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过硫酸钾促进 2-炔芳基腈与亚磺酸钠的自由基串联环化: 构筑稠环环戊烯并[gh]菲啶

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摘要 报道了一种以 2-炔芳基腈和亚磺酸钠为原料, 过硫酸钾为氧化剂, 通过自由基串联环化反应一步构筑环戊烯并[gh]菲啶的新方法. 该反应具有反应条件温和、原子经济性高、底物适应性较强等优势. 利用此方法简便地合成了多种潜在的具有生物活性的 4-磺化环戊烯并菲啶.

关键词 2-炔芳基腈; 亚磺酸钠; 4-磺化环戊[gh]菲啶; 自由基串联环化反应

$K_2S_2O_8$-Initiated Cascade Cyclization of 2-Alkynylnitriles with Sodium Sulfinates: Access to Fused Cyclopenta[gh]phenanthridines

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Abstract A convenient $K_2S_2O_8$-initiated radical cascade cyclization for the construction of 4-sulfonated cyclopenta[gh]-phenanthridines from 2-alkynylnitriles and sodium sulfinates has been explored under metal-free conditions. This protocol features mild conditions, good functional group tolerance and broad substrate scope. A variety of potentially bioactive 4-sulfonated cyclopenta[gh]phenanthridines were facilely synthesized via direct annulation.

Keywords 2-alkynylnitriles; sodium sulfinate; 4-sulfonated cyclopenta[gh]phenanthridine; radical cyclization cascade

1 Introduction

Cyclopenta[ij]isoquinoline, a unique N-heteropolycyclic skeleton, is widely found in natural and bioactive molecules, has exhibited diverse biological activities.[1] Among which, cyclopenta[gh]phenanthridine has attracted growing interest recently from organic chemists due to their anti-human immunodeficiency virus (HIV) activity.[2] Although some work on the synthesis of cyclopenta[gh]phenanthridine has been reported,[3] some disadvantages exist with these methods, such as complicated operation, low reaction efficiency and poor substrate adaptability. Therefore, the development of alternative approach for the facile and efficient synthesis of cyclopenta[gh]phenanthridine is of great significance.

Sulfone is also an important and essential structural scaffold in pharmaceuticals and biologically active compounds, as well as functional materials.[4] Numerous studies on the synthesis of sulfone derivatives have been reported.[5] The common means for preparing sulfones, including the oxidation of sulfides,[6] sulfonylation of arenes,[7] and transition metal catalyzed cross coupling, are available.[8] Among these, sulfinate salts offer operating convenience and commercial availability for the preparation of sulfones. Based on the importance of cyclopen-

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ta[gh]phenanthridine and sulfone in various fields, efficient methods for the synthesis of sulfonated cyclopenta[gh]phenanthridine are valuable. Recently, radical cascade cyclization has emerged as a powerful strategy for the preparation of heterocycles since core structures can be built in a single operation comprising multiple bond forming steps,[9] thereby increasing the economy of the overall process. Inspired by recent progress on cyano-participated radical addition/cyclization for the formation of cyclic compounds,[10] multifunctionalized 2-alkynylnitriles were designed as radical acceptors, and we envisioned that the oxidant-mediated sulfonylation of unactivated alkynes could generate secondary alkenyl radicals, which could be coupled with late-stage radical cyclization, leading to the functionalized polycyclic heterocycles. Herein, a $K_2S_2O_8$ mediated cascade cyclization of 2-alkynylnitriles with sodium sulfinates was disclosed to construct sulfonated cyclopenta[gh]phenanthridines.

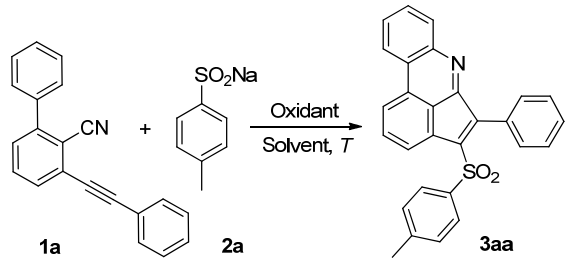
2 Results and discussion

Initially, 3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (**1a**) and sodium 4-methylbenzenesulfinate (**2a**) were utilized as the model substrates to optimize the reaction conditions. The results are summarized in Table 1. It was found that the desired product **3aa** was obtained in 41% yield when the reaction was performed in the presence of $NH_4S_2O_8$ as oxidant (3.5 equiv.) in CH_3CN/H_2O (V∶V= 4∶1) at 80 ℃ for 12 h under N_2 atmosphere (Entry 1). Encouraged by this result, the reaction conditions were further optimized by testing various oxidants. The investigation results showed that $K_2S_2O_8$ as an oxidant gave the best yield (83%), whereas other oxidants such as $Na_2S_2O_8$, *t*-butyl hydroperoxide (TBHP), di-*tert*-butyl peroxide (DTBP), *t*-butyl peroxybenzoate (TBPB), $PhI(OAc)_2$, $PhI(TFA)_2$ and oxone did not promote or only sluggishly promoted this reaction (Table 1, Entries 3～9). Among the solvents tested, CH_3CN/H_2O (V∶V=4∶1) was found to be the best one (Table 1, Entries 10～17). In contrast, the product **3aa** was isolated in low yield when the reaction was performed in the absence of H_2O or CH_3CN (Table 1, Entries 18 and 19). In addition, changing the loading of $K_2S_2O_8$ did not further improve the reaction either (Table 1, Entries 20 and 21). It should be noted that running the reaction at either 60 or 100 ℃ gave inferior results, which demonstrated that temperature is important (Table 1, Entries 22 and 23). The control experiment showed that no reaction occurred in the absence of $K_2S_2O_8$ (Table 1, Entry 24).

With the optimized conditions in hand (Table 1, Entry 2), the scope of substrates was then studied, as shown in Table 2. The substituent effect on the benzene ring was first examined. Both electron-donating and electron-withdrawing groups on the *para*-position of aromatic ring produced the corresponding cyclopenta[gh]phenanthridines **3aa**～**3af** in 49%～83% yields. When the *ortho* position on the benzene ring of the substrate was substituted with methyl, no desired product **3aj** was obtained perhaps due to the steric effect. Next, the effect of the substitution functional groups on the arene ring of the arylalkynyl moiety was investigated. The groups, such as methyl, ethyl, *tert*-butyl, methoxy, fluoro, chloro, and bromo groups, were examined and gave the corresponding products **3ah**～**3ap** in 56%～86% yields. When the arene ring of the arylalkynyl moiety was replaced by a heterocyclic ring, no desired products **3ax** and **3ay** were formed. Finally, the reactions of 3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (**1a**) with various sodium sulfinates were examined. Substituents in sodium arylsulfinates, such as *p*-H, *p*-F, *p*-Cl, *p*-Br, *m*-Br and *m*-F on the aromatic ring were compatible under the optimized conditions (**3aq**～**3av**). Moreover, when sodium cyclopropyl sulfinate were used as coupling partner, the desired product **3aw** was observed in 43% yield.

To shed light on the possible reaction mechanism, a radical-trapping experiment was carried out, as shown in

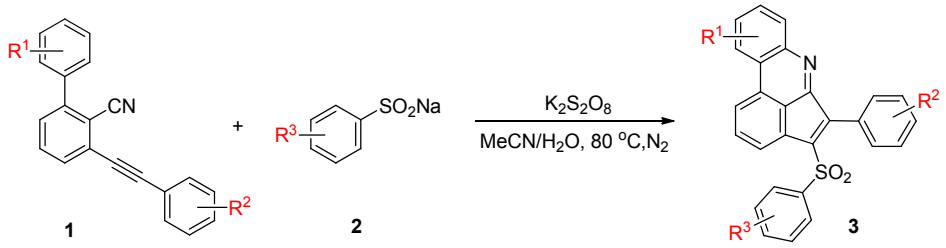
Table 1 Optimization of reaction conditions[a]

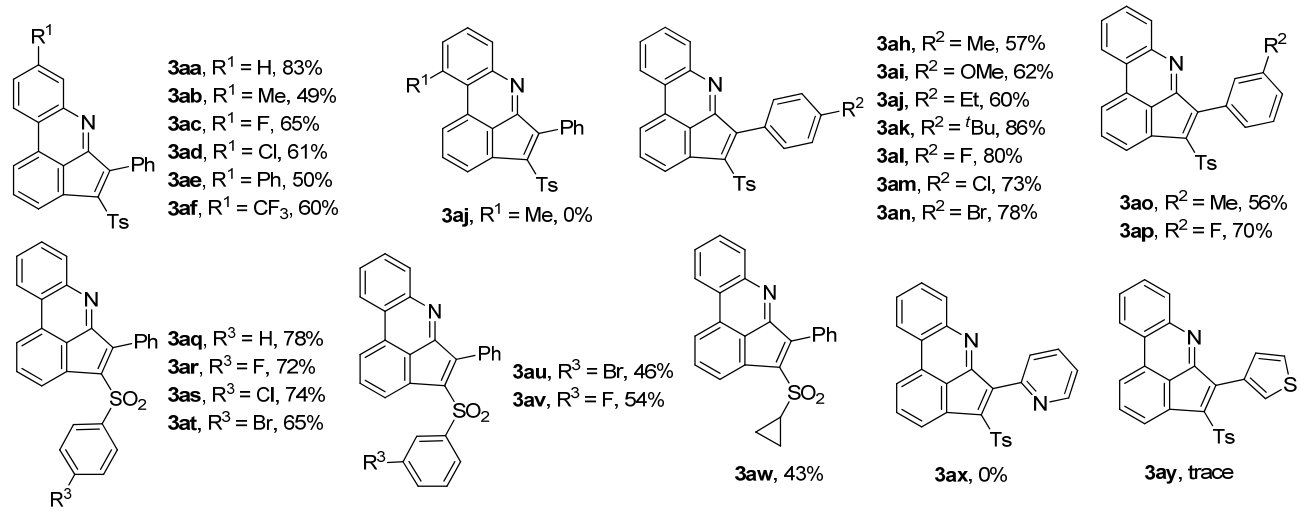


Entry	Oxidant	Solvent (V∶V)	Yiled[b]/%
1	$NH_4S_2O_8$	CH_3CN/H_2O (4∶1)	41
2	**$K_2S_2O_8$**	**CH_3CN/H_2O (4∶1)**	**83**
3	$Na_2S_2O_8$	CH_3CN/H_2O (4∶1)	69
4	TBHP	CH_3CN/H_2O (4∶1)	Trace
5	DTBP	CH_3CN/H_2O (4∶1)	N.r
6	TBPB	CH_3CN/H_2O (4∶1)	Trace
7	$PhI(OAc)_2$	CH_3CN/H_2O (4∶1)	Trace
8	$PhI(TFA)_2$	CH_3CN/H_2O (4∶1)	9
9	Oxone	CH_3CN/H_2O (4∶1)	18
10	$K_2S_2O_8$	Actone/H_2O (4∶1)	36
11	$K_2S_2O_8$	DMSO/H_2O (4∶1)	Trace
12	$K_2S_2O_8$	DCE/H_2O (4∶1)	Trace
13	$K_2S_2O_8$	CH_3CN/H_2O (1:1)	56
14	$K_2S_2O_8$	CH_3CN/H_2O (3∶1)	75
15	$K_2S_2O_8$	CH_3CN/H_2O (5∶1)	69
16	$K_2S_2O_8$	CH_3CN/H_2O (6∶1)	52
17	$K_2S_2O_8$	CH_3CN/H_2O (9∶1)	49
18	$K_2S_2O_8$	CH_3CN	39
19	$K_2S_2O_8$	H_2O	Trace
20[c]	$K_2S_2O_8$	CH_3CN/H_2O (4∶1)	54
21[d]	$K_2S_2O_8$	CH_3CN/H_2O (4∶1)	42
22[e]	$K_2S_2O_8$	CH_3CN/H_2O (4∶1)	60
23[f]	$K_2S_2O_8$	CH_3CN/H_2O (4∶1)	78
24	—	CH_3CN/H_2O (4∶1)	N.r

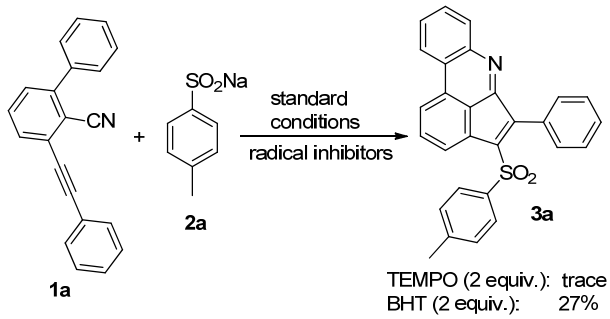
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), oxidant (0.7 mmol), solvent (3 mL), 80 ℃, 12 h, N_2 atmosphere. N.r.=no reaction; [b] Isolated yield; [c] $K_2S_2O_8$ (0.40 mmol); [d] $K_2S_2O_8$ (0.80 mmol); [e] 60 ℃; [f] 100 ℃.

Table 2 Scope of substrates[a,b]





[a] **1** (0.2 mmol), **2** (0.5 mmol), $K_2S_2O_8$ (0.7 mmol), CH_3CN/H_2O (V∶V=4∶1, 3 mL), at 80 ℃ for 12 h under N_2 atmosphere. [b] Isolated yield.



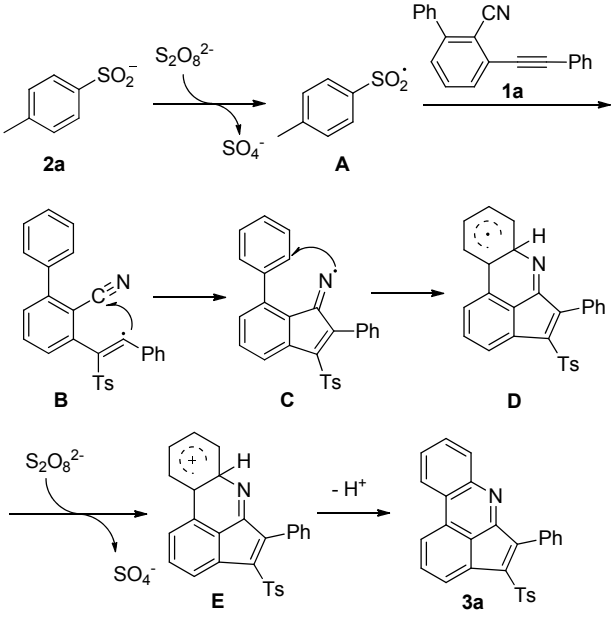
Scheme 1 Control experiments

Scheme 1. Addition of radical inhibitors, tetramethylpiperidin-1-oxyl and butylated hydroxytoluene, resulted in the inhibition of the reaction, suggesting that a radical process might be involved.

On the base of the above-mentioned experiments and literature reports,[11] a plausible mechanism is shown in Scheme 2. First, sodium benzenesulfinate **2a** was oxidized by $K_2S_2O_8$ to generate benzenesulfonyl radical **A**. Then, intermolecular addition of **A** to **1a** offered the alkenyl radical intermediate **B**, which underwent rapid intramolecular cyclization to give the iminyl radical **C**. Subsequently, radical intermediate **D** could be formed by intramolecular addition of iminyl radical **C** to the aromatic ring. Oxidation of **D** produced the corresponding cation **E**, which underwent deprotonation to yield the desired product **3a**.

3 Conclusions

In conclusion, a $K_2S_2O_8$ initiated cascade of sulfonyl radical addition and cyclization of 2-alkynylnitriles with sodium sulfinates were developed, providing direct access to various 4-sulfonated cyclopeanta[gh]phenanthridines with C—S/C—C/C—N bond formation in one pot. This protocol is practical under the mild conditions and has good tolerance towards various functional groups. When we prepare the manuscript, Zhou's group reported similar work.[12] Sulfurous acid was used as a free radical source, TBPB as an oxidant, and methylene chloride as a solvent



Scheme 2 Proposed reaction mechanism

in their procedure. In contrast, we use the cheaper inorganic salt $K_2S_2O_8$ as an oxidant, environmentally benign water as a co-solvent, which makes our reaction more economical and green.

4 Experimental section

4.1 General experimental information

^{1}H NMR spectra were recorded on 400 MHz spectrometer, and ^{13}C NMR spectra were recorded on 100 MHz spectrometer, Chemical shifts were recorded as residual signals relative to the solvent. High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70～230 mesh ASTM) using the reported eluent. Thin-layer chromatography (TLC) was carried out on 4 cm×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). All reagents were purchased from commercial suppliers and used directly after purchased. All solvents were used without special precautions to squeeze out moisture.

4.2 Experimental method

An oven-dried Schlenk tube was equipped with a magnetic stir bar, **1** (0.2 mmol), **2** (2.5 equiv., 0.5 mmol), $K_2S_2O_8$ (3.5 equiv., 0.7 mmol). The flask was evacuated and backfilled with N_2 for 3 times. Then CH_3CN/H_2O (V∶V=4∶1) (3 mL) was added. The tube was then sealed and the mixture was stirred for 12 h at 80 ℃ under N_2 (101 kPa). After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products **3**.

5-Phenyl-4-tosylcyclopenta[gh]phenanthridine (**3aa**): Yellow solid, 83% yield. m.p. 195～196 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (dd, J=6.2, 3.4 Hz, 1H), 8.36 (dd, J=9.9, 7.7 Hz, 2H), 8.31 (dd, J=6.2, 3.4 Hz, 1H), 7.87 (dd, J=8.1, 7.3 Hz, 1H), 7.78～7.72 (m, 2H), 7.70～7.64 (m, 2H), 7.57 (d, J=8.3 Hz, 2H), 7.53～7.47 (m, 3H), 7.11 (d, J=8.3 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4, 148.3, 148.2, 144.3, 142.8, 138.5, 135.3, 132.9, 132.4, 131.2, 129.8, 129.5,129.4, 129.0, 128.9, 128.7, 127.7, 127.6, 125.4, 124.5, 123.2, 122.9, 119.8, 21.5; HRMS (ESI) calcd for $C_{28}H_{20}NO_2S$ $[M+H]^+$ 434.1209; found 434.1211.

8-Methyl-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (**3ab**): Yellow solid, 49% yield. m.p. 184～186 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, J=8.2 Hz, 1H), 8.32 (t, J=7.8 Hz, 2H), 8.11 (s, 1H), 7.84 (t, J=7.7 Hz, 1H), 7.69～7.63 (m, 2H), 7.57 (d, J=8.3 Hz, 3H), 7.53～7.46 (m, 3H), 7.11 (d, J=8.1 Hz, 2H), 2.57 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.3, 148.5, 148.3, 144.2, 142.5, 139.2, 138.6, 135.2, 132.8, 131.9, 131.1, 130.5, 129.9, 129.4, 129.4, 129.0,127.6, 127.6, 125.0, 123.1, 122.6, 122.2, 119.5, 21.5; HRMS (ESI) calcd for $C_{29}H_{21}NO_2SNa$ $[M+Na]^+$ 470.1185, found 470.1183.

8-Fluoro-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (**3ac**): Yellow solid, 65% yield. m.p. 178～180 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53～8.45 (m, 1H), 8.31 (dd, J=13.8, 7.7 Hz, 2H), 7.95 (dd, J=10.0, 2.5 Hz, 1H), 7.86 (t, J=7.7 Hz, 1H), 7.65 (dd, J=7.6, 1.8 Hz, 2H), 7.56 (d, J=8.3 Hz, 2H), 7.54～7.47 (m, 4H), 7.11 (d, J=8.1 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.6, 162.5 (d, J=250.2 Hz), 149.5 (d, J=12.4 Hz), 147.9, 144.4, 143.3, 138.3, 135.4, 133.3, 131.1, 129.6, 129.4, 128.8, 127.7, 127.6, 125.4, 124.5 (d, J=9.4 Hz), 123.1, 121.2, 119.4, 117.7 (d, J=24.0 Hz), 116.8 (d, J=21.3 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −110.8 (s); HRMS (ESI) calcd for $C_{28}H_{18}FNO_2SNa$ $[M+Na]^+$ 474.0934, found 474.0936.

8-Chloro-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (**3ad**): Yellow solid, 61% yield. m.p. 193～194 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, J=8.7 Hz, 1H), 8.34 (d, J=7.1 Hz, 1H), 8.29 (dd, J=5.2, 3.1 Hz, 2H), 7.89～7.82 (m, 1H), 7.70～7.62 (m, 3H), 7.56 (d, J=8.3 Hz, 2H), 7.53～7.46 (m, 3H), 7.11 (d, J=8.1 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5, 148.7, 147.9, 144.4, 143.4, 138.3, 135.4, 134.6, 133.3, 131.4, 131.1, 129.6, 129.6, 129.4, 129.1, 128.6, 127.7, 127.6, 125.7, 124.0, 123.1, 122.9, 21.5; HRMS (ESI) calcd for $C_{28}H_{18}ClNO_2SNa$ $[M+Na]^+$ 490.0639, found 490.0639.

5,8-Diphenyl-4-tosylcyclopenta[gh]phenanthridine (**3ae**): Yellow solid, 50% yield. m.p. 190～191 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (dd, J=6.5, 5.3 Hz, 1H), 8.36 (dd, J=9.9, 7.7 Hz, 1H), 8.01 (dd, J=8.4, 1.9 Hz, 1H), 7.90～7.83 (m, 1H), 7.78～7.73 (m, 1H), 7.72～7.66 (m, 1H), 7.58 (d, J=8.3 Hz, 1H), 7.54～7.45 (m, 3H), 7.44～7.37 (m, 1H), 7.12 (d, J=8.1 Hz, 1H), 2.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.8, 148.7, 148.1, 144.3, 142.9, 141.7, 139.7, 138.5, 135.3, 133.0, 131.2, 130.2, 129.8, 129.6, 129.4, 129.0, 128.9, 127.9, 127.8, 127.7, 127.6, 127.3, 125.4, 123.5, 123.4, 123.3, 119.8, 21.5; HRMS (ESI) calcd for $C_{34}H_{23}NO_2SNa$ $[M+Na]^+$ 532.1342, found 532.1347.

5-Phenyl-4-tosyl-8-(trifluoromethyl)cyclopenta[gh]phenanthridine (**3af**): Yellow solid, 60% yield. m.p. 213～214 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (d, J=9.3 Hz, 1H), 8.39 (dd, J=11.5, 7.7 Hz, 1H), 7.95～7.88 (m, 1H), 7.66 (dd, J=7.6, 1.7 Hz, 1H), 7.57 (d, J=8.3 Hz, 1H), 7.54～7.47 (m, 1H), 7.12 (d, J=8.2 Hz, 1H), 2.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.8, 147.8, 147.4, 144.5, 143.7, 138.1, 135.4, 133.6, 130.7 (q, J=33.0 Hz), 131.0, 130.9, 130.6, 130.2, 129.7 (q, J=4.2 Hz), 129.5, 129.4, 128.4, 127.8, 127.6, 126.5, 124.4 (q, J=3.4 Hz), 123.9, 123.8 (q, J=271.3 Hz), 123.39, 120.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.2 (s); HRMS (ESI) calcd for $C_{29}H_{18}F_3NO_2S$ $[M+Na]^+$ 524.0903, found 524.0901.

5-(*p*-Tolyl)-4-tosylcyclopenta[gh]phenanthridine (**3ah**): Yellow solid, 57% yield. m.p. 197～198 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54～8.48 (m, 1H), 8.37～8.27 (m, 3H), 7.87～7.81 (m, 1H), 7.77～7.70 (m, 2H), 7.62 (d, J=8.2 Hz, 4H), 7.33 (d, J=7.9 Hz, 2H), 7.13 (d, J=8.2 Hz, 2H), 2.49 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5, 148.5, 148.2, 144.2, 142.0, 139.8, 138.7,

135.4, 132.8, 132.3, 131.2, 129.4, 129.0, 128.8, 128.7, 128.4, 127.5, 126.9, 125.1, 124.5, 123.09, 122.9, 119.9, 21.6, 21.5; HRMS (ESI) calcd for $C_{29}H_{21}NO_2SNa$ [M+Na]$^+$ 470.1185, found 470.1182.

5-(4-Methoxyphenyl)-4-tosylcyclopenta[gh]phenanthridine (**3ai**): Yellow solid, 62% yield. m.p. 190～192 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (dd, J=6.2, 3.4 Hz, 1H), 8.36～8.27 (m, 3H), 7.84 (dd, J=8.1, 7.3 Hz, 1H), 7.78～7.72 (m, 4H), 7.61 (d, J=8.3 Hz, 2H), 7.13 (d, J=8.2 Hz, 2H), 7.08～7.02 (m, 2H), 3.93 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5, 161.0, 148.2, 148.1, 144.2, 141.2, 138.7, 135.6, 133.1, 132.9, 132.3, 129.4, 129.0, 128.8, 128.7, 127.5, 125.0, 124.5, 122.9, 122.8, 122.1, 119.9, 113.3, 55.4, 21.5; HRMS (ESI) calcd for $C_{29}H_{21}NO_3SNa$ [M+Na]$^+$ 486.1134, found 486.1133.

5-(4-Ethylphenyl)-4-tosylcyclopenta[gh]phenanthridine (**3aj**): Yellow solid, 60% yield. m.p. 195～196 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55～8.48 (m, 1H), 8.32 (dt, J=9.8, 6.4 Hz, 3H), 7.85 (t, J=7.7 Hz, 1H), 7.78～7.70 (m, 2H), 7.61 (dd, J=14.8, 8.2 Hz, 4H), 7.33 (d, J=8.1 Hz, 2H), 7.10 (d, J=8.2 Hz, 2H), 2.78 (q, J=7.6 Hz, 2H), 2.32 (s, 3H), 1.35 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5, 148.3, 148.2, 146.0, 144.1, 142.1, 138.5, 135.4, 132.9, 132.3, 131.3, 129.3, 129.0, 128.8, 128.7, 127.6, 127.2, 127.1, 125.2, 124.5, 123.0, 122.9, 119.8, 28.9, 21.5, 15.5; HRMS (ESI) calcd for $C_{30}H_{24}NO_2S$ [M+H]$^+$ 462.1522, found 462.1522.

5-(4-(Tert-butyl)phenyl)-4-tosylcyclopenta[gh]phenanthridine (**3ak**): Yellow solid, 86% yield. m.p. 192～194 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53～8.47 (m, 1H), 8.36～8.28 (m, 3H), 7.84 (d, J=0.9 Hz, 1H), 7.76～7.69 (m, 2H), 7.64 (d, J=8.4 Hz, 2H), 7.56 (d, J=8.3 Hz, 2H), 7.49 (d, J=8.4 Hz, 2H), 7.06 (d, J=8.2 Hz, 2H), 2.30 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4, 152.7, 148.2, 148.1, 144.0, 142.3, 138.3, 135.5, 132.8, 132.3, 131.0, 129.2, 129.0, 128.8, 128.6, 127.6, 126.8, 125.2, 124.7, 124.5, 123.0, 122.9, 119.8, 34.8, 31.3, 21.5; HRMS (ESI) calcd for $C_{32}H_{27}NO_2SNa$ [M+Na]$^+$ 512.1655, found 512.1654.

5-(4-Fluorophenyl)-4-tosylcyclopenta[gh]phenanthridine (**3al**): Yellow solid, 80% yield. m.p. 195～197 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (dd, J=6.2, 3.3 Hz, 1H), 8.37～8.26 (m, 3H), 7.88～7.82 (m, 1H), 7.78～7.69 (m, 4H), 7.59 (d, J=8.3 Hz, 2H), 7.20 (t, J=8.7 Hz, 2H), 7.14 (d, J=8.2 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (d, J=250.1 Hz), 161.1, 148.1, 146.9, 144.5, 142.7, 138.4, 135.1, 133.4, 133.3, 131.4, 130.4, 129.5, 129.0 (d, J=13.6 Hz), 128.8, 127.5, 125.7 (d, J=3.8 Hz), 125.4, 124.5, 123.3, 122.9, 119.7, 114.9 (d, J=21.7 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −111.0 (s). HRMS (ESI) calcd for $C_{28}H_{18}FNO_2SNa$ [M+Na]$^+$ 474.0934, found 474.0939.

5-(4-Chlorophenyl)-4-tosylcyclopenta[gh]phenanthridine (**3am**): Yellow solid, 73% yield. m.p. 199～200 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (dd, J=6.2, 3.3 Hz, 1H), 8.33 (dd, J=16.4, 7.7 Hz, 2H), 8.30～8.26 (m, 1H), 7.85 (dd, J=8.2, 7.3 Hz, 1H), 7.79～7.71 (m, 2H), 7.68～7.58 (m, 4H), 7.51～7.45 (m, 2H), 7.15 (d, J=8.1 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 148.1, 146.6, 144.6, 143.0, 138.4, 135.9, 135.0, 132.9, 132.6, 132.2, 129.6, 129.0, 129.0, 128.9, 128.2, 128.0, 127.5, 125.4, 124.5, 123.4, 122.9, 119.7, 21.5; HRMS (ESI) calcd for $C_{28}H_{18}ClNO_2SNa$ [M + Na]$^+$ 490.0639, found 490.0639.

5-(4-Bromophenyl)-4-tosylcyclopenta[gh]phenanthridine (**3an**): Yellow solid, 78% yield. m.p. 206～208 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (dd, J=6.2, 3.3 Hz, 1H), 8.37 (s, 1H), 8.33 (dd, J=15.4, 7.7 Hz, 2H), 8.29～8.26 (m, 1H), 7.84 (dd, J=8.1, 7.3 Hz, 1H), 7.77～7.71 (m, 2H), 7.66～7.55 (m, 6H), 7.16 (d, J=8.2 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 148.1, 146.6, 144.6, 144.0, 138.3, 135.0, 132.9, 132.8, 132.2, 130.9, 129.6, 129.0, 129.0, 128.9, 128.7, 127.5, 125.4, 124.5, 124.3, 123.4, 122.9, 119.6, 21.5; HRMS (ESI) calcd for $C_{28}H_{18}BrNO_2SNa$ [M+Na]$^+$ 534.0134, found 534.0134.

5-(*m*-Tolyl)-4-tosylcyclopenta[gh]phenanthridine (**3ao**): Yellow solid, 56% yield, m.p. 196～198 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56～8.50 (m, 1H), 8.39～8.29 (m, 3H), 7.86 (dd, J=8.2, 7.2 Hz, 1H), 7.78～7.71 (m, 2H), 7.59 (d, J=8.3 Hz, 2H), 7.46～7.35 (m, 3H), 7.31 (d, J=7.5 Hz, 1H), 7.12 (d, J=8.1 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5, 148.4, 148.2, 144.2, 142.8, 138.5, 137.2, 135.3, 132.9, 132.4, 131.5, 130.3, 129.7, 129.3, 129.0, 128.8, 128.7, 128.1, 127.6, 127.6, 125.3, 124.5, 123.1, 122.9, 119.8, 21.5, 21.5; HRMS (ESI) calcd for $C_{29}H_{22}NO_2S$ [M+H]$^+$ 448.1366, found 448.1369.

5-(3-Fluorophenyl)-4-tosylcyclopenta[gh]phenanthridine (**3ap**): Yellow solid, 70% yield. m.p. 194～195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55～8.49 (m, 1H), 8.36 (dd, J=10.3, 7.7 Hz, 2H), 8.30 (dd, J=6.5, 3.1 Hz, 1H), 7.87 (dd, J=8.1, 7.3 Hz, 1H), 7.79～7.72 (m, 2H), 7.61 (d, J=8.3 Hz, 2H), 7.47 (dd, J=8.5, 3.4 Hz, 2H), 7.37～7.31 (m, 1H), 7.24～7.17 (m, 1H), 7.15 (d, J=8.1 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0 (d, J=245.7 Hz), 160.9, 148.2, 146.2, 144.6, 143.5, 138.2, 134.9, 132.9, 132.3, 131.8 (d, J=8.8 Hz), 129.5, 129.3 (d, J=8.4 Hz), 129.1, 129.0, 128.9, 127.6, 127.1 (d, J=2.9 Hz), 125.7, 124.5, 123.6, 122.9, 119.6, 118.1 (d, J=22.9 Hz), 116.4 (d, J=21.1 Hz), 21.53; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.5 (s); HRMS (ESI) calcd for $C_{28}H_{18}FNO_2SNa$ [M+Na]$^+$ 474.0934, found 474.0935.

5-Phenyl-4-(phenylsulfonyl)cyclopenta[gh]phenanthridine (**3aq**): Yellow solid, 78% yield. m.p. 193～194 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (dd, J=6.1, 3.4 Hz, 1H), 8.37 (dd, J=7.7, 3.0 Hz, 2H), 8.30 (dt, J=7.1, 3.5 Hz, 1H), 7.87 (dd, J=8.1, 7.3 Hz, 1H), 7.78～7.72 (m, 2H), 7.68 (td, J=8.1, 1.5 Hz, 4H), 7.55～7.42 (m, 4H), 7.31 (t, J=7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.2, 148.6, 148.3, 142.5, 141.3, 135.2, 133.2, 132.9, 132.4, 131.1, 129.7, 129.6, 129.0, 128.9, 128.8, 128.7, 127.7, 127.5, 125.4, 124.5, 123.3, 122.9, 119.7; HRMS (ESI) calcd for $C_{27}H_{17}NO_2SNa$ [M + Na]$^+$ 442.0872, found 442.0876.

4-((4-Fluorophenyl)sulfonyl)-5-phenylcyclopenta[gh]-phenanthridine (**3ar**): Yellow solid, 72% yield. m.p. 182～183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58～8.52 (m, 1H), 8.38 (dd, J=10.4, 7.7 Hz, 2H), 8.34～8.27 (m, 1H), 7.88 (dd, J=8.2, 7.2 Hz, 1H), 7.80～7.73 (m, 2H), 7.70～7.60 (m, 4H), 7.56～7.46 (m, 3H), 7.00～6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4 (d, J=256.9 Hz), 161.1, 148.5, 148.3, 142.5, 137.3 (d, J=3.0 Hz), 135.1, 132.9, 132.4, 131.1, 130.4, 130.3, 129.7, 129.1, 128.9 (d, J=10.0 Hz), 127.8, 125.4, 124.6, 123.4, 122.9, 119.7 (s), 115.9 (d, J=22.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −103.8 (s); HRMS (ESI) calcd for $C_{27}H_{16}FNO_2SNa$ $[M+Na]^+$ 460.0778, found 460.0777.

4-((4-Chlorophenyl)sulfonyl)-5-phenylcyclopenta[gh]-phenanthridine (**3as**): Yellow solid, 74% yield. m.p. 183～185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60～8.53 (m, 1H), 8.40 (dd, J=15.4, 7.7 Hz, 2H), 8.34 (dd, J=6.3, 3.3 Hz, 1H), 7.90 (dd, J=8.2, 7.2 Hz, 1H), 7.83～7.74 (m, 2H), 7.71～7.64 (m, 2H), 7.61～7.57 (m, 2H), 7.57～7.50 (m, 3H), 7.31～7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.0, 148.8, 148.3, 142.2, 139.9, 139.7, 135.0, 132.9, 132.4, 131.1, 129.7, 129.6, 129.1, 129.9, 128.9, 127.8, 125.4, 124.6, 123.4, 122.9, 119.7; HRMS (ESI) calcd for $C_{27}H_{16}ClNO_2SNa$ $[M+Na]^+$ 476.0482, found 476.0479.

4-((4-Bromophenyl)sulfonyl)-5-phenylcyclopenta[gh]-phenanthridine (**3at**): Yellow solid, 65% yield. m.p. 185～187 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (dd, J=6.1, 3.4 Hz, 1H), 8.39 (dd, J=15.9, 7.7 Hz, 2H), 8.33 (dt, J=7.1, 3.5 Hz, 1H), 7.90 (dd, J=8.2, 7.2 Hz, 1H), 7.82～7.76 (m, 2H), 7.68 (dt, J=3.9, 2.3 Hz, 2H), 7.59～7.48 (m, 5H), 7.47～7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.0, 148.9, 148.3, 142.1, 140.3, 135.0, 132.9, 132.4, 132.0, 131.1, 129.8, 129.6, 129.1, 129.0, 128.9, 128.5, 127.8, 125.4, 124.5, 123.4, 122.9, 119.7; HRMS (ESI) calcd for $C_{27}H_{17}BrNO_2S$ $[M+H]^+$ 498.0158, found 498.0162.

4-((3-Bromophenyl)sulfonyl)-5-phenylcyclopenta[gh]-phenanthridine (**3au**): Yellow solid, 46% yield. m.p. 186～188 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58～8.53 (m, 1H), 8.39 (dd, J=12.2, 7.7 Hz, 2H), 8.34～8.28 (m, 1H), 7.90 (dd, J=8.1, 7.3 Hz, 1H), 7.80～7.74 (m, 2H), 7.71 (t, J=1.7 Hz, 1H), 7.63 (dd, J=7.7, 1.7 Hz, 2H), 7.59～7.48 (m, 5H), 7.16 (t, J=8.0 Hz, 1H), 1.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.0, 149.1, 148.3, 142.9, 142.0, 136.2, 135.0, 133.0, 132.4, 131.0, 130.6, 130.2, 129.9, 129.5, 129.2, 129.0, 129.0, 127.9, 126.0, 125.5, 124.6, 123.5, 123.0, 122.6, 119.6; HRMS (ESI) calcd for $C_{27}H_{16}BrNO_2SNa$ $[M+Na]^+$ 519.9977, found 519.9974.

4-((3-Fluorophenyl)sulfonyl)-5-phenylcyclopenta[gh]-phenanthridine (**3av**): Yellow solid, 54% yield. m.p. 184～186 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57～8.50 (m, 1H), 8.37 (dd, J=13.5, 7.7 Hz, 2H), 8.31 (dt, J=7.0, 3.6 Hz, 1H), 7.88 (t, J=7.7 Hz, 1H), 7.79～7.73 (m, 2H), 7.66 (dd, J=7.6, 1.8 Hz, 2H), 7.57～7.48 (m, 3H), 7.46 (d, J=7.8 Hz, 1H), 7.36～7.31 (m, 1H), 7.29 (dd, J=8.0, 2.8 Hz, 1H), 7.14 (ddd, J=10.1, 7.9, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0 (d, J=251.3 Hz), 160.94 (s), 149.2, 148.3, 143.3, 143.2, 141.8, 135.0, 133.0, 132.4, 131.1, 130.5 (d, J=7.7 Hz), 129.8, 129.6, 129.1, 129.0 (d, J=6.7 Hz), 127.8, 125.4, 124.5, 123.5, 123.3 (d, J=3.3 Hz), 122.9, 120.5 (d, J=21.4 Hz), 119.6, 114.9 (d, J=24.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −109.8 (s); HRMS (ESI) calcd for $C_{27}H_{16}FNO_2SNa$ $[M+Na]^+$ 460.0778, found 460.0779.

4-(Cyclopropylsulfonyl)-5-phenylcyclopenta[gh]phenanthridine (**3aw**): Yellow solid, 43% yield. m.p. 227～229 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59～8.52 (m, 1H), 8.42～8.33 (m, 2H), 8.21 (d, J=7.1 Hz, 1H), 7.95～7.89 (m, 2H), 7.88～7.82 (m, 1H), 7.82～7.74 (m, 2H), 7.62～7.53 (m, 3H), 2.44 (tt, J=8.0, 4.8 Hz, 1H), 1.32～1.16 (m, 3H), 0.95～0.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.3, 148.3, 147.2, 141.9, 135.4, 132.9, 132.4, 131.2, 130.2, 129.8, 129.1, 128.9, 128.8, 128.0, 125.3, 124.5, 123.3, 123.0, 119.6, 33.0, 5.7; HRMS (ESI) calcd for $C_{24}H_{18}NO_2S$ $[M+H]^+$ 384.1053, found 384.1050.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **3aa**～**3aw**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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