properties (Figure S1).[6] Functionalization of C-2[7], C-3,[7] C-4[8] and C-7[9] C-H bonds of indole/indoline have thus been considerably investigated.[10] In contrast, the C-6 functionalization remains underdeveloped (Scheme S1a).[11] The groups of Yu, Baran, Shi and Frost demonstrated olefination,[11a] borylation,[11b] arylation[11c] and alkylation[11d] at C6 site, respectively. Contextually, a dual C-H functionalization of indolines would be valuable as it can lead to tandem C-C and carbon-heteroatom bond formation for the construction of complex structural scaffolds. In this line, azabenzonorbornadienes are realized as versatile building

blocks.[12] Herein, we report a dual C-7 and C-6 C-H functionalization of indolines with azabenzonorbornadienes using a Rh-catalysis to furnish pyrrolocarbazoles (Scheme S1b). The site-selectivity, substrate scope and functional group diversity are important practical features.

Scheme 1. Optimization of the Reaction Conditions[a]

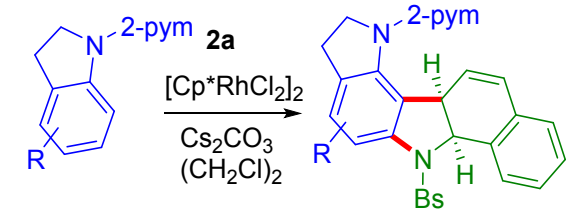


Our optimization studies commenced employing 1-(pyrimidin-2-yl)indoline **1a** and azabenzonorbornadiene **2a** as the model substrates (Scheme 1, Table S1). Delightfully, the reaction occurred to furnish pyrrolocarbazole **3a** in 48% yield when the substrates reacted using 4 mol % $[Cp^*RhCl_2]_2$, 2.5 equiv $Cu(OAc)_2 \cdot H_2O$ and 1 equiv K_2CO_3 for 24 h at 110 °C in 1,2-dichloroethane. Subsequent screening of the additives led to an enhance in the yield to 72% utilizing Cs_2CO_3, whereas KOAc, CsOPiv and CsOAc produced moderate results. The reaction utilizing $AgSbF_6$ inhibited the formation of **3a**, indicating cationic Rh**(**III**)** catalysis might not be involved. Further screening of the oxidants revealed that $Cu(OAc)_2 \cdot H_2O$ is the optimal oxidant. 1,2-Dichloroethane was found to be the solvent of choice. Aerobic condition as well as decreasing the temperature (100 °C) or the catalyst loading (2.5 mol %) led to drop the yield to <61% yield. Control experiments confirmed that the combination of the Rh-catalyst, oxidant and additive is crucial to produce **3a**. Moreover, directing groups, 3,4-dihydro-2*H*-pyrrole **I**, pyridinyl **II**, acetyl **III**, pivaloyl **IV** and *N*,*N*-dimethylcarbonyl **V**, were ineffective and the starting materials were recovered intact (Table S1).

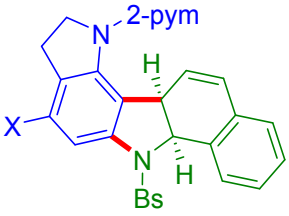
Having optimized the reaction conditions, the scope of the procedure was investigated for substituted indolines **1** utilizing **2a** as a standard substrate (Scheme 2). The substrates having

substitution at the 4-position of indoline with allyl **1b**, bromo **1c**, cyano **1d**, methoxy **1e** and phenyl **1f**, 3-chlorophenyl **1g** and 4-biphenyl **1h** groups underwent reaction to produce **3b-h** in 46-80% yields. In contrast, 5-substituted indolines **1i-k** were unsuccessful substrates, which might be due to steric hindrance near C6-site. However, a spiroindoline **1l** gave **3l** in 55% yield, whereas 1-(pyrimidin-2-yl)-1,2-dihydrobenzoindole **1m** and *N*-methyl-*N*-phenylpyrimidin-2-amine **1n** were found to be incompatible and formation of **3m** and **3n** was not observed.

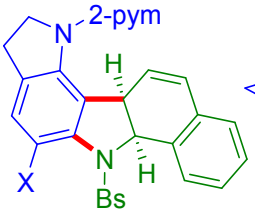
Scheme 2. Substrate Scope of Indolines 1 with 2a [a,b]



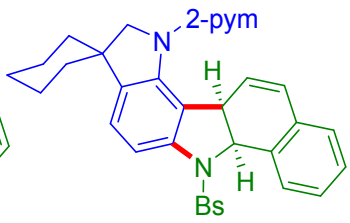
1b-n **3b-n**



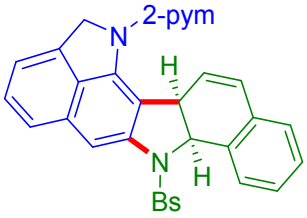
3b, X = allyl, 72%
3c, X = Br, 76%
3d, X = CN, 46%
3e, X = OMe, 80%
3f, X = Ph, 78%
3g, X = 3-ClC$_6$H$_4$, 67%
3h, X = 4-PhC$_6$H$_4$, 70%



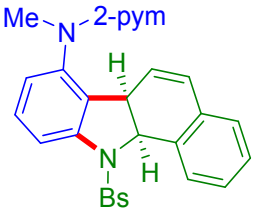
3i, trace (X=F)
3j, n.d. (X= Br)
3k, n.d (X=Me)



3l, 55%



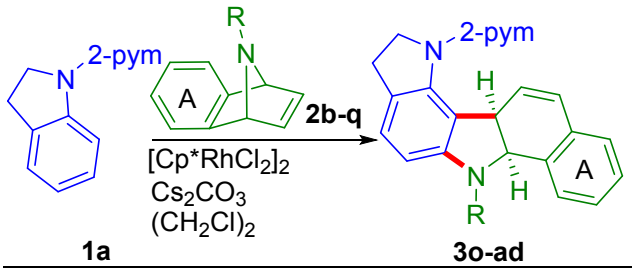
3m, n.d.

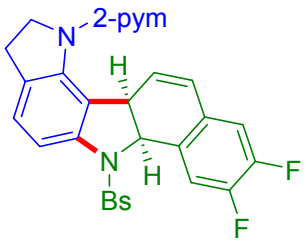


3n, n.d.

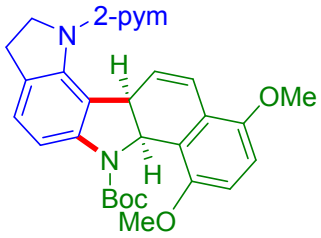
[a]Reaction conditions: **1b-n** (0.25 mmol), **2a** (0.3 mmol), [Cp*RhCl$_2$]$_2$ (4 mol %), Cu(OAc)$_2$·H$_2$O (0.63 mmol), Cs$_2$CO$_3$ (0.25 mmol), (CH$_2$Cl)$_2$ (2 mL), 110 °C, 24 h, N$_2$. [b]Isolated yield.

Scheme 3. Substrate Scope of Azabenzonorbornadienes 2 with 1a[a,b]

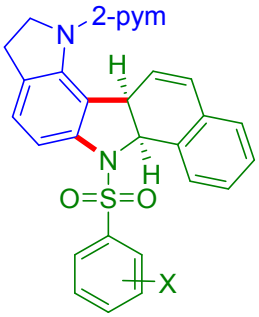




3o, 71%

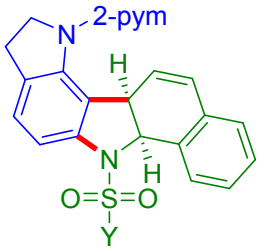


3p, 46%

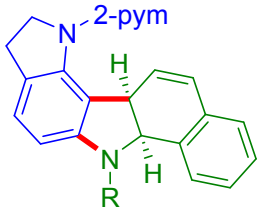


3q-y

3q, X = H, 43%
3r, X = 3-Me, 51%
3s, X = 3-CF_3, 63%
3t, X = 4-Cl, 69%
(CCDC 1948984)
3u, X = 4-I, 67%
3v, X = 4-Me, 54%
3w, X = 4-OMe, 58%
3x, X = 4-NO_2, 70%
3y, X = 4-*t*-Bu, 55%



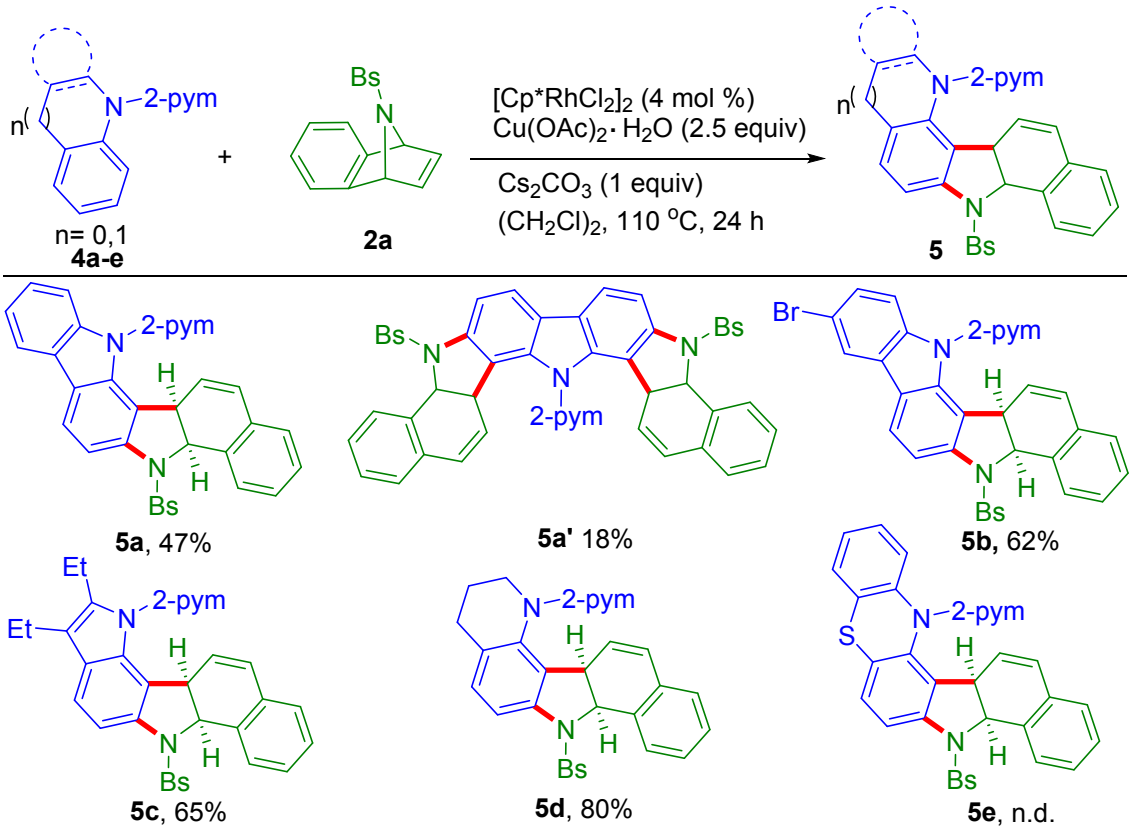
3z, Y = 2-naphthyl, 52%
3aa, Y = 2-thienyl, n.d.



3ab, R = Ms, 71%
3ac, R = Cbz, 66%
3ad, R = Boc, 63%

[a]Reaction conditions: **1a** (0.25 mmol), **2b-q** (0.3 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $Cu(OAc)_2 \cdot H_2O$ (0.63 mmol), Cs_2CO_3 (0.25 mmol), $(CH_2Cl)_2$ (2 mL), 110 °C, 24 h, N_2. [b]Isolated yield. n.d. = not detected.

Scheme 4. Scope of Carbazoles and Related Frameworks 4 with 1a. [a,b]



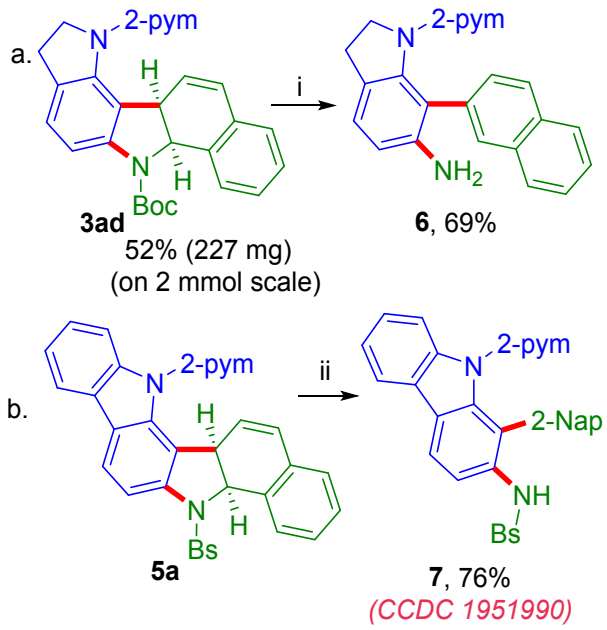
[a]Reaction conditions: **4a-e** (0.25 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $Cu(OAc)_2 \cdot H_2O$ (0.63 mmol), CsOAc (0.25 mmol), $(CH_2Cl)_2$ (2 mL), 110 °C, 24 h, N_2. [b]Isolated yield. n.d. = not detected.

The scope of the method was extended for diverse azabenzonorbornadienes **2** with indoline **1a** as a standard substrate (Scheme 3). Substrates with 6,7-difluoro **2b** and 5,8-dimethoxy **2c** groups in the aryl ring **A** reacted to give **3o** and **3p** in 71 and 46% yields, respectively. The reaction of **2d** having 9-phenylsulfonyl substituent afforded **3q** in 43% yield. In addition, the substrates containing 3-methyl **2e** and 3-trifluoromethyl **2f** groups in the 9-arylsulfonyl ring reacted to provide **3r** and **3s** in 51 and 63% yields, respectively. Further, the reaction of the substrates bearing substitution at the 4-position of the 9-arylsulfonyl ring *viz*; chloro **2g**, iodo **2h**, methyl **2i**, methoxy **2j**, nitro **2k** and *tert*-butyl **2l** groups, produced **3t-y** in 54-70% yields. Likewise, 9-naphthylsulfonyl substituted **2m** underwent reaction to furnish **3z** in 52% yield, whereas **2n** bearing 2-thiophene group was an unsuccessful substrate, which might be due to

the chelation to the Rh-catalyst. The substrates with 9-mesyl **2o**, 9-Cbz **2p** and 9-Boc **2q** protecting groups readily reacted to deliver **3ab-ad** in 63-71% yields. Notably, the products were obtained as a single diastereoisomer and stereochemistry was assigned by single-crystal X-ray of **3t** as a representative example (See SI).

The method was explored with carbazoles and related frameworks (Scheme 4). Thus, 9-(pyrimidin-2-yl)-9*H*-carbazole **4a** reacted to afford **5a** and **5a′** in 47 and 18% yields, respectively. The reaction of 3-bromo-9-(pyrimidin-2-yl)-9*H*-carbazole **4b** afforded **5b** in 62% yield. Interestingly, 2,3-diethyl-1-(pyrimidin-2-yl)-1*H*-indole **4c** and 1-(pyrimidin-2-yl)-1,2,3,4-tetrahydroquinoline **4d** conveyed **5c** and **5d** in 65 and 80% yields, respectively. However, 10-(pyrimidin-2-yl)-10*H*-phenothiazine **4e** failed to furnish **5e**, which might be due to the chelation of the thioether moiety to the Rh-catalyst.

Scheme 5. Post-Synthetic Modifications[a,b]



Reaction conditions: i. **3ad** (0.25 mmol), CF_3CO_2H (0.75 mmol), CH_2Cl_2 (2 mL), rt, 1 h; ii. **5a** (0. 25 mmol), NaOEt (1.25 mmol), DMSO (3 mL), 110 °C, 2 h.

The procedure was further examined for the reaction of 1-(pyrimidin-2-yl)indole **1a'** and 1,4-dihydro-1,4-epoxynaphthalene **2a'** (Scheme S2, See SI). However, they were unsuccessful substrates and formation of the target products **8** and **9** was not observed.

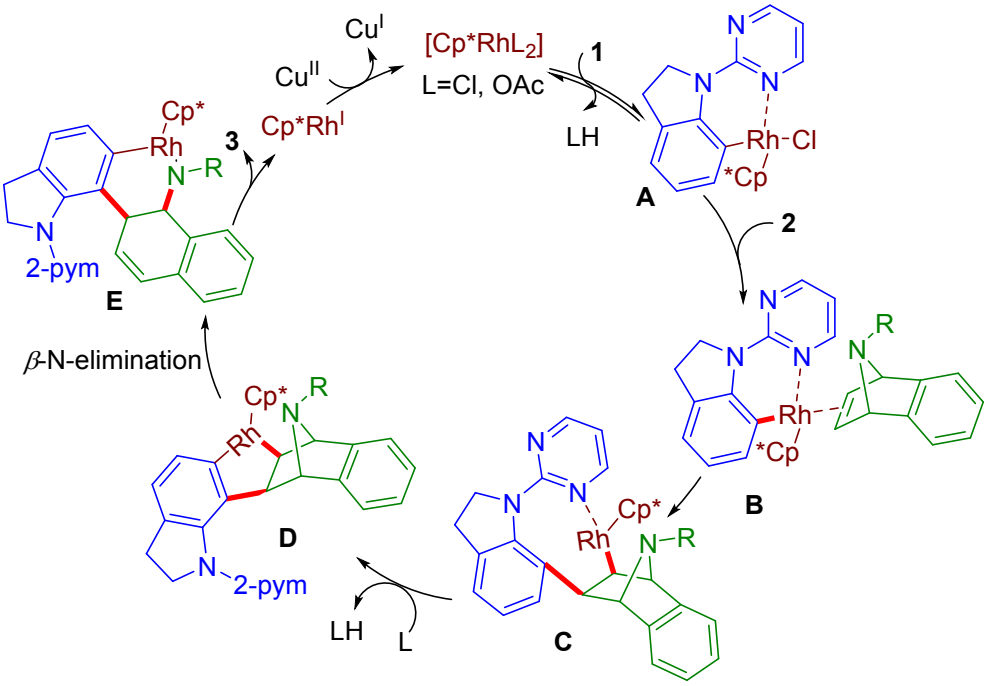
Finally, the scale up of the procedure was examined utilizing **1a** and **2q** as the representative examples (Scheme 5). The reaction occurred to provide **3ad** in 52% yield, which suggests that the procedure is scalable. The products can be further transformed into diverse scaffolds. For example, **3ad** could be converted to **6** in 69% yield employing trifluoroacetic acid *via* Boc deprotection and acid-mediated elimination. Similarly, **5a** could be transformed to **7** in 76% yield using base mediated elimination and the structure was determined using X-ray analysis (See SI).

To get insight into the mechanism, an H-D scrambling experiment was performed using **1a** in the presence of D_2O as a co-solvent, and 47% D incorporation was observed, while as using **1a** and **2a** in the presence of D_2O produced 20% D incorporation (Scheme S3). These results suggest that the migratory insertion of alkene is faster than H/D exchange and the initial C-H activation is reversible. In addition, the kinetic isotope experiments for C(7)-H activation exhibited $k_H/k_D = 1.32$ (one-pot) and $[P_H]/[P_D] = 1.20$ (parallel) (Scheme S4a-b). Similarly, the reaction of C(6)-H activation yielded $k_H/k_D = 1.38$ (one-pot) and $[P_H]/[P_D] = 1.12$ (parallel) (Scheme S4c-d). These results confide that the C-H bond cleavage might not be involved in the rate-determining step. Further, the stoichiometric reaction of $[Cp^*RhCl_2]_2$ with **1a** produced the rhodacycle **A** in 57% yield (Scheme S5a), whose structure was determined using the single-crystal X-ray analysis (CCDC 1948961, See SI). The complex **A** was catalytically competent to afford **3a** in 61% yield (Scheme S5b), suggesting an involvement of the rhodacycle as the active species in the catalytic cycle (See SI).

Preliminary mechanistic results and literature[12] suggest that 2-pyrimidine directed reversible fast C(7)-H activation can lead to the formation of the rhodacycle **A (**Scheme 6). Coordination of **A** with **2a** can give the Rh-species **B**, which can lead to the migratory insertion to yield **C**.

Concomitant activation of the C(6)-H bond can deliver **D**, which can undergo *β-N*-elimination to furnish **E** that may, in turn, undergo reductive elimination to deliver **3** and Rh^{I} species. Oxidation of Rh^{I} using Cu^{II} can regenerate the active Rh^{III} species to complete the catalytic cycle.

Scheme 6. Proposed Reaction Pathway



In summary, we have developed a Rh-catalyzed two-fold C-7 and C-6 functionalization of indolines with 7-azabenzonorbornadienes to produce pyrrolocarbazoles. The site-selectivity, substrate scope and functional group diversity are important practical features.

EXPERIMENTAL SECTION

General Information. $Cu(OAc)_2 \cdot H_2O$ (>98%), Cs_2CO_3 (99%), $[Cp^*RhCl_2]_2$, AgOAc (99.99%) and Ag_2CO_3 (99%) were purchased from Aldrich and used as received. Silica gel-G plates (Merck) were used for TLC analysis. Melting point was measured on MPB-540 Büchi melting point apparatus using open capillary tubes and are uncorrected. NMR spectra were recorded on Bruker 400 MHz and 600 MHz NMR instruments using TMS as an internal

standard and $CDCl_3$ as a solvent. Mestrenova software was used for the spectral analysis. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. HRMS was carried out using HA273 Q-Tof ESI-MS instrument. Infrared spectra were recorded on Perkin Elmer FT-IR instrument. 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).

1-(Pyrimidin-2-yl)indolines **1a-n** were synthesized as per reported procedure.[13]

1-(Pyrimidin-2-yl)indoline 1a.[13e] Yellow liquid; yield 73% (144 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 8.1 Hz, 1H), 7.15-7.07 (m, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.55 (t, *J* = 4.8 Hz, 1H), 4.12 (t, *J* = 8.7 Hz, 2H), 3.07 (t, *J* = 8.7 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{12}N_3$ 198.1026; Found 198.1026.

4-Allyl-1-(pyrimidin-2-yl)indoline 1b. Yellow solid, yield 67% (159 mg); mp 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.7 Hz, 2H), 8.29 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.79 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.68 (t, *J* = 4.7 Hz, 1H), 6.00-5.90 (m, 1H), 5.09-5.03(m, 2H), 4.25 (dd, *J* = 9.2, 8.1 Hz, 2H), 3.35 (dt, *J* = 6.6, 1.6 Hz, 2H), 3.13 (t, *J* = 8.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.4, 157.6, 143.7, 136.2, 135.8, 131.0, 127.8, 122.2, 115.9, 113.5, 111.5, 48.9, 37.7, 25.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}N_3$ 238.1339; Found 238.1339.

4-Bromo-1-(pyrimidin-2-yl)indoline 1c. Brown solid; yield 71% (195 mg); mp 114-115 °C; [13e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.6 Hz, 2H), 8.33 (dd, *J* = 6.4, 1.9 Hz, 1H), 7.06 (d, *J* = 6.7 Hz, 2H), 6.70-6.69 (m, 1H), 4.22 (t, *J* = 8.6 Hz, 2H), 3.14 (t, *J* = 8.7 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{11}BrN_3$ 276.0131; Found 276.0135.

1-(Pyrimidin-2-yl)indoline-4-carbonitrile 1d. Brown solid; yield 59% (131 mg); mp 174-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H), 8.48 (d, *J* = 4.8 Hz, 2H), 7.26-7.20 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 4.8 Hz, 1H), 4.28 (t, *J* = 8.8 Hz, 2H), 3.33 (t, *J* =

8.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.0, 157.7, 144.6, 136.8, 128.4, 124.0, 119.2, 117.6, 112.6, 108.8, 48.6, 26.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{11}N_4$ 223.0978; Found 223.0988.

4-Methoxy-1-(pyrimidin-2-yl)indoline 1e.[13e] Colorless solid; yield 64% (145 mg); mp 200-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.8 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.4 Hz, 1H), 6.67 (t, *J* = 4.8 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 4.25 (t, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.12 (t, *J* = 8.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.3, 157.5, 155.9, 145.1, 128.7, 119.2, 111.5, 108.8, 104.4, 55.4, 49.4, 24.3; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}N_3O$ 228.1131; Found 228.1134.

4-Phenyl-1-(pyrimidin-2-yl)indolines 1f. Yellow solid; yield 73% (199 mg); mp 117-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.8 Hz, 2H), 8.47 (d, *J* = 8.1 Hz, 1H), 7.45 (q, *J* = 7.9 Hz, 4H), 7.39-7.30 (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 4.8 Hz, 1H), 4.25 (t, *J* = 8.6 Hz, 2H), 3.25 (t, *J* = 8.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 157.6, 144.1, 140.9, 138.6, 130.0, 128.5, 127.9, 127.2, 122.4, 114.3, 111.6, 49.1, 27.3; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{16}N_3$ 274.1339; Found 274.1349.

4-(3-Chlorophenyl)-1-(pyrimidin-2-yl)indoline 1g. Brown liquid; yield 69% (212 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.7 Hz, 2H), 8.46 (d, *J* = 8.1 Hz, 1H), 7.44 (s, 1H), 7.38-7.35 (m, 1H), 7.34-7.30 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 4.7 Hz, 1H), 4.25 (t, *J* = 8.6 Hz, 2H), 3.23 (t, *J* = 8.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 159.4, 157.6, 144.2, 142.7, 137.2, 134.3, 130.0, 129.8, 128.6, 128.1, 127.3, 126.8, 122.2, 114.8, 111.8, 49.10, 27.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{15}ClN_3$ 308.0949; Found 308.0959.

4-([1,1'-Biphenyl]-4-yl)-1-(pyrimidin-2-yl)indoline 1h. Colorles solid; yield 71% (248 mg); mp 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.8 Hz, 2H), 8.46 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.68-7.64 (m, 4H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39-7.32 (m,

2H), 7.05 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.72 (t, *J* = 4.8 Hz, 1H), 4.27 (dd, *J* = 9.1, 8.0 Hz, 2H), 3.31 (t, *J* = 8.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.6, 144.1, 140.9, 140.1, 139.9, 138.2, 130.1, 128.98, 128.96, 128.0, 127.5, 127.2, 127.3, 122.5, 114.5, 111.7, 49.2, 27.5; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{20}N_3$ 350.1652; Found 350.1650.

5-Fluoro-1-(pyrimidin-2-yl)indoline 1i.[13e] Yellow solid; yield 63% (135 mg); mp 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 8.33 (dd, *J* = 8.6, 4.9 Hz, 1H), 6.93-6.86 (m, 2H), 6.68 (t, *J* = 4.8 Hz, 1H), 4.25 (t, *J* = 8.4 Hz, 2H), 3.18 (t, *J* = 8.6 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{11}FN_3$ 216.0932; Found 216.0932.

5-Bromo-1-(pyrimidin-2-yl)indoline 1j.[13e] Brown solid; yield 65% (179 mg); mp 109-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 4.8 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.02 (s, 1H), 6.48 (t, *J* = 4.7 Hz, 1H), 3.95 (t, *J* = 8.7 Hz, 2H), 2.89 (t, *J* = 8.7 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{11}BrN_3$ 276.0131; Found 276.0130.

5-Methyl-1-(pyrimidin-2-yl)indoline 1k.[13e] Brown liquid; yield 67% (141 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.65 (t, *J* = 4.8 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 2H), 3.16 (t, *J* = 8.4 Hz, 2H), 2.32 (s, 3H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}N_3$ 212.1182; Found 212.1185.

1'-(Pyrimidin-2-yl)spiro[cyclohexane-1,3'-indoline] 1l.[13e] Brown liquid; yield 46% (122 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.8 Hz, 2H), 8.32 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.17-7.11 (m, 1H), 7.10-7.06 (m, 1H), 6.90-6.87 (m, 1H), 6.59 (t, *J* = 4.8 Hz, 1H), 4.00 (s, 2H), 1.66 (d, *J* = 10.5 Hz, 5H), 1.60-1.53 (m, 3H), 1.44 (dd, *J* = 9.8, 3.4 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{20}N_3$ 266.1652; Found 266.1666.

1-(Pyrimidin-2-yl)-1,2-dihydrobenzo[*cd*]indole 1m. Brown solid; yield 49% (114 mg); mp 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 2H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.52-7.46 (m, 2H), 7.32 (dd, *J* = 7.6, 3.2 Hz, 2H), 6.80 (t, *J* = 4.8 Hz,

1H), 5.46 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.0, 157.9, 144.0, 136.1, 131.7, 129.6, 127.9, 123.0, 117.2, 116.5, 112.4, 108.5, 55.7; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{12}N_3$ 234.1026; Found 234.1037.

***N*-Methyl-*N*-phenylpyrimidin-2-amine 1n.**[13d] Yellow liquid; yield 86% (159 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.27-7.21 (m, 1H), 6.57 (t, *J* = 4.8 Hz, 1H), 3.53 (s, 3H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{12}N_3$ 186.1026; Found 186.1044.

9-(Pyrimidin-2-yl)-9*H*-carbazoles **4a-b** and 2,3-diethyl-1-(pyrimidin-2-yl)-1*H*-indole **4c** prepared as per literature.[13f]

9-(Pyrimidin-2-yl)-9*H*-carbazoles 4a. Colorless solid; yield 79% (194 mg); mp 112-113 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.4 Hz, 2H), 8.81 (d, *J* = 4.8 Hz, 2H), 8.10 (d, *J* = 7.7 Hz, 2H), 7.57-7.50 (m, 2H), 7.43-7.37 (m, 2H), 7.07 (t, *J* = 4.8 Hz, 1H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{12}N_3$ 246.1026; Found 246.1045.

3-Bromo-9-(pyrimidin-2-yl)-9*H*-carbazole 4b. Colorless solid; yield 74% (239 mg); mp 157-158 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 3.6 Hz, 1H), 8.83 (d, *J* = 4.4 Hz, 2H), 8.77 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 2.4 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.40-7.36 (m, 1H), 7.14 (t, *J* = 4.8 Hz, 1H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{11}BrN_3$ 324.0131; Found 324.0151.

2,3-Diethyl-1-(pyrimidin-2-yl)-1*H*-indole 4c. Yellow liquid; yield 69% (173 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.23-7.19 (m, 2H), 7.12 (t, *J* = 4.8 Hz, 1H), 3.19 (q, *J* = 7.4 Hz, 2H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}N_3$ 252.1495; Found 252.1513.

1-(Pyrimidin-2-yl)-1,2,3,4-tetrahydroquinoline was prepared as per literature.[13e]

1-(Pyrimidin-2-yl)-1,2,3,4-tetrahydroquinoline 4d. Yellow liquid; yield 87% (184 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.7 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.16 (dd, *J* = 17.1, 7.8 Hz, 2H), 7.04-6.98 (m, 1H), 6.66 (t, *J* = 4.7 Hz, 1H), 4.07-4.01 (m, 2H), 2.80 (t, *J* = 6.6 Hz, 2H), 2.02 (p, *J* = 6.5 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3$ 212.1182; Found 212.1201.

10-(Pyrimidin-2-yl)-10*H*-phenothiazine 4e. Phenothiazine (1.5 mmol, 298.5 mg), 2-bromopyrimidine (2.25 mmol, 355.5 mg), PCy_3 (7 mol %, 21.8 mg), NaO^{t}Bu (3.75 mmol, 360.4 mg) and $Pd_2(dba)_3$ (5 mol %, 68.7 mg) were stirred in toluene (10 ml) at 110 °C in a preheated oil-bath for 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was purified on silica gel column chromatography using 1:9 ethyl acetate and hexane to give the title compound. Green solid; yield 59% (163 mg); mp 211-212 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.38 (d, *J* = 4.7 Hz, 2H), 7.76 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.44 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.36 (td, *J* = 7.7, 1.5 Hz, 2H), 7.21 (td, *J* = 7.6, 1.4 Hz, 2H), 6.77 (t, *J* = 4.7 Hz, 1H; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 157.9, 140.1, 133.5, 128.7, 128.2, 126.6, 126.2, 113.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{12}N_3S$ 278.0746; Found 278.0750.

1-(3,4-Dihydro-2*H*-pyrrol-5-yl)indoline,[13b] 1-(pyridin-2-yl)indoline,[13a] 1-(indolin-1-yl)ethan-1-one,[13b] 1-(indolin-1-yl)-2,2-dimethylpropan-1-one[13d] and *N*,*N*-dimethylindoline-1-carboxamide were prepared as per literature and the data were accordance with literature.

1-(3,4-Dihydro-2*H*-pyrrol-5-yl)indoline I. Brown solid; yield 85% (158 mg); mp 186-187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.17-7.07 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 4.05 (t, *J* = 8.7 Hz, 2H), 3.81 (t, *J* = 7.1 Hz, 2H), 3.12 (t, *J* = 8.7 Hz, 2H), 2.82 (t, *J* = 8.1 Hz, 2H), 2.08-1.99 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.2, 144.8, 131.5, 127.4,

125.0, 121.0, 112.8, 56.7, 49.9, 33.4, 27.8, 23.5; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{15}N_2$ 187.1230; Found 187.1246.

1-(Pyridin-2-yl)indoline II. Brown liquid; yield 79% (157 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.4 Hz, 1H), 8.33-8.29 (m, 1H), 7.62-7.58 (m, 1H), 7.25 (dd, *J* = 15.9, 7.4 Hz, 2H), 6.98-6.90 (m, 1H), 6.84-6.79 (m, 1H), 6.78-6.74 (m, 1H), 4.04-3.98 (m, 2H), 3.21 (t, *J* = 8.5 Hz, 2H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2$ 197.1073; Found 197.1093.

1-(Indolin-1-yl)ethan-1-one III. Brown solid; yield 73% (118 mg); mp 102-103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 10.6, 7.7 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.21 (s, 3H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{12}NO$ 162.0913; Found 162.0934.

1-(Indolin-1-yl)-2,2-dimethylpropan-1-one IV. Brown liquid; yield 75% (152 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.12 (m, 1H), 7.08 (t, *J* = 6.9 Hz, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 4.11 (t, *J* = 8.2 Hz, 2H), 3.02 (t, *J* = 8.1 Hz, 2H), 1.28 (s, 9H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{18}NO$ 204.1383; Found 204.1400.

***N,N*-Dimethylindoline-1-carboxamide V.** Brown liquid; yield 72% (133 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 -7.03 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 3.83 (t, *J* = 8.2 Hz, 2H), 2.95 (t, *J* = 8.1 Hz, 2H), 2.87 (s, 6H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{15}N_2O$ 191.1179; Found 191.1198.

7-Azabenzonorbornadienes **2a-q** prepared as per literature.[12g]

9-((4-Bromophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2a. Brown solid; yield 80% (289 mg); mp 157-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.01 (dd, *J* = 5.2, 3.0 Hz, 2H), 6.86 (s, 2H), 6.80 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.44 (t, *J* = 1.5 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.0, 142.7, 137.2, 132.0, 129.8, 127.6, 125.3, 121.5, 67.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}BrNO_2S$ 361.9845; Found 361.9865.

9-((4-Bromophenyl)sulfonyl)-6,7-difluoro-1,4-dihydro-1,4-epiminonaphthalene 2b. Brown solid; yield 75% (240 mg); mp 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 6.93-6.85 (m, 4H), 5.42 (t, *J* = 1.3 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.4 (dd, *J* = 249.9, 14.9 Hz), 143.5 (t, *J* = 4.9 Hz), 142.8, 137.1, 132.19, 129.9, 128.2, 112.2 (t, *J* = 9.1 Hz), 112.0 (t, *J* = 9.2 Hz), 67.5; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{11}BrF_2NO_2S$ 397.9656; Found 397.9655.

***tert*-Butyl-5,8-dimethoxy-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate 2c.** Brown solid; yield 59% (201 mg); mp 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.97 (m, 2H), 6.51 (s, 2H), 5.71-5.69 (m, 2H), 3.76 (s, 6H), 1.37 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ154.9, 148.1, 147.9, 143.5, 142.2, 136.8, 111.3, 80.4, 64.3, 63.7, 56.4, 28.1; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{22}NO_4$ 304.1543; Found 304.1558.

9-Phenylsulfonyl-1,4-dihydro-1,4-epiminonaphthalene 2d. Brown solid; yield 69% (196 mg); mp 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.42-7.38 (m, 1H), 7.32-7.26 (m, 2H), 7.02 (dd, *J* = 5.2, 3.0 Hz, 2H), 6.80 (t, *J* = 1.6 Hz, 2H), 6.76 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.46 (t, *J* = 1.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 142.5, 138.2, 132.5, 128.8, 128.3, 125.2, 121.3, 67.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}NO_2S$ 284.0740; Found 284.0753.

9-(*m*-Tolylsulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2e. Colorless solid; yield 72% (214 mg); mp 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (td, *J* = 4.7, 4.2, 2.0 Hz, 1H), 7.30 (s, 1H), 7.20-7.16 (m, 2H), 7.00 (dd, *J* = 5.2, 3.0 Hz, 2H), 6.83 (t, *J* = 1.6 Hz, 2H), 6.75 (dd, *J* = 5.1, 3.0 Hz, 2H), 5.45 (s, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 142.6, 138.9, 137.8, 133.3, 128.8, 128.7, 125.5, 125.1, 121.3, 67.8, 21.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_2S$ 298.0896; Found 298.0909.

9-((3-(Trifluoromethyl)phenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2f. Colorless solid; yield 76% (267 mg); mp 115-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.41-7.37 (m, 1H), 6.96 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.93 (t, *J* = 1.7 Hz, 2H), 6.69 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.47 (t, *J* = 1.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.6, 143.0, 138.9, 131.8 (q, J_{C-F} = 33.3 Hz), 131.59, 131.58, 129.5, 129.0 (q, J_{C-F} = 3.6 Hz), 127.3 (q, J_{C-F} = 273.7 Hz), 125.5 (q, J_{C-F} = 4.2 Hz), 125.48, 121.6, 67.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{13}F_3NO_2S$ 352.0614; Found 352.0624.

9-((4-Chlorophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2g. Colorless solid; yield 84% (266 mg); mp 147-148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.01 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.86 (t, *J* = 1.6 Hz, 2H), 6.79 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.44 (t, *J* = 1.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.0, 142.7, 139.1, 136.7, 129.8, 129.0, 125.3, 121.5, 67.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}ClNO_2S$ 318.0350; Found 318.0365.

9-((4-Iodophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2h. Brown solid; yield 77% (314 mg); mp 168-169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.01 (dd, *J* = 5.2, 2.8 Hz, 2H), 6.86 (t, *J* = 1.5 Hz, 2H), 6.80 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.43 (t, *J* = 1.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 147.0, 142.7, 138.0, 137.8, 129.7, 125.3, 121.5, 100.1, 67.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}INO_2S$ 409.9706; Found 409.9713.

9-Tosyl-1,4-dihydro-1,4-epiminonaphthalene 2i. Colorless solid; yield 73% (217 mg); mp 172-173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.03 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.81-6.75 (m, 4H), 5.44 (s, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.4, 143.4, 142.5, 135.4, 129.5, 128.4, 125.2, 121.3, 67.9, 21.6; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_2S$ 298.0896; Found 298.0910.

9-((4-Methoxyphenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2j. Colorless solid; yield 61% (191 mg); mp 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.03 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.80-6.75 (m, 6H), 5.42 (t, *J* = 1.6 Hz, 2H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.0, 147.4, 142.5, 130.4, 129.9, 125.2, 121.3, 114.1, 67.8, 55.7; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_3S$ 314.0845; Found 314.0856.

9-((4-Nitrophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2k. Brown solid; yield 90% (296 mg); mp 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.00 (dd, *J* = 5.0, 3.0 Hz, 2H), 6.93 (s, 2H), 6.73 (dd, *J* = 5.1, 3.0 Hz, 2H), 5.49 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8, 144.0, 142.9, 130.7, 129.6, 125.5, 123.8, 121.7, 67.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}N_2O_4S$ 329.0591; Found 329.0600.

9-((4-(*tert*-Butyl)phenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2l. Colorless solid; yield 68% (230 mg); mp 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.99 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.90 (t, *J* = 1.7 Hz, 2H), 6.73 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.45 (s, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 156.2, 147.2, 142.9, 134.8, 128.2, 125.7, 125.1, 121.4, 67.8, 35.1, 31.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_2S$ 340.1366; Found 340.1373.

9-(Naphthalen-2-ylsulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2m. Brown solid; yield 65% (216 mg); mp 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.84-7.80 (m, 2H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.58-7.53 (m, 3H), 6.98 (dd, *J* = 5.1, 3.1 Hz, 2H), 6.78 (t, *J* = 1.6 Hz, 2H), 6.60 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.52 (t, *J* = 1.3 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 142.5, 135.2, 134.7, 132.2, 129.8, 129.2, 128.9, 128.8, 127.9, 127.4, 125.0, 123.5, 121.2, 67.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{16}NO_2S$ 334.0896; Found 334.0911.

9-(Thiophen-2-ylsulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2n. Brown solid; yield 77% (222 mg); mp 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.2 Hz, 1H), 7.22 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.88 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.84 (dd, *J* = 5.2, 3.0 Hz, 2H), 6.77 (t, *J* = 1.6 Hz, 2H), 5.48 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.0, 141.6, 138.7, 133.5, 133.0, 127.9, 125.4, 121.4, 68.0; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{12}NO_2S_2$ 290.0304; Found 290.0313.

9-(Methylsulfonyl)-1,4-dihydro-1,4-epiminonaphthalene 2o. Colorless solid; yield 63% (139 mg); mp 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.1, 3.0 Hz, 2H), 7.07 (t, *J* = 1.6 Hz, 2H), 7.02 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.47 (t, *J* = 1.6 Hz, 2H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.5, 143.2, 125.9, 121.7, 67.7, 39.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{12}NO_2S$ 222.0583; Found 222.0595.

Benzyl-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate 2p. Colorless solid; yield 52% (144 mg); mp 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.15 (m, 7H), 6.89 (dd, *J* = 5.2, 3.0 Hz, 4H), 5.51 (s, 2H), 4.99 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.4, 148.2, 143.6, 142.7, 136.4, 128.6, 128.2, 127.9, 125.3, 121.3, 121.0, 67.3, 66.4; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2$ 278.1176; Found 278.1174.

***tert*-Butyl-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate 2q.** Yellow liquid; yield 62% (903 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, 2H), 6.90-6.86 (m, 4H), 5.41 (s, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.2, 148.4, 125.0, 80.7, 28.3; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_2$ 244.1332; Found 244.1344.

General Procedure for Synthesis of Pyrrolocarbazoles. 1-(Pyrimidin-2-yl)indoline **1** (0.25 mmol, 1 equiv), 9-((aryl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene **2** (0.3 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (4 mol %, 0.01 mmol, 6.2 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.625 mmol, 2.5 equiv, 124.4 mg) and Cs_2CO_3 (0.25 mmol, 1 equiv, 81.5 mg) were stirred at 110 °C in a preheated oil

bath for 24 h in $(CH_2Cl)_2$ (2 mL, 0.13 M) under nitrogen atmosphere. Progress of the reaction was monitored using TLC with ethyl acetate and hexane as the eluent. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (20 mL) and passed through a short pad of celite. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford analytically pure functionalized pyrrolocarbazoles.

6-((4-Bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*] pyrrolo-[2,3-*g*]carbazole 3a. Brown solid; yield 72% (100 mg); mp 213-214 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.57-7.55 (m, 2H), 7.47-7.45 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.09 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.67-4.61 (m, 1H), 4.03 (q, *J* = 10.0 Hz, 1H), 3.66 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.29-3.20 (m, 1H), 2.88-2.80 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.6, 157.9, 140.9, 140.0, 136.5, 133.0, 132.5, 131.8, 131.6, 129.0, 128.6, 128.5, 128.2, 127.9, 127.2, 126.6, 126.4, 123.4, 123.0, 116.2, 112.7, 63.6, 51.8, 42.0, 29.0; FT-IR (KBr) 3128, 1630, 1576, 1550, 1400, 1166, 1088, 1014 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{22}BrN_4O_2S$ 557.0641; Found 557.0661.

4-Allyl-6-((4-bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo [*a*]-pyrrolo[2,3-*g*]carbazole 3b. Colorless solid; yield 72% (107 mg); mp 168-169 °C; R_f = 0.29 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.28-7.24 (m, 1H), 7.18 (s, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 4.8 Hz, 1H), 6.08 (d, *J* = 10.0 Hz, 1H), 5.95-5.85 (m, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.10-5.03 (m, 3H), 4.67-4.61 (m, 1H), 4.02 (q, *J* = 10.4 Hz, 1H), 3.66 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.31 (d, *J* = 6.4 Hz, 2H), 3.18-3.09 (m, 1H), 2.84-2.77 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.7, 157.8, 141.2,

139.7, 136.7, 135.8, 135.0, 132.4, 131.8, 131.7, 131.5, 129.0, 128.6, 128.5, 128.1, 127.9, 127.1, 126.6, 124.3, 123.2, 116.5, 116.4, 112.6, 63.7, 51.5, 41.9, 37.9, 27.6; FT-IR (KBr) 3130, 1631, 1575, 1400, 1167, 1085, 1066 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{26}BrN_4O_2S$ 597.0954; Found 597.0950.

4-Bromo-6-((4-bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydro-benzo-[*a*]pyrrolo[2,3-*g*]carbazole 3c. Brown solid; yield 76% (120 mg); mp 237-238 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.4 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.28-7.25 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.02 (dd, *J* = 9.6, 5.6 Hz, 1H), 4.61 (t, *J* = 10.0 Hz, 1H), 4.13-4.03 (m, 1H), 3.59 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.22-3.13 (m, 1H), 2.88 (dd, *J* = 16.4, 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.4, 157.8, 142.2, 140.5, 136.4, 133.2, 132.5, 131.6, 131.2, 128.9, 128.6, 128.5, 128.3, 128.1, 127.5, 126.7, 125.4, 122.4, 118.7, 117.3, 113.2, 63.8, 50.9, 41.7, 30.5; FT-IR (KBr) 3132, 1736, 1574, 1452, 1401, 1360, 1285, 1231, 1168, 1086 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{24}Br_2N_4O_2S$ 634.9746; Found 634.9746.

6-((4-Bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]-pyrrolo-[2,3-*g*]carbazole-4-carbonitrile 3d. Yellow solid; yield 46% (67 mg); mp 214-215 °C; R_f = 0.26 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.8 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.62-7.60 (m, 2H), 7.53 (s, 1H), 7.50-7.48 (m, 2H), 7.31-7.27 (m, 1H), 7.19-7.15 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 6.13 (d, *J* = 10.0 Hz, 1H), 5.61 (d, *J* = 10.4 Hz, 1H), 5.00 (dd, *J* = 9.6, 5.6 Hz, 1H), 4.73-4.67 (m, 1H), 4.13 (q, *J* = 10.0 Hz, 1H), 3.74-3.70 (m, 1H), 3.43-3.34 (m, 1H), 3.12-3.05 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.3, 158.0, 142.1, 141.2, 137.9, 136.3, 132.7, 131.5, 130.9, 130.8, 128.94, 128.90, 128.62, 128.57, 128.4, 128.3, 126.9, 121.3, 118.1, 116.9, 113.7, 107.8, 63.7,

51.5, 42.3, 28.7. FT-IR (KBr) 3129, 2225, 1574, 1400, 1288, 1168, 1067 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{21}BrN_5O_2S$ 582.0594; Found 582.0589.

6-((4-Bromophenyl)sulfonyl)-4-methoxy-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydro-benzo-[*a*]pyrrolo[2,3-*g*]carbazole 3e. Colorless solid; yield 80% (117 mg); mp 229-230 °C; R_f = 0.25 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.49-7.47 (m, 2H), 7.29-7.25 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.71 (t, *J* = 4.8 Hz, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 5.55 (d, *J* = 10.0 Hz, 1H), 5.07 (dd, *J* = 9.6, 5.6 Hz, 1H), 4.64-4.58 m, 1H), 4.03 (q, *J* = 10.8 Hz, 1H), 3.86 (s, 3H), 3.59 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.13-3.04 (m, 1H), 2.87-2.80 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.7, 157.8, 155.1, 142.1, 140.5, 136.5, 132.4, 131.8, 131.7, 129.0, 128.6, 128.4, 128.1, 127.9, 126.9, 126.6, 123.6, 119.8, 119.0, 112.6, 100.1, 64.0, 55.9, 51.9, 41.5, 26.0; FT-IR (KBr) 3125, 3011, 1630, 1575, 1400, 1169 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{24}BrN_4O_3S$ 587.0747; Found 587.0751.

6-((4-Bromophenyl)sulfonyl)-4-phenyl-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydro-benzo-[*a*]pyrrolo[2,3-*g*]carbazole 3f. Colorless solid; yield 78% (123 mg); mp 245-246 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.8 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 (q, *J* = 6.4 Hz, 5H), 7.35-7.28 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.75 (t, *J* = 4.8 Hz, 1H), 6.13 (d, *J* = 10.0 Hz, 1H), 5.63 (d, *J* = 10.0 Hz, 1H), 5.12 (dd, *J* = 9.6, 5.6 Hz, 1H), 4.68 (t, *J* = 9.6 Hz, 1H), 3.99 (q, *J* = 9.2 Hz, 1H), 3.72 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.43-3.34 (m, 1H), 2.80 (dd, *J* = 15.6, 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6, 157.9, 141.4, 140.1, 140.0, 137.7, 136.6, 132.5, 131.7, 131.6, 130.8, 129.0, 128.7, 128.5, 128.2, 127.9, 127.5, 127.3, 126.6, 125.3, 122.9, 116.7, 112.6, 63.7, 51.7, 41.9, 29.1; FT-IR (KBr) 3130, 1616, 1574, 1550, 1400, 1168, 1085 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{26}BrN_4O_2S$ 633.0954; Found 633.0959.

6-((4-Bromophenyl)sulfonyl)-4-(3-chlorophenyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazole 3g. Colorless solid; yield 67% (112 mg); mp 252-253 °C; R_f = 0.27 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.8 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.52-7.50 (m, 2H), 7.43-7.40 (m, 2H), 7.31 (s, 1H), 7.26-7.18 (m, 5H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 6.8 Hz, 1H), 6.65 (t, *J* = 4.8 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 4.99 (dd, *J* = 9.8, 5.6 Hz, 1H), 4.61-4.55 (m, 1H), 3.93-3.85 (m, 1H), 3.61-3.57 (m, 1H), 3.32-3.23 (m, 1H), 2.72-2.65 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.6, 157.9, 141.8, 141.7, 140.4, 136.7, 136.3, 134.5, 132.5, 131.8, 131.6, 130.8, 129.0, 128.7, 128.6, 128.3, 128.2, 128.0, 127.6, 127.4, 126.8, 126.7, 125.9, 122.7, 116.5, 112.8, 63.8, 51.7, 41.9, 29.0; FT-IR (KBr) 3129, 1634, 1574, 1400, 1167, 1087 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{25}BrClN_4O_2S$ 667.0565; Found 667.0562.

4-([1,1'-Biphenyl]-4-yl)-6-((4-bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazole 3h. Colorless solid; yield 70% (124 mg); mp 241-242 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.8 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.65-7.60 (m, 6H), 7.54-7.44 (m, 7H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.75 (t, *J* = 4.8 Hz, 1H), 6.14 (d, *J* = 10.0 Hz, 1H), 5.63 (d, *J* = 10.4 Hz, 1H), 5.12 (dd, *J* = 9.6, 5.6 Hz, 1H), 4.70 (t, *J* = 9.6 Hz, 1H), 4.00 (q, *J* = 9.2 Hz, 1H), 3.72 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.48-3.40 (m, 1H), 2.87 (q, *J* = 8.0, 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 157.9, 141.5, 140.8, 140.3, 140.3, 139.0, 137.3, 136.7, 132.5, 131.8, 131.7, 130.8, 129.01, 128.95, 128.7, 128.6, 128.2, 128.0, 127.5, 127.3, 127.24, 127.20, 126.7, 125.4, 122.9, 116.6, 112.7, 63.8, 51.8, 41.9, 29.3; FT-IR (KBr) 3128, 1633, 1569, 1550, 1400, 1168, 1072 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{40}H_{30}BrN_4O_2S$ 709.1267; Found 709.1288.

6-((4-Bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,6,6a,12a-tetrahydro-2H-spiro[benzo-[*a*]-pyrrolo[2,3-*g*]carbazole-3,1'-cyclohexane] 3l. Colorless solid; yield 55% (86 mg) mp

243-244 °C; R_f = 0.27 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29-7.25 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 1H), 6.72 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 9.6 Hz, 1H), 5.56 (d, *J* = 10.0 Hz, 1H), 5.08 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 3.70-3.63 (m, 2H), 1.81-1.74 (m, 3H), 1.64 (t, *J* = 11.6 Hz, 2H), 1.46 (t, *J* = 11.2 Hz, 2H), 1.35-1.26 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 157.9, 142.5, 141.0, 139.1, 136.4, 132.3, 131.8, 131.7, 129.0, 128.7, 128.5, 128.2, 127.9, 127.1, 126.6, 126.3, 123.1, 121.2, 116.4, 112.6, 63.5, 61.5, 45.3, 42.0, 37.1, 36.0, 25.7, 23.5, 23.0; FT-IR (KBr) 3128, 1631, 1576, 1548, 1400, 1167, 1088, 1068, 1019 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{33}H_{30}BrN_4O_2S$ 625.1267; Found 625.1282.

6-((4-Bromophenyl)sulfonyl)-8,9-difluoro-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydro-benzo[*a*]pyrrolo[2,3-*g*]carbazole 3o. Colorless solid; yield 71% (105 mg); mp 253-254 °C; R_f = 0.24 (1:9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.74 (dd, *J* = 10.8, 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.74 (t, *J* = 4.8 Hz, 1H), 6.64 (dd, *J* = 10.8, 7.8 Hz, 1H), 5.97 (d, *J* = 10.2 Hz, 1H), 5.46 (d, *J* = 10.2 Hz, 1H), 5.12 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.67-4.63 (m, 1H), 4.05 (q, *J* = 11.4 Hz, 1H), 3.64 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.29-3.23 (m, 1H), 2.87 (dd, *J* = 15.6, 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.5, 157.9, 150.8 (dd, *J* = 12.6, 10.0 Hz), 149.2 (dd, *J* = 21.0, 9.4 Hz), 140.5, 140.0, 136.1, 133.2, 132.5, 128.9, 128.7 (dd, *J* = 6.3, 3.6 Hz), 128.5 (t, *J* = 4.1 Hz), 128.1, 125.7, 125.3, 123.9, 123.7, 118.0 (d, *J* = 19.1 Hz), 116.1, 115.0 (d, *J* = 17.8 Hz), 112.8, 62.9, 51.7, 41.5, 28.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -137.2, -137.3, -139.5, -139.6; FT-IR (KBr) 3130, 1576, 1548, 1400, 1310, 1167, 1085 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{20}BrF_2N_4O_2S$ 593.0453; Found 593.0453.

***tert*-Butyl-7,10-dimethoxy-1-(pyrimidin-2-yl)-2,3,6a,12a-tetrahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazole-6(1*H*)-carboxylate 3p.** Thick liquid; yield 46% (57 mg); R_f = 0.23 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.8 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.72 (d, *J* = 9.2 Hz, 2H), 6.66 (t, *J* = 4.8 Hz, 1H), 5.71 (d, *J* = 7.6 Hz, 1H), 5.52 (dd, *J* = 10.0, 3.2 Hz, 1H), 4.60 (dd, *J* = 5.2, 2.4 Hz, 1H), 4.55-4.49 (m, 1H), 4.19 (q, *J* = 9.6 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.22-3.13 (m, 1H), 2.98-2.91 (m, 1H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.7, 157.7, 153.4, 149.3, 144.2, 139.5, 129.0, 127.0, 123.7, 123.0, 121.2, 121.1, 120.1, 112.2, 112.1, 111.3, 111.0, 80.2, 57.3, 56.4, 56.3, 52.2, 43.1, 29.8, 28.6, 28.4; FT-IR (KBr) 3131, 1690, 1633, 1579, 1552, 1460, 1400, 1328, 1259, 1158 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{31}N_4O_4$ 499.2340; Found 499.2356.

6-(Phenylsulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo[2,3-*g*]carb-azole 3q. Brown solid; yield 43% (51 mg); mp 196-197 °C; R_f = 0.25 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.8 Hz, 2H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.65-7.59 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29-7.27 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 6.4 Hz, 1H), 6.67 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 9.6 Hz, 1H), 5.61 (d, *J* = 10.4 Hz, 1H), 5.07 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.65-4.60 (m, 1H), 4.06-3.98 (m, 1H), 3.67 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.29-3.20 (m, 2H), 2.88-2.81 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.6, 157.7, 141.1, 139.9, 137.8, 132.6, 131.9, 131.8, 129.2, 128.7, 128.5, 128.1, 127.5, 127.2, 126.6, 126.5, 126.4, 123.3, 123.2, 116.1, 112.5, 63.5, 51.7, 42.0, 29.0; FT-IR (KBr) 3129, 1633, 1400, 1163, 1091 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}N_4O_2S$ 479.1536; Found 479.1551.

1-(Pyrimidin-2-yl)-6-(m-tolylsulfonyl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo[2,3-*g*]-carbazole 3r. Yellow solid; yield 51% (63 mg); mp 228-229 °C; R_f = 0.28 (1: 9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz,

1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 11.6 Hz, 1H), 7.32 (dd, *J* = 8.0, 3.2 Hz, 2H), 7.28-7.24 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 5.6 Hz, 1H), 6.68 (t, *J* = 4.8 Hz, 1H), 6.08 (d, *J* = 9.6 Hz, 1H), 5.57 (d, *J* = 10.4 Hz, 1H), 5.08 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.67-4.61 (m, 1H), 4.07-3.99 (m, 1H), 3.66 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.28-3.19 (m, 1H), 2.88-2.82 (m, 1H), 2.26 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 160.7, 157.6, 141.4, 139.8, 139.3, 137.7, 133.4, 132.5, 132.1, 131.8, 129.0, 128.8, 128.5, 128.0, 128.0, 127.2, 126.5, 126.5, 124.7, 123.3, 116.1, 112.5, 63.5, 51.8, 42.1, 29.0, 21.5; FT-IR (KBr) 3129, 1631, 1400, 1159 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{25}N_4O_2S$ 493.1693; Found 493.1705.

1-(Pyrimidin-2-yl)-6-((3-(trifluoromethyl)phenyl)sulfonyl)-1,2,3,6,6a,12a-hexahydro-benzo-[*a*]pyrrolo[2,3-*g*]carbazole 3s. Colorless solid; yield 63% (86 mg); mp 220-221 °C; R_f = 0.26 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$)) δ 8.19 (d, *J* = 4.8 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.4 Hz, 3H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30-7.28 (m, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.68 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 10.4 Hz, 1H), 5.67 (d, *J* = 10.0 Hz, 1H), 5.07 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.66-4.60 (m, 1H), 4.07-4.00 (m, 1H), 3.70 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.27-3.18 (m, 1H), 2.88-2.82 (m, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 160.4, 157.6, 140.6, 140.0, 138.6, 133.2, 132.1 (q, J_{C-F} = 33.2 Hz), 131.7, 131.4, 130.7, 129.8, 129.3 (q, J_{C-F} = 3.4 Hz), 128.7, 128.5, 128.2, 127.1, 126.6, 125.94 (q, J_{C-F} = 271.2 Hz), 125.90, 124.5 (q, J_{C-F} = 3.7 Hz), 123.5, 123.0, 115.8, 112.6, 63.7, 51.8, 42.0, 28.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.87. FT-IR (KBr) 3129, 1609, 1578, 1553, 1462, 1400, 1326, 1168, 1133, 1104 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{22}F_3N_4O_2S$ 547.1410; Found 547.1419.

6-((4-Chlorophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]-pyrrolo-[2,3-*g*]carbazole 3t. Colorless solid; yield 69% (59 mg); mp 240-241 °C; R_f = 0.28 (1: 9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J*

= 7.6 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.29-7.25 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 9.6 Hz, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.09 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.67-4.61 (m, 1H), 4.04 (q, *J* = 9.6 Hz, 1H), 3.65 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.29-3.20 (m, 1H), 2.88-2.82 (m, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6, 157.8, 141.0, 140.0, 139.5, 136.1, 133.0, 131.8, 131.7, 129.5, 129.0, 128.7, 128.6, 128.2, 127.3, 126.7, 126.4, 123.5, 123.0, 116.3, 112.7, 63.6, 51.8, 42.1, 29.0; FT-IR (KBr) 3125, 1719, 1631, 1577, 1400, 1166, 1088 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{22}ClN_4O_2S$ 513.1147; Found 513.1161.

6-((4-Iodophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo-[2,3-*g*]carbazole 3u. Colorless solid; yield 67% (101 mg); mp 246-247 °C; R_f = 0.29 (1: 9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.4 Hz, 3H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.74 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.56 (d, *J* = 10.2 Hz, 1H), 5.09 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.64 (t, *J* = 9.6 Hz, 1H), 4.04 (q, *J* = 10.2 Hz, 1H), 3.67 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.28-3.22 (m, 1H), 2.85 (dd, *J* = 15.6, 9.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6, 157.9, 140.9, 140.0, 138.4, 137.3, 132.9, 131.7, 131.6, 128.8, 128.6, 128.5, 128.1, 127.2, 126.6, 126.3, 123.4, 123.0, 116.1, 112.6, 100.3, 63.5, 51.7, 42.0, 28.9; FT-IR (KBr) 3129, 1573, 1546, 1400, 1163, 1087 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{22}IN_4O_2S$ 605.0503; Found 605.0513.

1-(Pyrimidin-2-yl)-6-tosyl-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazole 3v. Yellow solid; yield 54% (66 mg); mp 230-231 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.2 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 9.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.68 (t, *J* = 4.8 Hz, 1H), 6.08

(d, *J* = 10.2 Hz, 1H), 5.60 (d, *J* = 10.2 Hz, 1H), 5.08 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.65-4.61 (m, 1H), 4.02 (q, *J* = 10.2 Hz, 1H), 3.74 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.27-3.21 (m, 1H), 2.84 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 160.7, 157.6, 143.4, 141.3, 139.8, 135.1, 132.5, 132.1, 131.8, 129.7, 128.8, 128.5, 128.0, 127.6, 127.2, 126.5, 126.4, 123.4, 123.3, 116.2, 112.4, 63.4, 51.7, 42.1, 28.9, 21.8; FT-IR (KBr) 3129, 1631, 1571, 1544, 1400, 1163, 1091 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{25}N_4O_2S$ 493.1693; Found 493.1703.

6-((4-Methoxyphenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*] pyrrolo[2,3-*g*]carbazole 3w. Colorless solid; yield 58% (74 mg); mp 233-234 °C; R_f = 0.26 (1:9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 4.8 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 5.4 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.69 (t, *J* = 4.8 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 5.56 (d, *J* = 10.2 Hz, 1H), 5.09 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.65-4.61 (m, 1H), 4.02 (q, *J* = 10.8 Hz, 1H), 3.82 (s, 3H), 3.68 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.27-3.21 (m, 1H), 2.84 (dd, *J* = 15.6, 8.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 163.2, 160.6, 157.7, 141.4, 139.8, 132.5, 132.1, 131.7, 129.5, 129.3, 128.7, 128.5, 128.0, 127.1, 126.6, 126.5, 123.2, 123.2, 116.4, 114.4, 112.5, 63.3, 55.7, 51.7, 42.0, 29.0; FT-IR (KBr) 3130, 1632, 1595, 1400, 1260, 1155, 1091, 1021 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{25}N_4O_3S$ 509.1642; Found 509.1648.

6-((4-Nitrophenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]-pyrrolo-[2,3-*g*]carbazole 3x. Yellow solid; yield 70% (91 mg); mp 237-238 °C; R_f = 0.24 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.23 (m, 2H), 8.15 (d, *J* = 4.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81-7.79 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 4.8 Hz, 1H), 6.10 (d, *J* = 10.0 Hz, 1H), 5.65 (d, *J* = 10.0 Hz, 1H), 5.06 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.67-

4.61 (m, 1H), 4.04 (q, *J* = 11.2 Hz, 1H), 3.70 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.30-3.21 (m, 1H), 2.90-2.83 (m, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.5, 157.6, 150.4, 143.4, 140.4, 140.1, 131.7, 131.2, 128.7, 128.62, 128.61, 128.4, 127.3, 126.7, 125.8, 124.2, 123.6, 122.7, 115.8, 112.8, 63.8, 51.8, 42.0, 28.9; FT-IR (KBr) 3129, 1632, 1573, 1528, 1400, 1167, 1087 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{22}N_5O_4S$ 524.1387; Found 524.1391.

6-((4-(*tert*-Butyl)phenyl)sulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]-pyrrolo[2,3-*g*]carbazole 3y. Colorless solid; yield 55% (73 mg); mp 251-252 °C; R_f = 0.27 (1:9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.2 Hz, 2H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.28-7.25 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.63 (d, *J* = 10.2 Hz, 1H), 5.10 (dd, *J* = 10.0, 5.4 Hz, 1H), 4.65-4.62 (m, 1H), 4.03 (q, *J* = 10.8 Hz, 1H), 3.92 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.28-3.22 (m, 1H), 2.85 (dd, *J* = 15.6, 9.0 Hz, 1H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 160.5, 157.6, 156.6, 141.3, 139.8, 135.4, 132.4, 132.1, 131.8, 128.8, 128.5, 128.0, 127.4, 127.2, 126.4, 126.1, 126.0, 123.4, 123.3, 115.9, 112.3, 63.2, 51.6, 42.2, 35.3, 31.4, 28.9; FT-IR (KBr) 3129, 1577, 1551, 1400, 1166, 1113, 1084 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{31}N_4O_2S$ 535.2162; Found 535.2177.

6-(Naphthalen-2-ylsulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]-pyrrolo-[2,3-*g*]carbazole 3z. Brown solid; yield 52% (69 mg); mp 174-175 °C; R_f = 0.27 (1:9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 4.8 Hz, 2H), 8.0 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.44 (t, *J* = 4.8 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 5.68 (d, *J* = 9.6 Hz, 1H), 4.96 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.60-4.56 (m, 1H), 3.99 (q, *J* = 10.8 Hz, 1H), 3.52 (dd, *J* = 9.6, 5.4 Hz, 1H),

3.27-3.21 (m, 1H), 2.84 (dd, J = 15.6, 9.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 160.4, 157.4, 141.2, 139.9, 135.0, 134.9, 132.6, 132.4, 131.9, 131.7, 129.7, 129.1, 128.9, 128.71, 128.67, 128.5, 128.0, 127.8, 127.4, 127.0, 126.5, 126.4, 123.3, 123.1, 122.9, 116.2, 112.2, 63.5, 51.6, 41.9, 28.9; FT-IR (KBr) 3129, 1624, 1576, 1552, 1400, 1161, 1134, 1073 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{25}N_4O_2S$ 529.1693; Found 529.1705.

6-(Methylsulfonyl)-1-(pyrimidin-2-yl)-1,2,3,6,6a,12a-hexahydrobenzo[*a*]pyrrolo[2,3-*g*]-carbazole 3ab. Colorless solid; yield 71% (74 mg); mp 249-250 °C; R_f = 0.26 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.8 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.28-7.25 (m, 1H), 7.21-7.15 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.81 (t, J = 4.4 Hz, 1H), 6.23 (d, J = 10.0 Hz, 1H), 5.84 (d, J = 10.4 Hz, 1H), 5.36 (dd, J = 10.0, 5.6 Hz, 1H), 4.92 (dd, J = 10.4, 5.6 Hz, 1H), 4.75-4.70 (m, 1H), 4.17-4.10 (m, 1H), 3.30-3.21 (m, 1H), 2.95 (s, 3H), 2.93-2.87 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6, 158.0, 140.8, 140.1, 132.6, 132.0, 131.7, 129.0, 128.5, 128.2, 127.4, 126.5, 124.5, 123.7, 123.1, 114.6, 112.8, 63.7, 52.1, 42.7, 36.3, 28.9; FT-IR (KBr) 3126, 2927, 2855, 1637, 1577, 1553, 1400, 1263, 1156 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}N_4O_2S$ 417.1380; Found 417.1382.

Benzyl-1-(pyrimidin-2-yl)-2,3,6a,12a-tetrahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazol-6(1*H*)-yl)-sulfonyl)methanoate 3ac. Yellow solid; yield 66% (78 mg); mp 196-197 °C; R_f = 0.26 (1:9 ethyl acetate/hexane); ^1H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 4.8 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 1.8 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.35 (d, J = 14.6 Hz, 1H), 7.30 (d, J = 4.2 Hz, 1H), 7.12 (t, J = 6.0 Hz, 2H), 6.99 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 4.8 Hz, 1H), 6.76 (t, J = 4.8 Hz, 1H), 6.19 (d, J = 10.2 Hz, 1H), 6.05 (d, J = 10.8 Hz, 1H), 5.41-5.33 (m, 3H), 4.74 (dd, J = 10.2, 5.4 Hz, 1H), 4.67 (t, J = 9.6 Hz, 1H), 4.07 (q, J = 10.8 Hz, 1H), 3.23-3.17 (m, 1H), 2.82 (dd, J = 15.6, 9.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 160.9, 158.0, 139.6, 136.3, 133.1, 132.2, 130.3, 128.7, 128.5, 128.4, 128.2, 127.9, 127.5, 127.5, 126.6, 124.0,

123.1, 113.0, 112.5, 67.8, 60.9, 52.2, 42.0, 28.9; FT-IR (KBr) 3130, 1702, 1616, 1577, 1551, 1400, 1288, 1215, 1138 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{25}N_4O_2$ 473.1972; Found 473.1980.

***tert*-Butyl-1-(pyrimidin-2-yl)-2,3,6a,12a-tetrahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazole-6(1*H*)-carboxylate 3ad.** Brown solid; yield 63% (69 mg); mp 137-138 °C; R_f = 0.27 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.8 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 1H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.88-6.86 (m, 1H), 6.76 (t, *J* = 4.8 Hz, 1H), 6.19 (d, *J* = 10.0 Hz, 1H), 5.99 (d, *J* = 10.4 Hz, 1H), 5.35 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.73 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.70-4.65 (m, 1H), 4.11-4.03 (m, 1H), 3.24-3.15 (m, 1H), 2.81 (dd, *J* = 15.6, 8.8 Hz, 1H), 1.63 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.9, 158.0, 153.7, 141.9, 139.6, 133.8, 132.3, 129.8, 128.2, 127.7, 127.5, 127.4, 126.6, 124.1, 123.3, 122.9, 113.2, 112.5, 81.3, 60.5, 52.3, 41.9, 29.0, 28.7. FT-IR (neat) 3130, 1694, 1616, 1577, 1551, 1460, 1400, 1302, 1257, 1148 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{27}N_4O_2$ 439.2129; Found 439.2141.

5-((4-Bromophenyl)sulfonyl)-12-(pyrimidin-2-yl)-4b,5,12,12c-tetrahydrobenzo[*a*]indolo-[2,3-*g*]carbazole 5a. Brown solid; yield 47% (71 mg); mp 154-155 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.8 Hz, 2H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.95 (t, *J* = 6.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.46-7.42 (m, 3H), 7.35-7.27 (m, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 1H), 5.70 (d, *J* = 10.0 Hz, 1H), 4.51 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.64 (dd, *J* = 9.6, 5.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.3, 158.3, 141.1, 140.5, 135.9, 135.4, 132.3, 131.4, 131.1, 128.9, 128.6, 128.12, 128.05, 127.9, 126.9, 126.6, 126.1, 125.7, 123.7, 122.9, 121.5, 119.6, 119.2, 117.4, 116.2, 114.0, 63.5, 41.5; FT-IR (KBr) 3128, 1572, 1400, 1208, 1170, 1087 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{22}BrN_4O_2S$ 605.0641; Found 605.0656.

Bis-5,5'-((4-bromophenyl)sulfonyl)-8-(pyrimidine-2-yl)-4b,4'b,8c,8'c-tetrahydrobenzo[*a*]-indolo-[2,3-*g*]dicarbazole 5a'. Colorless solid; yield 18% (43 mg); mp 205-206 °C; R_f = 0.25 (1:9 ethyl acetate/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.8 Hz, 2H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.4 Hz, 4H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 4.8 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.18 (d, *J* = 10.2 Hz, 2H), 5.69 (dd, *J* = 10.2, 6.0 Hz, 2H), 5.65 (d, *J* = 10.2 Hz, 2H), 4.04 (dd, *J* = 9.6, 5.4 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 160.9, 157.6, 140.8, 139.7, 136.7, 132.4, 131.6, 131.0, 129.1, 128.7, 128.6, 128.3, 128.0, 127.99, 127.93, 127.6, 126.7, 122.6, 118.8, 118.1, 115.8, 63.7, 43.0, 29.9; FT-IR (KBr) 3129, 1641, 1572, 1400, 1261, 1168, 1087 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{48}H_{32}Br_2N_5O_4S_2$ 964.0257; Found 964.0256.

10-Bromo-5-((4-bromophenyl)sulfonyl)-12-(pyrimidin-2-yl)-4b,5,12,12c-tetrahydro-benzo-[*a*]indolo[2,3-*g*]carbazole 5b. Colorless solid; yield 62% (106 mg); mp 178-179 °C; R_f = 0.29 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.36 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.90-7.87 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.30-7.28 (m, 1H), 7.21 (t, *J* = 4.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 5.64 (d, *J* = 10.0 Hz, 1H), 4.43 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.58 (dd, *J* = 10.0, 5.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 158.5, 158.2, 141.3, 139.9, 136.0, 135.8, 132.5, 131.3, 131.1, 129.6, 129.0, 128.9, 128.7, 128.4, 128.3, 128.0, 127.8, 126.7, 125.0, 124.0, 122.5, 121.2, 119.6, 117.7, 116.8, 116.1, 115.8, 63.6, 41.6, 29.8; FT-IR (KBr) 3129, 1622, 1567, 1400, 1210, 1169, 1086 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{21}Br_2N_4O_2S$ 682.9746; Found 682.9746.

6-((4-Bromophenyl)sulfonyl)-2,3-diethyl-1-(pyrimidin-2-yl)-1,6,6a,12a-tetrahydrobenzo[*a*]-pyrrolo[2,3-*g*]carbazole 5c. Yellow solid; yield 65% (99 mg); mp 147-148 °C; R_f = 0.29

(1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.58-7.55 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.38-7.35 (m, 2H), 7.23 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.2 Hz, 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 5.50 (d, *J* = 9.6 Hz, 1H), 3.95 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.23 (dd, *J* = 9.6, 5.6 Hz, 1H), 3.16-3.06 (m, 1H), 2.74-2.64 (m, 3H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 158.7, 140.3, 137.3, 136.2, 132.5, 132.4, 131.6, 131.3, 130.2, 129.0, 128.7, 128.6, 128.2, 128.1, 127.7, 126.5, 121.5, 118.17, 118.15, 117.7, 115.2, 63.5, 41.0, 19.0, 17.8, 15.5, 15.3; FT-IR (KBr) 3129, 1628, 1565, 1400, 1288, 1261, 1169, 1091, 1026 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{28}BrN_4O_2S$ 611.1111; Found 611.1119.

7-((4-Bromophenyl)sulfonyl)-1-(pyrimidin-2-yl)-2,3,4,7,7a,13a-hexahydro-1*H*-benzo[*a*]-pyrido[2,3-*g*]carbazole 5d. Yellow solid; yield 80% (114 mg); mp 167-168 °C; R_f = 0.28 (1:9 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 7. 94 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.64 (t, *J* = 4.4 Hz, 1H), 6.14 (d, *J* = 10.0 Hz, 1H), 5.52 (d, *J* = 10.0 Hz, 1H), 5.05 (dd, *J* = 9.6, 5.6 Hz, 1H), 4.58-4.52 (m, 1H), 3.33 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.27-3.20 (m, 1H), 2.76-2.61 (m 2H), 2.12-2.03 (m, 1H), 1.79-1.69 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.0, 139.5, 137.2, 136.5, 132.5, 132.38, 132.35, 131.83, 131.81, 128.9, 128.4, 128.3, 128.2, 127.8, 127.7, 127.0, 126.5, 122.4, 116.7, 111.9, 63.7, 45.0, 41.8, 27.0, 24.1; FT-IR (KBr) 3129, 1577, 1552, 1471, 1400, 1355, 1298, 1165, 1086 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{24}BrN_4O_2S$ 571.0798; Found 571.0809.

7-(Naphthalen-2-yl)-1-(pyrimidin-2-yl)indolin-6-amine 6. To a stirred solution of *tert*-butyl-1-(pyrimidin-2-yl)-2,3,6a,12a-tetrahydrobenzo[*a*]pyrrolo[2,3-*g*]carbazole-6(1*H*) carbox -ylate **3ab** (0.25 mmol, 109.5 mg) in CH_2Cl_2 (7 mL), trifluoroacetic acid (0.75 mmol, 57 μL)

was added at 0 ˚C. The resultant solution was stirred at room temperature for 1 h. After completion, as indicated by TLC, the reaction mixture was diluted with CH_2Cl_2 (15 mL). The mixture was successively washed with brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford 7-(naphthalen-2-yl)-1-(pyrimidin-2-yl)indolin-6-amine **6** as a brown solid. R_f = 0.24 (1:9 ethyl acetate/hexane); yield 69% (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 4.8 Hz, 2H), 7.74-7.68 (m, 4H), 7.50 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.41-7.35 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.08 (t, *J* = 4.8 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 3.56 (br s, 2H), 3.07 (t, *J* = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 159.2, 156.4, 143.7, 142.8, 135.9, 133.7, 132.2, 128.1, 128.0, 127.7, 127.6, 127.5, 125.7, 125.7, 124.8, 124.6, 116.8, 111.6, 110.9, 53.4, 29.3; FT-IR (KBr) 3128, 1617, 1576, 1550, 1401, 1278 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}N_4$ 339.1604; Found 339.1606.

4-Bromo-*N*-(1-(naphthalen-2-yl)-9-(pyrimidin-2-yl)-9*H*-carbazol-2-yl)benzenesulfon-amide 7. To a stirred solution of **5a** (0.25 mmol, 151 mg) in DMSO (3 mL), NaOEt (1.5 mmol, 102 mg) in EtOH (0.2 mL) was added. The mixture was warmed up to 110 °C in a preheated oil bath and stirred for 2 h. The reaction mixture was cooled to room temperature and diluted with ethyl acetate (15 mL). The resultant mixture was washed with 2 N HCl (1 x 5 mL), brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford 4-bromo-*N*-(1-(naphthalen-2-yl)-9-(pyrimidin-2-yl)-9*H*-carbazol-2-yl)benzenesulfon-amide **7** as a brown solid. R_f = 0.32 (1:9 ethyl acetate/hexane); yield 76% (115 mg); mp 139-140 ˚C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 4.8 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.74 (dd, *J* = 13.8, 7.8 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.51-7.48 (m, 1H), 7.47-7.43 (m, 2H), 7.42-7.39 (m, 1H), 7.37-7.35 (m, 1H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 3H), 6.96 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.80

(s, 1H), 6.33 (t, J = 4.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 157.4, 157.0, 141.1, 138.0, 137.8, 133.1, 132.10, 132.06, 131.93, 131.9, 128.6, 128.44, 128.40, 127.9, 127.8, 127.6, 126.7, 126.8, 126.6, 124.6, 124.0, 122.2, 120.7, 120.5, 120.2, 118.2, 117.0, 111.5; FT-IR (KBr) 3128, 2800, 1913, 1566, 1454, 1401, 1329, 1267, 1216, 1160, 1088, 1046 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{22}BrN_4O_2S$ 605.0641; Found 605.0656.

H/D Exchange Studies in $(CH_2Cl)_2$:D_2O (Scheme S2). 1-(Pyrimidin-2-yl)indoline **1a** (0.25 mmol, 49.3 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.62 mmol, 124 mg), Cs_2CO_3 (0.25 mmol, 81.5 mg), D_2O (1 mmol, 18 μL) and $[Cp^*RhCl_2]_2$ (4 mol %, 6.2 mg) were stirred in $(CH_2Cl)_2$ (2 mL) under nitrogen at 110 ˚C in a preheated oil bath for 6 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane (15 mL). The combined organic layer was washed with water (5 mL) and dried over Na_2SO_4. Evaporation of the solvent gave a residue which was purified on silica gel column chromatography using a 1:9 mixture of ethyl acetate and hexanes. The ^{1}H NMR analysis showed 47% D incorporation at C-7.

H/D Exchange Studies $(CH_2Cl)_2$:D_2O with 2a (Scheme S2). 1-(Pyrimidin-2-yl)indoline **1a** (0.25 mmol, 49.3 mg), 9-((4-bromophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene **2a** (0.30, 108.7 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.62 mmol, 124 mg), Cs_2CO_3 (0.25 mmol, 81.5 mg), D_2O (1 mmol, 18 μL) and $[Cp^*RhCl_2]_2$ (4 mol %, 6.2 mg) were stirred in $(CH_2Cl)_2$ (2 mL) under nitrogen at 110 ˚C in a preheated oil bath for 12 h. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2 (15 mL). The combined organic layer was washed with water (5 mL) and dried over Na_2SO_4. Evaporation of the solvents gave a residue that was purified on silica gel column chromatography using a 1:9 mixture of ethyl acetate and hexanes. The ^{1}H NMR analysis showed 20% D incorporation at C-7.

Preparation of 1-(pyrimidin-2-yl)indoline-7-*d*.[14] The titled compound was prepared according to the reported procedure as a pale yellow liquid. The deuterium incorporation was determined using 400 MHz ^{1}H NMR as 89%.

Synthesis of 1-(pyrimidin-2-yl)indoline-4,6-d_2. The titled compound was prepared using the following procedure.

Step-1. **2-Nitrobenzen-4,6-d_2-amine**: Trifluoroacetic anhydride (1.40 mL, 10 mmol) was added slowly to D_2O (4 mL) in a screw-capped pressure tube at 0 °C. Then, 2-nitroaniline (1.380 g, 10 mmol) was added in portion wise. The tube was sealed and heated at 120 °C for 24 h. The reaction mixture was cooled to room temperature and then 2 M NaOH solution (20 mL) was added. The resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic layer was dried over Na_2SO_4. Evaporation of the solvent afforded 2-nitrobenzen-4,6-d_2-amine in 98% (1.40 g) yield as a yellow solid that was used for step-2 without further purification. ^{1}H NMR showed 89% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.27 (s, 1H).

Step-2. **1-Iodo-2-nitrobenzene-4,6-d_2** : To a solution of 2-nitrobenzen-4,6-d_2-amine (5 mmol, 691 mg) in water (25 mL), concentrated HCl (10 mL) was added and the resultant solution was cooled to 0 °C. Then, $NaNO_2$ (6 mmol, 414 mg) in water (10 mL) was added dropwise over 30 min and the stirring continued for additional 1 h. The resultant diazonium salt solution was treated with NaI (15 mmol, 2.25 g) and the stirring was continued for an additional 1 h. Sodium thiosulfate was added to quench the excess iodine present, and the product was extracted using ethyl acetate (3 × 15 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using 2% ethyl acetate in hexane to afford the 1-iodo-2-nitrobenzene-4,6-d_2 in 84% (1.05 g) yield as a yellow solid. ^{1}H NMR showed 89% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 1.6 Hz, 1H), 7.20 (d, J = 3.5 Hz, 1H).

Step-3. **2-Iodobenzen-3,5-d_2-amine**. To a stirring solution of 1-iodo-2-nitrobenzene-4,6-d_2 (4 mmol, 1 g), $FeCl_3$ (1.5 mol %, 9.7 mg) and activated charcoal (20 mol %, 9.6 mg) at 70 °C in methanol (10 mL), hydrazine hydrate (8 mmol, 256 mg) was added and the stirring was continued for an additional 2 h. The reaction mixture was then passed through a pad of celite

and the solvent was evaporated. The residue was diluted with ethyl acetate (15 mL) and washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using a 1:4 mixture of ethyl acetate and hexane to provide 2-iodobenzen-3,5-d_2-amine in 92% (813 mg) yield as yellow oil. ^{1}H NMR showed 89% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, J = 1.3 Hz, 1H), 6.54-6.42 (m, 1H), 3.52 (br s, 2H).

Step-4. **2-Ethynylbenzen-3,5-d_2-amine**: To a solution of 2-iodobenzen-3,5-d_2-amine (3.5 mmol, 721 mg), $PdCl_2(PPh_3)_2$ (5 mol %, 123 mg), CuI (5 mol %, 33 mg), triethylamine (15 mL) and trimethylsilylacetylene (5.25 mmol, 500 μL) were added under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h, and then concentrated to give a residue, which was diluted with dichloromethane (10 mL). The solution was washed with water (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave brown oil that was dissolved in a 1:1 mixture of methanol and CH_2Cl_2, treated with K_2CO_3 (10.5 mmol, 1.45 g) and stirred for 2 h at room temperature. The mixture was then concentrated in vacuo, and the residue was extracted using ethyl acetate (20 mL) and washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent provided a residue that was purified on silica gel chromatography using a 3:7 mixture of ethyl acetate and hexane to provide 2-ethynylbenzen-3,5-d_2-amine in 93% (387 mg) yield as a brown oil. ^{1}H NMR showed that 89% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, J=5.3 Hz, 2H), 4.11 (br s, 2H), 3.25 (s, 1H).

Step-5. **1*H*-Indole-4,6-d_2**: To a mixture of 2-ethynylbenzen-3,5-d_2-amine (250 mg, 2.1 mmol), triethylamine (3.5 mmol, 0.5 mL,) and DMAP (0.21 mmol, 26 mg,) in dichloromethane (10 mL) was added acetyl chloride (3.23 mmol, 230 μL) at 0 °C. The resultant mixture was warmed to room temperature and stirred for 24 h. The reaction was quenched using water and extracted with CH_2Cl_2 (15 mL). Drying (Na_2SO_4) and evaporation of the solvent furnished as brown solid, which was used for the next step without further purification. The resultant *N*-(2-

ethynylphenyl-3,5-d_2)acetamide (2.1 mmol, 338 mg) was dissolved with toluene (5 mL) and treated with Cs_2CO_3 (2 equiv, 1.40 g) in a screw capped pressure tube. The tube was sealed and stirred at 150 °C for 12 h. The reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography to provide 1*H*-indole-4,6-d_2 in 76% (190 mg) yield as brown solid. ^{1}H NMR showed 89% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.40 (s, 1H), 7.21 (t, *J* = 2.8 Hz, 1H), 7.15 (s, 1H), 6.58 (t, *J* = 1.6 Hz, 1H).

Step-6. Finally, the 1-(pyrimidin-2-yl)indoline-4,6-d_2 was prepared from 1*H*-indole-4,6-d_2 as per literature.[13] ^{1}H NMR showed 89% D incorporation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.8 Hz, 2H), 8.40 (s, 1H), 6.94 (s, 1H), 6.69 (t, *J* = 4.8 Hz, 1H). 4.25 (dd, *J* = 9.2, 8.1 Hz, 2H), 3.21 (dd, *J* = 9.3, 8.1 Hz, 2H).

Preparation of Cyclometalted Rh-complex A. 1-(Pyrimidin-2-yl)indoline **1a** (1 mmol, 197 mg), $[Cp^*RhCl_2]_2$ (0.25 mmol, 154.5 mg) and NaOAc (5.0 mmol, 410 mg) were stirred in CH_2Cl_2 (3 mL) for 46 h at room temperature under N_2. The solution was passed through a short pad of celite and the solvent was evaporated under reduced pressure. The residue was washed with diethyl ether (10 mL) to afford a residue that was recrystallized using a mixture of diethyl ether and CH_2Cl_2 to afford analytically pure red crystals in 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 5.6, 2.4 Hz, 1H), 8.29 (dd, *J* = 4.5, 2.4 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.71 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.60 (dd, *J* = 5.6, 4.5 Hz, 1H), 4.21 (ddd, *J* = 11.8, 10.1, 6.5 Hz, 1H), 3.94 (ddd, *J* = 11.8, 10.2, 7.0 Hz, 1H), 3.13 (td, *J* = 9.6, 6.5 Hz, 2H), 1.35 (s, 15H).

Catalytic Studies with Rhodacycle A. 1-(Pyrimidin-2-yl)indoline **1a** (0.25 mmol, 49.3 mg), 9-((4-bromophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene **2a** (0.30 mmol, 108.7 mg) $Cu(OAc)_2 \cdot H_2O$ (0.62 mmol, 124 mg), Cs_2CO_3 (0.25 mmol, 81.5 mg) and rhodacycle **A** (5 mol %, 7.7 mg) in $(CH_2Cl)_2$ (5 mL) stirred at 110 °C in a preheated oil bath for 24 h under nitrogen.

The resultant mixture was treated with dichloromethane (10 mL) and washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent afforded a residue that was purified on silica gel column chromatography using a 1:4 mixture of ethyl acetate and hexane to furnish the target product in 61% yield.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information having scheme S1-S5, table S1, figure S1-S4, crystal structure of **3t**, **A** and **7** including NMR spectra (^1H, ^{13}C and ^{19}F) of all the starting materials and products (PDF) is available free of charge on the ACS Publications website at DOI:

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tpunni@iitg.ac.in

Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Science and Engineering Research Board (CRG/2018/000406) and Council of Scientific and Industrial Research (02(0255)-2016-EMR-II) for the financial supports. We are grateful to Central Instrumentation Facility and Department of Chemistry, IIT Guwahati for mass (FIST) and COE FAST for NMR (F. No. 22-3/2016-TS-II/TC) analysis.

REFERENCES

(1) For some recent reviews, see: (a) Colby, D. A.; Bergman, R. G.; Ellman, J. A. Rhodium-Catalyzed C−C Bond Formation via Heteroatom-Directed C−H Bond Activation. *Chem. Rev.* **2010**, *110*, 624–655. (b) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. Towards Mild

Metal-Catalyzed C–H Bond Activation. *Chem. Soc. Rev.* **2011**, *40*, 4740-4761. (c) Ackermann, L. Carboxylate-Assisted Transition-Metal-Catalyzed C−H Bond Functionalizations: Mechanism and Scope. *Chem. Rev.* **2011**, *111*, 1315-1345. (d) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. Weak Coordination as a Powerful Means for Developing Broadly Useful C–H Functionalization Reactions. *Acc. Chem. Res.* **2012**, *45*, 788-802. (e) Arockiam, P. B.; Bruneau C.; Dixneuf, P. H. Ruthenium(II)-Catalyzed C–H Bond Activation and Functionalization. *Chem. Rev.* **2012**, *112*, 5879-5918. (f) Park, Y.; Kim, Y.; Chang, S. Transition Metal-Catalyzed C–H Amination: Scope, Mechanism, and Applications. *Chem. Rev.* **2017**, *117*, 9247-9301. (g) Shang, R.; Ilies, L.; Nakamura, E. Iron-Catalyzed C–H Bond Activation. *Chem. Rev*. **2017**, *117*, 9086-9139. (h) Rej, S.; Chatani, N. Rhodium-Catalyzed C(sp^2)- or C(sp^3)−H Bond Functionalization Assisted by Removable Directing Groups. *Angew. Chem. Int. Ed.* **2019**, *58*, 8304-8329.

(2) For some recent examples, see: (a) Zhu, C.; Kuniyil, R.; Ackermann, L. Manganese(I)-Catalyzed C–H Activation/Diels-Alder/retro-Diels-Alder Domino Alkyne Annulation by Transformable Pyridines. *Angew. Chem. Int. Ed.* **2019**, *58*, 5338-5342. (b) Xia, G.; Weng, J.; Liu, L.; Verma, P.; Li, Z.; Yu, J.-Q. Reversing Conventional Site-Selectivity in C(sp^3)-H Bond Activation. *Nat. Chem.* **2019**, *11*, 571–577. (c) Lu, Q.; Mondal, S.; Cembellín, S.; Greßies, S.; Glorius, F. Site-selective C–H Activation and Regiospecific Annulation Using Propargylic Carbonates. *Chem. Sci.* **2019**, *10*, 6560-6564. (d) Zhang, J.; Jung, H.; Kim, D.; Park, S.; Chang, S. Sequential C−H Borylation and *N*-Demethylation of 1,1'-Biphenylamines: An Alternative Route to Polycyclic *BN*-Heteroarenes. *Angew. Chem. Int. Ed.* **2019**, *58*, 7361-7365. (e) Wen, J.; Wang, D.; Qian, J.; Wang, D.; Zhu, C.; Zhao, Y.; Shi, Z. Rhodium-Catalyzed P^{III}-Directed ortho-C-H Borylation of Arylphosphines, *Angew. Chem. Int. Ed.* **2019**, *58*, 2078-2082. (f) Phipps, E. J. T.; Rovis, T. Rh(III)-Catalyzed C–H Activation-Initiated Directed Cyclopropanation of Allylic Alcohols. *J. Am. Chem. Soc.* **2019**, *141*, 6807-6811. (g) Pitzer, L.; Schäfers, F.; Glorius, F. Rapid Assessment of the Reaction-Condition-Based Sensitivity of

Chemical Transformations. *Angew Chem Int Ed.* 2019, *58*, 8572-8576. (h) Pinkert, T.; Wegner, T.; Mondal, S.; Glorius, F. Intermolecular 1,4-Carboamination of Conjugated Dienes Enabled by Cp*RhIII -Catalyzed C-H Activation. *Angew. Chem. Int. Ed*. 2019, *58*,15041-15045.

(3) For biological properties, see: (a) Kochanowska-Karamyan, A. J.; Hamann, M. T. Marine Indole Alkaloids: Potential New Drug Leads for the Control of Depression and Anxiety. *Chem. Rev.* **2010**, *110*, 4489-4497. (b) Kaushik, N. K.; Kaushik, N.; Attri, P.; Kumar, N.; Kim, C. H.; Verma, A. K.; Choi, E. H. Biomedical Importance of Indoles. *Molecules* **2013**, *18*, 6620-6662. (c) Lepri, S.; Buonerba, F.; Goracci, L.; Velilla, I.; Ruzziconi, R.; Schindler, B. D.; Seo, S. M.; S. Kaatz, G. W.; Cruciani, G. Indole Based Weapons to Fight Antibiotic Resistance: A Structure–Activity Relationship Study. *J. Med. Chem.* **2016**, *59*, 867-891. (d) Singh, T. P.; Singh, O. M. Recent Progress in Biological Activities of Indole and Indole Alkaloids. *Mini. Rev. Med. Chem.* **2018**, *18*, 9-25.

(4) For pyrrolocarbazole/indolocarbazole natural products, see: (a) Steglich, W.; Steffan, B.; Kopanski, L.; Eckhardt, G. Indole Pigments from the Fruiting Bodies of the Slime Mold *Arcyria denudate*. *Angew. Chem. Int. Ed.* **1980**, *19*, 459-460. (b) Meragelman, K. M.; West, L. M.; Northcote, P. T.; Pannell, L. K.; McKee, T. C.; Boyd, M. R. Unusual Sulfamate Indoles and a Novel Indolo[3,2-*a*]carbazole from Ancorina sp.[1] *J. Org. Chem.* **2002**, *67*, 6671-6677. (c) Warabi, K.; Matsunaga, S.; van Soest, R. W. M.; Fusetani, N. Dictyodendrins A−E, the First Telomerase-Inhibitory Marine Natural Products from the Sponge *Dictyodendrilla verongiformis*[1] *J. Org. Chem.* **2003**, *68*, 72765-2770. (d) Russell, F.; Harmody, D.; McCarthy, P. J.; Pomponi, S. A.; Wright, A. E. Indolo[3,2-*a*]carbazoles from a Deep-Water Sponge of the *Genus Asteropus*. *J. Nat. Prod.* **2013**, *76*, 1989-1992. (e) Liu, D.-Q.; Mao, S.-C.; Zhang, H.-Y.; Yu, X.-Q.; Feng, M.-T.; Wang, B.; Feng, L.- H.; Guo, Y.-W. Racemosins A and B, Two Novel Bisindole Alkaloids from the Green Alga *Caulerpa racemosa*. *Fitoterapia* **2013***, 91,* 15-20.

(5) For biological properties, see: (a) Sánchez, C.; Méndez, C.; Salas, J. A. Indolocarbazole Natural Products: Occurrence, Biosynthesis, and Biological Activity. *Nat. Prod. Rep.* **2006**, *23*, 1007-1045. (b) Fousteris, M. A.; Papakyriakou, A.; Koutsourea, A.; Manioudaki, M.; Lampropoulou, E.; Papadimitriou, E.; Spyroulias, G. A.; Nikolaropoulos, S. S. Pyrrolo[2,3-*a*]carbazoles as Potential Cyclin Dependent Kinase 1 (CDK1) Inhibitors. Synthesis, Biological Evaluation, and Binding Mode through Docking Simulations. *J. Med. Chem.* **2008**, *51*, 1048-1052. (c) Nakano, H.; Ōmura, S. Chemical Biology of Natural Indolocarbazole Products: 30 Years since the Discovery of Staurosporine. *J. Antibiot.* **2009**, *62*, 17-26. (d) Lampropoulou, E.; Manioudaki, M.; Fousteris, M.; Koutsourea, A.; Nikolaropoulos, S.; Papadimitriou, E. Pyrrolo[2,3-*a*]carbazole Derivatives as Topoisomerase I Inhibitors that Affect Viability of Glioma and Endothelial Cells *in vitro* and Angiogenesis *in vivo*. *Biomed. Pharmacother.* **2011**, *65*, 142–150. (e) Giraud, F.; Akué-Gédu, R.; Nauton, L.; Candelon, N.; Debiton, E.; Théry, V.; Anizon, F.; Moreau, P. Synthesis and Biological Activities of 4-Substituted Pyrrolo[2,3-a]carbazole Pim Kinase Inhibitors. *Eur. J. Med. Chem.* **2012**, *56*, 225-236.

(6) For material applications, see: (a) Belletête, M.; Blouin, N.; Boudreault, P.-L. T.; Leclerc, M.; Durocher, G. Optical and Photophysical Properties of Indolocarbazole Derivatives. *J. Phys. Chem. A* **2006**, *110*, 13696-13704. (b) Lai, C.-C.; Huang, M.-J.; Chou, H.-H.; Liao, C.-Y.; Rajamalli, P.; Cheng, C.-H. *m*-Indolocarbazole Derivative as a Universal Host Material for RGB and White Phosphorescent OLEDs. *Adv. Funct. Mater.* **2015**, *25*, 5548–5556. (c) Ohisa, S.; Takahashi, T.; Igarashi, M.; Fukuda, H.; Hikichi, T.; Komatsu, R.; Ueki, E.; Pu, Y.-J.; Chiba, T.; Kido, J. An Indolocarbazole-Based Thermally Activated Delayed Fluorescence Host for Solution-Processed Phosphorescent Tandem Organic Light-Emitting Devices Exhibiting Extremely Small Efficiency Roll-Off. *Adv. Funct. Mater.* **2019**, *29*, 1808022.

(7) For C-2 and C-3 Functionalization, see: (a) Phipps, R. J.; Grimster, N. P.; Gaunt, M. J. Cu(II)-Catalyzed Direct and Site-Selective Arylation of Indoles Under Mild Conditions. *J. Am. Chem. Soc.* **2008**, *130*, 8172-8174. (b) Ding, S.; Jiao, N. Direct Transformation of *N, N*-

Dimethylformamide to -CN: Pd-Catalyzed Cyanation of Heteroarenes via C–H Functionalization. *J. Am. Chem. Soc.* **2011**, *133*, 12374-12377. (c) Kim, J.; Kim, H.; Chang, S. Copper-Mediated Selective Cyanation of Indoles and 2-Phenylpyridines with Ammonium Iodide and DMF. *Org. Lett.* **2012**, 14, 3924-3927. (d) Lu, P.; Feng, C.; Loh, T.-P. Divergent Functionalization of Indoles with Acryloyl Silanes via Rhodium-Catalyzed C–H Activation. *Org. Lett.* **2015**, *17*, 3210-3213. (e) Tayu, M. Nomura, K.; Kawachi, K.; Higuchi, K.; Saito, N.; Kawasaki, T. Direct C2-Functionalization of Indoles Triggered by the Generation of Iminium Species from Indole and Sulfonium Salt. *Chem. Eur. J.* **2017**, *23*, 10925-10930. (f) Cabrero-Antonino, J. R.; Adam, R.; Junge, K.; Beller, M. Cobalt-Catalysed Reductive C–H Alkylation of Indoles using Carboxylic Acids and Molecular Hydrogen. *Chem. Sci*. **2017**, *8*, 6439-6450. (g) Lu, Q.; Cembellín, S.; Greßies, S.; Singha, S.; Daniliuc, C. G.; Glorius, F. Manganese(I)-Catalyzed C-H (2-Indolyl)methylation: Expedient Access to Diheteroarylmethanes. *Angew. Chem. Int. Ed.* **2018**, *57*, 1399-1403.

(8) For examples of C-4 Functionalization, see: (a) Yang, Y.; Gao, P.; Zhao, Y.; Shi, Z. Regiocontrolled Direct C-H Arylation of Indoles at the C4 and C5 Positions, *Angew. Chem. Int. Ed.* **2017**, *56*, 3966-3971. (b) Kalepu, J.; Gandeepan, P.; Ackermann, L.; Pilarski, L. T. C4-H Indole Functionalisation: Precedent and Prospects. *Chem. Sci.* **2018**, *9*, 4203-4216. (c) Lv, J.; Wang, B.; Yuan, K.; Wang, Y.; Jia, Y. Regioselective Direct C-4 Functionalization of Indole: Total Syntheses of (−)-Agroclavine and (−)-Elymoclavine. *Org. Lett.* **2017**, *19*, 3664-3667.

(9) For examples of C-7 functionalization, see: (a) Paul, S.; Chotana, G. A.; Holmes, D.; Reichle, R. C.; Maleczka, R. E., Jr.; Smith, M. R., Ir-Catalyzed Functionalization of 2-Substituted Indoles at the 7-position: Nitrogen-directed Aromatic Borylation. *J. Am. Chem. Soc.* **2006**, *128*, 15552-15553. (b) Robbins, D. W.; Boebel, T. A.; Hartwig, J. F. Iridium-Catalyzed, Silyl-Directed Borylation of Nitrogen-Containing Heterocycles. *J. Am. Chem. Soc.* **2010**, *132*, 4068-4069. (c) Pitts, A. K.; OÏHara, F.; Snell, R. H.; Gaunt, M. J. A Concise and

Scalable Strategy for the Total Synthesis of Dictyodendrin B Based on Sequential C-H Functionalization. *Angew. Chem. Int. Ed.* **2015**, *54*, 5451-5455. (d) Kim, Y.; Park, J.; Chang, S. A Direct Access to 7-Aminoindoles via Iridium-Catalyzed Mild C−H Amidation of N-Pivaloylindoles with Organic Azides. *Org. Lett.* **2016**, *18*, 1892-1895. (e) Yang, Y.; Qiu, X.; Zhao, Y.; Mu, Y. Shi, Z. Palladium-Catalyzed C–H Arylation of Indoles at the C7 Position. *J. Am. Chem. Soc.* **2016**, *138*, 495-498. (f) Gandeepan, P.; Koeller, J.; Ackermann, L. Expedient C-H Chalcogenation of Indolines and Indoles by Positional-Selective Copper Catalysis. *ACS Catal.* **2017**, *7*, 1030-1034. (g) De, P. B.; Pradhan, S.; Banerjee, S.; Punniyamurthy, T. Expedient Cobalt(II)-Catalyzed Site-Selective C7-Arylation of Indolines with Arylboronic Acids. *Chem. Commun.* **2018**, *54*, 2494-2497. (h) De, P. B.; Banerjee, S.; Pradhan, S.; Punniyamurthy, T. Ru(II)-Catalyzed C7-Acyloxylation of Indolines with Carboxylic Acids. *Org. Biomol. Chem.* **2018**, *16*, 5889-5898. (i) Qiu, X.; Deng, H.; Zhao, Y. and Shi, Z. Rhodium-catalyzed, P-directed selective C7 arylation of indoles. *Sci. Adv*. **2018**, *4*, aau6468. (j) Borah, A. J. and Shi, Z. Rhodium-Catalyzed, Remote Terminal Hydroarylation of Activated Olefins through a Long-Range Deconjugative Isomerization. *J. Am. Chem. Soc*. **2018**, *140*, 6062−6066. (k) Shah, T. A.; De, P. B.; Pradhan, S.; Punniyamurthy, T. Transition-Metal-Catalyzed Site-Selective C7-Functionalization of Indoles: Advancement and Future Prospects. *Chem. Commun.* **2019**, *55*, 572-587. (l) Qiu, X.; Wang, P.; Wang, D.; Wang, M.; Yuan, Y.; Shi, Z. P^{III}-Chelation-Assisted Indole C7-Arylation, Olefination, Methylation, and Acylation with Carboxylic Acids/Anhydrides by Rhodium Catalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 1504-1508. (m) Lv, J.; Chen, X.; Xue, X.-S.; Zhao, B.; Liang, Y.; Wang, M.; Jin, L.; Yuan, Y.; Han, Y.; Zhao, Y.; Lu, Y.; Zhao, J.; Sun, W.-Y.; Houk, K. N. and Shi, Z. Metal-free directed sp^2-C–H borylation. *Nature* **2019,** *575***,** 336–340.

(10) For indoles reviews, see: (a) Cacchi, S.; Fabrizi, G. Synthesis and Functionalization of Indoles Through Palladium-Catalyzed Reactions. *Chem. Rev.* **2005**, *105*, 2873-2920. (b) Bandini, M.; Eichholzer, A. Catalytic Functionalization of Indoles in a New Dimension.

Angew. Chem. Int. Ed. **2009**, *48*, 9608-9644. (c) Sandtorv, A. H. Transition Metal-Catalyzed C-H Activation of Indoles. *Adv. Synth. Catal.* **2015**, *357*, 2403-2435. (d) Leitch, J. A.; Bhonoah, Y.; Frost, C. G. Beyond C2 and C3: Transition-Metal-Catalyzed C−H Functionalization of Indole. *ACS Catal.* **2017**, *7*, 5618-5627. (e) Yang, Y.; Shi, Z. Regioselective Direct Arylation of Indoles on the Benzenoid Moiety. *Chem.Commun.* **2018**, *54*, 1676-1685.

(11) For C-6 functionalization of indole/indolines, see: (a) Yang, G.; Lindovska, P.; Zhu, D.; Kim, J.; Wang, P.; Tang, R.-Y.; Movassaghi, M.; Yu, J.-Q. Pd(II)-Catalyzed meta-C−H Olefination, Arylation, and Acetoxylation of Indolines Using a U-Shaped Template. *J. Am. Chem. Soc.* **2014**, *136*, 10807-10813. (b) Feng, Y.; Holte, D.; Zoller, J.; Umemiya, S.; Simke, L. R.; Baran, P. S. Total Synthesis of Verruculogen and Fumitremorgin A Enabled by Ligand-Controlled C−H Borylation. *J. Am. Chem. Soc*. **2015**, *137*, 10160−10163. (c) Yang, Y.; Li, R.; Zhao, Y.; Zhao, D.; Shi, Z. Cu-Catalyzed Direct C6-Arylation of Indoles. *J. Am. Chem. Soc.* **2016**, *138*, 8734−8737. (d) Leitch, J. A.; McMullin, C. L.; Mahon, M. F.; Bhonoah, Y.; Frost, C. G. Remote C6-Selective Ruthenium-Catalyzed C−H Alkylation of Indole Derivatives via σ-Activation. *ACS Catal.* **2017**, *7*, 2616-2623.

(12) For examples, see: (a) Qi, Z.; Li, X. Rhodium(III)-Catalyzed Coupling of Arenes with 7-Oxa/azabenzonorbornadienes by C-H Activation. *Angew. Chem. Int. Ed.* **2013**, *52*, 8995-9000. (b) Cheng, H.; Dong, W.; Dannenberg, C. A.; Dong, S.; Guo, Q.; Bolm, C. Ruthenium-Catalyzed Hydroarylations of Oxa- and Azabicyclic Alkenes. *ACS Catal.* **2015**, *5*, 2770-2773. (c) Wang, X.; Lerchen, A.; Gensch, T.; Knecht, T.; Daniliuc, C. G.; Glorius, F. Combination of Cp*RhIII -Catalyzed C-H Activation and a Wagner-Meerwein-Type Rearrangement. *Angew. Chem. Int. Ed.* **2017**, *56*, 1381-1384. (d) Wang, X.; Li, Y.; Knecht, T.; Daniliuc, C. G.; Houk K. N. and Glorius, F. Unprecedented Dearomatized Spirocyclopropane in a Sequential Rhodium(III)-Catalyzed C-H Activation and Rearrangement Reaction. *Angew. Chem. Int. Ed.* **2018**, *57*, 5520–5524. (e) Yan, Q.; Xiong, C.; Chu, S.; Liu, Z.; and Yuhong Zhang, Y.

Ruthenium-Catalyzed Ring-Opening Addition of Anilides to 7-Azabenzonorbornadienes: A Diastereoselective Route to Hydronaphthylamines. *J. Org. Chem.* **2018**, *83*, 5598−5608. (f) Li, D.-Y.; Huang, Z.-L.; Liu, P.-N. Heterobicyclic Core Retained Hydroarylations through C–H Activation: Synthesis of Epibatidine Analogues. *Org. Lett.* **2018**, *20*, 2028-2032. (g) Mi, R.; Zheng, G.; Qi, Z.; Li, X. Rhodium-Catalyzed Enantioselective Oxidative [3+2] Annulation of Arenes and Azabicyclic Olefins via Twofold C-H Activation. *Angew. Chem. Int. Ed*. **2019**, *58*, 17666-17670. (h) Kumar, S. V.; Banerjee, S.; Punniyamurthy, T. Rh-catalyzed C-C/C-N bond formation via C-H activation: Synthesis of 2H-indazol-2-yl-benzo[a]carbazoles. *Org. Chem. Front.* **2019**, *6*, 3885-3890. (i) Wang, P.; Xu, Y.; Sun, J.; Li, X. Rhodium(III)-Catalyzed Chemo-divergent Couplings of Sulfoxonium Ylides with Oxa/azabicyclic Olefins. *Org. Lett.* **2019**, *21*, 8459-8463.

(13) (a) Chatani, N.; Asaumi, T.; Yorimitsu, S.; Ikeda, T.; Kakiuchi, F.; Murai, S. $\upsilon_3(CO)_{12}$-Catalyzed Coupling Reaction of sp^3 C−H Bonds Adjacent to a Nitrogen Atom in Alkylamines with Alkenes. *J. Am. Chem. Soc*. **2001**, *123*, 10935-10941. (b) Pastine, J. L.; Gribkov, V. D.; Sames, D. sp^3 C−H Bond Arylation Directed by Amidine Protecting Group: α-Arylation of Pyrrolidines and Piperidines. *J. Am. Chem. Soc*. **2006**, *128*, 14220-14221. (c) Jiang, Z.; Zhang, L.; Dong, C.; Su, X.; Li, H.; Tang, W.; Xu, L.; Fan, Q. Direct Synthesis of 8-Aryl Tetrahydroquinolines *via* Pd-Catalyzed *ortho*-Arylation of Arylureas in Water. *RSC Adv*. **2013**, *3*, 1025-1028. (d) Jeon, M.; Mishra, N. K.; De, U.; Sharma, S.; Oh, Y.; Choi, M.; Jo, H.; Sachan, R.; Kim, H. S.; Kim, I. S. Rh(III)-Catalyzed C–H Functionalization of Indolines with Readily Accessible Amidating Reagent: Synthesis and Anticancer Evaluation. *J. Org. Chem.* **2016**, *81*, 9878-9885. (e) Mishra, N. K.; Jeon, M.; Oh, Y.; Jo, H.; Park, J.; Han, S.; Sharma, S.; Han, S. H.; Jung, Y. H.; Kim, I. S. Site-selective Cp*Rh(III)-Catalyzed C–H Amination of Indolines with Anthranils. *Org. Chem. Front*. **2017**, *4*, 241-249. (f) Leitch, J. A.; Heron, C. J.; McKnight, J.; Kociok-Köhn, G.; Bhonoahd, Y.; Frost, C. G. Ruthenium Catalyzed Remote C4-Selective C–H Functionalisation of Carbazoles *via* σ-Activation. *Chem. Commun*. **2017**, *53*, 13039-13042.

(14) Xie, W.; Li, B.; Wang, B. Rh(III)-Catalyzed C7-Thiolation and Selenation of Indolines. *J. Org. Chem*. **2016**, *812*, 396-403.