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基于原位形成的氮杂邻亚甲基苯醌和卤代萘酚的分子间[4＋1]螺环化/去芳香化反应

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摘要 报道了一种碱促进的卤代萘酚与 *N*-(邻氯甲基)芳基酰胺[4＋1]螺环化/去芳构化策略, 以此来直接有效地合成氮杂螺环化合物. 在温和条件下以中等至优秀的收率、高非对映选择性地合成了一系列氮杂螺环化合物. 该反应可以兼容各种官能团, 如醛基、游离羟基和不同的 N 保护基, 如 Bz 和 Ts 等. 对产物进行了转化, 并提出了可能的反应机理.
关键词 氮杂螺环; [4＋1]环加成反应; 脱芳构化; 螺环化

Dearomatization of Halonaphthols via an Intermolecular [4＋1] Spiroannulation with *in situ* Formed Aza-*ortho*-quinone Methides

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Abstract A base promoted dearomatization strategy for [4＋1] spiroannulation of halonaphthols with *N*-(*o*-chloromethyl) aryl amides is reported, which is used to efficiently synthesize azaspirocycles. A range of azaspirocycles were obtained in satisfactory to excellent yield with high diastereoselectivity under mild conditions. Variety functional groups including aldehyde and free hydroxyl group, and different *N*-protecting groups, such as Bz and Ts are compatibility. The transformation of the product and a possible mechanism were also provided.
Keywords azaspirocyclic compound; [4＋1] cycloaddition reaction; dearomatization; spiroannulation

1 Introduction

Organic nitrogen-containing compounds are widely found in natural products, bioactive molecules, and functional materials.[1] Among these, azaspirocyclic rings are of particular important because of their unique three-dimensional property. This subunit is also broadly existing in many natural products including cephalotaxine,[2a] stemonamide,[2b] serratinine,[2c] and clinical drugs, such as fluspirilene [2d] and enilospirone.[2d] Moreover, many molecules with azaspirocyclic ring could also be used as organo-catalysts[3a-3c] or ligands[3d] in organic synthesis. Therefore, it is of great significance to develop highly efficient and selective methodologies to construct complex nitrogen heterocyclic, especially azaspirocyclic rings under mild conditions, even though still with great challenge (Figure 1).[4]

The dearomatization reaction of aromatic compounds could directly convert simple and abound distributed planar aromatic compounds into a variety of valuable, complex three-dimensional skeletons with multiple functional groups, thereby providing an irreplaceable platform for further functional group modification. The dearomatization C—C bond formation process is well established,[5] which has also been used extensively to construct azaspirocyclic rings through intramolecular dearomatization of 2-substituted pyrroles or indoles as reported by You[6a-6c] and Jia,[6d-6f] however, the similar process involving dearomatization C—N bond formation is much less developed. Nevertheless, many elegant strategies, especially intramo-

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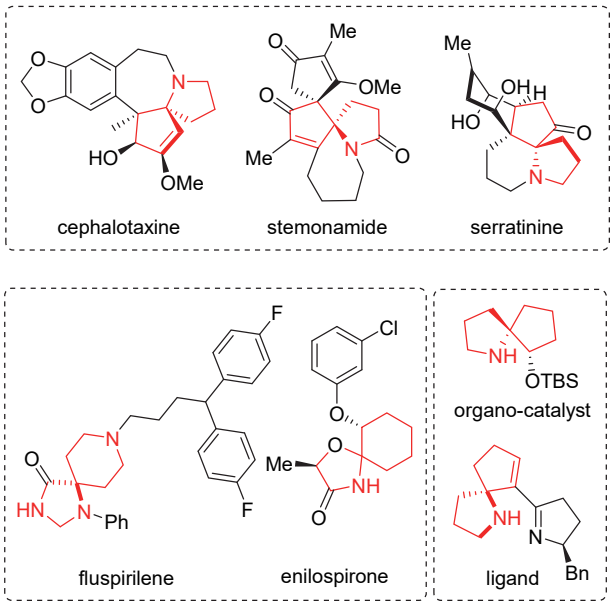


Figure 1 Representative molecules containing azaspirocycles

lecular dearomatization C—N bond formation reaction, were revealed recently. For example, hypervalent iodine compounds mediated dearomatization of phenol derivatives is a reliable strategy to access spiropyrrolidines via nitrenium ions (Figure 2A),[7-8] while other electrophilic nitrogen initialed dearomatizations C—N bond formation reactions were also reported by Narasaka's[9a-9b] and Bower's group (Figure 2B),[9c-9d] respectively. Different from the intramolecular process, the product diversification of which relies heavily on pre-prepared single raw materials, intermolecular reactions can make it much easier to prepare a broad range of structural diversity compounds by altering the substituted groups in the two reaction substrates separately, and ultimately facilitate the drug discovery. However, the development of intermolecular dearomatization C—N bond formation to access a new *N*-heterocyclic ring is challenging, and was only realized by Luan's group[10] very recently via a [4+1] annulation of bromophenols with *α*-ester activated *α*,*β*-unsaturated phenyl ketone imines (Figure 2C). Meanwhile, it has been well established that *ortho*-quinone methides could be used in [4+*n*] annulations to access diversified heterocyclic molecules,[11] we have also shown the possibility of using the *in situ* formed aza-*ortho*-quinone methides (aza-*o*-QMs) to synthesis of indazoles.[11f] Inspired by Luan's works,[10] and due to our continuous interesting in pursuing efficient dearomatization process under mild conditions,[9c-9d,12] we herein developed a base promoted [4+1] azaspiroannulation of halogenoated naphthols with *N*-(*o*-chromomethyl) aryl amides (Figure 2D).[13] The readily access, bench stable and easily diversity of aza-*ortho*-quinone methides precursor plus with the mild reaction conditions made the procedure reported herein an attractive complementarity to current dearomatization C—N bond formation reactions.

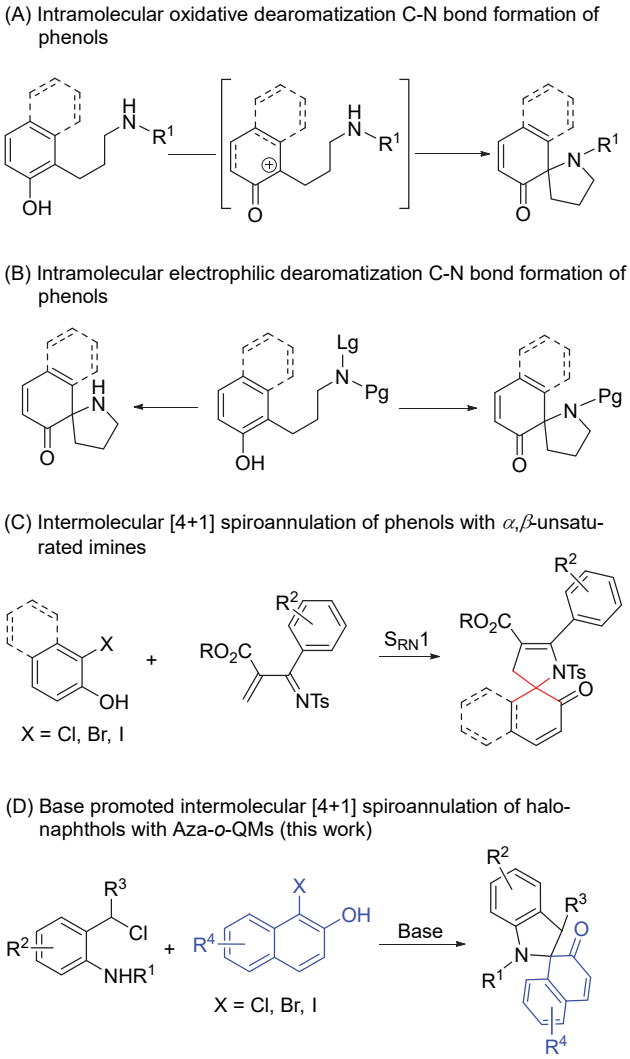
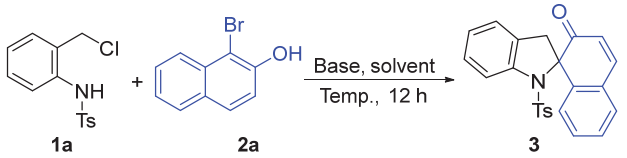


Figure 2 Construction of azaspirocycles by dearomatization

2 Results and discussion

To begin with our study, the reaction between aza-*o*-QMs precursor **1a** and 1-bromo-2-naphthol **2a** was investigated. We were pleased to find that the reaction proceeded smoothly and afforded the corresponding spirocyclic product **3a** in 83% yield using Cs_2CO_3 as a base and 1,2-dichloroethane (DCE) as a solvent (Table 1, Entry 1). Further optimization of bases (Entries 2～5) shown that K_2CO_3 was the most suitable one for this transformation, which offered the product in 92% isolated yield (Entry 3). Different solvents were also examined and it was found that the reaction went smoothly in nonpolar or low polar solvent including dichloromethane (DCM), tetrahydrofuran (THF) and toluene, in which the product was produced in 82%～90% yields. However, higher polar solvent such as DMF only leaded to the decomposition of **1a** (Entries 6～9). Further optimization of the temperature demonstrated that it has negligible influence on the yield of the reaction when the temperature was changed from 10～50 ℃ (Entries 10～12).

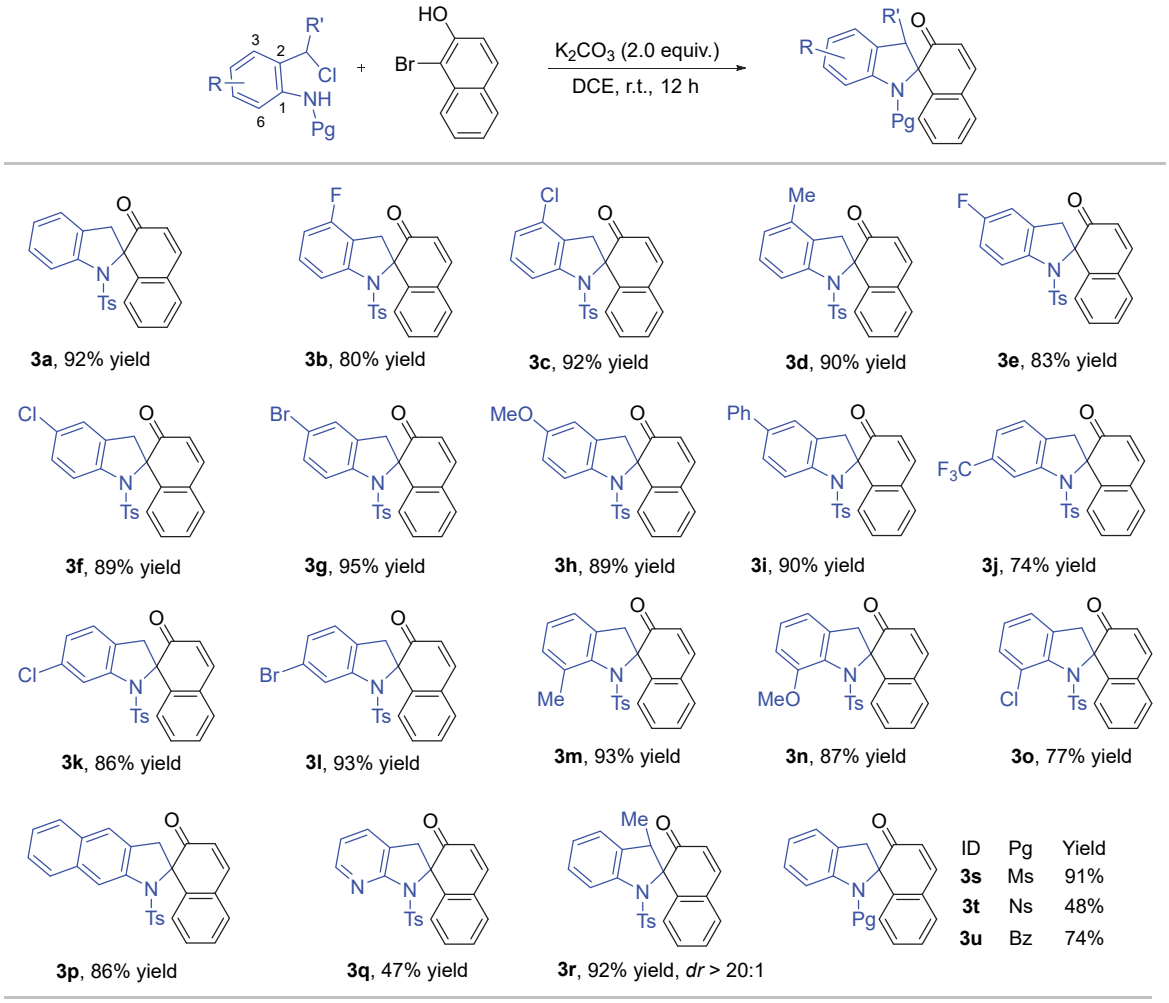
Table 1 Optimization of the reaction conditions[a]



Entry	Base	Solvent	*T*/℃	Yield[b]/%
1	Cs_2CO_3	DCE	25	83
2	MeONa	DCE	25	60
3	**K_2CO_3**	**DCE**	**25**	**93 (92)**
4	DBU	DCE	25	0
5	DIPEA	DCE	25	0
6	K_2CO_3	DCM	25	85
7	K_2CO_3	THF	25	82
8	K_2CO_3	DMF	25	0
9	K_2CO_3	Toluene	25	90
10	K_2CO_3	DCE	40	92
11	K_2CO_3	DCE	50	92
12	K_2CO_3	DCE	10	90

[a] Reaction conditon: 0.1 mmol of **1a**, 0.2 mmol of **2a** and 0.2 mmol of base in solvent (1.0 mL) were stirred at corresponding temperature for 12 h. [b] NMR yield using CH_2Br_2 as standard, isolated yield in parentheses.

With the optimal reaction conditions in hand, the substrate scope of the *o*-chloromethylaniline was then investigated (Scheme 1). It was found that the reaction is not sensitive to the electron property of the substitutes on benzene. For example, when F, Cl or methyl substitute was preinstalled at 3-position of *o*-chloromethylaniline, under the standard reaction conditions, the corresponding product was isolated in 80%～92% yields (**3b**～**3d**). The similar high efficiency was also obtained when an electron withdrawing group including F, Cl, Br or electron donating group such as MeO was substituted at 4-position, all of which delivered the products in higher than 80% yield (**3e**～**3i**). Even though a strong electron withdrawing group such as CF_3 at 5-position gave the product (**3j**) in a slight reduced yield (74%), the corresponding Cl and Br substituted products (**3k**, **3l**) were produced in 86% and 93% yields, respectively. The *o*-chloromethylanilines with a substitute at 6-position were also suitable for this transformation, which gave the products (**3m**～**3o**) in 77%～87% yields. The conversion could proceed successfully when benzene was replaced with naphthalene, which led to the formation of the corresponding product (**3p**) in 86% yield.



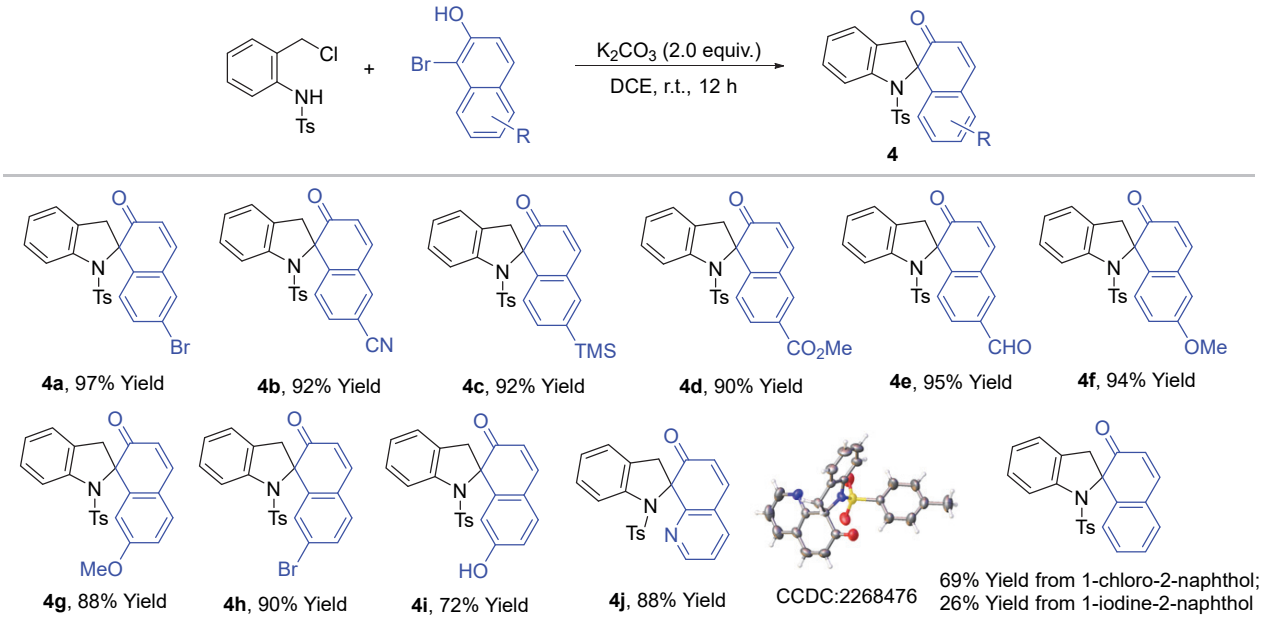
Scheme 1 Scope of *o*-chloromethylanilines

Heterocyclic *o*-chloromethylaniline could also be converted to the product (**3q**), even though with the reduced yield (47%). Notably, the substrate with a methyl at the 2-chloroalkyl group can also use to this dearomatization process, and the substituted azaspirocyclic product (**3r**) was obtained in high yield (82%) and excellent diastereoselectivity (>20∶1), which further highlight the generality of this transformation. Finally, the different protecting groups on the amine were studied. The dearomatization process worked smoothly for the substrate with amine was protected by mesyl (Ms), which gave the product (**3s**) in 91% yield, while Ns protected amine resulted in the decrease of the yield (**3t**) due to the stability of the starting material. The *o*-chloromethylaniline substrate protecting with benzoyl (Bz) also delivered the product (**3u**) in satisfactory yield.

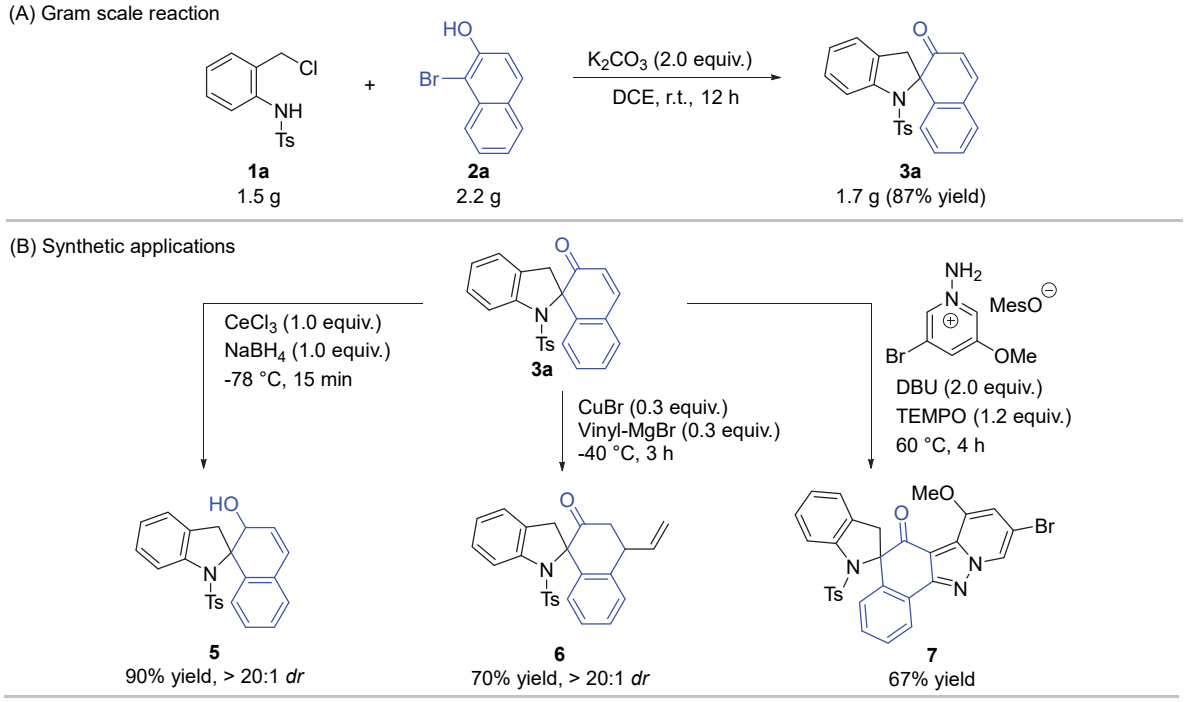
Next, the substrate scopes of the 1-halo-2-naphthols were investigated (Scheme 2). It was found that a series of functional groups, such as halide, CN, trimethylsilyl (TMS), ester, and especially the aldehyde group are well tolerated under the standard conditions, providing the corresponding products (**4a**~**4e**) in 90%~97% yields. The reaction is also insensitive to the position of substitutes on the naphthol as both 6-MeO and 7-MeO substituted naphthols, offering the product (**4f** or **4g**) in around 90% yield. It is worth noting that naphthol with a free hydroxyl group at 7-position was also smoothly converted into the product (**4i**) in 72% yield, which demonstrated the good functional group compatibility of the reaction. To our delight, dearomatization of 8-bromoquinolin-7-ol also underwent smoothly under the standard conditions delivering the product (**4j**) in 88% yield. Furthermore, the reactions of 1-chloro-2-naphthol and 1-iodo-2-naphthol with benzenesulfon amide **1a** were also tested, both of which gave the product in synthetically useful yield.

To further explore the potential application of the reaction, a gram scale reaction was carried out, therefore, starting from 1.5 g of **1a** and 2.2 g of **1b**, 1.7 g (87% yield) of **3a** was isolated under standard reaction conditions (Scheme 3A). In addition, the obtained spirocyclic product could be further transformed to a variety of other synthetically useful intermediates (Scheme 3B). For example, Luche reduction of **3a** proceeded smoothly to provide **4** in 90% yield with excellent diastereoselectivity (>20∶1). 1,4-Michael addition of vinyl-cuprate to **3a** was also produced the corresponding product in good yield with excellent diastereoselectivity (>20∶1). The *α*,*β*-unsaturated ketone sub-unit in the product could also be used to the synthesis of pyrazolo[1,5-*a*]pyridines under our recently disclosed conditions.[12c]

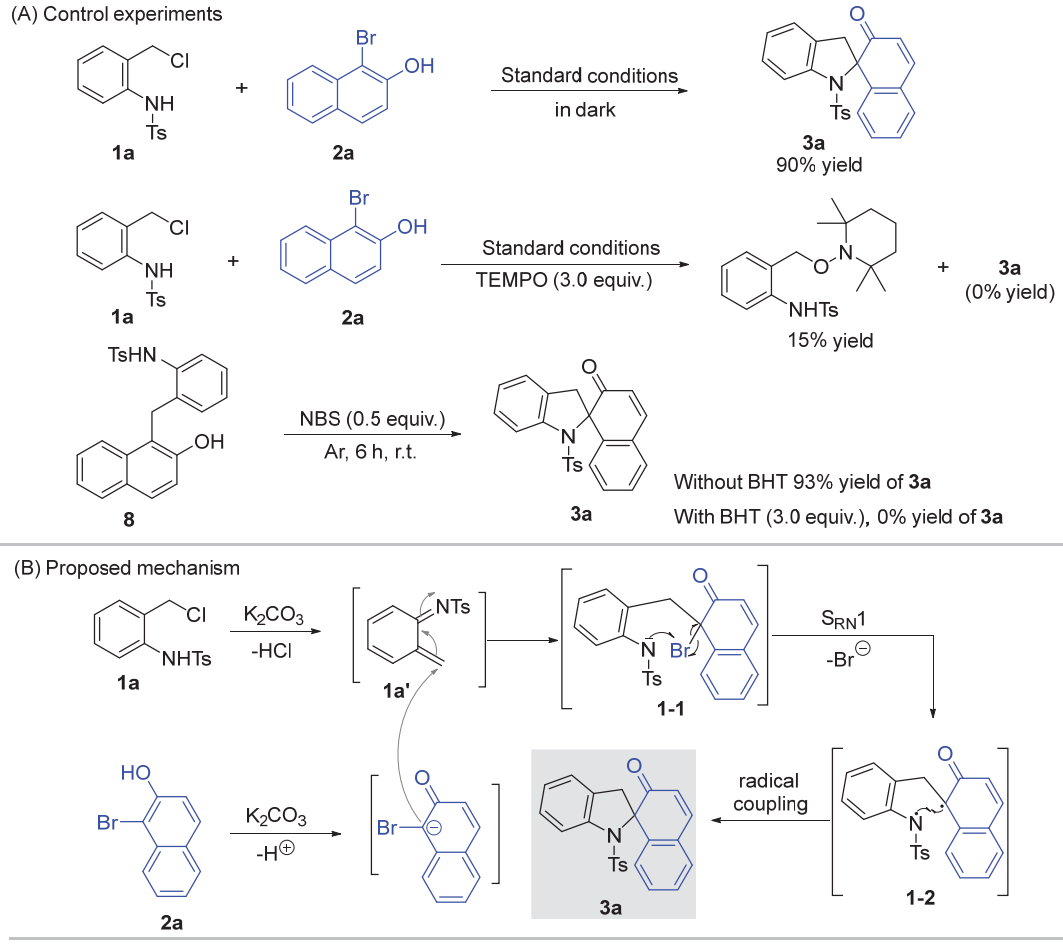
The classical S_N1 and S_N2 reaction mechanism was first ruled out based on the following observations: (i) The reaction generally works well in nonpolar solvents, such as DCM, DCE, toluene (Table 1, Entries 5, 6, 9), and 1-chloro-2-naphthol gives the product in significantly higher yield than that of 1-iodo-2-naphthol. These may exclude the S_N1 process, which always needs a polar solvent and a good leaving group such as iodo-substituted substrate. (ii) S_N2 reaction is highly sensitive to steric hindrance, and needs a strong nucleophile. In our case, the *in situ* formed intermediate **1-1** is a tetra-substituted quaternary carbon center, where the *N*-atom was protected with a strong electron withdraw group such as Ts or Bz. The S_N2 reaction for such a substrate should be highly impossible. A series of control reactions were then carried out to understand the reaction mechanism. It was found that the reaction is not sensitive to light as when the reaction was shielded from ambient lab light, the product was isolated in



Scheme 2 Scope of 1-halo-2-naphthols



Scheme 3 Gram-scale reaction and synthetic applications



Scheme 4 Control experiments and proposed mechanism

a similar yield (90%), while the reaction was inhibited completely by the addition of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (Scheme 4A).[14] Compound **8** according a literature's procedure was then synthesized[15] and

subjected to the reaction. It was found that the reaction underwent smoothly in the presence of 0.5 equiv. of *N*-bromo-succinimide (NBS) providing spirocyclic product **3a** in 93% yield. The process even does not need an extra base. Meanwhile, when BHT (butylated hydroxytoluene, 3.0 equiv.) was added under the same condition, no product was generated. This experiment highly suggested that a free radical process may involve in the spirocyclization. Based on these control experiments and according to the previous literatures,[9] a possible reaction mechanism was proposed for this transformation (Scheme 4B). Elimination of hydrogen chloride from *N*-(2-(chloromethylphenyl)-4-methylbenzennesulfonamide (**1a**) under assistance of base could produce aza-*o*-QMs intermediate **1a'**.[11f] Michael addition of bromo naphthol **2a** to intermediate **1a'**[10,16] would form intermediate **1-1**. Then, the nitrogen anion attacked to the bromine atom by single electron transfer (SET), causing the C—Br bond to homolysis, followed by the departure of bromine anion obtained intermediate **1-2**, in which containing carbon and nitrogen free radicals. Finally, radical-radical coupling of **1-2** could obtain the product **3a**. We speculated that the reaction took place through Michael addition and free radical single molecule nucleophilic substitution ($S_{RN}1$) cascade reaction. The similar $S_{RN}1$ process has also been proposed by Luan and co-workers,[10,16-17] providing further evidence for this transformation.

3 Conclusions

In summary, we have developed an intermolecular [4＋1] annulation strategy to synthesize various azaspiro molecules through the dearomatization of halonaphthols with simple starting materials. The reaction undergoes a cascade process of Michael addition, C—X (X＝Cl, Br, I) bond homolysis and free radical coupling with the assistance of base. The procedure is easily handling, and provides a wide range of azaspirobicyclic compounds with various functional groups in good to excellent yields with high diastereoselective under mild conditions. The transformation of the obtained products highlighting the application of our methodology in the synthesis of high-value compounds. The study of this intermolecular [4＋1] annulation strategy to other dearomatization process is ongoing in our laboratory.

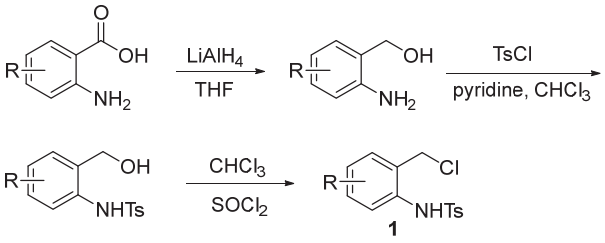
4 Experimental section

4.1 General information

All materials were purchased from commercial sources (Acros, Aldrich, Adamas, Casmart) and used without any further treatment unless otherwise stated. Flash column chromatography was performed using silica gel (Qindao Haiyang, 200～300). Thin layer chromatography (TLC) was performed using aluminium backed $60F_{254}$ silica plates. Visualization was achieved by UV fluorescence or a basic $KMnO_4$ solution and heat. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker Avance 400 MHz and were relative to $CDCl_3$ (δ 7.26). ^{13}C NMR spectra were recorded at 101 MHz and were relative to $CDCl_3$ (δ 77.16). *In situ* yields were determined by integration of the ^1H NMR of the crude material employing dibromomethane as internal standard. High-resolution mass spectra (HRMS) were recorded on a BioTOFQ. Melting point (m.p.) experiments were performed on digital micro-melting point tester (Beijing Fukai Instrument Co., Ltd).

4.2 General procedure for the synthesis of 1

The synthesis of *N*-(2-(chloromethyl)phenyl)-4-methylbenzenesulfonamides with different substituent **1** is shown in Scheme 5.



Scheme 5 Synthesis of compound **1**

Under argon atmosphere, to a solution of corresponding 2-aminobenzoic acid (1.0 equiv., 2.0 mmol) in dry THF (10 mL) was added $LiAlH_4$ (3.0 equiv., 2.5 mL, 2.4 mol/L in *n*-hexane) slowly at 0 ℃ and stirred for 0.5 h at this temperature. Then, the reaction was moved to room temperature and was stirred for another 3.5 h. After the reaction was completed as indicated by TLC analysis, the reaction was quenched by the addition of ice water (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (10 mL×3). The combined organic phase was dried over sodium sulfate and concentrated. The crude material was used directly to the next step without further purification (yield≈100%).[18]

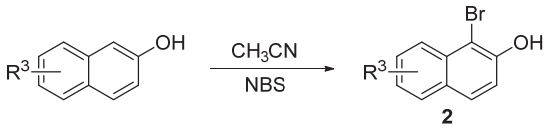
To a solution of substituted 2-aminobenzyl alcohol (1.0 equiv., 2.0 mmol) in $CHCl_3$ (12 mL) was added pyridine (0.4 mL, 0.5 mmol) dropwise over 2 min. The reaction was stirred for 25 min, and a solution of TsCl (418 mg, 1.1 equiv., 2.2 mmol) in $CHCl_3$ (5 mL) was added dropwise over 20 min. The resulted mixture was stirred at same temperature for another 2 h, and the reaction was quenched with saturated aqueous NH_4Cl (10 mL). The layers were separated and the aqueous layer was extracted with $CHCl_3$ (10 mL×3). The combined organic layers were then washed with brine (10 mL), and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded crude N-protected 2-aminobenzyl alcohol, which was used in the subsequent transformation without further purification.[19]

N-Protected 2-aminobenzyl alcohol (1.0 equiv., 2 mmol) in $CHCl_3$ (10 mL) was added to a solution of dichlorosulfoxide (1.2 equiv., 2.4 mmol) in $CHCl_3$ (5 mL) over 1 min. The reaction was heated at 40 ℃ overnight. After the reaction was completed as indicated by TLC analysis, the

reaction was cooled to room temperature, then quenched with ice water (10 mL). The layers were separated and the aqueous layer was extracted with $CHCl_3$ (10 mL×3). The combined organic layers were washed with brine (30 mL), and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded product **1**, which was purified by flash chromatography on silica gel.[20]

4.3 General procedure for the synthesis of 2

The synthesis of 1-bromo-2-naphthols with different substituent **2** is shown in Scheme 6.



Scheme 6 Synthesis of compound **2**

To a solution of corresponding 2-hydroxynaphthalene (1.0 equiv., 3.0 mmol) in CH_3CN (15 mL) was added NBS (1.1 equiv., 3.3 mmol, 0.58 g) at 0 ℃ and the resulted mixture was stirred for 30 min at this temperature. Then, the reaction was move to room temperature and stirred overnight. After the reaction was completed as indicated by TLC analysis, the reaction was quenched by water (10 mL) and extracted with EtOAc (20 mL×3). The combined organic phase was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by flash chromatography on silica gel to provide desired products **2**.[21]

4.4 General procedure for the synthesis of 3 and 4

In an oven dried round-bottom flask, substrate **1** (0.1 mmol, 1.0 equiv.), 1-halo-2-naphthol **2** (0.2 mmol, 2.0 equiv.) and K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.) were dissolved in DCE (1.0 mL) at room temperature. The resulted mixture was stirred at the same temperature for 12 h. The reaction was quenched with water and extracted with DCM (5 mL×3). The combined organic phase was washed with brine (5 mL×2) and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by flash chromatography on silica gel (EtOAc/petroleum ether, *V*∶*V*=1∶10).

1-Tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3a**): 37.3 mg, 93% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 215～216 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.84 (d, *J*=8.1 Hz, 2H), 7.47 (d, *J*=9.9 Hz, 1H), 7.32 (d, *J*=7.5 Hz, 1H), 7.26 (t, *J*=7.3 Hz, 2H), 7.18 (t, *J*=5.8 Hz, 3H), 7.16～7.08 (m, 2H), 6.98 (d, *J*=7.4 Hz, 1H), 6.89 (t, *J*=7.1 Hz, 1H), 6.27 (d, *J*=9.9 Hz, 1H), 3.53 (d, *J*=15.7 Hz, 1H), 3.06 (d, *J*=15.7 Hz, 1H), 2.32 (s,3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 198.1, 145.7, 144.7, 144.1, 142.7, 136.8, 130.7, 129.9, 129.4, 128.4, 128.3, 128.1, 127.8, 126.3, 125.6, 124.3, 122.8, 111.7, 75.1, 46.7, 21.6. HRMS (ESI) calcd for $C_{24}H_{19}NO_3SNa$ $[M+Na]^+$ 424.0983, found 424.0985.

4-Fluoro-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3b**): 33.5 mg, 80% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 66～67 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.87 (d, *J*=8.3 Hz, 2H), 7.55 (d, *J*=9.9 Hz, 1H), 7.40 (d, *J*=7.3 Hz, 1H), 7.37～7.31 (m, 2H), 7.27 (s, 1H), 7.25 (s, 2H), 7.17 (dd, *J*=13.9, 8.2 Hz, 1H), 7.01 (d, *J*=8.1 Hz, 1H), 6.68 (t, *J*=8.4 Hz, 1H), 6.34 (d, *J*=9.9 Hz, 1H), 3.56 (d, *J*=16.1 Hz, 1H), 3.17 (d, *J*=16.1 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.5, 160.5, 158.1, 145.9, 145.1, 145.0, 144.3, 144.2, 136.4, 130.8, 130.2, 130.2, 130.0, 129.5, 128.6, 128.3, 127.8, 125.6, 124.1, 112.8, 112.6, 109.9, 109.7, 107.5, 107.5, 75.5, 42.9, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −117.52. HRMS (ESI) calcd for $C_{24}H_{18}FNO_3SNa$ $[M+Na]^+$ 442.0889, found 442.0890.

4-Chloro-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3c**): 40.0 mg, 92% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 226～227 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.10 (d, *J*=7.8 Hz, 2H), 7.56 (d, *J*=6.0 Hz, 1H), 7.52 (d, *J*=9.9 Hz, 1H), 7.36 (dd, *J*=7.9, 5.0 Hz, 3H), 7.27 (d, *J*=8.0 Hz, 2H), 7.14 (d, *J*=7.7 Hz, 1H), 6.98 (d, *J*=7.0 Hz, 1H), 6.92 (t, *J*=7.6 Hz, 1H), 6.31 (d, *J*=9.9 Hz, 1H), 3.59 (d, *J*=15.7 Hz, 1H), 3.13 (d, *J*=15.7 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 198.2, 145.6, 145.1, 143.4, 140.1, 139.6, 131.5, 130.7, 130.4, 130.2, 129.4, 128.4, 127.5, 127.4, 124.8, 124.3, 124.1, 117.3, 76.3, 45.5, 21.5. HRMS (ESI) calcd for $C_{24}H_{18}ClNO_3SNa$ $[M+Na]^+$ 458.0594, found 458.0593.

4-Methyl-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3d**): 37.4 mg, 90% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 167～168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.90 (d, *J*=8.3 Hz, 2H), 7.55 (d, *J*=9.9 Hz, 1H), 7.41～7.37 (m, 1H), 7.37～7.30 (m, 2H), 7.29～7.27 (m, 1H), 7.25 (t, *J*=3.1 Hz, 2H), 7.10 (t, *J*=7.8 Hz, 1H), 7.04 (d, *J*=7.9 Hz, 1H), 6.78 (d, *J*=7.3 Hz, 1H), 6.34 (d, *J*=9.9 Hz, 1H), 3.49 (d, *J*=15.8 Hz, 1H), 3.05 (d, *J*=15.8 Hz, 1H), 2.38 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 198.2, 145.7, 145.0, 144.0, 142.3, 136.8, 135.2, 130.8, 129.8, 129.4, 128.3, 128.3, 128.3, 127.7, 125.6, 124.8, 124.2, 123.9, 109.1, 74.9, 45.8, 21.5, 18.3. HRMS (ESI) calcd for $C_{25}H_{21}NO_3SNa$ $[M+Na]^+$ 438.1140, found 438.1149.

5-Fluoro-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3e**): 34.8 mg, 83% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 224～225 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.87 (d, *J*=8.2 Hz, 2H), 7.55 (d, *J*=9.9 Hz, 1H), 7.40 (d, *J*=7.3 Hz, 1H), 7.38～7.31 (m, 2H), 7.28 (s, 1H), 7.26 (s, 2H), 7.14 (dd, *J*=8.8, 4.3 Hz, 1H), 6.94～6.84 (m, 1H), 6.79 (d, *J*=7.8 Hz, 1H), 6.35 (d, *J*=9.9 Hz, 1H), 3.58 (d, *J*=16.1 Hz, 1H), 3.11 (d, *J*=16.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.8, 160.3, 145.8, 144.4, 144.2, 138.8, 136.6, 130.8, 130.0, 129.5, 128.5, 128.3, 127.9, 125.6, 124.3, 114.6, 114.4, 113.1, 112.9, 112.1, 112.1, 100.0, 75.4, 46.4, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −121.27. HRMS (ESI) calcd for $C_{24}H_{18}FNO_3SNa$ $[M+Na]^+$ 442.0889, found 442.0891.

5-Chloro-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3f**): 38.7 mg, 89% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 220～221 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.77 (d, *J*=8.3 Hz, 2H), 7.46 (d, *J*=9.9 Hz, 2H), 7.31 (d, *J*=6.8 Hz, 1H), 7.25 (td, *J*=7.3, 1.3 Hz, 1H), 7.23～7.14 (m, 4H), 7.09～7.03 (m, 2H), 6.95 (s, 1H), 6.25 (d, *J*=9.9 Hz, 1H), 3.48 (d, *J*=16.0 Hz, 1H), 3.02 (d, *J*=16.1 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.6, 145.8, 144.3, 144.2, 141.4, 136.4, 130.7, 130.0, 129.5, 128.6, 128.3, 128.2, 128.0, 127.9, 127.9, 125.6, 125.5, 124.2, 112.4, 75.2, 46.3, 21.5. HRMS (ESI) calcd for $C_{24}H_{18}ClNO_3SNa$ $[M+Na]^+$ 458.0594, found 458.0593.

5-Bromo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3g**): 35.5 mg, 95% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 199～200 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.85 (d, *J*=8.2 Hz, 2H), 7.54 (d, *J*=9.9 Hz, 1H), 7.39 (d, *J*=7.2 Hz, 1H), 7.34 (t, *J*=7.3 Hz, 1H), 7.30 (d, *J*=7.4 Hz, 2H), 7.26 (d, *J*=7.2 Hz, 3H), 7.18 (s, 1H), 7.09 (d, *J*=8.6 Hz, 1H), 6.33 (d, *J*=9.9 Hz, 1H), 3.57 (d, *J*=16.0 Hz, 1H), 3.11 (d, *J*=16.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.6, 145.8, 144.4, 144.1, 141.9, 136.4, 130.9, 130.8, 130.0, 129.5, 128.7, 128.6, 128.5, 128.5, 127.8, 125.5, 124.2, 115.2, 112.9, 75.2, 46.2, 21.6. HRMS (ESI) calcd for $C_{24}H_{18}BrNO_3SNa$ $[M+Na]^+$ 502.0088, found 502.0081.

5-Methoxy-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3h**): 38.3 mg, 89% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 165～166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.87 (d, *J*=8.3 Hz, 2H), 7.53 (d, *J*=9.9 Hz, 1H), 7.34 (dt, *J*=21.7, 7.1 Hz, 3H), 7.26～7.18 (m, 3H), 7.12 (d, *J*=8.8 Hz, 1H), 6.72 (dd, *J*=8.8, 2.4 Hz, 1H), 6.64 (s, 1H), 6.32 (d, *J*=9.9 Hz, 1H), 3.71 (s, 3H), 3.57 (d, *J*=15.9 Hz, 1H), 3.08 (d, *J*=15.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 198.0, 155.9, 145.7, 144.6, 143.9, 136.8, 136.3, 130.6, 129.8, 129.4, 128.3, 128.2, 127.8, 127.7, 125.5, 124.2, 112.8, 112.0, 111.9, 75.1, 55.7, 46.7, 21.5. HRMS (ESI) calcd for $C_{25}H_{21}NO_4SNa$ $[M+Na]^+$ 454.1089, found 454.1097.

5-Phenyl-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3i**): 42.9 mg, 90% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 122～123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.91 (d, *J*=8.2 Hz, 2H), 7.53 (d, *J*=10.0 Hz, 1H), 7.47 (d, *J*=7.6 Hz, 2H), 7.43～7.34 (m, 5H), 7.34～7.27 (m, 3H), 7.26～7.19 (m, 4H), 6.34 (d, *J*=9.9 Hz, 1H), 3.64 (d, *J*=15.8 Hz, 1H), 3.16 (d, *J*=15.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.9, 145.8, 144.5, 144.1, 142.0, 140.4, 136.6, 136.2, 130.6, 129.9, 129.4, 128.7, 128.4, 128.2, 127.8, 127.0, 127.0, 126.9, 126.6, 125.6, 124.2, 124.2, 111.7, 75.2, 46.6, 21.5. HRMS (ESI) calcd for $C_{30}H_{23}NO_3SNa$ $[M+Na]^+$ 500.1296, found 500.1299.

1-Tosyl-6-(trifluoromethyl)-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3j**): 34.7 mg, 74% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 152～153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.80 (d, *J*=8.3 Hz, 2H), 7.54 (d, *J*=10.0 Hz, 1H), 7.51 (s, 1H), 7.39 (d, *J*=7.5 Hz, 1H), 7.35～7.29 (m, 1H), 7.27 (s, 1H), 7.25～7.18 (m, 4H), 7.14 (d, *J*=7.8 Hz, 1H), 6.33 (d, *J*=9.9 Hz, 1H), 3.60 (d, *J*=16.4 Hz, 1H), 3.16 (d, *J*=16.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.5, 145.9, 144.6, 143.9, 143.1, 136.0, 130.7, 130.5, 130.0, 129.5, 128.6, 128.2, 127.9, 125.7, 125.6, 124.0, 119.9, 119.8, 108.3, 108.2, 75.1, 46.3, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −62.33. HRMS (ESI) calcd for $C_{25}H_{18}F_3NO_3SNa$ $[M+Na]^+$ 492.0857, found 492.0856.

6-Chloro-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3k**): 37.4 mg, 86% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 164～165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.85 (d, *J*=8.2 Hz, 2H), 7.54 (d, *J*=9.9 Hz, 1H), 7.39 (d, *J*=7.4 Hz, 1H), 7.34 (t, *J*=7.2 Hz, 1H), 7.31～7.26 (m, 3H), 7.24 (t, *J*=4.5 Hz, 2H), 7.01～6.90 (m, 1H), 6.34 (d, *J*=9.9 Hz, 1H), 3.53 (d, *J*=15.9 Hz, 1H), 3.08 (d, *J*=15.9 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.6, 145.8, 144.4, 144.2, 143.8, 136.3, 133.9, 130.7, 130.0, 129.6, 128.5, 128.2, 127.9, 126.2, 125.5, 124.9, 124.2, 122.8, 112.2, 75.7, 46.1, 21.6. HRMS (ESI) calcd for $C_{24}H_{18}ClNO_3SNa$ $[M+Na]^+$ 458.0594, found 458.0595.

6-Bromo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3l**): 44.5 mg, 93% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 232～233 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.85 (d, *J*=8.3 Hz, 2H), 7.55 (d, *J*=9.9 Hz, 1H), 7.39 (d, *J*=6.7 Hz, 1H), 7.34 (td, *J*=7.3, 1.5 Hz, 1H), 7.31～7.25 (m, 5H), 7.18 (s, 1H), 7.09 (d, *J*=8.6 Hz, 1H), 6.34 (d, *J*=9.9 Hz, 1H), 3.57 (d, *J*=16.0 Hz, 1H), 3.11 (d, *J*=16.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 197.6, 145.9, 144.4, 144.2, 141.9, 136.4, 130.9, 130.8, 130.0, 129.5, 128.7, 128.6, 128.5, 128.3, 127.9, 125.5, 124.2, 115.2, 112.9, 75.2, 46.2, 21.6. HRMS (ESI) calcd for $C_{24}H_{18}BrNO_3SNa$ $[M+Na]^+$ 502.0088, found 502.0096.

7-Methyl-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3m**): 38.6 mg, 93% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 147～148 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.21 (d, *J*=8.2 Hz, 2H), 7.61～7.55 (m, 1H), 7.52 (d, *J*=9.9 Hz, 1H), 7.40～7.36 (m, 1H), 7.34 (dd, *J*=9.3, 5.8 Hz, 3H), 7.30 (s, 1H), 7.00～6.89 (m, 3H), 6.31 (d, *J*=9.9 Hz, 1H), 3.62 (d, *J*=15.5 Hz, 1H), 3.12 (d, *J*=15.5 Hz, 1H), 2.41 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 198.7, 145.7, 145.4, 143.5, 141.7, 139.4, 132.7, 130.4, 129.9, 129.4, 128.1, 127.8, 127.3, 127.2, 124.5, 124.2, 123.4, 123.4, 122.2, 75.9, 45.5, 21.4, 21.3. HRMS (ESI) calcd for $C_{25}H_{22}NO_3S$ $[M+H]^+$ 416.1320, found 416.1318.

7-Methoxy-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3n**): 37.5 mg, 87% yield, ethyl acetate/petroleum ether (*V*∶*V*=1∶10), yellow solid. m.p. 206～207 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.04 (s, 2H), 7.61 (dd, *J*=5.9, 2.8 Hz, 1H), 7.52 (d, *J*=9.9 Hz, 1H), 7.42～7.29 (m, 3H), 7.27 (d, *J*=8.3 Hz, 2H), 6.94 (t, *J*=7.8 Hz, 1H), 6.75 (d, *J*=8.2 Hz, 1H), 6.69 (d, *J*=7.4 Hz, 1H), 6.33 (d, *J*=9.9 Hz, 1H), 3.58 (d, *J*=15.6 Hz, 1H), 3.41 (s, 3H), 3.12 (d, *J*=15.6 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ: 198.7, 145.8, 145.5, 142.6, 139.8, 132.1, 130.5, 129.9, 129.0, 128.5, 128.2, 127.6, 127.3, 125.1, 124.3, 124.3, 118.2, 113.0, 75.7, 55.3, 46.2, 21.5. HRMS (ESI) calcd for $C_{25}H_{21}NO_4SNa$ $[M+Na]^+$ 454.1089, found 454.1088.

7-Chloro-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3o**): 33.5 mg, 77% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 206～207 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J=8.2 Hz, 2H), 7.57 (d, J=10.0 Hz, 1H), 7.41 (d, J=7.4 Hz, 1H), 7.37 (d, J=6.9 Hz, 1H), 7.35～7.29 (m, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 7.18～7.07 (m, 2H), 6.95 (d, J=7.4 Hz, 1H), 6.35 (d, J=9.9 Hz, 1H), 3.57 (d, J=16.5 Hz, 1H), 3.17 (d, J=16.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.6, 146.0, 144.4, 143.8, 136.4, 131.3, 130.9, 130.0, 129.7, 129.5, 128.6, 128.3, 127.9, 125.6, 124.8, 124.1, 122.8, 109.8, 74.7, 45.9, 21.6. HRMS (ESI) calcd for $C_{24}H_{18}ClNO_3SNa$ $[M+Na]^+$ 458.0594, found 458.0602.

1-Tosyl-1,3-dihydro-2'*H*-spiro[benzo[*f*]indole-2,1'-naphthalen]-2'-one (**3p**): 38.8 mg, 86% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 194～195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=8.4 Hz, 2H), 7.73 (d, J=8.1 Hz, 1H), 7.65 (d, J=8.0 Hz, 1H), 7.55 (d, J=10.0 Hz, 1H), 7.52 (s, 1H), 7.49 (s, 1H), 7.44～7.36 (m, 2H), 7.34～7.25 (m, 5H), 7.21～7.14 (m, 1H), 6.37 (d, J=9.9 Hz, 1H), 3.71 (dd, J=16.0, 1.2 Hz, 1H), 3.25 (d, J=16.1 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.0, 145.78, 144.4, 144.3, 140.9, 136.4, 133.6, 130.7, 130.2, 129.9, 129.5, 128.4, 127.9, 127.4, 127.3, 126.2, 125.5, 124.5, 124.4, 124.4, 107.5, 75.3, 46.3, 21.5. HRMS (ESI) calcd for $C_{28}H_{21}NO_3SNa$ $[M+Na]^+$ 474.1140, found 474.1139.

1'-Tosyl-1',3'-dihydro-2*H*-spiro[naphthalene-1,2'-pyrrolo[2,3-*b*]pyridin]-2-one (**3q**): 18.9 mg, 47% yield, ethyl acetate/petroleum ether (V∶V=1∶1), yellow solid. m.p. 112～113 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J=5.0 Hz, 1H), 8.01 (d, J=8.1 Hz, 2H), 7.56 (d, J=9.9 Hz, 1H), 7.40 (t, J=9.3 Hz, 2H), 7.35 (d, J=7.5 Hz, 2H), 7.32～7.28 (m, 2H), 7.24 (s, 1H), 6.89～6.81 (m, 1H), 6.34 (d, J=9.9 Hz, 1H), 3.49 (d, J=16.3 Hz, 1H), 3.05 (d, J=16.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.4, 156.3, 147.2, 145.9, 144.6, 144.0, 136.6, 133.3, 130.9, 130.0, 129.4, 128.7, 128.4, 127.9, 125.5, 123.7, 119.1, 117.6, 72.9, 43.5, 21.6. HRMS (ESI) calcd for $C_{23}H_{19}N_2O_3S$ $[M+H]^+$ 403.1116, found 403.1124.

3-Methyl-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3r**): 34.0 mg, 82% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 182～183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, J=8.3 Hz, 2H), 7.54 (d, J=9.9 Hz, 1H), 7.38 (d, J=7.5 Hz, 1H), 7.35～7.27 (m, 3H), 7.27～7.20 (m, 2H), 7.16 (ddd, J=17.1, 8.9, 4.7 Hz, 2H), 7.02～6.92 (m, 2H), 6.37 (d, J=9.9 Hz, 1H), 3.80 (q, J=7.0 Hz, 1H), 2.39 (s, 3H), 0.82 (d, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 199.4, 146.0, 144.1, 142.2, 140.3, 136.7, 131.9, 130.1, 129.9, 129.5, 129.4, 128.6, 128.2, 126.8, 124.9, 123.9, 122.7, 111.2, 80.9, 51.0, 21.6, 12.6. HRMS (ESI) calcd for $C_{25}H_{21}NO_3SNa$ $[M+Na]^+$ 438.1140, found 438.1144.

1-(Methylsulfonyl)-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3s**): 30.0 mg, 91% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 151～152 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53～7.45 (m, 2H), 7.40 (d, J=8.1 Hz, 1H), 7.37～7.26 (m, 4H), 7.10 (d, J=7.3 Hz, 1H), 7.03 (t, J=7.4 Hz, 1H), 6.22 (d, J=9.9 Hz, 1H), 3.65 (d, J=16.1 Hz, 1H), 3.25 (s, 3H), 3.11 (d, J=16.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.8, 146.4, 145.9, 142.5, 131.2, 129.9, 128.4, 128.1, 127.3, 125.9, 125.7, 125.0, 123.3, 123.0, 111.2, 75.9, 45.8, 40.5. HRMS (ESI) calcd for $C_{18}H_{15}NO_3SNa$ $[M+Na]^+$ 348.0670, found 348.0679.

1-((4-Nitrophenyl)sulfonyl)-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3t**): 20.7 mg, 48% yield, ethyl acetate/petroleum ether (V∶V=1∶4), yellow solid. m.p. 108～109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, J=8.9 Hz, 2H), 8.21 (d, J=8.9 Hz, 2H), 7.58 (d, J=9.9 Hz, 1H), 7.42 (d, J=6.9 Hz, 1H), 7.35 (td, J=7.4, 1.2 Hz, 1H), 7.31 (dd, J=7.4, 2.6 Hz, 2H), 7.27 (d, J=1.3 Hz, 1H), 7.25～7.21 (m, 1H), 7.11 (d, J=7.3 Hz, 1H), 7.04 (t, J=7.3 Hz, 1H), 6.33 (d, J=9.9 Hz, 1H), 3.63 (d, J=15.8 Hz, 1H), 3.17 (d, J=15.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.7, 150.2, 146.2, 145.4, 144.3, 141.9, 130.9, 130.1, 129.4, 128.7, 128.4, 127.7, 126.4, 126.0, 125.2, 124.1, 123.9, 123.7, 111.7, 75.6, 46.6. HRMS (ESI) calcd for $C_{23}H_{16}N_2O_5SNa$ $[M+Na]^+$ 455.0678, found 455.0680.

1-Benzoyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**3u**): 26.0 mg, 74% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 145～146 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 2H), 7.51 (dd, J=14.0, 8.3 Hz, 2H), 7.43 (d, J=6.4 Hz, 2H), 7.39～7.33 (m, 2H), 7.33～7.25 (m, 2H), 7.09 (d, J=7.4 Hz, 1H), 6.99～6.85 (m, 2H), 6.33 (d, J=9.5 Hz, 1H), 6.09 (d, J=6.2 Hz, 1H), 3.57 (d, J=16.2 Hz, 1H), 3.11 (d, J=16.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.9, 167.5, 145.1, 144.7, 143.2, 135.5, 131.0, 130.6, 129.6, 128.7, 127.8, 127.6, 127.3, 125.8, 124.3, 123.5, 123.4, 113.6, 72.7, 43.0, 29.6. HRMS (ESI) calcd for $C_{24}H_{17}NO_2Na$ $[M+Na]^+$ 374.1157, found 374.1162.

6'-Bromo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**4a**): 46.5 mg, 97% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 192～193 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J=8.1 Hz, 2H), 7.53 (s, 1H), 7.46 (d, J=10.0 Hz, 1H), 7.33 (d, J=8.4 Hz, 1H), 7.27 (t, J=6.7 Hz, 2H), 7.19 (t, J=9.9 Hz, 3H), 7.06 (d, J=7.3 Hz, 1H), 7.01～6.92 (m, 1H), 6.37 (d, J=10.0 Hz, 1H), 3.58 (d, J=15.8 Hz, 1H), 3.10 (d, J=15.8 Hz, 1H), 2.40 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.4, 144.3, 144.0, 143.3, 142.4, 136.5, 133.3, 132.3, 129.7, 129.5, 128.2, 127.2, 125.9, 125.6, 125.5, 122.9, 122.1, 111.7, 74.6, 46.5, 21.5. HRMS (ESI) calcd for $C_{24}H_{18}BrNO_3SNa$ $[M+Na]^+$ 502.0088, found 502.0089.

2'-Oxo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalene]-6'-carbonitrile (**4b**): 39.2 mg, 92% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 212～

213 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=8.1 Hz, 2H), 7.70 (s, 1H), 7.53 (dd, J=12.5, 7.0 Hz, 3H), 7.31 (d, J=8.0 Hz, 2H), 7.20 (q, J=8.2 Hz, 2H), 7.07 (d, J=7.3 Hz, 1H), 6.99 (t, J=7.0 Hz, 1H), 6.46 (d, J=10.0 Hz, 1H), 3.61 (d, J=15.8 Hz, 1H), 3.11 (d, J=15.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.5, 149.1, 144.6, 143.2, 142.3, 136.3, 133.7, 132.9, 129.6, 128.9, 128.5, 128.3, 126.4, 126.3, 125.7, 125.5, 123.2, 117.7, 112.6, 111.8, 74.9, 46.3, 21.6. HRMS (ESI) calcd for $C_{25}H_{18}N_2O_3SNa$ $[M+Na]^+$ 449.0936, found 449.0941.

1-Tosyl-6'-(trimethylsilyl)-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**4c**): 43.5 mg, 93% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 144～145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J=8.0 Hz, 2H), 7.57 (d, J=9.9 Hz, 1H), 7.50 (s, 1H), 7.36 (d, J=7.6 Hz, 1H), 7.29 (d, J=7.7 Hz, 1H), 7.24 (d, J=4.8 Hz, 2H), 7.21 (s, 1H), 7.20～7.15 (m, 1H), 7.04 (d, J=7.2 Hz, 1H), 6.95 (t, J=7.1 Hz, 1H), 6.34 (d, J=9.9 Hz, 1H), 3.59 (d, J=15.7 Hz, 1H), 3.12 (d, J=15.7 Hz, 1H), 2.38 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.2, 146.1, 144.9, 144.0, 142.6, 141.0, 136.7, 135.7, 134.9, 129.4, 128.3, 128.0, 127.0, 126.3, 125.5, 124.6, 124.2, 122.7, 111.6, 75.1, 46.7, 21.5, −1.3. HRMS (ESI) calcd for $C_{27}H_{27}NO_3SSiNa$ $[M+Na]^+$ 496.1379, found 496.1388.

Methyl 2'-oxo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalene]-6'-carboxylate (**4d**): 41.3 mg, 90% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 176～177 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (s, 1H), 7.92 (d, J=8.1 Hz, 3H), 7.61 (d, J=10.0 Hz, 1H), 7.45 (d, J=8.2 Hz, 1H), 7.28 (d, J=8.1 Hz, 2H), 7.21 (d, J=3.8 Hz, 2H), 7.06 (d, J=7.4 Hz, 1H), 7.02～6.95 (m, 1H), 6.41 (d, J=10.0 Hz, 1H), 3.93 (s, 3H), 3.61 (d, J=15.8 Hz, 1H), 3.12 (d, J=15.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.3, 165.9, 149.1, 144.8, 144.3, 142.5, 136.5, 131.5, 130.9, 130.3, 129.5, 128.3, 128.3, 128.0, 125.8, 125.7, 125.6, 125.1, 123.0, 111.7, 75.1, 52.4, 46.4, 21.6. HRMS (ESI) calcd for $C_{26}H_{21}NO_5SNa$ $[M+Na]^+$ 482.1038, found 482.1047.

2'-Oxo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalene]-6'-carbaldehyde (**4e**): 40.8 mg, 95% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 150～151 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.00 (s, 1H), 7.95 (d, J=8.3 Hz, 2H), 7.91 (d, J=0.8 Hz, 1H), 7.77 (dd, J=8.0, 1.3 Hz, 1H), 7.63 (d, J=10.0 Hz, 1H), 7.58 (d, J=8.0 Hz, 1H), 7.30 (d, J=8.2 Hz, 2H), 7.24～7.17 (m, 2H), 7.07 (d, J=7.4 Hz, 1H), 7.03～6.95 (m, 1H), 6.44 (d, J=10.0 Hz, 1H), 3.62 (d, J=15.8 Hz, 1H), 3.13 (d, J=15.9 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.0, 190.9, 150.5, 144.4, 144.4, 142.4, 136.4, 136.3, 131.8, 130.4, 129.6, 128.6, 128.4, 128.3, 126.3, 125.7, 125.5, 123.1, 111.7, 75.2, 46.3, 21.6. HRMS (ESI) calcd for $C_{25}H_{19}NO_4SNa$ $[M+Na]^+$ 452.0932, found 452.0932.

6'-Methoxy-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**4f**): 40.5 mg, 94% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 89～90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J=8.3 Hz, 2H), 7.48 (d, J=9.9 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.22 (d, J=8.6 Hz, 1H), 7.20～7.14 (m, 2H), 7.06 (d, J=7.4 Hz, 1H), 6.99～6.92 (m, 1H), 6.89 (d, J=2.6 Hz, 1H), 6.75 (dd, J=8.7, 2.7 Hz, 1H), 6.35 (d, J=9.9 Hz, 1H), 3.80 (s, 3H), 3.58 (d, J=15.7 Hz, 1H), 3.11 (d, J=15.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.5, 159.4, 145.5, 144.0, 142.6, 136.8, 136.7, 129.4, 129.0, 128.3, 128.0, 126.8, 126.4, 125.5, 124.9, 122.7, 116.0, 114.7, 111.6, 74.6, 55.4, 46.9, 21.5. HRMS (ESI) calcd for $C_{25}H_{19}NO_4SNa$ $[M+Na]^+$ 454.1089, found 454.1095.

7'-Methoxy-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**4g**): 37.9 mg, 88% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 194～195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=8.1 Hz, 2H), 7.41 (d, J=9.9 Hz, 1H), 7.24 (d, J=8.2 Hz, 1H), 7.20 (s, 1H), 7.18 (s, 1H), 7.16 (d, J=8.6 Hz, 1H), 7.10 (t, J=7.7 Hz, 1H), 6.97 (d, J=7.4 Hz, 1H), 6.88 (t, J=7.3 Hz, 1H), 6.75 (m, J=11.0, 2.6 Hz, 2H), 6.13 (d, J=9.9 Hz, 1H), 3.56～3.47 (m, 4H), 3.05 (d, J=15.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.0, 161.7, 146.8, 145.7, 144.0, 142.7, 137.0, 131.5, 129.4, 128.3, 128.1, 126.1, 125.6, 122.8, 121.6, 121.1, 113.7, 111.7, 75.4, 55.2, 46.7, 21.5. HRMS (ESI) calcd for $C_{25}H_{19}NO_4SNa$ $[M+Na]^+$ 454.1089, found 454.1090.

7'-Bromo-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**4h**): 43.1 mg, 90% yield, ethyl acetate/petroleum ether (V∶V=1∶10), yellow solid. m.p. 189～190 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J=8.3 Hz, 2H), 7.51～7.42 (m, 2H), 7.35 (d, J=8.1 Hz, 1H), 7.28～7.25 (m, 3H), 7.24～7.20 (m, 2H), 7.07 (d, J=7.3 Hz, 1H), 6.99 (t, J=7.4 Hz, 1H), 6.35 (d, J=9.9 Hz, 1H), 3.59 (d, J=16.0 Hz, 1H), 3.13 (d, J=16.0 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.9, 145.8, 144.3, 144.3, 142.5, 136.7, 131.6, 131.0, 129.6, 129.2, 128.3, 127.7, 127.2, 125.7, 125.6, 125.2, 124.5, 123.0, 111.9, 74.0, 46.3, 21.6. HRMS (ESI) calcd for $C_{24}H_{18}BrNO_3SNa$ $[M+Na]^+$ 502.0088, found 502.0092.

7'-Hydroxy-1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**4i**): 30.0 mg, 72% yield, ethyl acetate/petroleum ether (V∶V=1∶1), yellow solid. m.p. 201～202 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, J=8.2 Hz, 1H), 7.45 (d, J=9.9 Hz, 1H), 7.37 (d, J=8.3 Hz, 2H), 7.34 (d, J=8.4 Hz, 1H), 7.28 (d, J=7.6 Hz, 1H), 7.14 (d, J=8.2 Hz, 2H), 7.09 (d, J=8.4 Hz, 2H), 7.00 (t, J=7.4 Hz, 1H), 6.24 (d, J=9.9 Hz, 1H), 5.95 (s, 1H), 3.44 (d, J=16.4 Hz, 1H), 3.33 (d, J=16.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.2, 154.5, 145.4, 144.0, 141.2, 136.5, 131.4, 129.1, 128.0, 127.5, 127.4, 125.3, 124.7, 122.7, 121.3, 115.2, 114.0, 112.1, 72.3, 42.4, 21.5. HRMS (ESI) calcd for $C_{24}H_{20}NO_4S$ $[M+H]^+$ 418.1113, found 418.1074.

1-Tosyl-7'*H*-spiro[indoline-2,8'-quinolin]-7'-one (**4j**): 35.3 mg, 88% yield, ethyl acetate/petroleum ether (V∶V=1∶1), yellow solid. m.p. 196～197 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, J=4.8 Hz, 1H), 7.78 (d, J=8.2 Hz, 2H), 7.69 (d, J=7.7 Hz, 1H), 7.52 (d, J=10.0 Hz, 1H), 7.29～7.25 (m, 1H), 7.24～7.19 (m, 3H), 7.16 (t, J=

7.6 Hz, 1H), 7.05 (d, J=7.4 Hz, 1H), 6.95 (t, J=7.3 Hz, 1H), 6.43 (d, J=10.0 Hz, 1H), 3.53 (d, J=15.7 Hz, 1H), 3.30 (d, J=15.7 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.5, 161.4, 150.2, 143.8, 143.0, 142.9, 137.0, 136.3, 129.4, 127.9, 127.9, 126.5, 125.6, 125.0, 124.3, 123.3, 122.6, 111.6, 75.8, 44.1, 21.5. HRMS (ESI) calcd for $C_{23}H_{19}N_2O_3S$ $[M+H]^+$ 403.1116, found 403.1125.

4.5 Procedure for the synthesis of **5**

To a solution of **3a** (21.3 mg, 0.1 mmol, 1.0 equiv.) and $CeCl_3$•$7H_2O$ (37.3 mg, 0.1 mmol, 1.0 equiv.) in MeOH (2.5 mL) and THF (2.5 mL) was added $NaBH_4$ (3.8 mg, 0.1 mmol, 1.0 equiv.) at −78 ℃. After stirring for 15 min, the reaction mixture was diluted with EtOAc and washed with 1 mol/L HCl (1 mL) and brine (2 mL), respectively. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography chromatography (EtOAc/petroleum ether, V∶V=1∶1) to give 1-tosyl-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-ol (**5**):[22] 38.7 mg, 90% yield, *dr*>20∶1, yellow solid. m.p. 166～167 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (t, J=8.0 Hz, 3H), 7.23 (d, 1H), 7.19 (t, J=7.9 Hz, 1H), 7.12 (dd, J=15.6, 7.5 Hz, 2H), 7.02 (dd, J=14.6, 7.6 Hz, 3H), 6.94 (dd, J=15.1, 7.6 Hz, 2H), 6.37 (d, J=9.8 Hz, 1H), 6.19 (dd, J=9.8, 3.7 Hz, 1H), 4.49 (d, J=6.6 Hz, 1H), 3.74 (d, J=16.2 Hz, 1H), 3.48 (d, J=10.6 Hz, 1H), 3.32 (d, J=16.2 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.3, 143.1, 137.6, 136.5, 131.3, 130.6, 129.1, 128.2, 128.1, 127.9, 127.2, 126.8, 126.6, 126.0, 124.5, 123.1, 114.3, 75.8, 71.8, 46.4, 21.4. HRMS (ESI) calcd for $C_{24}H_{21}NO_3SNa$ $[M+Na]^+$ 426.1140, found 426.1141.

4.6 Procedure for the synthesis of **6**

A solution of **3a** (40 mg, 0.1 mmol) in dry THF (0.3 mL) was added through a syringe to a solution of CuBr•Me_2S (6.2 mg, 0.03 mmol) and Me_2S (0.05 mL) in the same solvent (0.2 mL) and cooled to −40 ℃. Then vinylmagnesium bromide (0.3 mL, 0.3 mmol, 1 mol/L in THF) was added dropwise with stirring whilst keeping the reaction temperature below −40 ℃. The reaction mixture was stirred at −40 ℃ for 3 h, poured into ice and aqueous hydrochloride (*ca*. 1 mol/L, 2.0 mL), and then extracted with diethyl ether (10 mL×3). The crude product was left to evaporation to dryness under reduced pressure and the residue was subjected to flash column chromatography (EtOAc/petroleum ether, V∶V=1∶1) to afford 1-tosyl-4'-vinyl-3',4'-dihydro-2'*H*-spiro[indoline-2,1'-naphthalen]-2'-one (**6**):[9c] 30.0 mg, 70% yield, *dr*>20∶1, yellow solid. m.p. 124～125 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J=8.0 Hz, 2H), 7.30 (q, J=7.9 Hz, 2H), 7.20 (dt, J=12.7, 8.2 Hz, 5H), 7.12 (dd, J=13.4, 5.7 Hz, 1H), 7.02 (d, J=7.3 Hz, 1H), 6.94 (t, J=7.2 Hz, 1H), 5.95 (ddd, J=16.9, 10.2, 6.5 Hz, 1H), 5.23 (d, J=10.2 Hz, 1H), 5.13 (d, J=17.2 Hz, 1H), 4.06 (dd, J=11.8, 5.9 Hz, 1H), 3.57 (d, J=16.1 Hz, 1H), 3.25～3.13 (m, 2H), 2.98 (dd, J=15.1, 6.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 208.2, 143.9, 142.2, 140.0, 139.9, 136.7, 136.2, 129.3, 128.1, 128.1, 128.0, 127.9, 127.8, 126.4, 126.2, 125.1, 122.8, 116.7, 111.5, 74.9, 47.7, 43.4, 42.7, 21.5. HRMS (ESI) calcd for $C_{26}H_{23}NO_3SNa$ $[M+Na]^+$ 452.1296, found 452.1294.

4.7 Procedure for the synthesis of **7**

To a stirring suspension of *N*-aminopyridines (32.3 mg, 0.1 mmol, 1.0 equiv.) and **3a** (80.2 mg, 0.2 mmol, 2.0 equiv.) in toluene (1 mL, 0.1 mol/L) was added TEMPO (19.0 mg, 0.12 mmol, 1.2 equiv.). After being cooled down to 0 ℃, 1,5-dizzabicyclo[5.4.0]undecen-5-ene (DBU) (29.8 μL, 0.2 mmol, 2.0 equiv.) was added dropwise. Then the resulting mixture was allowed to stir at 60 ℃ (oil bath) for 4 h. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was subjected to flash column chromatography (EtOAc/petroleum ether, V∶V=1∶3) to afford 9-bromo-7-methoxy-1'-tosyl-6*H*-spiro[benzo[*g*]pyrido[1,2-*b*]indazole-5,2'-indolin]-6-one (**7**):[13] 40.0 mg, 67% yield, brown solid. m.p. 144～145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.40 (s, 1H), 8.23 (d, J=7.7 Hz, 1H), 7.80 (d, J=7.9 Hz, 2H), 7.40 (t, J=7.5 Hz, 1H), 7.31 (d, J=8.2 Hz, 1H), 7.24 (s, 1H), 7.20 (d, J=7.7 Hz, 4H), 7.05 (d, J=7.4 Hz, 1H), 6.95 (t, J=7.4 Hz, 1H), 6.86 (s, 1H), 4.03 (s, 3H), 3.81 (d, J=16.1 Hz, 1H), 3.22 (d, J=16.1 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 187.9, 154.6, 152.3, 143.7, 143.7, 143.0, 137.2, 133.6, 130.5, 129.3, 128.3, 128.2, 128.0, 127.0, 126.4, 125.4, 124.1, 123.9, 122.9, 122.6, 111.9, 110.3, 109.9, 107.0, 56.8, 47.0, 21.6. HRMS (ESI) calcd for $C_{30}H_{23}BrN_3O_4S$ $[M+H]^+$ 600.0593, found 600.0584.

4.8 Procedure for the synthesis of **8**

In an oven dried round-bottom flask, finely grounded 2-naphthol (144.0 mg, 1.0 mmol, 1.0 equiv.) and LiOH (48.0 mg, 2.0 mmol, 2.0 equiv.) were mixed and stirred for 15 min. Substrate **1a** (590.0 mg, 2.0 mmol, 2.0 equiv.) in DCE (10.0 mL) was added to the above mixture. The resulted mixture was stirred at 85 ℃ for 2 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite®, washed with ethyl ether and evaporated the solvent under reduced pressure to afford the crude product **8**, which was purified by flash chromatography on silica gel (EtOAc/petroleum ether, V∶V=1∶3).[15] *N*-(2-((2-Hydroxynaphthalen-1-yl)methyl)phenyl)-4-methylbenzenesulfonamide (**8**): 88.7 mg, 22% yield, white solid. m.p. 195～196 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 1H), 7.85 (d, J=8.6 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.68 (d, J=8.8 Hz, 1H), 7.37 (t, J=7.9 Hz, 4H), 7.33～7.27 (m, 2H), 7.19 (d, J=8.8 Hz, 1H), 7.16 (s, 1H), 7.09 (t, J=7.7 Hz, 1H), 7.03 (d, J=7.5 Hz, 1H), 6.98 (d, J=8.2 Hz, 2H), 4.19 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 153.41, 143.62, 138.38, 137.23, 135.09, 133.80, 130.21, 128.73, 128.63, 128.51, 127.26, 126.68, 126.53, 126.41, 123.24, 122.75, 118.44, 116.61, 26.27, 21.54. HRMS (ESI) calcd for $C_{24}H_{21}NO_3SNa$ $[M+Na]^+$ 426.1140, found 426.1135.

Supporting Information ^{1}H NMR, ^{13}C NMR and HRMS spectra of **1i**, **1p**, **3a**～**3u**, **4a**～**4j**, **5**, **6**, **7** and **8**. The Supporting Information is available free of charge via the internet at http://sioc-journal.cn/.

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[13] During our preparation of this manuscript, a similar process was disclosed in a patent, in which 2.5 equiv. of **1** and 4.0 equiv. of Na_2CO_3 were employed in toxic CH_3NO_2 to maintain high yield with limited functional group tolerance, see: Zhang, J; He, Z; Cheng, X. *CN 114835630*, **2022**.

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