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Pd(0)-Catalyzed Intramolecular Heck reaction of 2/3-Aryl(amino)methyl-3/2-bromoindoles: Syntheses of 3,4-Benzo[*c*]-β-carbolines, Benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-Dioxides, and 1,2-Benzo[*a*]-γ-carbolines

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Cite This: *J. Org. Chem.* 2021, 86, 1925−1937 Read Online

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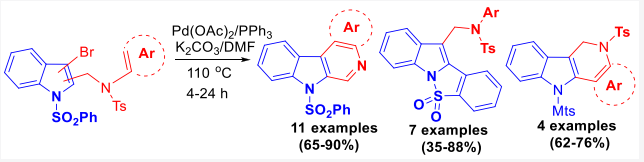
ABSTRACT: One-pot synthesis of 3,4-benzo[*c*]-β-carbolines was achieved from 2-aryl(tosylamino)methyl-3-bromoindoles via 10 mol % $Pd(OAc)_2/PPh_3$-mediated intramolecular Heck coupling using K_2CO_3 as a base in DMF at 110 °C with concomitant aromatization through an elimination of tosylsulfinic acid. Under identical conditions, the isomeric 3-aryl(tosylamino)methyl-2-bromoindoles upon intramolecular Heck reaction furnished benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxides instead of the expected γ-carbolines. However, synthesis of the expected γ-carboline framework, 3-tosyl-6,9-dihydro-1,2-benzo[*a*]-γ-carbolines, could be achieved from 3-aryl(tosylamino)methyl-2-bromoindoles containing a mesitylene sulfonyl unit as a protecting group on the indole nitrogen.



Carbolines are pyridine-fused indole heterocycles present in many natural products and bioactive compounds. Among the four regioisomeric α-, β-, γ-, and δ-carbolines, β-carbolines are most extensively dispersed in nature. β-Carboline units are present in a wide variety of indole alkaloids.[1] The β-carboline-based alkaloids possess significant biological activities such as antiplasmodial, antithrombotic, parasiticidal, anti-HIV, anti-Alzheimer, and antifungal effects.[2] These compounds are known for their cytotoxicity, DNA intercalation, and topoisomerase inhibition.[3] Traditionally, β-carbolines and their derivatives are obtained via Bischler−Napieralski, Fischer indolization, and Pictet−Spengler cyclization reactions.[4]

Some of the recently reported methodologies to access β-carbolines (Figure 1) involve Pd-catalyzed coupling of 3-iodo-2-iminoindole with substituted acetylene derivatives followed by cyclization,[5] Bu_3SnH-mediated radical cyclization of 3-bromo-2-aryl-(*N*-tosylamino)methylindole,[6] and regioselective Buchwald−Hartwig amination followed by Heck-type intramolecular arylation of 3-(2-bromophenylamino)quinolines,[7] electrocyclization of imino ether precursors,[8] Pd(0)-catalyzed coupling of indole with 1-iodo-2-nitrobenzene followed by reductive cyclization,[9] Pd(II)-catalyzed coupling of 2-iminoindole with acetylene derivatives followed by cyclization,[10] Ullmann cross-coupling of 2-iodocyclohex-2-en-1-ones with 3-nitro-4-iodopyrdine followed by Pd-catalyzed sequential reductive cyclization and dehydrogenation,[11] and condensation of an in situ generated 1,5-diketone with ammonia.[12] Apart from these reports, Mulcahy and co-workers outlined the synthesis of pyrido[3,4-*b*]indoles utilizing Rh(I)-catalyzed cyclization methodology.[13] Tilve and Volvoikar reported the synthesis of indolo[2,3-*c*]quinoline and indolo[3,2-*c*]quinoline salts involving I_2/TBHP-mediated intramolecular dehydrogenative coupling reaction.[14] Very recently, Vyalyh and co-workers reported the synthesis of carbolines involving LDA-mediated

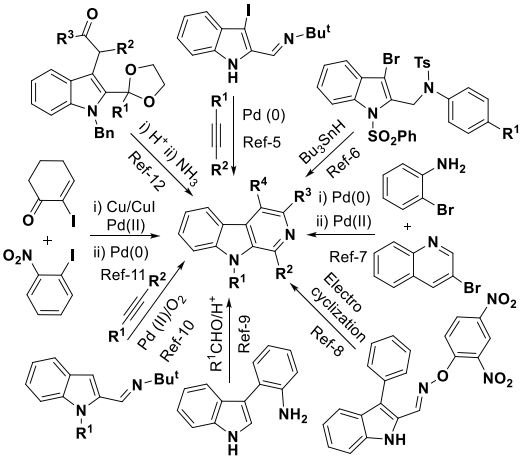


Figure 1. Summary of recent strategies for β-carboline synthesis.

Received: September 6, 2020
Published: January 4, 2021

https://dx.doi.org/10.1021/acs.joc.0c02152
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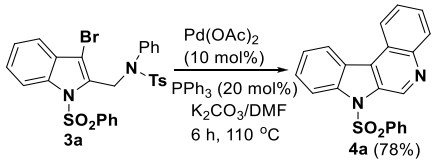
cycloaddition of 3-benzoyl-2-methylindole with nitriles.[15] Invariably, most of these methods suffer from disadvantages such as restricted substitution and harsh reaction conditions.

Our strategy is to utilize *N*-aryltryptamine as well as *N*-arylisotryptamine precursors for the construction of cyclo-fused carbolines via intramolecular Heck coupling of *N*-((3/2-bromo-1-(phenylsulfonyl)-1*H*-indol-2/3-yl)methyl)-4-methyl-*N*-arylbenzenesulfonamides. To initiate this work, the known 3-bromo-2-bromomethylindole **1**[6] was reacted with 4-methyl-*N*-phenylbenzenesulfonamide **2a** in the presence of K_2CO_3 in DMF to afford 2-(phenylaminomethyl)-3-bromoindole **3a** in 75% yield. Initially, intramolecular Heck coupling of 2-(phenylaminomethyl)-3-bromoindole **3a** using 10 mol % $Pd(PPh_3)_4$ in the presence of K_2CO_3 in DMF at 100 °C for 12 h led to the isolation of benzo-*β*-carboline **4a** in 36% yield. Subsequently, the intramolecular coupling reaction employing an in situ generated zerovalent Pd (10 mol %) using $Pd(OAc)_2$−PPh_3 in the presence of K_2CO_3 in DMF at 110 °C for 6 h gave the benzo-*β*-carboline **4a** in 78% yield (Scheme 1).

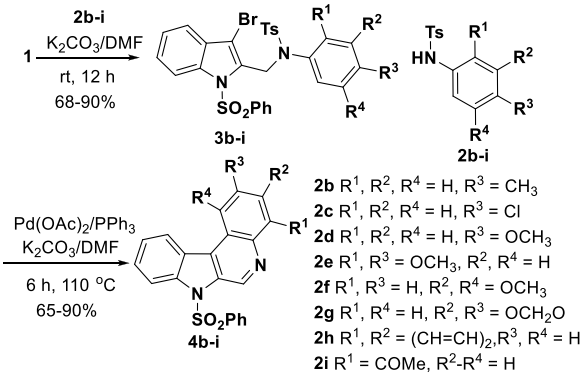
Scheme 1. Synthesis of Benzo-*β*-carboline 4a

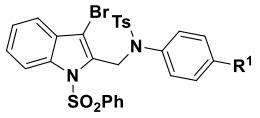
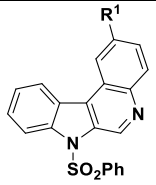
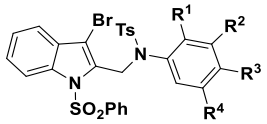
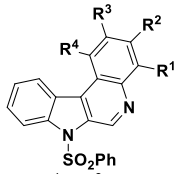
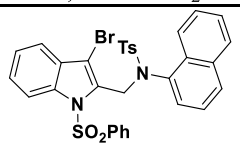
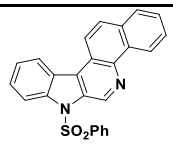
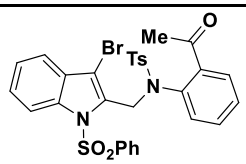
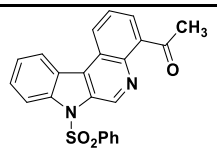


Having achieved the synthesis of *β*-carboline **4a**, next, synthesis of *β*-carboline derivatives having different substituents on the benzene portion was planned. With that idea in mind, the required 2-arylaminomethyl-3-bromoindoles **3b**−**i** were prepared via the reaction of 3-bromo-2-bromomethylindole **1** with substituted 4-methyl-*N*-arylbenzenesulfonamides **2b**−**i** using K_2CO_3 in DMF at room temperature for 12 h. As expected, 2-arylaminomethyl-3-bromoindole **3b**−**i** upon reaction with 10 mol % $Pd(OAc)_2$−PPh_3(20 mol %) and K_2CO_3 in DMF at 110 °C for 6 h underwent intramolecular coupling followed by a subsequent tosyl group elimination to furnish the respective *β*-carbolines **4b**−**i** in 65−90% yields (Table 1). It should be noted that the Pd-catalyzed intramolecular coupling of 2-piperonylaminomethyl-3-bromoindole **3g** furnished *β*-carboline **4g** as an exclusive product in 78% yield. To our delight, the synthesis of naptho[*b*]-*β*-carboline **4h** was also achieved by an intramolecular Heck coupling of the respective 2-naphthylaminomethyl-3-bromoindole **3h**. The 2-phenylaminomethyl-3-bromoindole **3i** containing an electron-withdrawing acetyl unit in the benzene portion also underwent the Pd-catalyzed intramolecular coupling reaction followed by aromatization to afford the respective *β*-carboline **4i** in 65% yield. Except in the case of 3-bromoindole **3i**, in all other cases, the 10% Pd(0)-catalyzed intramolecular cyclization followed by base-mediated elimination of *p*-toulenesulfinic acid furnished the corresponding *β*-carbolines in very good yields. The structures of the *β*-carbolines **4a** and **4h** were confirmed by single-crystal X-ray diffraction analyses (see the SI).

Based on the facile synthesis of benzo-*β*-carbolines **4a**−**i**, next, the synthesis of 4-susbtituted *β*-carboline was planned by employing the similar sequence of reactions. As expected, the reaction of 3-bromo-2-phenylsulfonylaminomethylindole **5**[16] with allyl bromide/cinnamyl bromide using K_2CO_3 in CH_3CN at reflux led to the formation of 3-bromoindoles **6a** and **6b**, respectively. Using the established conditions as mentioned above, compound **6a**/**6b** underwent smooth Pd(0)-catalyzed

Table 1. Synthesis of Benzo-*β*-carbolines 4b−i



3-Bromo-2-arylamino methylindoles **3b-i**	β-carbolines **4b-i**[a]	Yield (%)[b]
 **3b** R^1 = Me **3c** R^1 = Cl **3d** R^1 = OMe	 **4b** R^1 = Me **4c** R^1 = Cl **4d** R^1 = OMe	88 75 79
 **3e** R^1, R^3 = OMe; R^2, R^4 = H **3f** R^1, R^3 = H; R^2, R^4 = OMe **3g** R^1, R^4 = H; R^2, R^3 = OCH_2O	 **4e** R^1, R^3 = OMe; R^2, R^4 = H **4f** R^1, R^3 = H; R^2, R^4 = OMe **4g** R^1, R^2 = H; R^3, R^4 = OCH_2O	85 90 78
 **3h**	 **4h**	90
 **3i**	 **4i**	65

[a]*β*-Carbolines **4b**−**i** were obtained using 3-bromoindole **3b**−**i** (1 equiv), $Pd(OAc)_2$ (10 mol %), PPh_3(20 mol %), and K_2CO_3 (3 equiv) in DMF at 110 °C under N_2 atmosphere for 6 h. [b]Isolated yield of *β*-carbolines **4b**−**i** by column chromatography.

https://dx.doi.org/10.1021/acs.joc.0c02152
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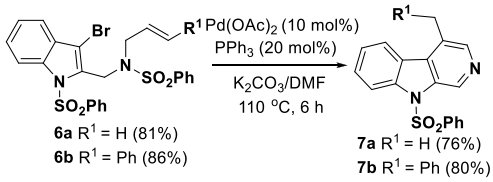
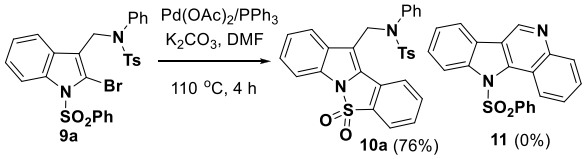
intramolecular Heck coupling followed by aromatization to furnish β-carbolines **7a** and **7b** in 76% and 80% yields, respectively (Scheme 2).

Scheme 2. Synthesis of 4-Substituted β-Carbolines 7a and 7b



Having achieved the synthesis of β-carboline derivatives **4a–i/7a/7b**, next, the synthesis of γ-carboline congeners involving the Pd-catalyzed intramolecular coupling reaction of isomeric 2-bromoindoles was initiated. Accordingly, the required starting material, 2-bromo-3-arylaminomethylindole **9a**, was prepared via the reaction of 2-bromo-3-bromomethyl-1-phenylsulfonylindole **8** with 4-methyl-*N*-phenylbenzenesulfonamide **2a** using K_2CO_3 as base in DMF at room temperature. However, the Pd-catalyzed intramolecular Heck coupling reaction of 2-bromo-3-phenylaminomethylindole **9a** in the presence of K_2CO_3 in DMF at 110 °C for 4 h failed to produce the expected benzo-γ-carboline **11** (Scheme 3). On the basis of

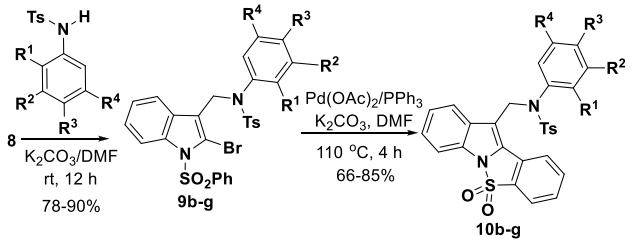
Scheme 3. Pd-Catalyzed Cyclization of 2-Bromo-3-phenylaminomethylindole 9a

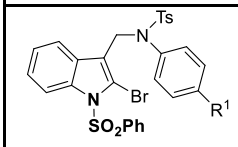
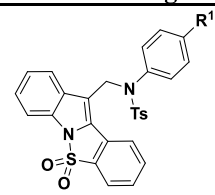
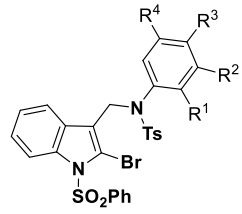
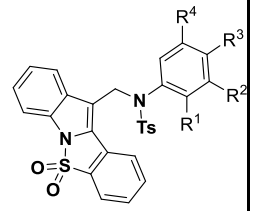


the ^{1}H and ^{13}C NMR spectral data, the structure of the unusual product obtained during the Pd-catalyzed intramolecular coupling reaction of **9a** was assigned as a sulfonamide **10a**. The formation of the sulfonamide **10a** clearly confirmed that the phenyl group of 3-phenylaminomethylindole **9a** is not in the proximal position of the intermediate 2-indolyl-Pd species to induce the required coupling reaction with the 2-position of *N*-tosylaniline to yield the expected γ-carboline **11**. Obviously, the 2-indolyl-Pd species formed underwent facile intramolecular coupling reaction with the *N*-phenylsulfonyl group to give the sulfonamide **10a**. A survey of the literature indicated that Laha and co-workers[17] recently observed a similar type of sulfonamide formation involving Pd-catalyzed CH activation of *N*-phenylsulfonylindoles.

Toward unravelling the electronic influence of aryl units on the observed Pd-catalyzed coupling reaction, a series of 2-bromo-3-arylaminomethylindoles **9b–g** containing different substituents were prepared from 3-bromomethylindole **8**. As expected, the coupling reaction of 2-bromo-3-arylaminomethylindoles **9b–g** using $Pd(OAc)_2$–PPh_3 in the presence of K_2CO_3 as a base in DMF followed by workup afforded, only, the respective sulfonamides **10b–g** as the exclusive products (Table 2). The ^{1}H and ^{13}C NMR spectral data of sulfonamides **10b–g** were consistent with their structures.

Table 2. Synthesis of Benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxides 10b–g



2-Bromo-3-arylamino methylindoles **9b-g**	Benzo[4,5]isothiazolo [2,3-*a*]indole 5,5-dioxides **10b-g**[a]	Yield (%)[b]
 **9b** R^1 = Me **9c** R^1 = OMe	 **10b** R^1 = Me **10c** R^1 = OMe	82 85
 **9d** R^1, R^3 = OMe; R^2, R^4 = H **9e** R^1, R^3 = H; R^2, R^4 = OMe **9f** R^1, R^4 = H; R^2, R^3 = OMe **9g** R^1 = COMe R^2-R^4 = H	 **10d** R^1, R^3 = OMe; R^2, R^4 = H **10e** R^1, R^3 = H; R^2, R^4 = OMe **10f** R^1, R^4 = H; R^2, R^3 = OMe **10g** R^1 = COMe R^2-R^4 = H	85 85 80 66

[a]Indole sulfonamides **10b–g** were obtained using 2-bromoindole **9b–g** (1 equiv), $Pd(OAc)_2$ (10 mol %), PPh_3(20 mol %), and K_2CO_3 (3 equiv) in DMF at 110 °C under N_2 atmosphere for 4 h. [b]Isolated yield of indole sulfonamides **10b–g** by column chromatography.

The 2-bromo-3-bromomethyl-1-phenylsulfonylindole **8** upon reaction with 3,4-methylenedioxyanilinylsulfonamide **2g** using K_2CO_3 in dry DMF gave compound **9h** in 78% yield. To our surprise, intramolecular Heck coupling reaction of **9h** using $Pd(OAc)_2$/PPh_3 and K_2CO_3 in DMF at 110 °C for 6 h followed by workup furnished sulfonamide **10h** and γ-carboline **12** in 35% and 34% yields, respectively. The formation of γ-carboline **12** could be realized through the intramolecular coupling reaction of **9h** followed by base-mediated migration of the tosyl group to give dihydrocarboline **14**. The dihydrocarboline **14** uponsubsequent aromatization could lead to the formation of γ-carboline **12** (Scheme 4). As a representative case, the structure of sulfonamide **10h** could be confirmed by a single-crystal X-ray diffraction analysis (see SI).

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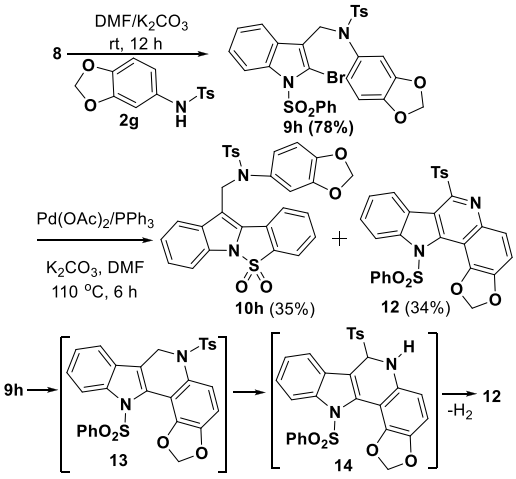
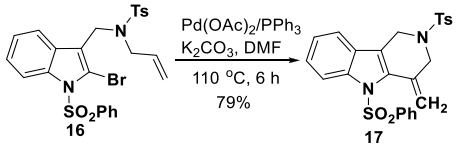
Scheme 4. Pd-Catalyzed Cyclization of 2-Bromo-3-piperonylaminomethylindole 9h



Next, 2-bromo-3-bromomethyl-1-phenylsulfonylindole **8** upon reaction with the 4-methylbenzenesulfonamide in acetonitrile at reflux gave 2-bromo-3-*N*-tosylaminomethyl-1-phenylsulfonylindole **15**. Then the subsequent *N*-alkylation of compound **15** with allyl bromide afforded allylaminomethylindole **16** in 85% yield. As expected, the Pd(0)-catalyzed Heck coupling reaction of compound **16** led to the formation of γ-carboline derivative **17** as an exclusive product in 79% yield (Scheme 5).

Scheme 5. Pd-Catalyzed Cyclization of 2-Bromo-3-allyl-*N*-tosylaminomethylindole 16

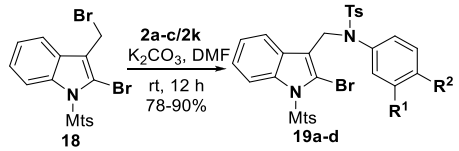


Contrary to the 2-bromo-3-arylaminomethylindoles **9b−g**, the allylaminomethylindole **16** underwent an exclusive intramolecular Heck coupling with vinyl unit rather than the intramolecular coupling reaction with an *N*-phenylsulfonyl group.

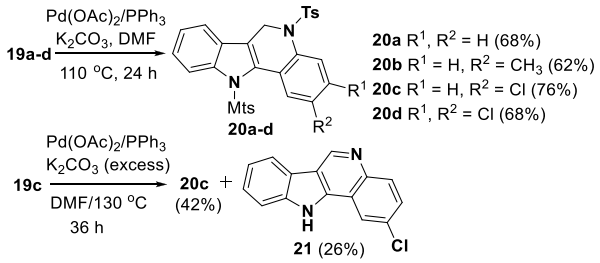
To overcome the unexpected intramolecular Heck coupling of 2-bromoindole with the *N*-benzenesulfonyl unit, synthesis of 2-bromomethylindoles containing a 2-mesitylenesulfonyl (Mts) unit at the indole-1-position was initiated. Accordingly, the required bromomethylindole **18** was prepared via *N*-mesitylsulfonylation of 3-methylindole followed by ring bromination and subsequent benzylic bromination to give 1-(mesitylenesulfonyl)-2-bromo-3-bromomethylindole **18**. The *N*-alkylation of bromomethylindole **18** with *N*-arylbenzenesulfonamide **2a,b/2j/2k** in the presence of K_2CO_3 as a base in DMF at room temperature furnished the 3-arylaminomethyl-2-bromoindoles **19a−d** in 78−90% yields (Scheme 6).

Gratifyingly, the intramolecular Heck coupling reaction of the 3-phenylaminomethyl-2-bromoindoles **19a−d** using Pd(0) in the presence of K_2CO_3 in DMF at 110 °C for 24 h gave the respective dihydro-γ-carbolines **20a−d** in 62−76% yields (Scheme 7). As a representative case, the intramolecular Heck coupling reaction of the 3-(4-methylphenyl)-

Scheme 6. Synthesis of 1-Mesitylenesulfonyl-2-bromo-3-aryl-*N*-tosylaminomethylindoles 19a−d



Scheme 7. Pd-Catalyzed Cyclization of 1-Mesitylenesulfonyl-2-bromo-3-aryl-*N*-tosylaminomethylindoles 19a−d

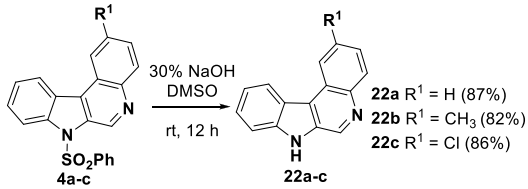


tosylaminomethyl-2-bromoindole **19b** using Pd(0) with an excess of K_2CO_3 in DMF at 130 °C for 36 h led to the isolation dihydro-γ-carboline **20c** and benzo-γ-carboline **21** in 42% and 26% yields, respectively.

The probable mechanism for the formation of carbolines **4a** and **20a** as well as benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxide **10a** is outlined (see SI Figure 1 [DMH]).

Finally, the representative *N*-sulfonyl-β-carbolines **4a−c** could be hydrolyzed using 30% NaOH in DMSO at room temperature to give *N*-free β-carbolines **22a−c** (Scheme 8). As a representative case, gram-scale synthesis of benzo-β-carboline **4a** as well as benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxide **10f** could be achieved in acceptable yields.

Scheme 8. Cleavage of the *N*-Phenylsulfonyl Unit of Representative β-Carbolines 4a−c [DM2]



In summary, we have developed an efficient one pot synthesis of 3,4-benzo[*c*]-β-carbolines involving the Pd-catalyzed intramolecular Heck coupling reaction of 2-aryl-(tosylamino)methyl-3-bromoindoles. The methodology was found to be useful for accessing 4-substituted β-carbolines as well. In the case of isomeric 3-aryl(tosylamino)methyl-2-bromoindoles, the Pd-catalyzed intramolecular Heck coupling led to the formation of benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxides instead of the expected γ-carbolines. However, the 3-aryl(tosylamino)methyl-2-bromoindoles containing mesitylenesulfonyl unit on the indole nitrogen underwent Pd(0)-mediated intramolecular Heck coupling reaction to furnish the

https://dx.doi.org/10.1021/acs.joc.0c02152
J. Org. Chem. 2021, 86, 1925−1937

required γ-carboline frameworks in reasonable yields. Thus, by the appropriate choice of protecting group on the indole nitrogen, the Pd(0)-catalyzed Heck coupling reaction can be fine tuned to access a wide variety of carboline as well as benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxide heterocycles. The structures of the representative benzo[*c*]β-carbolines and benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxide were confirmed through single-crystal X-ray analyses.

EXPERIMENTAL SECTION

General Methods. All melting points were uncorrected. Solvents were dried by standard procedures. All of the experiments were carried out under nitrogen atmosphere unless otherwise stated. Reactions other than room temperature were carried out in an oil bath. The progression of all of the reactions was monitored by TLC using a hexanes/ethyl acetate (EA) mixture. Column chromatography was carried out on silica gel (230−400 mesh, Merck) by increasing the polarity. ^{1}H, ^{13}C, and DEPT spectra were recorded in $CDCl_3$ using TMS as an internal standard on Bruker 300 and 400 MHz spectrometers at room temperature. Chemical shift values are quoted in parts per million (ppm), and coupling constants are quoted in hertz (Hz). HRMS were recorded on Xevo G2S QTof instrument.

3-Bromo-2-(bromomethyl)-1-(phenylsulfonyl)-1*H*-indole (1). To a solution of 3-bromo-2-methyl-1-phenylsulfonylindole (1 g, 2.86 mmol) in CCl_4 (30 mL) were added NBS (0.66 g, 3.72 mmol) and AIBN (0.1 g, 0.28 mmol), and the solution was refluxed for 1 h. After completion of the reaction (monitored by TLC), the floated succinimide was filtered off and filtrate was concentrated under reduced pressure. The crude product was crystallized from methanol (3 mL) to afford 3-bromo-2-bromomethylindole **1** as a colorless solid (1.12 g, 92%). Mp: 100−102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.14 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.60−7.52 (m, 2H), 7.48−7.37 (m, 3H), 7.35−7.32 (m, 1H), 5.14 (s, 2H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)138.5, 136.3, 134.2, 133.3, 129.3, 128.6, 127.1, 124.6, 120.3, 115.0, 106.1, 22.6 ppm.

General Procedure for the Preparation of Compounds 3a−i. To a solution of 3-bromo-2-bromomethylindole **1** (0.58 mmol) in DMF (10 mL) were added *N*-tosylanilines **2a−i** (0.70 mmol) and K_2CO_3 (1.75 mmol). The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), the mixture was poured over crushed ice containing concd HCl (5 mL). The solid obtained was filtered, washed with water (2 × 20 mL), and dried (Na_2SO_4). The crude product was recrystallized from methanol (5 mL) to afford sulfonamides **3a−i**.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-4-methyl-N-phenylbenzenesulfonamide (**3a**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosylaniline **2a** (172 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) following the general procedure as mentioned above furnished sulfonamide **3a** as a colorless solid (260 mg, 75%). Mp: 220−222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.25−7.13 (m, 5H), 7.00−6.93 (m, 3H), 6.70 (d, *J* = 7.2 Hz, 2H), 5.26 (s, 2H), 2.33 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.7, 138.2, 137.9, 136.4, 134.6, 134.1, 130.8, 129.4, 129.3, 128.5, 128.3, 128.2, 128.1, 126.7, 126.5, 124.2, 120.0, 115.1, 107.3, 45.9, 21.6 ppm. Anal. Calcd for $C_{28}H_{23}BrN_2O_4S_2$: C, 56.47; H, 3.89; N, 4.70; S, 10.77. Found: C, 56.32; H, 3.65; N, 4.38; S, 10.92.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-4-methyl-N-p-tolylbenzenesulfonamide (**3b**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-4-methylaniline **2b** (183 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) adopting the above-mentioned general procedure afforded sulfonamide **3b** as a colorless solid (290 mg, 82%). Mp: 185−187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.1 Hz, 1H) 7.82 (d, *J* = 7.5 Hz, 2H), 7.60−7.55 (m, 3H), 7.47−7.42 (m, 2H), 7.37−7.35 (m, 2H), 7.31−7.26 (m, 3H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 2H), 5.35 (s, 2H), 2.44 (s, 3H), 2.19 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.5, 138.6, 137.9, 136.6, 135.6, 135.3, 134.0, 131.3, 129.3 (2C), 129.1, 128.8, 128.4, 126.8, 126.4, 124.3, 120.1, 115.3, 107.3, 46.0, 21.5, 21.0 ppm. Anal. Calcd for $C_{29}H_{25}BrN_2O_4S_2$: C, 57.14; H, 4.13; N, 4.60; S, 10.52. Found: C, 57.31; H, 3.96; N, 4.81; S, 10.37.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-N-(4-chlorophenyl)-4-methylbenzenesulfonamide (**3c**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-4-chloroaniline **2c** (196 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) following the general procedure gave sulfonamide **3c** as a colorless solid (249 mg, 68%). Mp: 188−190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.52−7.46 (m, 3H), 7.36 (t, *J* = 7.35 Hz, 2H), 7.26 (t, *J* = 7.35 Hz, 2H), 7.20−7.14 (m, 3H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 5.23 (s, 2H), 2.35 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.0, 138.3, 136.6, 136.4, 134.3, 134.2, 134.0, 130.7, 130.4, 129.5, 129.4, 128.6, 128.4, 128.2, 126.7 (2C), 124.4, 120.1, 115.2, 107.4, 45.8, 21.6 ppm. Anal. Calcd for $C_{28}H_{22}BrClN_2O_4S_2$: C, 53.38; H, 3.52; N, 4.45; S, 10.18. Found: C, 53.21; H, 3.36; N, 4.58; S, 9.96.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (**3d**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-4-methoxyaniline **2d** (194 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) adopting the general procedure afforded sulfonamide **3d** as a colorless solid (288 mg, 79%). Mp: 175−177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.50−7.48 (m, 3H), 7.39−7.35 (m, 2H), 7.28−7.17 (m, 5H), 6.59 (d, *J* = 7.2 Hz, 2H), 6.46 (d, *J* = 7.8 Hz, 2H), 5.23 (s, 2H), 3.58 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.0, 143.6, 138.4, 136.4, 134.8, 134.1, 130.9, 130.7, 130.2, 129.3, 128.5, 128.3, 126.7, 126.5, 124.2, 120.1, 115.2, 113.6, 107.3, 55.2, 45.9, 21.6 ppm. Anal. Calcd for $C_{29}H_{25}BrN_2O_5S_2$: C, 55.68; H, 4.03; N, 4.48; S, 10.25. Found: C, 55.58; H, 4.26; N, 4.57; S, 10.01.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-N-(2,4-dimethoxyphenyl)-4-methylbenzenesulfonamide (**3e**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-2,4-dimethoxyaniline **2e** (215 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) following the general procedure furnished sulfonamide **3e** as a colorless solid (286 mg, 75%). Mp: 70−72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.32−7.11 (m, 5H), 6.79 (d, *J* = 8.7 Hz, 1H), 6.11−6.04 (m, 4H), 5.43−5.27 (m, 2H), 3.60 (s, 3H), 3.15 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 160.8, 157.8, 142.6, 138.0, 137.3, 136.4, 134.0, 133.9, 132.1, 129.1, 128.9, 128.7, 128.0, 126.6, 126.3, 124.2, 120.0, 118.5, 115.3, 107.6, 103.7, 98.5, 55.3, 54.4, 45.1, 21.5 ppm. Anal. Calcd for $C_{30}H_{27}BrN_2O_6S_2$: C, 54.96; H, 4.15; N, 4.27; S, 9.78. Found: C, 55.23; H, 4.43; N, 4.00; S, 10.02.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-N-(3,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**3f**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-3,5-dimethoxyaniline **2f** (241 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) adopting the general procedure afforded sulfonamide **3f** as a colorless solid (344 mg, 90%). Mp: 110−112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.35 Hz, 1H), 7.40−7.19 (m, 7H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.19−6.16 (m, 1H), 6.12 (s, 1H), 5.50−5.35 (m, 2H), 3.68 (s, 3H), 3.23 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 160.8, 157.9, 142.6, 138.0, 137.4, 136.4, 134.6, 133.9, 132.2, 129.2, 129.0, 128.8, 128.0, 126.6, 126.3, 124.2, 120.1, 118.6, 115.4, 107.6, 163.7, 98.5, 21.5 ppm. Anal. Calcd for $C_{30}H_{27}BrN_2O_6S_2$: C, 54.96; H, 4.15; N, 4.27; S, 9.78. Found: C, 55.23; H, 4.43; N, 4.00; S, 10.02.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-N-(3,4-methylenedioxyphenyl)-4-methylbenzenesulfonamide (**3g**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-3,4-methyledioxyaniline **2g** (203 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) following the general procedure furnished sulfonamide **3g** as a colorless solid (283 mg,

https://dx.doi.org/10.1021/acs.joc.0c02152
J. Org. Chem. 2021, 86, 1925−1937

76%). Mp: 168−170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.55−7.54 (m, 1H), 7.45−7.42 (m, 2H), 7.35−7.31 (m, 2H), 7.25−7.21 (m, 2H), 6.41 (d, *J* = 5.1 Hz, 1H), 6.24−6.23 (m, 1H), 6.21−6.19 (m, 1H), 5.80 (s, 2H), 5.27 (s, 2H), 2.41 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 147.3, 147.1, 143.8, 138.3, 136.4, 134.6, 134.2, 131.4, 10.7, 129.4 (2C), 128.5, 128.3, 126.7, 126.6, 126.3, 123.1, 120.1, 115.2, 110.7, 107.3, 101.5, 46.0, 21.6 ppm. Anal. Calcd for $C_{29}H_{23}BrN_2O_6S_2$: C, 54.46; H, 3.63; N, 4.38; S, 10.03. Found; C, 54.24; H, 3.39; N, 4.51; S, 10.15.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-4-methyl-N-(naphthalen-1-yl)benzenesulfonamide (**3h**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-1-naphthylamine **2h** (207 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) following the general procedure gave sulfonamide **3h** as a colorless solid (330 mg, 88%). Mp: 70−72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28−8.25 (m, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.72−7.61 (m, 4H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.34−7.20 (m, 8H), 7.17−7.11 (m, 3H), 5.76 (d, *J* = 13.8 Hz, 1H), 5.37 (d, *J* = 13.8 Hz, 1H), 2.43 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.6, 137.7, 136.6, 135.8, 134.8, 134.3, 133.9, 133.5, 131.3, 129.3, 129.2, 129.1, 129.0, 128.6, 128.3 127.4, 126.5, 126.4, 126.2, 126.0, 124.6, 124.5, 124.4, 120.0, 115.6, 109.3, 47.0, 21.5 ppm. Anal. Calcd for $C_{32}H_{25}BrN_2O_4S_2$: C, 59.54; H, 3.90; N, 4.34; S, 9.93. Found; C, 59.42; H, 3.67; N, 4.48; S, 9.76.

*N-(2-Acetylphenyl)-N-((3-bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-4-methylbenzenesulfonamide (**3i**).* The reaction of 3-bromo-2-bromomethylindole **1** (250 mg, 0.58 mmol) with *N*-tosyl-2-acetylaniline **2i** (202 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) following the general procedure afforded sulfonamide **3i** as a colorless solid (278 mg, 75%). Mp: 180−182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.61−7.52 (m, 5H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.32−7.25 (m, 6H), 7.22−7.11 (m, 3H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 2H), 2.56 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.9, 143.4, 141.9, 137.2, 137.1, 136.8, 135.8, 133.9, 132.4, 132.2, 130.9, 129.6, 129.3, 129.2, 129.1, 128.6, 128.4, 126.8, 126.5, 124.9, 120.3, 116.2, 110.4, 47.3, 29.8, 21.5 ppm. Anal. Calcd for $C_{30}H_{25}BrN_2O_5S_2$: C, 56.52; H, 3.95; N, 4.39; S, 10.06. Found: C, 56.28; H, 4.14; N, 4.18; S, 9.81.

General Procedure for the Preparation of β-Carbolines 4a−i. To a solution of 3-bromo-2-arylaminomethylindoles **3a−i** (0.25 mmol) in DMF (8 mL) were added $Pd(OAc)_2$ (0.025 mmol), PPh_3 (0.052 mmol), and K_2CO_3(0.63 mmol). Then the reaction mixture was stirred at 110 °C for 6 h. After completion of the reaction (monitored by TLC), it was filtered through a Celite bed. It was then washed with ethyl acetate (10 mL). The combined filtrate was diluted with ethyl acetate (20 mL), washed with brine solution (2 × 10 mL), and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, EtOAc−hexane) afforded β-carbolines **4a−i** in good yields.

*7-(Phenylsulfonyl)-7H-indolo[2,3-c]quinoline (**4a**).* The intramolecular cyclization of 3-bromo-2-aminomethylindoles **3a** (150 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3(87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and chromatographic purification (silica gel, EtOAc−hexane 1:9) furnished β-carboline **4a** as a colorless solid (70 mg, 78%). Mp: 232−234 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.55 (d, *J* = 6.9 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.67−7.59 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.27−7.22 (m, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.9, 139.5, 138.5, 137.5, 134.2, 131.6, 130.5, 129.3, 128.9, 127.9, 127.7, 126.5, 125.3, 124.9, 123.4, 115.5 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{21}H_{14}N_2O_2S$ 358.0776, found 358.0775.

*2-Methyl-7-(phenylsulfonyl)-7H-indolo[2,3-c]quinoline (**4b**).* The cyclization reaction of 3-bromo-2-aminomethylindole **3b** (154 mg, 0.25 mmol) using $Pd(OAc)_2$(6 mg, 0.025 mmol), PPh_3(13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded β-carboline **4b** as a colorless solid (82 mg, 88%). Mp: 204−206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.55 (d, *J* = 7.4 Hz, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 8.37 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.59−7.54 (m, 2H), 7.46 (t, *J* = 6.9 Hz, 1H), 7.36−7.28 (m, 2H), 2.67 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.5, 138.5, 138.4, 137.9, 137.5, 134.2, 131.7, 130.1, 130.0, 129.3, 128.7, 126.5, 125.9, 125.5, 124.8, 123.5, 123.4, 122.5, 115.5, 22.1 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{22}H_{16}N_2O_2S$ 372.0932, found 372.0930.

*2-Chloro-7-(phenylsulfonyl)-7H-indolo[2,3-c]quinoline (**4c**).* To a solution of 3-bromo-2-aminomethylindole **3c** (158 mg, 0.25 mmol) in DMF (8 mL) were added $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3(13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol), and the mixture was stirred at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded β-carboline **4c** as a colorless solid (74 mg, 75%). Mp: 189−190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.47−8.44 (m, 2H), 8.34 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.65−7.58 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.29−7.24 (m, 2H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.2, 139.6, 138.5, 137.4, 134.4, 133.7, 131.9, 130.7, 130.3, 129.8, 129.4, 129.2, 128.7, 127.5, 126.8, 126.5, 125.5, 125.0, 124.0, 123.5, 123.2, 122.5, 115.6 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{21}H_{13}ClN_2O_2S$ 392.0386, found 392.0385.

*2-Methoxy-7-(phenylsulfonyl)-7H-indolo[2,3-c]quinoline (**4d**).* The intramolecular Heck reaction of 3-bromo-2-aminomethylindoles **3d** (158 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 1.5:8.5) furnished β-carboline **4d** as a colorless solid (77 mg, 79%). Mp: 235−237 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.79 (s, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 3H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.49−7.22 (m, 5H), 3.97 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.9, 140.8, 138.4, 137.6, 136.8, 134.2, 132.0, 131.9, 129.3, 128.6, 126.5, 125.5 (2C), 124.7, 124.4, 123.0, 119.5, 115.5, 102.5, 55.7 ppm. HRMS (ESI-TOF): *m*/*z* calcd for $[M]^+$ $C_{22}H_{16}N_2O_3S$ 388.0882, found 388.0880.

*2,4-Dimethoxy-7-(phenylsulfonyl)-7H-indolo[2,3-c]quinoline (**4e**).* The cyclization reaction of 3-bromo-2-aminomethylindole **3e** (165 mg, 0.25 mmol) using $Pd(OAc)_2$(6 mg, 0.025 mmol), PPh_3(13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded β-carboline **4e** as a colorless solid (89 mg, 85%). Mp: 200−202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.71−7.66 (m, 1H), 7.58−7.53 (m, 1H), 7.45−7.28 (m, 4H), 6.77 (s, 1H), 4.13 (s, 3H), 4.06 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.9, 157.1, 138.5, 137.6, 135.3, 134.2, 133.0, 132.6, 129.2, 128.6, 126.5, 125.6, 125.2, 124.7, 123.0, 115.5, 99.5, 93.9, 56.2, 55.6 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{23}H_{18}N_2O_4S$ 418.0987, found 418.0985.

*1,3-Dimethoxy-7-(phenylsulfonyl)-7H-indolo[2,3-c]quinoline (**4f**).* The cyclization reaction of 3-bromo-2-aminomethylindole **3f** (165 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded β-carboline **4f** as a colorless solid (95 mg, 90%). Mp: 228−230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.87 (d, *J* = 6.3 Hz, 1H), 8.52 (d, *J* = 6.3 Hz, 1H), 7.79 (d, *J* = 6 Hz, 2H), 7.64 (t, *J* = 6 Hz, 1H), 7.45 (m, 2H), 7.31−7.26 (m, 3H), 6.72 (s, 1H), 4.09 (s, 3H), 3.98 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.9, 156.4, 148.2, 140.1, 139.8, 138.2, 133.9, 131.4, 129.2, 128.9, 128.0, 127.9, 126.6, 126.2, 124.1, 115.2, 102.4, 100.4, 55.7, 55.4 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{23}H_{18}N_2O_4S$ 418.0987, found 418.0983.

*8-(Phenylsulfonyl)-8H-[1,3]dioxolo[4,5-f]indolo[2,3-c]quinoline (**4g**).* The cyclization reaction of 3-bromo-2-aminomethylindoles **3a** (101 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13

https://dx.doi.org/10.1021/acs.joc.0c02152
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mg, 0.052 mmol.), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and chromatographic purification (silica gel, EtOAc−hexane 2:8) furnished β-carboline **4g** as a colorless solid (79 mg, 78%). Mp: 202−204 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.81 (s, 1H), 9.01 (d, *J* = 8.1 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 7.91−7.85 (m, 3H), 7.67 (t, *J* = 8.1 Hz, 1H), 7.49−7.32 (m, 5H), 6.18 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.1, 141.7, 139.9, 138.3, 137.8, 137.5, 134.2, 131.4, 129.3, 128.8, 126.5, 125.8, 125.1, 125.0, 124.4, 124.0, 114.8, 111.4, 110.0, 101.6 ppm. Anal. Calcd for $C_{22}H_{14}N_2O_4S$: C, 65.66; H, 3.51; N, 6.96; S, 7.97. Found: C, 65.42; H, 3.67; N, 6.86; S, 8.11.

*7-(Phenylsulfonyl)-7H-benzo[h]indolo[2,3-c]quinolone (**4h**).* The intramolecular cyclization of 3-bromo-2-aminomethylindole **3h** (160 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded β-carboline **4h** as a colorless solid (91 mg, 90%). Mp: 186−188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.09 (s, 1H), 9.38 (d, *J* = 6.3 Hz, 1H), 8.56−8.53 (m, 3H), 8.00 (d, *J* = 6.6 Hz, 1H), 7.95 (d, *J* = 5.7 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 2H), 7.79 (t, *J* = 6 Hz, 1H) 7.70 (t, *J* = 5.7 Hz, 2H), 7.56 (t, *J* = 5.55 Hz, 1H), 7.45 (t, *J* = 5.55 Hz, 1H), 7.32 (t, *J* = 5.7 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 142.4, 138.8, 137.5, 137.0, 134.2, 132.7, 132.4, 131.9, 129.3, 129.1, 129.0, 127.8, 127.7, 127.5, 127.3, 126.5, 125.5, 124.8, 124.7, 123.8, 121.2, 120.9, 115.5 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{25}H_{16}N_2O_2S$ 408.0932, found 408.0928.

*1-(7-(Phenylsulfonyl)-7H-indolo[2,3-c]quinolin-4-yl)ethanone (**4i**).* The cyclization of 3-bromo-2-aminomethylindole **3i** (160 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded β-carboline **4h** as a colorless solid (66 mg, 65%). Mp: 182−184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.71 (d, *J* = 1.2 Hz, 1H), 8.68 (d, *J* = 1.2 Hz, 1H), 8.47 (d, *J* = 1.2 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 3H), 7.72−7.63 (m, 3H), 7.51 (t, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 8.1 Hz, 1H), 2.91 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 204.6, 141.9, 141.1, 139.4, 138.5, 137.5, 134.4, 131.6, 129.4, 129.2, 127.3, 126.9, 126.5, 126.3, 125.1, 124.9, 123.6, 123.5, 115.6, 32.8 ppm. HRMS (ESI-TOF, MeOH): *m*/*z* calcd $[M]^+$ for $C_{23}H_{16}N_2O_3S$ 400.0882, found 400.0880.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-benzenesulfonamide (**5**).* To a solution of 3-bromo-2-bromomethylindole **1** (2 g, 4.66 mmol) in DMF (15 mL) were added benzenesulfonamide (0.98 g, 5.59 mmol), and K_2CO_3 (1.28 g, 9.32 mmol). The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), the mixture was poured over crushed ice (100 g) containing Conc. HCl (5 mL). The solid obtained was filtered, washed with water (2 × 30 mL), and dried (Na_2SO_4). Purification of the crude product by column chromatography (silica gel, EtOAc−hexane 2:8) afforded sulfonamide **5** as a colorless solid (1.93 g, 82%). Mp: 140−142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.76−7.75 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.39−7.26 (m, 5H), 7.17−7.16 (m, 3H), 5.75−5.73 (m, 1H), 4.64 (d, *J* = 6.9 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 140.2, 137.7, 135.8, 134.4, 132.0, 131.9, 129.6, 128.6, 128.4, 126.8, 126.7, 126.3, 124.8, 120.4, 114.8, 105.9, 39.6 ppm. Anal. Calcd for $C_{21}H_{17}BrN_2O_4S_2$: C, 49.91; H, 3.39; N, 5.54; S, 12.69. Found: C, 49.68; H, 3.52; N, 5.49; S, 12.51.

*N-Allyl-N-((3-bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-benzenesulfonamide (**6a**).* To a solution of 3-bromo-2-(amino)-methylindole **5** (250 mg, 0.49 mmol) in acetonitrile (20 mL), allyl bromide (72 mg, 0.59 mmol), and K_2CO_3 (204 mg, 1.48 mmol) were added, and the reaction mixture was stirred at reflux for 6 h. After completion of the reaction (monitored by TLC), it was concentrated under reduced pressure. Then the residue was diluted with ethyl acetate (15 mL), washed with water (2 × 10 mL), and dried (Na_2SO_4). Evaporation of the solvent followed by trituration of the crude product with methanol afforded *N*-allyl sulfonamide **6a** as a colorless solid (218 mg, 81%). Mp: 168−170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.86−7.79 (m, 4H), 7.59−7.54 (m, 2H), 7.51−7.38 (m, 6H), 7.34−7.28 (m, 2H), 5.32−5.23 (m, 1H), 4.91 (s, 2H), 4.84 (d, *J* = 17.4 Hz, 1H), 4.69 (d, *J* = 10.2 Hz, 1H), 3.82 (d, *J* = 6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.9, 137.9, 136.3, 134.2, 132.9, 132.5, 130.8, 129.3, 128.8, 128.7, 126.7, 124.5, 120.9, 117.3, 115.3, 107.9, 51.3, 43.8 ppm. Anal. Calcd for $C_{25}H_{23}BrN_2O_4S_2$: C, 53.67; H, 4.14; N, 5.01; S, 11.46. Found; C, 53.42; H, 4.31; N, 5.26; S, 11.72.

*N-((3-Bromo-1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-N-cinnamylbenzenesulfonamide (**6b**).* To a solution of 3-bromo-2-amino-methylindole **5** (250 mg, 0.49 mmol) in acetonitrile (20 mL) were added cinnamyl bromide (117 mg, 0.59 mmol) and K_2CO_3 (204 mg, 1.48 mmol), and the reaction mixture was stirred at reflux for 6 h. Then the usual workup adopting the above-mentioned procedure furnished **6b** as a colorless solid (264 mg, 86%). Mp: 124−126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.58−7.23 (m, 9H), 7.14−7.12 (m, 3H), 6.81−6.80 (m, 2H), 6.01 (d, *J* = 15.9 Hz, 1H), 5.60−5.50 (m, 1H), 4.99 (s, 2H), 3.90 (d, *J* = 6.9 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.5, 137.8, 136.3, 135.9, 134.0, 132.5, 132.3, 130.5, 129.1, 128.8, 128.4, 127.9, 127.4, 127.2, 126.7, 126.0, 124.3, 123.9, 119.9, 115.1, 107.6, 50.5, 43.8 ppm. Anal. Calcd for $C_{30}H_{25}BrN_2O_4S_2$: C, 57.97; H, 4.05; N, 4.51; S, 10.32. Found: C, 58.12; H, 3.80; N, 4.61; S, 10.04.

*4-Methyl-9-(phenylsulfonyl)-9H-pyrido[3,4-b]indole (**7a**).* The intramolecular cyclization reaction of 3-bromo-2-phenylaminomethylindole **6a** (140 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h adopting the above-mentioned general procedure for **4a**−**i** followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded β-carboline **7a** as a colorless solid (61 mg, 76%). Mp: 208−210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (s, 1H) 8.14 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30−7.11 (m, 4H), 2.50 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 144.1, 138.5, 136.9, 134.2, 134.0, 131.1, 129.4, 129.2, 126.3, 126.2, 124.8, 124.4, 123.7, 114.7, 17.1 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{18}H_{14}N_2O_2S$ 322.0776, found 322.0775.

*4-Benzyl-9-(phenylsulfonyl)-9H-pyrido[3,4-b]indole (**7b**).* To a solution of 3-bromo-2-cinnamylaminomethylindole **6b** (157 mg, 0.25 mmol) in DMF were added $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (86 mg, 0.62 mmol). The reaction mixture was then stirred at 110 °C for 6 h. The usual workup adopting the general procedure as mentioned above followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) furnished β-carboline **7b** as a colorless solid (80 mg, 80%). Mp: 192−194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.65 (s, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.38 (s, 1H), 7.92−7.88 (m, 3H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.40−7.23 (m, 6H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.51 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.4, 138.9, 137.9, 137.4, 135.6, 134.7, 134.2, 131.1, 129.5, 129.3, 129.1, 128.8, 128.4, 126.7, 126.6, 124.5, 124.4, 124.0, 115.0, 36.8 ppm. HRMS (ESI-TOF): *m*/*z* calcd $[M]^+$ for $C_{24}H_{18}N_2O_2S$ 398.1089, found 398.1088.

*2-Bromo-3-(bromomethyl)-1-(phenylsulfonyl)-1H-indole (**8**).* To a solution of 2-bromo-3-methylindole (1 g, 2.86 mmol) in CCl_4(30 mL), NBS (0.66 g, 3.72 mmol), and AIBN (0.1 g, 0.28 mmol) were added and refluxed for 1 h. After completion of the reaction (monitored by TLC), the floated succinimide was filtered off and filtrate was concentrated under reduced pressure. The crude product was recrystallized from methanol (3 mL) to afford 2-bromo-3-bromomethylindole **8** as a colorless solid (1.05 g, 86%). Mp: 108−110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.60−7.52 (m, 2H), 7.48−7.37 (m, 3H), 7.35−7.32 (m, 1H), 5.14 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.5, 136.3, 134.2, 133.3, 129.3, 128.6, 127.1, 124.6, 120.3, 115.0, 106.1, 22.6 ppm. Anal. Calcd for $C_{15}H_{11}Br_2NO_2S$: C, 41.98; H, 2.58; N, 3.26. Found: C, 41.78; H, 2.45; N, 3.42.

https://dx.doi.org/10.1021/acs.joc.0c02152
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*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-4-methyl-N-phenylbenzenesulfonamide (**9a**).* The reaction of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol) with *N*-tosylaniline **2a** (172 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) at room temperature stirring for 12 h following the general procedure furnished sulfonamide **9a** as a colorless solid (270 mg, 78%). Mp: 118−120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19−8.16 (m, 1H), 7.99−7.96 (m, 1H), 7.59−7.48 (m, 5H), 7.35−7.26 (m, 6H), 7.12−7.07 (m, 1H), 7.00 (t, J = 7.5 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 4.80 (s, 2H), 2.46 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.8, 137.9, 137.7, 137.3, 134.8, 133.9, 131.6, 130.1, 129.6, 129.1, 128.7, 128.5, 128.0, 127.8, 126.6, 125.5, 124.4, 119.8, 119.2, 115.0, 111.5, 46.0, 21.6 ppm. Anal. Calcd for $C_{28}H_{23}BrN_2O_4S_2$: C, 56.47; H, 3.89; N, 4.70; S, 10.77. Found: C, 56.42; H, 3.78; N, 4.92; S, 10.56.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-4-methyl-N-p-tolylbenzenesulfonamide (**9b**).* A mixture of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol), *N*-tosyl-4-methylaniline **2b** (183 mg, 0.70 mmol), and K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the usual workup adopting the above-mentioned general procedure afforded sulfonamide **9b** as a colorless solid (319 mg, 90%). Mp: 206−208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J = 5.1 Hz, 1H), 7.91 (d, J = 3.6 Hz, 1H), 7.52−7.40 (m, 5H), 7.24−7.19 (m, 6H), 6.71 (d, J = 7.8 Hz, 2H), 6.53 (d, J = 7.8 Hz, 2H), 4.70 (s, 2H), 2.36 (s, 3H), 2.14 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.7, 137.9, 137.7, 137.3, 135.0, 134.8, 133.8, 129.5, 129.2, 129.0, 128.7, 128.4, 127.8, 126.6, 125.4, 124.4, 119.8, 119.3, 115.0, 111.5, 46.0, 21.6, 21.1 ppm. Anal. Calcd for $C_{29}H_{25}BrN_2O_4S_2$: C, 57.14; H, 4.13; N, 4.60; S, 10.52. Found: C, 57.03; H, 3.96; N, 4.28; S, 10.37.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (**9c**).* A mixture of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol), *N*-tosyl-4-methoxyaniline **2d** (194 mg, 0.70 mmol), and K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the workup adopting the above-mentioned general procedure gave sulfonamide **9c** as a colorless solid (291 mg, 80%). Mp: 108−110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22−8.19 (m, 1H), 7.99−7.96 (m, 1H), 7.61−7.48 (m, 5H), 7.36−7.28 (m, 6H), 6.65 (d, J = 9 Hz, 2H), 6.52 (d, J = 9 Hz, 2H), 4.81 (s, 2H), 3.73 (s, 3H), 2.47 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.1, 143.7, 138.3, 137.6, 135.4, 133.8, 130.5, 130.0, 129.6, 129.0, 128.9, 128.0, 126.8, 125.5, 124.5, 119.9, 119.6, 115.2, 113.9, 111.8, 55.3, 46.2, 21.6 ppm. Anal. Calcd for $C_{29}H_{25}BrN_2O_5S_2$: C, 55.68; H, 4.03; N, 4.48; S, 10.25. Found: C, 55.45; H, 4.16; N, 4.32; S, 10.47.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-N-(2,4-dimethoxyphenyl)-4-methylbenzenesulfonamide (**9d**).* To a solution of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol) in DMF (10 mL), *N*-tosyl-2,4-dimethoxyaniline **2e** (215 mg, 0.70 mmol), and K_2CO_3 (241 mg, 1.75 mmol) were added, and it was stirred at room temperature for 12 h. Then the usual workup produced sulfonamide **9d** as a colorless solid (297 mg, 78%). Mp: 160−162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13−8.10 (m, 1H), 7.91−7.88 (m, 1H), 7.53 (t, J = 8.55 Hz, 4H), 7.44 (t, J = 7.2 Hz, 1H), 7.28−7.23 (m, 4H), 7.18 (t, J = 7.8 Hz, 2H), 6.49 (d, J = 8.4 Hz, 1H), 6.01 (s, 1H), 5.94 (d, J = 8.7 Hz, 1H), 4.97 (d, J = 13.2 Hz, 1H), 4.70 (d, J = 13.2 Hz, 1H), 3.64 (s, 3H), 3.05 (s, 3H), 2.35 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 160.6, 157.4, 142.8, 137.9, 137.3, 137.2, 133.8, 133.5, 129.0, 127.6, 126.7, 125.2, 124.3, 120.1, 119.9, 117.8, 114.9, 111.6, 104.0, 98.5, 55.3, 54.4, 44.1, 21.5 ppm. Anal. Calcd for $C_{30}H_{27}BrN_2O_6S_2$: C, 54.96; H, 4.15; N, 4.27; S, 9.78. Found: C, 55.19; H, 4.38; N, 4.08; S, 10.02.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-N-(3,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**9e**).* A mixture of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol), *N*-tosyl-3,5-dimethoxyaniline **2f** (241 mg, 0.70 mmol), and K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the usual workup adopting the above-mentioned general procedure afforded sulfonamide **9e** as a colorless solid (309 mg, 81%). Mp: 130−132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11−8.08 (m, 1H), 7.91−7.88 (m, 1H), 7.50 (d, J = 7.5 Hz, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.26−7.18 (m, 6H), 6.11 (s, 1H), 5.83 (s, 2H), 4.68 (s, 2H), 3.40 (s, 6H), 2.37 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 160.0, 143.8, 139.4, 137.8, 137.3, 134.6, 133.9, 129.5, 129.0, 128.7, 127.9, 126.5, 125.4, 124.4, 119.8, 115.1, 111.5, 106.7, 101.0, 55.2, 46.1, 21.6 ppm. Anal. Calcd for $C_{30}H_{27}BrN_2O_6S_2$: C, 54.96; H, 4.15; N, 4.27; S, 9.78. Found: C, 54.81; H, 4.29; N, 4.19; S, 9.52.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-N-(3,4-dimethoxyphenyl)-4-methylbenzenesulfonamide (**9f**).* A mixture of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol), *N*-tosyl-3,4-dimethoxyaniline **2j** (241 mg, 0.70 mmol), and K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the usual workup adopting the above-mentioned general procedure afforded sulfonamide **9f** as a colorless solid (305 mg, 80%). Mp: 100−102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21−8.18 (m, 1H), 8.00−7.97 (m, 1H), 7.58 (d, J = 8.4 Hz, 4H), 7.50 (t, J = 7.5 Hz, 1H), 7.36−7.28 (m, 6H), 6.48 (d, J = 8.7 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 6.21 (s, 1H), 4.81(s, 2H), 3.80 (s, 3H), 3.45 (s, 3H), 2.47 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 148.9, 148.6, 143.4, 138.2, 137.6, 135.3, 133.9, 130.7, 129.5, 129.0, 128.9, 128.1, 126.6, 125.5, 124.4, 121.3, 119.9, 119.5, 115.3, 112.8, 111.8, 110.6, 55.9, 55.7, 46.3, 21.5 ppm. Anal. Calcd for $C_{30}H_{27}BrN_2O_6S_2$: C, 54.96; H, 4.15; N, 4.27; S, 9.78. Found: C, 55.08; H, 4.00; N, 4.52; S, 9.92.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-N-(2-acetylphenyl)-4-methylbenzenesulfonamide (**9g**).* The reaction of 2-bromo-3-bromomethylindole **8** (600 mg, 1.40 mmol) with *N*-tosyl-2-acetylaniline **2i** (480 mg, 1.69 mmol) using K_2CO_3 (290 mg, 2.11 mmol) in DMF (10 mL) at room temperature stirring for 12 h followed by usual workup furnished sulfonamide **9g** as a colorless solid (710 mg, 79%). Mp: 176−178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, J = 8.1 Hz 1H), 7.77−7.70 (m, 3H), 7.58−7.51 (m, 3H), 7.43 (d, J = 1.2 Hz, 1H), 7.38−7.27 (m, 7H), 7.11 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 5.2 (m, 1H), 4.87 (m, 1H), 2.46 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.4, 143.9, 141.5, 138.3, 137.4, 135.9, 135.6, 144.0, 131.1, 130.9, 129.6, 129.4, 129.3, 129.1, 128.5, 128.2, 127.0, 125.6, 124.4, 119.9, 119.7, 115.2, 112.8, 46.5, 29.6, 21.5 ppm. Anal. Calcd for $C_{30}H_{25}BrN_2O_5S_2$: C, 56.52; H, 3.95; N, 4.39; S, 10.06. Found; C, 56.68; H, 4.02; N, 4.26; S, 9.87.

*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-N-(3,4-methylendioxyphenyl)-4-methylbenzenesulfonamide (**9h**).* The reaction of 2-bromo-3-bromomethylindole **8** (250 mg, 0.58 mmol) with *N*-tosyl-3,4-methylenedioxyaniline **2g** (203 mg, 0.70 mmol) using K_2CO_3 (241 mg, 1.75 mmol) in DMF (10 mL) at room temperature stirring for 12 h followed by usual workup furnished sulfonamide **9h** as a colorless solid (290 mg, 78%). Mp: 98−100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22−8.19 (m, 1H), 7.97−7.94 (m, 1H), 7.63−7.49 (m, 5H), 7.36−7.26 (m, 6H), 6.37 (d, J = 8.1 Hz, 1H), 6.25 (d, J = 1.2 Hz, 1H), 6.13 (d, J = 8.4 Hz, 1H), 5.89 (s, 2H), 4.73 (s, 2H), 2.45 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 147.3, 147.2, 143.8, 137.8, 137.3, 134.6, 133.9, 131.3, 129.6, 129.0, 128.7, 127.7, 126.7, 125.5, 124.5, 122.3, 119.7, 119.2, 115.1, 111.6, 109.8, 107.5, 101.4, 46.2, 21.6 ppm. Anal. Calcd for $C_{29}H_{23}BrN_2O_6S_2$: C, 54.46; H, 3.63; N, 4.38; S, 10.03. Found; C, 54.58; H, 3.57; N, 4.16; S, 9.87.

*N-((5,5-Dioxidobenzo[4,5]isothiazolo[2,3-a]indol-11-yl)methyl)-4-methyl-N-phenylbenzenesulfonamide (**10a**).* The intramolecular cyclization reaction of 2-bromo-3-aminomethylindole **9a** (150 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (90 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure for **4a−i** followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded sulfonamide **10a** as a colorless solid (99 mg, 76%). Mp: 186−188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.60−7.57 (m, 3H), 7.51−7.48 (m, 2H), 7.32−7.26 (m, 3H), 7.17−7.09 (m, 4H), 6.90−6.87 (m, 2H), 5.10 (s, 2H), 2.47 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.0, 138.4, 138.0, 134.8, 134.2, 132.7, 132.1, 131.3, 129.6, 129.2, 129.0, 128.9, 128.5, 128.0, 127.0,

https://dx.doi.org/10.1021/acs.joc.0c02152
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126.1, 123.7, 123.3, 122.5, 120.7, 111.6, 110.9, 44.8, 21.6 ppm. Anal. Calcd for $C_{28}H_{22}N_2O_4S_2$: C, 65.35; H, 4.31; N, 5.44; S, 12.46. Found: C, 65.14; H, 4.50; N, 5.21; S, 12.35.

*N-((5,5-Dioxidobenzo[4,5]isothiazolo[2,3-a]indol-11-yl)methyl)-4-methyl-N-(p-tolyl)benzenesulfonamide (**10b**).* The cyclization reaction of 2-bromo-3-aminomethylindole **9b** (154 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded sulfonamide **10b** as a colorless solid (109 mg, 82%). Mp: 250−252 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.61−7.57 (m, 3H), 7.55−7.46 (m, 2H), 7.33−7.26 (m, 3H), 7.18 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 5.10 (s, 2H), 2.47 (s, 3H), 2.17 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.9, 138.5, 138.1, 135.6, 134.9, 134.2, 132.8, 132.1, 131.3, 129.7, 129.6, 129.2, 128.5, 128.0, 127.1, 126.1, 123.8, 123.4, 122.5, 120.9, 111.6, 111.1, 44.8, 21.6, 21.0 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{29}H_{24}N_2O_4S_2$528.1177, found 528.1175.

*N-((5,5-Dioxidobenzo[4,5]isothiazolo[2,3-a]indol-11-yl)methyl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (**10c**).* The cyclization reaction of 3-bromo-2-aminomethylindole **9c** (158 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 1.5:8.5) furnished sulfonamide **10c** as a colorless solid (117 mg, 85%). Mp: 200−202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.69−7.60 (m, 4H), 7.55−7.47 (m, 2H), 7.35−7.28 (m, 3H), 7.18 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 9.0 Hz, 2H), 6.60 (d, J = 9.0 Hz, 2H), 5.11 (s, 2H), 3.66 (s, 3H), 2.48 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 159.5, 143.8, 138.4, 135.5, 134.1, 132.9, 132.4, 131.4, 131.0, 130.2, 129.6, 129.2, 128.1, 127.3, 126.1, 123.8, 123.4, 122.5, 120.9, 114.4, 111.7, 111.3, 53.3, 45.0, 21.5 ppm. Anal. Calcd for $C_{29}H_{24}N_2O_5S_2$: C, 63.95; H, 4.44; N, 5.14; S, 11.77. Found C, 63.72; H, 4.21; N, 5.36; S, 11.92.

*N-(2,4-Dimethoxyphenyl)-N-((5,5-dioxidobenzo[4,5]isothiazolo-[2,3-a]indol-11-yl)methyl)-4-methylbenzenesulfonamide (**10d**).* The cyclization reaction of 2-bromo-3-aminomethylindole **9d** (165 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded sulfonamide **10d** as a colorless solid (123 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.65−7.58 (m, 5H), 7.45 (t, J = 7.5 Hz, 1H), 7.35−7.28 (m, 3H), 7.19 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.17−6.10 (m, 2H), 5.32 (d, J = 12.6 Hz, 1H), 5.08 (d, J = 13.8 Hz, 1H), 3.63 (s, 3H), 3.23 (s, 3H), 2.45 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.9, 157.2, 143.0, 138.0, 137.1, 134.0, 133.9, 133.1, 132.1, 131.3, 129.0, 127.7, 127.2, 126.0, 123.6, 123.3, 122.3, 121.2, 118.1, 111.8, 111.4, 104.3, 99.0, 55.3, 54.6, 43.0, 21.5 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{30}H_{26}N_2O_6S_2$574.1232, found 574.1230.

*N-(3,5-Dimethoxyphenyl)-N-((5,5-dioxidobenzo[4,5]isothiazolo-[2,3-a]indol-11-yl)methyl)-4-methylbenzenesulfonamide (**10e**).* The intramolecular cyclization reaction of 2-bromo-3-aminomethylindole **9e** (165 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded sulfonamide **10e** as a colorless solid (123 mg, 85%). Mp: 215−217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 6.9 Hz, 1H), 7.61−7.55 (m, 5H), 7.42 (t, J = 6.9 Hz, 1H), 7.31−7.28 (m, 3H), 7.16 (t, J = 6.9 Hz, 1H), 6.17 (s, 1H), 6.00 (s, 2H), 4.98 (s, 2H), 3.46 (s, 6H), 2.43 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.4, 143.9, 140.0, 137.7, 134.7, 133.9, 132.6, 131.8, 131.0, 129.4, 129.1, 127.8, 126.7, 125.9, 123.5, 123.2, 122.1, 120.9, 111.3, 110.9, 107.0, 100.6, 55.1, 44.8, 21.4 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{30}H_{26}N_2O_6S_2$ 574.1232, found 574.1231.

*N-(3,4-Dimethoxyphenyl)-N-((5,5-dioxidobenzo[4,5]isothiazolo-[2,3-a]indol-11-yl)methyl)-4-methylbenzenesulfonamide (**10f**).* The cyclization reaction of 2-bromo-3-aminomethylindole **9f** (165 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.052 mmol), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded sulfonamide **10f** as a colorless solid (116 mg, 80%). Mp: 218−220 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.68−7.63 (m, 4H), 7.53−7.47 (m, 2H), 7.36−7.28 (m, 3H), 7.18 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 8.4 Hz, 1H), 6.45 (dd, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 1H), 6.34 (d, J = 2.1 Hz, 1H), 5.12 (s, 2H), 3.74 (s, 3H), 3.50 (s, 3H), 2.48 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.5, 149.2, 143.9, 138.5, 135.6, 134.1, 133.0, 131.5, 131.3, 129.6, 129.3, 128.2, 127.3, 126.2, 123.8, 123.5, 122.6, 121.7, 120.9, 113.3, 111.8, 111.4, 111.3, 56.0, 55.9, 45.2, 21.6 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{30}H_{26}N_2O_6S_2$ 574.1232, found 574.1224.

*N-(2-Acetylphenyl)-N-((5,5-dioxidobenzo[4,5]isothiazolo[2,3-a]-indol-11-yl)methyl)-4-methylbenzenesulfonamide (**10g**).* The cyclization reaction of 2-bromo-3-aminomethylindole **9g** (310 mg, 0.488 mmol) using $Pd(OAc)_2$ (32 mg, 0.048 mmol), PPh_3 (25 mg, 0.097 mmol), and K_2CO_3 (168 mg, 1.220 mmol) in DMF (8 mL) at 110 °C for 4 h adopting the above-mentioned general procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded sulfonamide **10g** as a colorless solid (179 mg, 66%). Mp: 170−172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.53−7.47 (m, 2H), 7.44−7.39 (m, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.25−7.22 (m, 3H), 7.17 (d, J = 8.1 Hz, 1H), 7.14−7.07 (m, 1H), 6.55 (d, J = 7.8 Hz, 1H), 5.46 (s, 2H), 2.44 (s, 3H), 2.32 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 200.7, 143.8, 142.0, 138.4, 136.9, 135.1, 133.9, 133.0, 132.9, 132.5, 132.3, 131.3, 129.6, 129.1, 128.9, 128.7, 128.0, 127.1, 126.2, 123.6, 123.5, 122.3, 121.3, 111.8, 111.4, 45.7, 29.6, 21.5 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{30}H_{24}N_2O_5S_2$ 556.1127, found 556.1122.

Palladium-Catalyzed Coupling Reaction of *N*-((2-Bromo-1-(phenylsulfonyl)-1*H*-indol-3-yl)methyl)-*N*-(3,4-methylendioxyphenyl)-4-methylbenzenesulfonamide (9h). The cyclization reaction of 2-bromo-3-aminomethylindole **9h** (101 mg, 0.25 mmol) using $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.500 mmol.), and K_2CO_3 (87 mg, 0.63 mmol) in DMF (8 mL) at 110 °C for 6 h followed by usual workup and column chromatographic purification (silica gel, EtOAc−hexane 1:9) furnished γ-carboline **12**. Further elution of the column (EtOAc−hexane 2:8) afforded sulfonamide **10h**.

*12-(Phenylsulfonyl)-7-tosyl-12H-[1,3]dioxolo[4,5-f]indolo[3,2-c]-quinoline (**12**).* Colorless solid (48 mg, 34%). Mp: 145−147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66−7.62 (m, 1H), 7.58 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.35−7.28 (m, 5H), 7.19−7.16 (m, 2H), 7.03 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.4 Hz, 1H), 5.68 (s, 2H), 2.17 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 146.9, 143.9, 142.8, 139.5, 139.2, 136.1, 133.0, 130.6, 129.5, 129.1, 128.7, 127.4, 126.7, 126.0, 125.3, 124.3, 122.3, 121.0, 118.8, 116.4, 109.6, 107.2, 101.1, 21.4 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{29}H_{20}N_2O_6S_2$ 556.0763, found 556.0761.

*N-(Benzo[d][1,3]dioxol-5-yl)-N-((5,5-dioxidobenzo[4,5]-isothiazolo[2,3-a]indol-11-yl)methyl)-4-methylbenzenesulfonamide (**10h**).* Colorless solid (49 mg, 35%). Mp: 216−218 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.62−7.53 (m, 4H), 7.44 (t, J = 9.0 Hz, 2H), 7.26−7.19 (m, 3H), 7.09 (t, J = 7.5 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 6.37 (s, 1H), 6.20 (d, J = 8.1 Hz, 1H), 5.75 (s, 2H), 4.93 (s, 2H), 2.40 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.8, 147.7, 144.1, 138.0, 134.6, 134.3, 132.8, 132.1, 131.9, 131.3, 129.7, 129.3, 128.0, 127.0, 126.1, 123.7, 123.5, 122.6, 122.1, 120.8, 111.6, 110.8, 110.0, 107.9, 101.6, 45.0, 21.7 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{29}H_{22}N_2O_6S_2$558.0919, found 558.0902.

https://dx.doi.org/10.1021/acs.joc.0c02152
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*N-((2-Bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide (**15**).* To a solution of 2-bromo-3-bromomethylindole **8** (5 g, 11.60 mmol) in acetonitrile (80 mL), 4-methylbenzenesulfonamide (2.2 g, 13.90 mmol), and K_2CO_3 (3.21 g, 23.3 mmol) were added and the reaction mixture was stirred at reflux for 6 h. After completion of reaction (monitored by TLC), the usual workup procedure similar to that of **3a−i** led to sulfonamide **15** as a colorless solid (4.8 g, 80%). Mp: 146−148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, J = 7.4 Hz, 1H), 7.85 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.46−7.41 (m, 3H), 7.33 (t,, J = 6.9 Hz, 1H), 7.28−7.23 (m, 1H), 7.19−7.15 (m, 2H), 4.88−4.75 (m, 1H), 4.23 (d, J = 6.0 Hz, 2H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.6, 138.5, 137.3, 136.8, 134.3, 129.5, 129.3, 128.3, 127.1, 125.5, 124.2, 119.4, 118.8, 115.1, 110.9, 38.4, 21.4 ppm. Anal. Calcd for $C_{22}H_{19}BrN_2O_4S_2$: C, 50.87; H, 3.69; N, 5.39; S, 12.34. Found: C, 51.04; H, 3.42; N, 5.16; S, 12.18.

*N-Allyl-N-((2-bromo-1-(phenylsulfonyl)-1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide (**16**).* To a solution of 2-bromo-3-aminomethylindole **15** (250 mg, 0.48 mmol) in acetonitrile (20 mL) were added allyl bromide (70 mg, 0.58 mmol) and K_2CO_3 (199 mg, 1.44 mmol), and the reaction mixture was stirred at reflux for 6 h. Then the usual workup adopting the above-mentioned procedure gave 2-bromo-3-allylaminomethylindole **16** as a colorless solid (228 mg, 85%). Mp: 108−110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 3.9 Hz, 1H), 7.33−7.26 (m, 4H), 5.26−5.08 (m, 1H), 4.72−4.61 (m, 2H), 4.40 (s, 2H), 3.52 (d, J = 6.0 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.6, 138.1, 137.4, 136.2, 134.2, 131.9, 129.8, 129.1, 128.9, 127.3, 127.0, 125.6, 124.4, 120.0, 119.3, 118.1, 115.1, 111.2, 50.2, 43.6, 21.5 ppm. Anal. Calcd for $C_{25}H_{23}BrN_2O_4S_2$: C, 53.67; H, 4.14; N, 5.01; S, 11.46. Found: C, 53.90; H, 3.93; N, 5.25; S, 11.26.

*4-Methylene-5-(phenylsulfonyl)-2-tosyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (**17**).* To a solution of 2-bromo-3-allylaminomethylindole **16** (150 mg, 0.27 mmol) in DMF (8 mL) were added $Pd(OAc)_2$ (6 mg, 0.027 mmol), PPh_3 (14 mg, 0.054 mmol), and K_2CO_3 (92 mg, 0.67 mmol). The reaction mixture was then stirred at 110 °C for 6 h followed by workup using the above-mentioned general procedure gave compound **17** as a colorless solid (101 mg, 79%). Mp: 162−164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.32−7.28 (m, 4H), 7.17−7.11 (m, 7H), 5.86 (s, 1H), 5.40 (s, 1H), 4.23 (s, 2H), 3.87 (s, 2H), 2.28 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.9, 139.4, 136.3, 134.0, 133.9, 133.7, 129.6, 128.6, 128.5, 127.5, 126.5, 126.4, 125.1, 121.3, 118.6, 118.6, 117.9, 51.6, 42.6, 21.4 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{25}H_{22}N_2O_4S_2$478.1021, found 478.1020.

*2-Bromo-3-(bromomethyl)-1-(2-mesitylenesulfonyl)-1H-indole (**18**). Stage 1: 1-(2-Mesitylenesulfonyl)-3-methyl-1H-indole.* To a solution of 3-methylindole (5 g, 38.16 mmol) in distilled benzene (100 mL) were added 2-mesitylenesulfonyl chloride (9.15 g, 41.98 mmol) and 60% aqueous NaOH solution (25 g in 40 mL) along with tetra-*n*-butylammonium hydrogen sulfate (1.0 g) at room temperature. Then this two-phase system was warmed to 60 °C for 1 h with continuous stirring. After the reaction was completed (TLC), the mixture was diluted with water (200 mL), and the organic layer was separated. The aqueous layer was extracted with benzene (2 × 30 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by trituration of the crude product with MeOH afforded *N*-mesitylenesulfonylindole as a dull white solid (9.31 g, 78%). Mp: 128−130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51−7.46 (m, 1H), 7.40−7.34 (m, 1H), 7.31 (d, J = 0.9 Hz, 1H), 7.23−7.17 (m, 2H), 6.92 (s, 2H), 2.53 (s, 6H), 2.56 (s, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.8, 140.2, 135.1, 133.3, 132.4, 131.1, 124.2, 123.3, 122.4, 119.5, 115.9, 112.6, 22.7, 21.0, 9.6 ppm.

Stage 2: 2-Bromo-1-(2-mesitylenesulfonyl)-3-methyl-1H-indole. To a solution of 1-(2-mesitylenesulfonyl)-3-methyl-1*H*-indole (5 g, 15.97 mmol) in dry DCM (30 mL) at 0 °C was added NBS (3.12 g, 17.57 mmol) in portions (10 times). After the reaction was completed (TLC), the mixture was poured into ice−water and the organic layer was separated. The aqueous layer was extracted with DCM (2 × 30 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by trituration of the crude product with methanol afforded 1-mesitylenesulfonyl-2-bromo-3-methylindole as a colorless solid (5.13 g, 82%). Mp: 136−138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.35−7.25 (m, 2H), 6.94 (s, 2H), 2.44 (s, 6H), 2.31 (s, 3H), 2.18 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.9, 140.3, 137.8, 134.9, 132.0, 128.7, 124.6, 122.8, 119.1, 118.6, 115.3, 108.2, 22.6, 21.1, 10.0 ppm.

*Stage 3: 2-Bromo-3-(bromomethyl)-1-(2-mesitylenesulfonyl)-1H-indole (**18**).* To a solution of 2-bromo-1-(mesitylenesulfonyl)-3-methylindole (4.0 g, 10.20 mmol) and AIBN (0.05 g) in dry carbon tetrachloride (80 mL) was added finely powdered NBS (2.0 g, 11.22 mmol). The reaction mixture was refluxed for 0.5 h and cooled to room temperature. The floated succinimide was filtered off and washed with carbon tetrachloride (15 mL). The combined filtrate was concentrated in vacuo to afford bromo compound **18** as a light brown solid (3.65 g, 76%). Mp: 118−120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 7.8 Hz, 1H), 7.65−7.62 (m, 1H), 7.40−7.31 (m, 2H), 6.96 (s, 2H), 4.58 (s, 2H), 2.43 (s, 6H), 2.32 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.4, 140.3, 138.0, 134.4, 132.2, 126.4, 125.3, 123.4, 119.1, 118.7, 115.5, 110.9, 23.1, 22.5, 21.1 ppm. Anal. Calcd for $C_{18}H_{17}Br_2NO_2S$: C, 45.88; H, 3.64; N, 2.97; S, 6.80. Found C, 45.64; H, 3.52; N, 3.15; S, 6.58.

General Procedure for Preparation of *N*-Phenylbenzenesulfonamides (19a−d). To a solution of 2-bromo-3-bromomethylindole **18** (1 equiv) in DMF (10 mL) were added *N*-tosylanilines (**2a-c**/**2k**) (1.2 equiv) and K_2CO_3 (3 equiv). The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), it was then poured over crushed ice containing concd HCl (5 mL). The solid obtained was filtered, washed with water (2 × 20 mL), and dried (Na_2SO_4). The crude product was crystallized from methanol (5 mL) to afford sulfonamides **19a−d**.

*N-((2-Bromo-1-(2-mesitylenesulfonyl)-1H-indol-3-yl)methyl)-4-methyl-N-phenylbenzenesulfonamide (**19a**).* To a solution of 2-bromo-3-bromomethylindole **18** (300 mg, 0.637 mmol) in DMF (10 mL) were added *N*-tosylaniline **2a** (189 mg, 0.764 mmol) and K_2CO_3 (263 mg, 1.91 mmol). The reaction mixture was stirred at room temperature for 12 h. Then the usual workup adopting the above-mentioned general procedure gave sulfonamide **19a** as a colorless solid (341 mg, 84%). Mp: 194−196. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08−8.05 (m, 1H), 7.97−7.94 (m, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.31−7.25 (m, 4H), 7.10 (t, J = 7.35 Hz, 1H), 7.01 (t, J = 7.5 Hz, 2H), 6.81−6.79 (m, 4H), 4.82 (s, 2H), 2.43 (s, 3H), 2.27 (s, 3H), 2.09 (s, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.7, 143.6, 140.1, 138.1, 138.0, 135.2, 134.9, 131.9, 129.5, 128.9, 128.5, 127.9, 127.8, 127.0, 125.0, 123.4, 119.7, 116.5, 115.0, 111.0, 45.7, 22.1, 21.5, 21.0 ppm. Anal. Calcd for $C_{31}H_{29}BrN_2O_4S_2$: C, 58.40; H, 4.58; N, 4.39; S, 10.06. Found C, 58.22; H, 4.46; N, 4.52; S, 9.84.

*N-((2-Bromo-1-(2-mesitylenesulfonyl)-1H-indol-3-yl)methyl)-4-methyl-N-(p-tolyl)benzenesulfonamide (**19b**).* A mixture of 2-bromo-3-bromomethylindole **18** (300 mg, 0.637 mmol), *N*-tosyl-4-methylaniline **2b** (199 mg, 0.764 mmol), and K_2CO_3 (263 mg, 1.91 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the workup adopting the above-mentioned procedure furnished sulfonamide **19b** as a colorless solid (323 mg, 78%). Mp: 232−234 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02−7.99 (m, 1H), 7.94−7.91 (m, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.26−7.18 (m, 4H), 6.74−6.71 (m, 4H), 6.56 (d, J = 8.1 Hz, 2H), 4.70 (s, 2H), 2.36 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.99 (s, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.7, 143.6, 140.1, 137.9, 137.6, 135.1, 134.9, 134.7, 131.8, 129.5, 129.1, 128.6, 127.9, 126.8, 125.1, 123.4, 119.7, 116.4, 114.9, 110.8, 45.6, 22.2, 21.6, 21.2, 21.1 ppm. Anal. Calcd for $C_{32}H_{31}BrN_2O_4S_2$: C, 58.98; H, 4.80; N, 4.30; S, 9.84. Found C, 58.72; H, 4.76; N, 4.11; S, 9.98.

*N-((2-Bromo-1-(2-mesitylenesulfonyl)-1H-indol-3-yl)methyl)-N-(4-chlorophenyl)-4-methylbenzenesulfonamide (**19c**).* A mixture of 2-bromo-3-bromomethylindole **18** (300 mg, 0.637 mmol), *N*-tosyl-4-

https://dx.doi.org/10.1021/acs.joc.0c02152
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chloroaniline **2c** (214 mg, 0.764 mmol), and K_2CO_3 (263 mg, 1.91 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the usual workup adopting the above-mentioned procedure afforded sulfonamide **19c** as a colorless solid (385 mg, 90%). Mp: 198−200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05−8.01 (m, 1H), 7.88−7.85 (m, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.24−7.17 (m, 4H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 2H), 2.35 (s, 3H), 2.22 (s, 3H), 1.97 (s, 6H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.0, 143.9, 140.1, 138.1, 136.6, 134.8, 133.6, 131.8, 130.1, 129.7, 128.6, 127.8, 126.6, 125.2, 123.5, 119.5, 116.0, 115.1, 111.0, 45.5, 22.0, 21.5, 20.9 ppm. Anal. Calcd for $C_{31}H_{28}BrClN_2O_4S_2$: C, 55.40; H, 4.20; N, 4.17; S, 9.54. Found C, 55.26; H, 4.04; N, 3.91; S, 9.29.

*N-((2-Bromo-1-(2-mesitylenesulfonyl)-1H-indol-3-yl)methyl)-N-(3,4-dichlorophenyl)-4-methylbenzenesulfonamide (**19d**).* A mixture of 2-bromo-3-bromomethylindole **18** (300 mg, 0.637 mmol), *N*-tosyl-3,4-dichloroaniline **2k** (241 mg, 0.764 mmol), and K_2CO_3 (263 mg, 1.91 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. Then the usual workup adopting the above-mentioned procedure gave sulfonamide **19d** as a colorless solid (342 mg, 86%). Mp: 200−202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (dd, J^1 = 6.1 Hz, J^2 = 3.1 Hz, 1H), 7.98 (dd, J^1 = 6 Hz, J^2 = 3 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.34−7.28 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.84−6.82 (m, 3H), 4.85 (s, 2H), 2.45 (s, 3H), 2.30 (s, 3H), 2.12 (s, 6H) ppm. ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ 143.72, 143.68, 140.1, 138.1, 138.0, 135.2, 134.9, 131.9, 129.5, 128.9, 128.5, 127.9, 127.8, 127.1, 125.0, 123.4, 119.7, 116.5, 115.0, 111.0, 45.7, 22.1, 21.5, 21.0 ppm. Anal. Calcd for $C_{31}H_{27}BrC1_2N_2O_4S_2$: C, 52.70; H, 3.85; N, 3.97; S, 9.08. Found C, 52.86; H, 3.97; N, 3.74; S, 9.31.

*11-(2-Mesitylenesulfonyl)-5-tosyl-6,11-dihydro-5H-indolo[3,2-c]-quinolone (**20a**).* To a solution of 2-bromo-3-aminomethylindole **19a** (159 mg, 0.25 mmol) in DMF (8 mL) were added $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.05 mmol), and K_2CO_3 (86 mg, 0.625 mmol). Then the reaction mixture was stirred at 110 °C for 24 h. Then the usual workup adopting the above-mentioned procedure for **4a−i** followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded carboline **20a** as a colorless solid (94 mg, 68%). Mp: 184−186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09−8.06 (m, 1H), 8.00−7.97 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.32−7.25 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.65 Hz, 2H), 6.79 (d, *J* = 4.8 Hz, 2H), 4.80 (s, 2H), 2.42 (s, 3H), 2.27 (s, 3H), 2.06 (s, 6H) ppm. ^{13}C{^{1}HNMR (75 MHz, $CDCl_3$): δ 143.8, 140.0, 137.9, 137.8, 134.7, 134.6, 131.9, 129.6, 128.8, 128.5, 127.9, 127.8, 126.8, 125.1, 123.4, 119.7, 116.3, 115.0, 110.9, 45.6, 22.2, 21.6, 21.0 ppm. HRMS (ESI-TOF): *m*/*z* calcd [M]$^+$ for $C_{31}H_{28}N_2O_4S_2$556.1490, found 556.1496.

*11-(2-Mesitylenesulfonyl)-2-methyl-5-tosyl-6,11-dihydro-5H-indolo[3,2-c]quinolone (**20b**).* To a solution of 2-bromo-3-aminomethylindole **19b** (163 mg, 0.25 mmol) in DMF (8 mL) were added $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.05 mmol), and K_2CO_3 (86 mg, 0.625 mmol). Then the reaction mixture was stirred at 110 °C for 24 h. Then the usual workup adopting the above-mentioned procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded carboline **20b** as a colorless solid (88 mg, 62%). Mp: 194−196 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76−7.74 (m, 1H), 7.68−7.65 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.31−7.29 (m, 4H), 7.14−7.11 (m, 4H), 6.96−6.95 (m, 4H), 4.93 (s, 2H), 2.28 (s, 3H), 2.21 (s, 6H), 2.15 (s, 3H), 2.11 (m, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.9, 143.3, 138.2, 137.6, 135.6, 135.2, 132.8, 132.2, 132.1, 129.4, 128.4, 127.0, 126.2, 126.1, 125.8, 125.3, 123.7, 123.5, 119.9, 119.7, 42.7, 21.5, 20.9, 20.5, 20.4 ppm. HRMS (ESI-TOF): *m*/*z* calcd [M]$^+$ for $C_{32}H_{30}N_2O_4S_2$ 570.1647, found 570.1653.

*2-Chloro-11-(2-mesitylenesulfonyl)-5-tosyl-6,11-dihydro-5H-indolo[3,2-c]quinolone (**20c**).* A mixture of 2-bromo-3-aminomethylindole **19c** (0.168 g, 0.25 mmol), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.05 mmol), and K_2CO_3 (86 mg, 0.625 mmol) in DMF (8 mL) was stirred at 110 °C for 24 h. Then the usual workup adopting the above-mentioned procedure followed by column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded carboline **20c** as a colorless solid (112 mg, 76%). Mp: 156−158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87−7.85 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.47−7.44 (m, 1H), 7.29−7.12 (m, 7H), 6.95 (s, 2H), 6.84−6.82 (m, 2H), 4.88 (s, 2H), 2.32−2.30 (m, 9H), 2.16 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.9, 143.8, 138.9, 136.7, 135.6, 134.4, 132.5, 132.1, 131.7, 129.5, 129.2, 127.7, 126.7, 126.1, 126.0, 125.9, 125.7, 123.6, 119.9, 119.1, 116.3, 43.2, 22.3, 21.4, 20.9 ppm. HRMS (ESI-TOF): *m*/*z* calcd [M]$^+$ for $C_{31}H_{27}ClN_2O_4S_2$ 590.1101, found 590.1098.

*2,3-Dichloro-11-(2-mesitylenesulfonyl)-5-tosyl-6,11-dihydro-5H-indolo[3,2-c]quinolone (**20d**).* A mixture of 2-bromo-3-arylaminomethylindole **19d** (176 mg, 0.25 mmol), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PPh_3 (13 mg, 0.05 mmol), and K_2CO_3 (86 mg, 0.625 mmol) in DMF (8 mL) was stirred at 110 °C for 24 h. Then the usual workup and column chromatographic purification (silica gel, EtOAc−hexane 1:9) afforded carboline **20d** as a colorless solid (106 mg, 68%). Mp: 140−142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25−7.20 (m, 2H), 7.17−7.14 (m, 1H), 6.98 (d, *J* = 2.1 Hz, 1H), 6.87 (s, 2H), 6.76 (dd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, 1H), 4.80 (s, 2H), 2.45 (s, 3H), 2.26−2.23 (m, 9H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.3, 144.2, 140.1, 138.2, 135.1, 134.7, 132.9, 132.7, 132.4, 132.1, 130.5, 130.3, 129.8, 128.7, 128.1, 127.8, 126.0, 124.8, 123.2, 120.2, 113.6, 112.6, 45.8, 22.1, 21.5, 21.0 ppm. HRMS (ESI-TOF): *m*/*z* calcd [M]$^+$ for $C_{31}H_{26}Cl_2N_2O_4S_2$ 624.0711, found 624.0704.

*2-Chloro-11H-indolo[3,2-c]quinoline (**21**).* A mixture of 2-bromo-3-arylaminomethylindole **19c** (150 mg, 0.22 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), PPh_3 (13 mg, 0.044 mmol), and K_2CO_3 (150 mg, 1.11 mmol) in DMF (8 mL) was stirred at 130 °C for 36 h. Then the usual workup adopting the above-mentioned procedure followed by column chromatic purification (silica gel, EtOAc−hexane 1:9) furnished *N*-tosyldihydrocarboline **20c** as a colorless solid (55 mg, 42%). Further elution of the column afforded carboline **21** as a pale yellow solid (15 mg, 26%). Mp: 292−294 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.70 (s, 1H), 9.61 (s, 1H), 8.64 (d, *J* = 2.4 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.35 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 145.2, 143.8, 138.9, 131.6, 129.9, 128.2, 125.9, 121.7, 121.2, 120.8, 120.2, 117.9, 114.9, 112.0 ppm. HRMS (ESI-TOF): *m*/*z* calcd [M]$^+$ for $C_{15}H_9ClN_2$52.0454, found 252.0451.

*7H-Indolo[2,3-c]quinoline (**22a**).* To a stirred solution of *N*-(phenylsulfonyl)carboline **4a** (80 mg, 0.22 mmol) in DMSO (5 mL) was added 30% NaOH (2 mL) and the mixture stirred at room temperature for 12 h. After the completion of the reaction (TLC), the mixture was poured over crushed ice (50 g) containing concd HCl (5 mL). The precipitate obtained was filtered and dried ($CaCl_2$). Trituration of the crude product with MeOH (5 mL) afforded *N*-free carboline **22a** as a yellow solid (42 mg, 87%). Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.19 (s, 1H), 9.29 (s, 1H), 8.80 (d, *J* = 8.1 Hz, 1H), 8.68 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.79−7.70 (m, 2H), 7.70−7.57 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.2, 139.4, 138.8, 132.7, 129.9, 127.0, 126.7, 125.2, 124.3, 123.2, 122.9, 121.3, 120.3, 119.4, 112.7 ppm. HRMS (ESI-TOF): *m*/*z* calcd for [M]$^+$ $C_{15}H_{10}N_2$ 218.0844, found 218.0857.

*2-Methyl-7H-indolo[2,3-c]quinolone (**22b**).* To a stirred solution of *N*-(phenylsulfonyl)carboline **4b** (80 mg, 0.21 mmol) in DMSO (5 mL), 30% NaOH (2 mL) was added. The heterogeneous solution was stirred at room temperature for 12 h. The usual workup followed by trituration of the crude product with MeOH (5 mL) gave *N*-free carboline **22b** as a brown solid (41 mg, 82%). Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.10 (s, 1H), 9.20 (s, 1H), 8.71 (d, *J* = 8.1 Hz, 1H), 8.57 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 8.1 Hz, 1H), 7.61−7.56 (m, 1H), 7.51−7.47 (m, 1H), 7.42−7.37 (m, 1H), 2.66 (m, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 140.6, 139.3, 137.7, 136.7, 132.8, 129.7, 127.2, 126.5, 124.2, 123.0, 122.3, 121.3, 120.2, 119.0, 112.6, 21.5 ppm. HRMS (ESI-TOF): *m*/*z* calcd [M]$^+$ for $C_{16}H_{12}N_2$ 232.1000, found 232.0993.

https://dx.doi.org/10.1021/acs.joc.0c02152
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*2-Chloro-7H-indolo[2,3-c]quinolone (**22c**).* The heterogeneous solution of *N*-(phenylsulfonyl)carboline **6c** (80 mg, 0.20 mmol) in DMSO (5 mL) and 30% NaOH (2 mL) was stirred at room temperature for 12 h. Then the usual workup followed by trituration of the crude product with MeOH (5 mL) gave *N*-free carboline **22c** as a brown solid (44 mg, 86%). Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.32 (s, 1H), 9.31 (s, 1H), 8.75 (d, J = 2.1 Hz, 1H), 8.70 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.70−7.60 (m, 2H), 7.42 (t, J = 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 140.5, 139.4, 139.3, 131.9, 131.7, 129.1, 127.0, 125.7, 122.9, 121.9, 120.9, 120.6, 118.5, 112.8 ppm. HRMS (ESI-TOF): m/z calcd $[M]^+$ for $C_{15}H_9ClN_2$252.0454, found 252.0451.

Gram-Scale Synthesis of Benzo-β-carboline (4a). The intramolecular cyclization of 3-bromo-2-aminomethylindole **3a** (1.17 g, 1.96 mmol) using $Pd(OAc)_2$ (133 mg, 0.196 mmol), PPh_3 (103 mg, 0.393 mmol), and K_2CO_3 (679 mg, 4.9 mmol) in DMF (30 mL) at 110 °C for 8 h followed by workup and chromatographic purification (silica gel, EtOAc−hexane 1:9) furnished β-carboline **4a** (510 mg, 72%).

Gram-Scale Synthesis of Benzo[4,5]isothiazolo[2,3-*a*]indole 5,5-dioxides (10f). The intramolecular cyclization of 2-bromo-3-aminomethylindole **9f** (1.4 g, 2.15 mmol) using $Pd(OAc)_2$ (144 mg, 0.214 mmol), PPh_3 (113 mg, 0.428 mmol), and K_2CO_3 (738 mg, 5.35 mmol) in DMF (30 mL) at 110 °C for 6 h followed by workup and column chromatographic purification (silica gel, EtOAc−hexane 2:8) afforded **10f** as a colorless solid (940 mg, 76%).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02152.

Copies of ^{1}H and ^{13}C NMR spectra for **1**, **3a−i**, **4a−i**, **5**, **6a,b**, **7a,b**, **8**, **9a−h**, **10a−h**, **12**, **15−18**, **19a−d**, **20a−d**, **21**, and **22a−c** (PDF)

Accession Codes

CCDC 1894094, 1936760, and 1990919 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors graciously acknowledge the Council of Scientific and Industrial Research (CSIR) Project (02(0376)/19/EMR-II) and University Grants Commission (UGC)-Mid Career Award (F-19-230/20189(BSR)) New Delhi for financial support. P.R. thanks the University Grants Commission (UGC) New Delhi for fellowship. V.S. thanks the Council of Scientific and Industrial Research (CSIR) New Delhi for a fellowship. The authors thank the Department of Science and Technology Funds for the Improvement of Science and Technology (DST-FIST) New Delhi for NMR and HRMS facilities.

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J. Org. Chem. 2021, 86, 1925−1937