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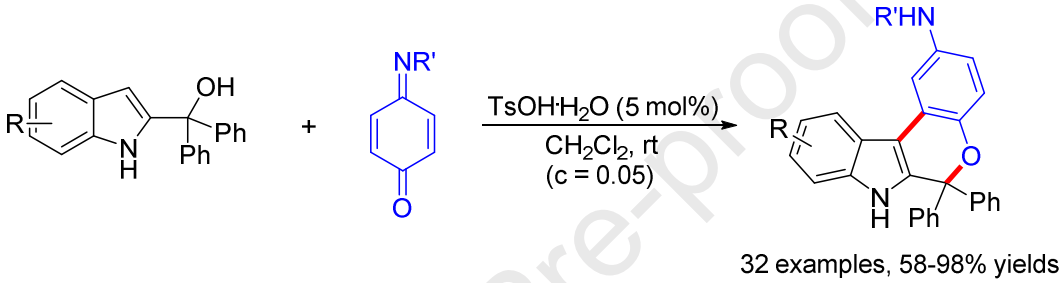

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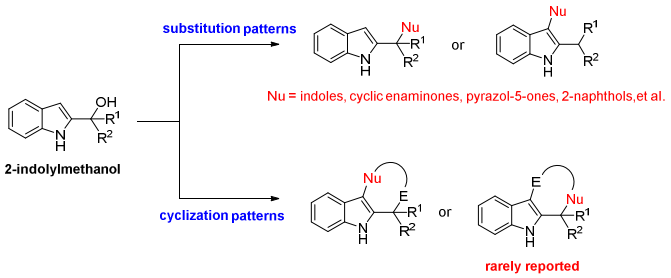
ABSTRACT

A formal [3+3] cyclization reaction of 2-indolylmethanols with quinones was realized to furnish indole-fused scaffolds in moderate to excellent yields. This protocol was proceeded smoothly under acid condition, with high high yields and broad substrate scope.

Introduction

Among the numerous heterocyclic compounds, indole-fused derivatives which serve as the core structures have been found in biologically natural products and pharmaceuticals.[1] Thus the development of novel and efficient methodologies to construct structurally diverse indole-fused heterocycles has attracted considerable attention from the chemistry community. Among the various reported approaches, the synthesis of indole-fused scaffolds from indole skeletons has been proved to be one of the most straightforward procedure.



Scheme 1. Two reaction patterns of 2-indolylmethanols.

In recent years, 2-indolylmethanols which serve as versatile reactants have been extensively explored in organic synthesis. [2] As shown in Scheme 1, two main reaction patterns of 2-indolylmethanols have been developed to synthesize indole derivatives or construct indole-fused scaffolds. First, nucleophilic substitutions of 2-indolylmethanols have been well studied by the Shi group. Nowadays, various nucleophiles including indoles, [3] cyclic enaminones, [4] pyrazol-5-ones, [5] 2-naphthols, [6] phosphine nucleophiles [7] *et al.* [8] were successfully added to the C3-position of the indole moiety, providing versatile indole derivatives. Second, 2-indolylmethanols involved in cycloaddition reaction, including [3+2], [9] [3+3], [10] [4+3] cyclizations, [11] have been recently developed to construct indole-fused cyclic frameworks. However, among these reported cyclization reactions, the C3 position of 2-indolylmethanols as nucleophilic site has been very limited investigated to construct indole-fused cyclic frameworks. To the best of our knowledge, there are only two examples employing C3-position of 2-indolylmethanols as nucleophilic site reported by the Shi group, including [3+3] cyclization of 2-indolylmethanols with vinylcyclopropanes10 and [4+3] cyclization of o-hydroxybenzyl alcohols with 2-indolylmethanols. [11] In this regard, it is highly desired to develop cyclization reaction of 2-indolylmethanols, and C3-position of 2-indolylmethanols display nucleophilicity. As a continuous work of our research towards the catalytic reaction of quinone imines, [12] we designed the [3+3] cycloaddition reaction of 2-indolylmethanols with quinone imines, to construct indole-fused heterocycles. Herein, we report the novel cyclization reaction, providing access to structurally diverse indole-fused frameworks in high yield (up to 98%).

Result and Discussion

At the outset, the reaction of 2-indolylmethanol **1a** and quinone imine **2a** was examined as a model reaction to test our hypothesis under acid condition (Table 1). However, initially, no reaction occurred under weak acids condition, such as AcOH, $PhCO_2H$ (entries 1-2, Table 1). Therefore, the stronger acids were examined (entries 3-4, Table 1) and found that $TsOH{\cdot}H_2O$

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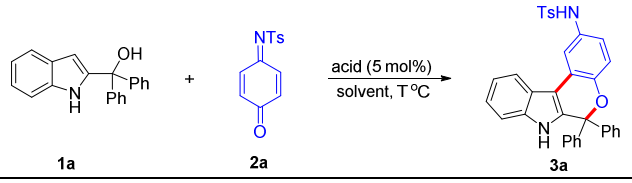
generated the desired product **3a** in 78% yield. Furthermore, the structure of the product **3a** was confirmed by X-ray single-crystal analysis (see the supporting information for details). [13] Then, a series of commonly used solvents were evaluated (entries 5-9, Table 1), and CH_2Cl_2 was found to be the optimization reaction medium as it could afford product **3a** in 78% yield (entry 5, Table 1). To improve the yield of the reaction, the reaction temperature and the concentration of the reaction was further investigated (entries 10-12, Table 1), lowering the temperature had no influence on the reaction. However, when the concentration of the reaction was decreased to 0.05 mol/L, the yield could increase to 85%, then the concentration was further lowered, the yield was almost be maintained. Thus, the optimal reaction condition was confirmed as following: **1a** (0.36 mmol), **2a** (0.30 mmol), $TsOH{\cdot}H_2O$ (5 mol%), CH_2Cl_2 (6.0 mL), 25 °C.

Table 1. Reaction Optimization. [a]

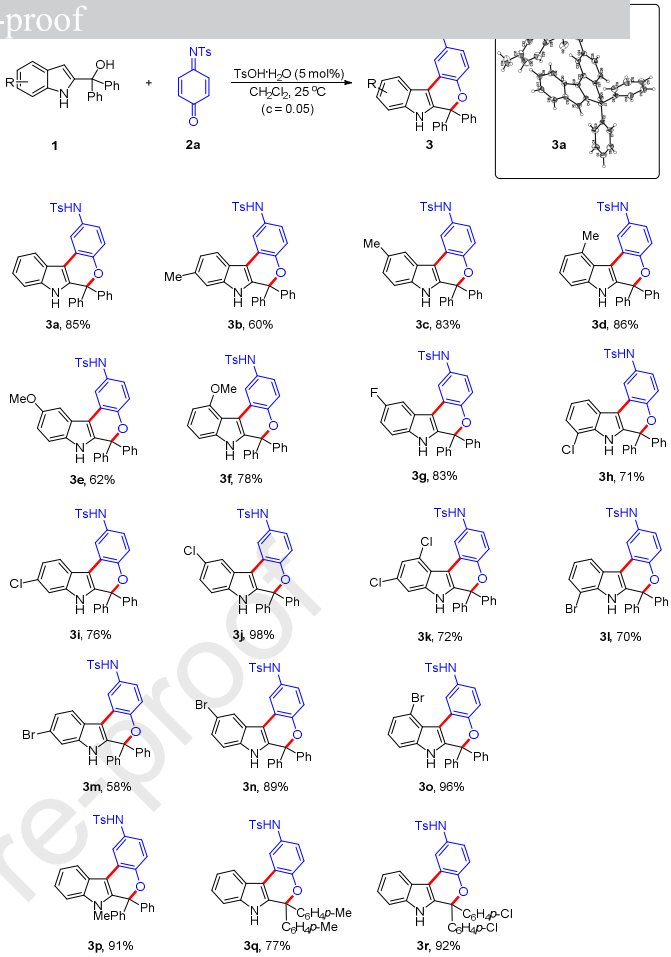


1a 2a 3a

entry	acid	solvent	T (°C)	yield (%)[b]
1	AcOH	CH_2Cl_2	25	NR
2	$PhCO_2H$	CH_2Cl_2	25	NR
3	$(PhO)_2PO_2H$	CH_2Cl_2	25	36
4	CF_3SO_3H	CH_2Cl_2	25	49
5	$TsOH{\cdot}H_2O$	CH_2Cl_2	25	78
6	$TsOH{\cdot}H_2O$	CH_3CN	25	27
7	$TsOH{\cdot}H_2O$	DCE	25	75
8	$TsOH{\cdot}H_2O$	EtOH	25	66
9	$TsOH{\cdot}H_2O$	DMF	25	NR
10	$TsOH{\cdot}H_2O$	CH_2Cl_2	0	75
11 [c]	**$TsOH{\cdot}H_2O$**	**CH_2Cl_2**	**25**	**85**
12 [d]	$TsOH{\cdot}H_2O$	CH_2Cl_2	25	87

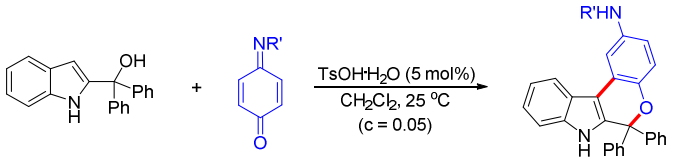
[a] Reaction conditions: **1a** (0.36 mmol), **2a** (0.30 mmol), acid (5 mol%), solvent (3.0 mL), 25 °C. [b] Isolated yield. [c] using CH_2Cl_2 (6.0 mL). [d] using CH_2Cl_2 (12.0 mL).

With optimal reaction condition in hands, we next explored the substrates with different substituted 2-indolylmethanols and quinone imines. As illustrated in Scheme 2, a wide range of 2-indolylmethanols **1** bearing different substituents on the indole core could be proceeded smoothly, generating the cyclization product **3** (**3a-3o**) in moderate to excellent yields (58-98%), different electron-withdrawing and electron-donating substituents were well tolerated in this transformation. It is worth noting that N-Me-2-indolylmethanol **1p** could serve as a suitable substrate to give product **3p** in excellent yield (91%). Meanwhile, 2-indolylmethanols bearing other aromatic groups could be participated in the [3+3] cyclization, affording the desire products in good yields (77-92%).



Scheme 2. Substrate scope of 2-indolylmethanols. Reaction conditions: **1** (0.36 mmol), **2a** (0.3 mmol), $TsOH{\cdot}H_2O$ (5 mol%), CH_2Cl_2 (6.0 mL), 25 °C.

Table 2. Substrate scope of substituted quinone imines. [a]



1a 2 4

entry	2	4	yield (%)[b]
1	**2b**, R' = *p*-$MeOC_6H_4SO_2$	**4b**	81
2	**2c**, R' = *p*-^{t}Bu$C_6H_4SO_2$	**4c**	93
3	**2d**, R'= *p*-$PhC_6H_4SO_2$	**4d**	82
4	**2e**, R'= *p*-$ClC_6H_4SO_2$	**4e**	69
5	**2f**, R'= *m*-$BrC_6H_4SO_2$	**4f**	90
6	**2g**, R'= *o*-$ClC_6H_4SO_2$	**4g**	96
7	**2h** R'= 3,4-$Cl_2C_6H_3SO_2$	**4h**	73
8	**2i**, R'= *m*-$FC_6H_4SO_2$	**4i**	86
9	**2j**, R'= *m*-$CNC_6H_4SO_2$	**4j**	73
10	**2k**, R'= *m*-$NO_2C_6H_4SO_2$	**4k**	70
11	**2l**, R'= *m*-$CF_3C_6H_4SO_2$	**4l**	78
12	**2m**, R'= $EtSO_2$	**4m**	74
13	**2n**, R'= ^{n}$PrSO_2$	**4n**	82
14	**2o**, R'= cyclopropylSO_2	**4o**	94

[a] Reaction conditions: **1a** (0.36 mmol), **2** (0.3 mmol), $TsOH{\cdot}H_2O$ (5 mol%), CH_2Cl_2 (6.0 mL), 25 °C. [b] Isolated yield.

Moreover, a series of quinone imines bearing different Ar and alkyl substituents were also employed in the [3+3] cyclization reaction, affording the desired product **4b-4o** in good yields (69-96%) (Table 2). Substituted quinone imines bearing electron-

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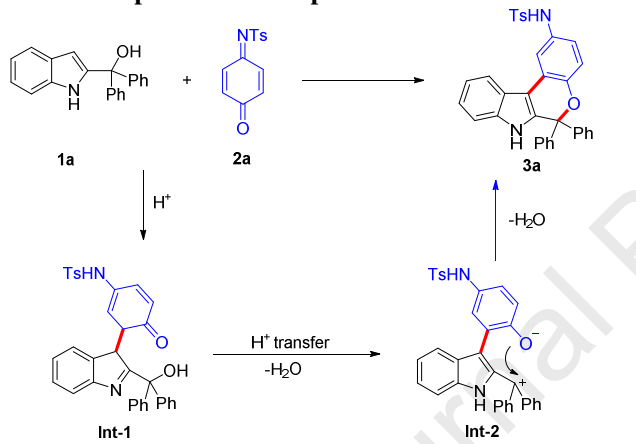
group (Cl, Br, NO_2, CN, CF_3) on the aromatic ring, were obtained with high to excellent yields (69-96% yields). Overall, the substitution pattern and electronic effects of the substituents had limited influence on the reactivity of this transformation. We also examined the reactivity of the alkyl substituted quinone imines (Et, *n*-Pr, cyclopropyl), pleasingly, the reaction proceeded smoothly, affording the desired products in 74-94% yields. However, the other protecting groups on the quinone imine (such as Ac and Boc), the desired products could not be obtained under optimized condition.

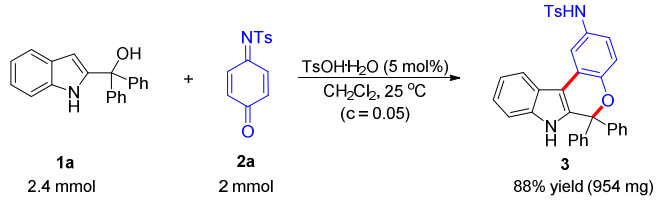
A proposed reaction process to explain this transformation of the [3+3] cyclization reaction was depicted in Scheme 3. Initially, the 2-indolylmethanol **1a** utilized the nucleophilicity of the C3-position of the indole to attack quinone imine **2a** under acid condition, leading to the intermediate **Int-1**, which could rapidly undergo proton transfer and lose one molecular water to afford **Int-2**. Then **Int-2** could occur an intramolecular nucleophilic attack pathway to give cyclization product **3a**.

Scheme 3. Proposed reaction process.



In addition, this [3+3] cyclization reaction of 2-indolylmethanol **1a** and quinone imine **2a** could be carried out at 2 mmol scale under the optimization condition, affording the indole-fused framework **3a** in 88% yield (Scheme 4). This result revealed that this [3+3] cyclization reaction could be scaled up.

Scheme 4. Two mmol scale reaction.



Conclusion

In summary, a formal [3+3] cyclization reaction of 2-indolylmethanols and quinone imines was developed and this transformation provides an efficient method for the synthesis of fused-indole scaffolds under acid condition. We next speculate that 2-indolylmethanols as 1,3-dipole could be involved in other cyclization reactions to give rapid access to fused-indole heterocycles.

^{1}H and ^{13}C NMR spectra were recorded on an ACF* 300Q Bruker or ACF* 500Q Bruker spectrometer. Low- and high-resolution mass spectra (LRMS and HRMS) were recorded in electron impact mode. The mass analyzer type used for the HRMS measurements was TOF. Reactions were monitored by TLC on silica gel 60 F254 plates (Qingdao Ocean Chemical Company, China). Column chromatography was carried out on silica gel (200-300 mesh, Qingdao Ocean Chemical Company, China). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br s = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Commercially available reagents and solvents were used without further purification.

General procedure for TsOH·H_2O catalyzed [3+3] cyclization reaction of 2-indolylmethanols and quinone imines.

To the mixture of 2-indolylmethanols **1** (0.36 mmol), quinone imines **2** (0.30 mmol) in CH_2Cl_2 (6 mL) was added the catalyst TsOH·H_2O in one portion, which was stirred at 25 °C for 2 h. After the completion of the reaction indicated by TLC, the reaction mixture was directly purified through flash column chromatography on silica gel to afford pure products **3** and **4**.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3a)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 85% yield (138.6 mg), white solid; m.p. 280-281 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.29 (s, 1H), 9.91 (s, 1H), 7.71-7.57 (m, 3H), 7.48-7.41 (m, 1H), 7.40-7.28 (m, 9H), 7.25-7.14 (m, 6H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.29, 143.51, 142.41, 137.46, 137.30, 136.52, 132.33, 130.03, 128.66, 128.57, 128.02, 127.22, 123.11, 122.93, 122.50, 121.04, 119.07, 118.97, 117.78, 115.49, 113.16, 105.78, 84.23, 21.37. HRMS (ESI) exact mass calcd. for $[C_{34}H_{26}N_2O_3S+Na]^+$ requires 565.1556, found 565.1556.

4-methyl-N-(9-methyl-6,6-diphenyl-6,7-dihydrochromeno [3,4-b]indol-2-yl)benzenesulfonamide (3b)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 83% yield (140.0 mg), white solid; m.p. 252-255 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.13 (s, 1H), 9.88 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.42-7.28 (m, 9H), 7.26-7.16 (m, 5H), 7.02 (d, *J* = 8.1Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.74 (dd, *J* = 8.4, 2.1 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.72, 146.74, 142.98, 142.02, 137.41, 136.85, 135.35, 131.78, 131.23, 129.51, 128.10, 128.02, 127.51, 126.70, 122.49, 122.14, 120.55, 118.27, 117.13, 114.86, 112.43, 105.20, 95.26, 91.63, 83.75, 21.30, 20.87. HRMS (ESI) exact mass calcd. for $[C_{35}H_{28}N_2O_3S+Na]^+$ requires 579.1718, found 579.1713.

5-methyl-N-(10-methyl-6,6-diphenyl-6,7-dihydrochromeno [3,4-b]indol-2-yl)benzenesulfonamide (3c)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 83% yield (140.0 mg), white solid; m.p. 252-255 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.14 (s, 1H), 9.90 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.44 (s, 1H), 7.41-7.28 (m, 10H), 7.27-7.16 (m, 4H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.47 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.77, 142.98, 142.05, 136.95, 136.10, 135.37, 131.89, 129.55, 129.21, 128.15, 128.08, 127.55, 126.74, 123.51, 122.98, 122.69, 118.35, 118.20,

exact mass calcd. for $[C_{35}H_{28}N_2O_3S+Na]^+$ requires 579.1718, found 579.1713.

4-methyl-N-(11-methyl-6,6-diphenyl-6,7-dihydrochromeno [3,4-b]indol-2-yl)benzenesulfonamide (3d)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 86% yield (145.5 mg), white solid; m.p. 231-233 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.14 (s, 1H), 9.80 (s, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 2.1 Hz, 1H), 7.38-7.30 (m, 6H), 7.30-7.23 (m, 3H), 7.22-7.13 (m, 4H), 7.03 (dd, *J* = 8.1, 7.8 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.1 Hz, 1H), 2.54 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.69, 142.85, 141.51, 138.18, 137.44, 136.54, 131.66, 129.43, 129.32, 128.17, 128.00, 127.82, 126.58, 123.47, 122.61, 122.55, 122.04, 119.04, 118.92, 118.39, 110.24, 106.82, 83.56, 23.60, 20.89. HRMS (ESI) exact mass calcd. for $[C_{35}H_{28}N_2O_3S+Na]^+$ requires 579.1713, found 579.1711.

N-(10-methoxy-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3e)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 62% yield (107.0mg), white solid; m.p. 267-269 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.13 (s, 1H), 9.94 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.47-7.26 (m, 10H), 7.26-7.15 (m, 5H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.86 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.43, 146.46, 143.01, 141.93, 136.70, 136.57, 132.00, 129.53, 128.11, 128.04, 127.48, 126.61, 123.01, 122.60, 117.41, 117.24, 114.18, 113.30, 111.49, 105.10, 101.12, 83.67, 55.46, 20.82. HRMS (ESI) exact mass calcd. for $[C_{35}H_{28}N_2O_4S+Na]^+$ requires 595.1662, found 595.1661.

N-(11-methoxy-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3f)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 78% yield (136.0 mg), white solid; m.p. 235-238 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.16 (s, 1H), 9.84 (s, 1H), 8.17 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.39-7.30 (m, 6H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.23-7.15 (m, 4H), 7.13-6.98 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.70-6.58 (m, 2H), 3.95 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.58, 147.91, 143.17, 142.41, 139.01, 137.40, 135.92, 135.59, 132.04, 129.85, 128.59, 128.47, 128.15, 127.01, 123.54, 123.23, 120.51, 119.61, 117.86, 113.87, 106.93, 106.10, 101.36, 83.57, 55.32, 21.33. HRMS (ESI) exact mass calcd. for $[C_{35}H_{28}N_2O_4S+Na]^+$ requires 595.1662, found 595.1664.

N-(10-fluoro-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3g)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 83% yield (104.3 mg); white solid; m.p. 282-285 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.42 (s, 1H), 9.86 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.45 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.42-7.25 (m, 10H), 7.25-7.16 (m, 4H), 7.12-7.02 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.30, 156.20, 146.72, 143.10, 141.72, 137.93, 136.84, 133.68, 131.99, 129.58, 128.27, 128.16, 127.55, 126.76, 122.65 (d, *J* = 10.1 Hz), 121.99, 118.59, 117.44, 114.86, 113.85 (d, *J* = 9.7 Hz), 110.15 (d, *J* = 25.5 Hz), 105.63 (d, *J* = 4.5 Hz), 103.41 (d, *J* = 24.0 Hz), 95.32, 83.73, 20.86. HRMS (ESI) exact mass calcd. for $[C_{35}H_{25}FN_2O_3S+Na]^+$ requires 538.1462, found 538.1462.

N-(8-chloro-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamid (3h)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 71% yield (128.5 mg), white solid; m.p. 246-248 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.76 (s, 1H), 9.91 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.44-7.18 (m, 15H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.85-6.74 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.01, 143.08, 141.50, 137.65, 136.82, 133.88, 131.90, 129.59, 128.25, 128.06, 127.93, 126.77, 124.60, 122.16, 121.68, 121.57, 119.13, 117.54, 117.35, 116.94, 115.13, 106.88, 91.68, 84.25, 20.92. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}ClN_2O_3S+Na]^+$ requires 599.1167, found 599.1164.

N-(9-chloro-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3i)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 76% yield (131.0 mg), white solid; m.p. 272-274 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.44 (s, 1H), 9.91 (s, 1H), 7.70-7.57 (m, 3H), 7.45 (s, 1H), 7.42-7.30 (m, 9H), 7.30-7.14 (m, 5H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.83-6.73 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.27, 143.54, 142.12, 137.92, 137.46, 137.24, 132.46, 130.04, 128.78, 128.65, 128.00, 127.22, 127.18, 122.31, 121.88, 121.40, 120.31, 119.23, 117.96, 115.41, 112.80, 106.06, 84.12, 21.37. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}ClN_2O_3S+Na]^+$ requires 599.1167, found 599.1165.

N-(10-chloro-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3j)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 98% yield (169.4 mg), white solid; m.p. 266-269 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.52 (s, 1H), 9.89 (s, 1H), 7.76 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.45-7.30 (m, 10H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.25-7.14 (m, 4H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.15, 143.57, 142.05, 137.94, 137.14, 136.17, 132.52, 130.04, 128.78, 128.64, 128.00, 127.19, 125.06, 124.72, 122.23, 121.25, 118.98, 117.98, 115.21, 115.16, 113.56, 105.52, 84.13, 21.40. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}ClN_2O_3S+Na]^+$ requires 599.1163, found 599.1165.

N-(9,11-dichloro-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3k)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 72% yield (132.0 mg), white solid; m.p. 295-297 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.66 (s, 1H), 9.82 (s, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.39-7.30 (m, 6H), 7.29-7.21 (m, 3H), 7.21-7.11 (m, 4H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.33, 143.29, 141.32, 140.84, 138.97, 137.14, 135.60, 132.06, 129.87, 128.91, 128.64, 128.26, 127.01, 126.89, 125.23, 122.04, 121.91, 121.27, 120.81, 120.53, 118.86, 111.75, 106.67, 83.74, 21.36. HRMS (ESI) exact mass calcd. for $[C_{34}H_{24}Cl_2N_2O_3S+Na]^+$ requires 633.0777, found 633.0779.

N-(8-bromo-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3l)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 70% yield (124.0 mg), white solid; m.p. 242-245 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.56 (s, 1H), 9.90 (s, 1H), 7.70-7.60 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.41-7.23 (m, 13H), 7.16 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.31 (s, 3H). ^{13}C

NM
137.23, 135.82, 135.59, 132.32, 130.04, 128.70, 128.55, 128.35, 127.21, 125.83, 124.86, 122.50, 122.02, 119.60, 118.43, 117.81, 115.58, 107.42, 105.53, 84.71, 21.37. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}BrN_2O_3S+H]^+$ requires 621.0842, found 621.0844.

N-(9-bromo-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3m)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 58% yield (94.0 mg), white solid; m.p. 271-274 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.44 (s, 1H), 9.91 (s, 1H), 7.73-7.52 (m, 4H), 7.47-7.28 (m, 10H), 7.27-7.15 (m, 4H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.82-6.73 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.26, 143.53, 142.08, 138.33, 137.34, 137.26, 132.45, 130.03, 128.77, 128.64, 127.99, 127.21, 123.93, 122.28, 122.12, 120.67, 119.22, 117.94, 115.74, 115.43, 115.10, 106.10, 84.10, 21.35. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}BrN_2O_3S+H]^+$ requires 621.0842, found 621.0840.

N-(10-bromo-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3n)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 89% yield (167.6 mg), white solid; m.p. 280-282 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.49 (s, 1H), 9.88 (s, 1H), 7.66 (s, 1H), 7.64 (s, 1H), 7.63-7.56 (m, 2H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.42-7.30 (m, 8H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.26-7.15 (m, 5H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.17, 143.57, 142.06, 138.13, 137.17, 135.94, 132.50, 130.05, 128.78, 128.64, 128.00, 127.19, 125.61, 124.03, 122.49, 122.24, 119.02, 118.21, 117.96, 115.27, 114.72, 105.63, 84.14, 21.36. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}BrN_2O_3S+H]^+$ requires 621.0842, found 621.0866.

N-(11-bromo-6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3o)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 96% yield (174.5 mg), white solid; m.p. 262-263 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.58 (s, 1H), 9.80 (s, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.55-7.42 (m, 3H), 7.40-7.30 (m, 7H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.22-7.14 (m, 4H), 7.07 (appt, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.80 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.55, 143.25, 141.48, 140.67, 138.90, 137.24, 135.60, 131.59, 129.85, 128.80, 128.55, 128.31, 127.09, 125.91, 123.56, 123.16, 122.61, 122.55, 120.91, 118.76, 112.46, 106.56, 84.01, 21.37. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}BrN_2O_3S+H]^+$ requires 621.0842, found 621.0843.

5-methyl-N-(7-methyl-6,6-diphenyl-6,7-dihydrochromeno [3,4-b]indol-2-yl)benzenesulfonamide (3p)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 91% yield (152.9 mg), white solid; m.p. 218-220 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.88 (s, 1H), 7.73-7.59 (m, 3H), 7.58-7.49 (m, 1H), 7.47-7.25 (m, 11H), 7.24-7.13 (m, 4H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.80-6.69 (m, 1H), 3.05 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.81, 143.49, 141.72, 138.40, 137.51, 137.29, 132.43, 130.01, 129.15, 128.76, 128.64, 127.19, 122.94, 122.73, 122.53, 121.45, 119.20, 119.12, 117.87, 115.56, 111.33, 106.56, 84.74, 31.77, 21.37. HRMS (ESI) exact mass calcd. for $[C_{35}H_{28}N_2O_3S+Na]^+$ requires 579.1713, found 579.1711.

methylbenzenesulfonamide (3q)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 77% yield (132.9 mg), white solid; m.p. 170-172 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.19 (s, 1H), 9.88 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.60 (dd, *J* = 6.0, 2.9 Hz, 1H), 7.43 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.39-7.30 (m, 3H), 7.22-7.11 (m, 6H), 7.07 (d, *J* = 8.1 Hz, 4H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.73 (dd, *J* = 8.5, 2.2 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.40, 143.48, 139.61, 137.90, 137.37, 136.92, 135.60, 132.19, 130.02, 129.05, 127.96, 127.21, 123.14, 123.03, 122.36, 120.94, 118.97, 117.75, 115.49, 113.12, 105.64, 84.02, 21.38, 21.06. HRMS (ESI) exact mass calcd. for $[C_{34}H_{25}BrN_2O_3S+Na]^+$ requires 593.1869, found 593.1869.

N-(6,6-bis(4-chlorophenyl)-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methylbenzenesulfonamide (3r)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 92% yield (165.0 mg), white solid; m.p. 155-156 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.33 (s, 1H), 9.91 (s, 1H), 7.70-7.60 (m, 3H), 7.50-7.38 (m, 6H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25-7.15 (m, 6H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 146.40, 143.05, 140.39, 137.08, 136.82, 135.16, 133.25, 132.23, 129.52, 129.45, 128.31, 127.49, 126.75, 122.64, 122.38, 122.29, 120.75, 118.71, 118.61, 117.44, 115.09, 112.75, 105.61, 95.32, 82.89, 20.90. HRMS (ESI) exact mass calcd. for $[C_{34}H_{24}Cl_2N_2O_3S+Na]^+$ requires 609.0812, found 609.0810.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-4-methoxybenzenesulfonamide (4b)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 81% yield (135.8 mg), white solid; m.p. 251-253 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.28 (s, 1H), 9.81 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.67-7.59 (m, 1H), 7.49-7.29 (m, 8H), 7.27-7.14 (m, 6H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.80, 147.25, 142.43, 137.46, 136.49, 132.46, 131.84, 129.35, 128.64, 128.56, 128.02, 123.13, 122.92, 122.50, 121.00, 119.11, 118.93, 117.74, 115.48, 114.75, 113.15, 105.81, 84.23, 56.01. HRMS (ESI) exact mass calcd. for $[C_{34}H_{26}N_2O4S+Na]^+$ requires 581.1506, found 581.1506.

4-(tert-butyl)-N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)benzenesulfonamide (4c)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 93% yield (164.0 mg), white solid; m.p. 260-262 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.29 (s, 1H), 9.95 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.66-7.51 (m, 3H), 7.48-7.28 (m, 8H), 7.27-7.13 (m, 6H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 1.22 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.73, 146.76, 141.96, 137.02, 136.10, 131.94, 128.19, 128.10, 127.57, 126.58, 125.99, 122.67, 122.52, 122.03, 120.56, 118.61, 118.32, 117.36, 114.78, 112.70, 105.35, 83.78, 34.78, 30.69. HRMS (ESI) exact mass calcd for $[C_{37}H_{32}N_2O_3S+Na]^+$ requires 607.2026, found 607.2029.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-[1,1'-biphenyl]-4-sulfonamide (4d)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 82% (148.7 mg); white solid; m.p. 213-232 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.29 (s, 1H), 10.05 (s, 1H), 7.85 (s, 4H), 7.72-7.62 (m, 3H), 7.52-7.40 (m, 5H), 7.39-7.28 (m, 6H), 7.26-7.09 (m, 6H), 6.97 (d, *J* = 8.5

Hz, DMSO-d_6) δ 147.44, 144.69, 142.44, 138.97, 138.75, 137.50, 136.64, 132.28, 129.51, 128.99, 128.72, 128.62, 128.08, 127.94, 127.83, 127.51, 123.17, 123.11, 122.55, 121.14, 119.10, 117.95, 115.59, 113.22, 105.81, 84.30. HRMS (ESI) exact mass calcd. for $(C_{39}H_{28}N_2O_3S+Na)^+$ requires m/z 627.1713, found m/z 627.1713.

4-chloro-N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)benzenesulfonamide (4e)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 69% yield (116.9 mg), white solid; m.p. 292-295 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.30 (s, 1H), 10.04 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.65-7.55 (m, 3H), 7.48-7.42 (m, 1H), 7.41-7.28 (m, 7H), 7.27-7.15 (m, 6H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.79-6.70 (m, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.66, 142.37, 138.93, 138.15, 137.48, 136.58, 131.82, 129.79, 129.13, 128.68, 128.58, 128.04, 123.12, 123.09, 122.53, 121.12, 119.51, 119.02, 117.92, 116.00, 113.19, 105.72, 84.30. HRMS (ESI) exact mass calcd. for $[C_{33}H_{23}ClN_2O_3S+Na]^+$ requires 585.1010, found 585.1012.

3-bromo-N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)benzenesulfonamide (4f)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, reaction time = 2 h, 90% yield (165.0 mg), white solid; m.p. 220-223 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.30 (s, 1H), 10.06 (s, 1H), 7.97 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.66-7.57 (m, 1H), 7.53-7.42 (m, 2H), 7.41-7.29 (m, 7H), 7.29-7.14 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.83-6.72 (m, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.76, 142.37, 142.10, 137.48, 136.53, 136.02, 131.87, 131.60, 129.57, 128.66, 128.56, 128.01, 126.23, 123.09, 122.53, 121.11, 119.78, 119.05, 117.90, 116.11, 113.18, 105.67, 84.33. HRMS (ESI) exact mass calcd. for $[C_{33}H_{23}BrN_2O_3S+NH_4]^+$ requires 624.0951, found 624.0954.

2-chloro-N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)benzenesulfonamide (4g)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 96% (162.9 mg); white solid; m.p. 270-272 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.30 (s, 1H), 10.30 (s, 1H), 8.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.72-7.58 (m, 3H), 7.56-7.48 (m, 1H), 7.47-7.40 (m, 2H), 7.40-7.29 (m, 6H), 7.27-7.15 (m, 6H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.77 (dd, *J* = 8.6, 2.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.25, 142.40, 137.47, 137.36, 136.62, 135.03, 132.36, 131.98, 131.60, 131.28, 128.74, 128.63, 128.25, 128.06, 128.05, 123.10, 123.08, 123.08, 122.57, 121.17, 119.06, 118.29, 117.90, 114.77, 113.24, 105.68, 84.28, 65.39, 15.65. HRMS (ESI) exact mass calcd. for $(C_{33}H_{23}ClN_2O_3S+Na)^+$ requires m/z 585.1010, found m/z 585.1012.

3,4-dichloro-N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)benzenesulfonamide (4h)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 72% (130.3 mg); white solid; m.p. 283-284 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.33 (s, 1H), 10.12 (s, 1H), 7.98 (d, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.64-7.56 (m, 1H), 7.51-7.42 (m, 1H), 7.42-7.30 (m, 7H), 7.29-7.16 (m, 6H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.82, 148.01, 142.36, 140.29, 137.53, 136.68, 136.48, 132.70, 132.11, 131.42, 128.99, 128.76, 128.64, 128.07, 127.41, 123.24, 123.14, 122.64, 121.24, 120.17, 118.98, 118.12, 116.44, 113.29, 105.67, 84.39, 60.25, 21.22, 14.54. HRMS (ESI) m/z 619.0620, found m/z 619.0625.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-3-fluorobenzenesulfonamide (4i)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 86% (141.1 mg); white solid; m.p. 244-246 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.32 (s, 1H), 10.10 (s, 1H), 7.67-7.54 (m, 4H), 7.53-7.43 (m, 2H), 7.42-7.39 (m, 1H), 7.39-7.29 (m, 6H), 7.27-7.16 (m, 6H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.14, 161.16, 147.72, 142.41, 142.18 (d, *J* = 6.5 Hz), 137.52, 136.65, 132.13 (d, *J* = 7.8 Hz), 131.81, 128.75, 128.64, 128.08, 123.57 (d, *J* = 3.1 Hz), 123.16, 122.63, 121.16, 120.48 (d, *J* = 21.2 Hz), 119.49, 119.08, 118.00, 115.98, 114.25 (d, *J* = 24.2 Hz), 113.27, 105.73, 84.36. HRMS (ESI) exact mass calcd. for $(C_{33}H_{23}FN_2O_3S+Na)^+$ requires m/z 569.1306, found m/z 569.1301.

3-cyano-N-(6,6-diphenyl-6,7-dihydro- chromeno[3,4-b]indol-2-yl)benzene-Sulfonamide (4j)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 72% (121.0 mg); white solid; m.p. 259-262 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.32 (s, 1H), 10.14 (s, 1H), 8.23 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.75 (appt, *J* = 7.9 Hz, 1H), 7.67-7.57 (m, 1H), 7.51-7.41 (m, 1H), 7.41-7.29 (m, 7H), 7.28-7.15 (m, 6H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.77 (dd, *J* = 8.6, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.87, 142.36, 141.33, 137.50, 136.86, 136.65, 131.72, 131.48, 131.26, 130.76, 128.77, 128.65, 128.06, 123.20, 123.11, 122.63, 121.19, 119.81, 119.04, 118.05, 117.87, 116.24, 113.27, 112.97, 105.64, 84.37. HRMS (ESI) exact mass calcd. for $(C_{34}H_{23}F_3N_2O_3S-H)^-$ requires m/z 552.1460, found m/z 552.1374.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-3-nitrobenzenesulfonamide (4k)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 70% (120.9 mg); white solid; m.p. 208-210 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.32 (s, 1H), 10.29 (s, 1H), 8.60 (appt, *J* = 1.8 Hz, 1H), 8.48-8.37 (m, 1H), 8.19-8.08 (m, 1H), 7.82 (appt, *J* = 8.0 Hz, 1H), 7.71-7.58 (m, 1H), 7.51-7.41 (m, 2H), 7.41-7.28 (m, 6H), 7.28-7.14 (m, 6H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.79 (dd, *J* = 8.5, 2.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.31, 147.88, 142.33, 141.61, 141.59, 137.48, 136.63, 133.24, 131.82, 131.42, 131.40, 128.76, 128.64, 128.17, 128.03, 127.92, 123.21, 123.08, 122.63, 121.99, 121.12, 119.78, 118.97, 118.07, 116.22, 113.26, 105.59, 84.35. HRMS (ESI) exact mass calcd. for $(C_{33}H_{23}N_3O_5S+Na)^+$ requires m/z 592.1251, found m/z 592.1252.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)-3-(trifluoromethyl)benzene sulfonamide (4l)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 77% (139.1 mg); white solid; m.p. 135-137 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.31 (s, 1H), 10.13 (s, 1H), 8.12 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.77 (appt, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.42-7.30 (m, 7H), 7.29-7.13 (m, 6H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.95, 142.36, 141.13, 137.49, 136.61, 131.46, 131.31, 131.29, 130.38 (q, *J* = 32.7 Hz), 129.95 (q, *J* = 3.7 Hz), 128.74, 128.62, 128.05, 124.89, 123.81 (q, *J* = 273.4 Hz), 123.79 (q, *J* = 4.0 Hz), 123.10, 123.10, 122.60, 121.04, 120.09, 118.97, 118.02, 116.37, 113.24, 105.61, 84.36. HRMS (ESI) exact mass

calc
m/z 619.1273.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)ethanesulfonamide(4m)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 74% (107.3 mg); white solid; m.p. 142-145 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.31 (s, 1H), 9.48 (s, 1H), 7.92-7.84 (m, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.51-7.43 (m, 1H), 7.43-7.31 (m, 6H), 7.31-7.16 (m, 6H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.06 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.06, 142.62, 137.56, 136.61, 133.11, 128.74, 128.66, 128.12, 123.28, 123.27, 122.59, 121.15, 119.36, 117.94, 117.86, 114.82, 113.22, 105.91, 84.30, 45.26, 8.53. HRMS (ESI) exact mass calcd. for $(C_{29}H_{24}N_2O_3S+Na)^+$ requires m/z 503.1400, found m/z 579.1400.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)propane-1-sulfonamide (4n)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 82% (122.4 mg); white solid; m.p. 152-154 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.32 (s, 1H), 9.47 (s, 1H), 7.94-7.81 (m, 1H), 7.67 (s, 1H), 7.53-7.31 (m, 7H), 7.31-7.14 (m, 6H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 3.03 (t, *J* = 7.2 Hz, 2H), 1.84-1.60 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.06, 142.59, 137.54, 136.62, 133.1, 128.74, 128.66, 128.10, 123.27, 123.24, 122.59, 121.14, 119.33, 117.95, 117.90, 114.84, 113.22, 105.91, 84.29, 52.54, 17.32, 13.08. HRMS (ESI) exact mass calcd. for $(C_{30}H_{26}N_2O_3S+Na)^+$ requires m/z 517.1556, found m/z 517.1555.

N-(6,6-diphenyl-6,7-dihydrochromeno[3,4-b]indol-2-yl)cyclopropanesulfonamide (4o)

Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 2 h; yield: 94% (140.0 mg); white solid; m.p. 150-152 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.31 (s, 1H), 9.40 (s, 1H), 7.93-7.83 (m, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.52-7.43 (m, 1H), 7.43-7.33 (m, 6H), 7.31-7.16 (m, 6H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.3 Hz, 1H), 2.66-2.54 (m, 1H), 0.93-0.88 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.26, 142.57, 137.54, 136.63, 133.00, 128.73, 128.65, 128.25, 128.13, 123.30, 123.14, 122.56, 121.13, 119.35, 118.83, 117.86, 115.68, 113.21, 105.96, 84.29, 29.66, 5.40. HRMS (ESI) exact mass calcd. for $(C_{30}H_{24}N_2O_3S+Na)^+$ requires m/z 515.1400, found m/z 515.1399.

THE ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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[13] CCDC 1983979 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Highlights

A formal [3+3] cyclization reaction of 2-indolylmethanols with quinone imines was realized to afford fused-indole scaffolds in moderate to excellent yields. In this transformation, the reaction was employing C3-position of 2-indolylmethanols as nucleophilic site.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: