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可见光促进异腈插入反应合成硒代螺环[吲哚-3,3'-喹啉]衍生物

刘浩阳 孙爽爽 马献力* 陈艳艳 徐燕丽*
(桂林医学院药学院 广西桂林 541004)

摘要 发展了一种无光敏剂参与的可见光促进异腈插入反应合成硒代螺环[吲哚-3,3'-喹啉]衍生物的方法. 该反应操作简便, 具有官能团兼容性好、底物适用性广和产率高的优点. 通过噻唑蓝(MTT)测试, 发现产物 2-苯基-2'-苯硒基-6'-三氟甲基-4'*H*-螺[吲哚-3,3'-喹啉](**3g**)、2-苯基-2'-(4-氟苯硒基)-5'-溴-4'*H*-螺[吲哚-3,3'-喹啉](**4d**)、2-苯基-2'-(4-(三氟甲基)苯硒基)-4'*H*-螺[吲哚-3,3'-喹啉](**4g**)能有效抑制肿瘤细胞的增长.

关键词 可见光促进; 异腈; 螺环化反应; 硒代螺环[吲哚-3,3'-喹啉]

Synthesis of Selenylated Spiro[indole-3,3'-quinoline] Derivatives via Visible-Light-Promoted Isocyanide Insertion

Liu, Haoyang Sun, Shuangshuang Ma, Xianli* Chen, Yanyan Xu, Yanli*
(*College of Pharmacy*, *Guilin Medical University*, *Guilin*, *Guangxi 541004*)

Abstract A photosensitizer-free visible-light-promoted isocyanide insertion protocol for the synthesis of selenylated spiro[indole-3,3'-quinoline] derivatives has been developed, which has the advantages of functional group tolerance, broad substrate scope, simple operation, and good yield. 2-Phenyl-2'-(phenylselanyl)-6'-(trifluoromethyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3g**), 5-bromo-2'-((4-fluorophenyl)selanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4d**) and 2-phenyl-2'-((4-(trifluoromethyl)phenyl)selanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**4g**) showed potent cancer-cell-growth inhibitory activities by methyl thiazolyl tetrazolium (MTT) assay.

Keywords visible-light-promoted; isocyanides; spirocyclization; selenylated spiro[indole-3,3'-quinoline]

1 Introduction

Organoselenium compounds have been extensively studied due to their wide application in drug design[1] and fluorescent molecular probes.[2] Because of their well-known biological activities,[3] much research effort has been directed at methods for introducing selenium groups to organic compounds,[4] which can be used in drug design and development.

Spirocyclic scaffolds are incorporated in various approved drugs and drug candidates,[5] which have attracted great attention in the chemical world due to their original stereostructure and challenging complexity of their synthesis.[6] Aza-spirocyclic compounds such as spiroindole derivatives are common structural scaffolds with diverse pharmacological activities[7] and found in many bioactive natural products[8] (Figure 1). Therefore, the development of new methods for the preparation of spiroindole derivatives as a key structure is of great importance in pharmaceutical and medicinal chemistry.[9]

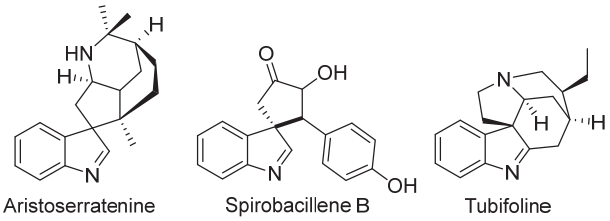

Figure 1 Spiroindolenine natural products

Isocyanides are important building blocks for the construction of organic selenium compounds,[10] and visible-light-promoted isocyanide insertion has been used to prepare 2,4-bis-(selanyl)quinolones[11] and 2,3-bis-(selanyl)-quinoxalines[12] via radical-mediated cascade cyclization. However, no studies have obtained spiroindole-containing

* Corresponding authors. E-mail: mxl78@glmc.edu.cn; yanli.xu@163.com
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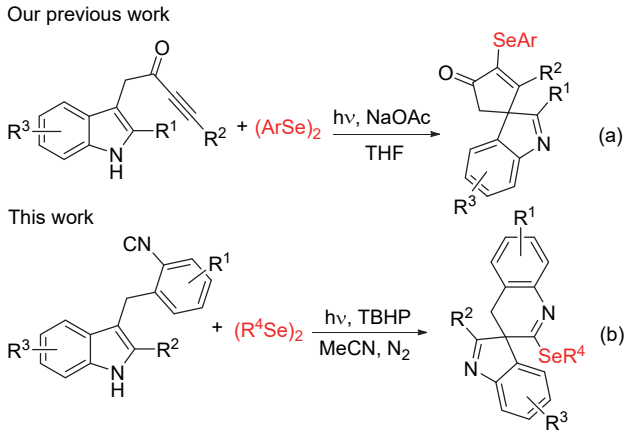
selenium compounds from isocyanides. Therefore, efficient and practical synthetic methods to synthesize spiroindole-containing selenium compounds need to be developed. Recently, our group has reported a metal-free visible-light-induced spirocyclization of indolyl-ynones with diselenides to construct 3-selenospiroindolenine compounds (Scheme 1a).[13] Two of the 3-selenospiroindolenine compounds have been found to display potent inhibitory activities against MGC-803 and HeLa cell lines, and one kind of 3-selenospiroindolenine was found to be cytotoxic against T-24 cell lines. Inspired by this result and with our continued interest in the synthesis of heterocycle-containing selenium compounds,[14] we developed an efficient visible-light-promoted isocyanide insertion protocol for the synthesis of selenylated spiro[indole-3,3'-quinoline] derivatives from 3-(2-isocyanobenzyl)-indoles and diselenides (Scheme 1b). This transformation is performed in mild conditions, without transition metal catalyst and photocatalyst, providing a rapid method to obtain selenylated spiro[indole-3,3'-quinoline] derivatives.

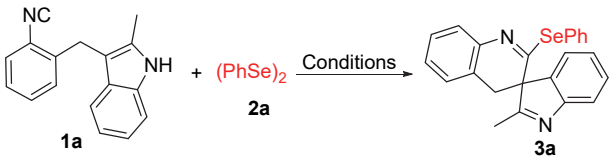


Scheme 1 Synthesis of selenylated spiroindolenine compounds

2 Results and discussion

At the beginning, isocyanide **1a** and diphenyl diselenide (**2a**) were reacted under irradiation by 60 W white LEDs to screen optimized reaction conditions (Table 1). **1a** and **2a** were reacted in MeCN under air atmosphere, providing the desired product of **3a** in 30% yield (Table 1, Entry 1). The reaction was performed in the presence of 1 equiv. of *tert*-butyl hydroperoxide (TBHP), resulting in **3a** in 57% yield, and the yield of **3a** increased up to 83% when 2 equiv. of TBHP was added (Table 1, Entries 2～4). Using H_2O_2 as an oxidant, the yield of **3a** decreased to 50% (Table 1, Entry 5). The data showed that the reactions were seriously inhibited when other solvents such as dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and ethanol were used (Table 1, Entries 3 vs. 6～8). The reactions were performed in different molar ratios of **1a**∶**2a** such as 1∶1, 1∶0.5, and 1∶0.4, affording the desired product of **3a** in 83%, 83%, and 73% yields, respectively (Table 1, Entries 3 vs 9～10). Moreover, the desired product of **3a** was obtained in 10% yield when the reaction was performed in dark condition (Table 1, Entry 11). In addition, when the reaction was performed on a 4.2 mmol scale and the reaction time was extended to 10 h, the desired product **3a** was afforded in 78% yield (Table 1, Entry 12). Thus, the best conditions leading to the formation of **3a** involved reaction in a MeCN/TBHP system under irradiation of 60 W white LEDs in N_2 atmosphere.

Table 1 Optimized conditions[a]

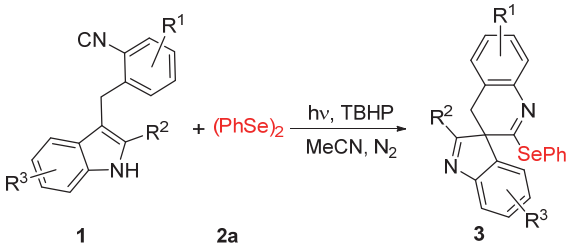


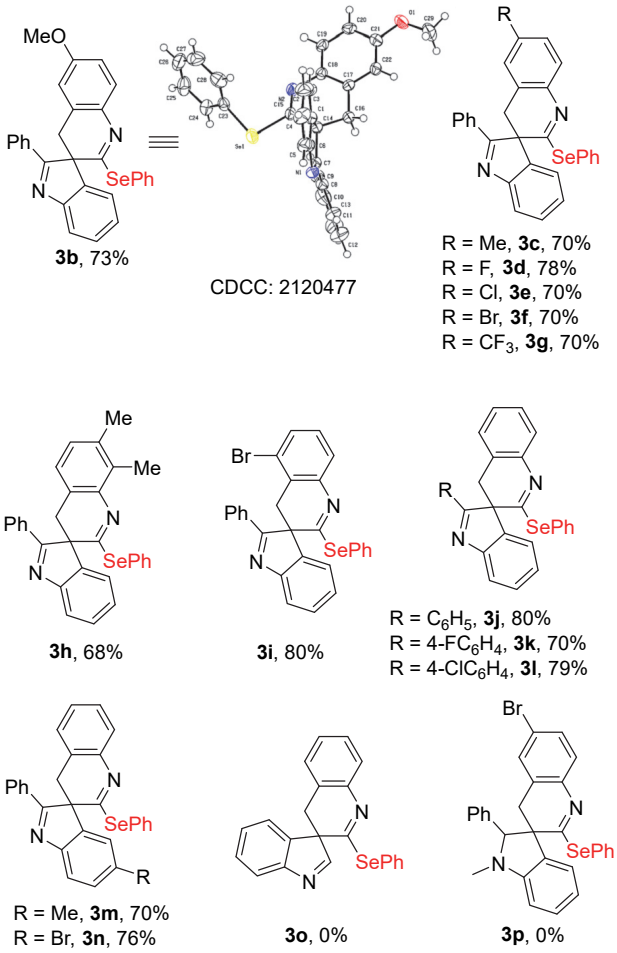
Entry	Oxidant	Solvent	Yield/%
1[b]	—	MeCN	30
2[c]	TBHP	MeCN	57
3	TBHP	MeCN	83
4[d]	TBHP	MeCN	77
5	H_2O_2	MeCN	50
6	TBHP	DMSO	Trace
7	TBHP	THF	31
8	TBHP	EtOH	Trace
9[e]	TBHP	MeCN	83
10[f]	TBHP	MeCN	73
11[g]	TBHP	MeCN	10
12[h]	TBHP	MeCN	78

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), solvent (1.0 mL), oxidant (0.2 mmol), and 60 W white LEDs in N_2 at room temperature for 3 h, isolated yield based on **1a**. [b] The reaction was performed in air atmosphere. [c] 0.1 mmol of TBHP was used. [d] 0.3 mmol of TBHP was used. [e] **2a** (0.05 mmol). [f] **2a** (0.04 mmol). [g] The reaction was carried out in the dark. [h] The reaction of **1a** (4.2 mmol) and **2a** (2.1 mmol) in the mixture of MeCN (10 mL), TBHP (8.4 mmol), and 60 W white LEDs in N_2 for 10 h.

With the optimal reaction conditions identified, the substrate scope of the reaction with respect to the isocyanides was explored (Table 2). The isocyanides (R^1 groups) with different substitutions at the benzene ring, including electron-donating (Me, MeO) and electron-withdrawing (F, Cl, Br, and CF_3), were suitable substrates, giving the corresponding products **3b**～**3i** in 68%～80% yields. The single crystals of **3b** were obtained by gradual crystallization in chloroform and characterized as 6'-methoxy-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (for details see Supporting Information). This reaction is also compatible with the substituent R^2 group containing aryl group, which was treated with **2a** providing the desired product of **3j**～**3l** in 70%～80% yields. In addition, the process is compatible with the substituent R^3 groups containing methyl and bromo substituents, which reacted with **2a** affording the desired products **3m** and **3n** in 70% and 76% yields, respectively. However, the substrate **1o** or **1p** did not react with **2a** under the standard condition. Most of the substrates were decomposed, and no desired products of **3o** and **3p** were detected.

Table 2 Substrate scope of isocyanides[a]

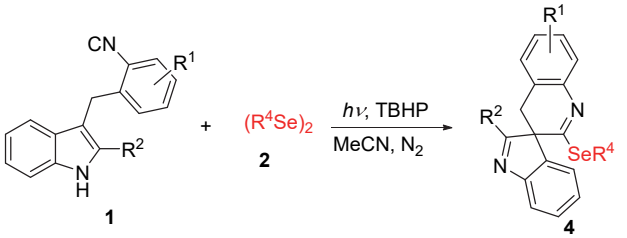


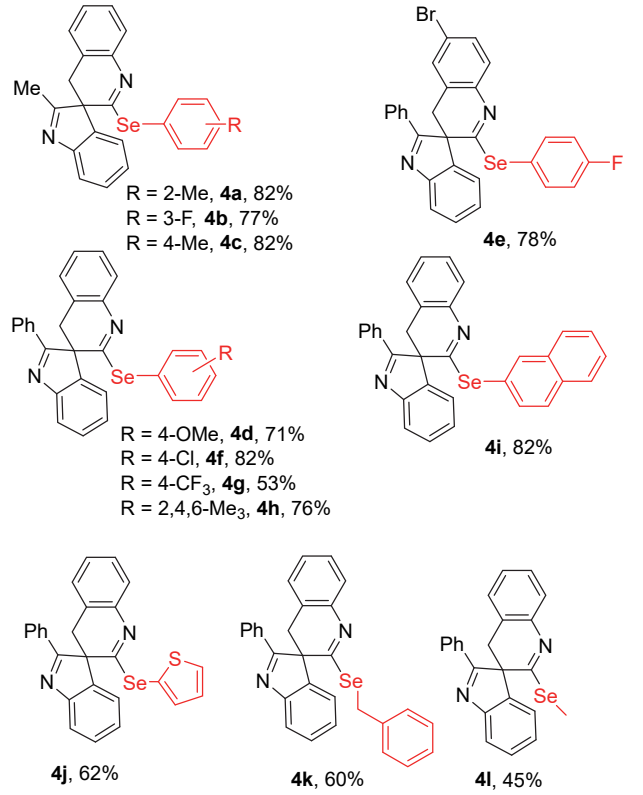


[a] Reaction conditions: **1** (0.2 mmol), $(PhSe)_2$ (0.1 mmol), TBHP (0.4 mmol), MeCN (2.0 mL), and 60 W white LEDs in N_2 at room temperature for 3 h. Isolated yield.

Next, we explored the substrate scope of the reaction with respect to various diselenides **2** (Table 3). The diaryldiselenides bearing a methyl group at the *ortho*-position or a fluoro group at the *meta*-position of benzene ring were tolerated and provided the desired product of **4a** and **4b** in 82% and 77% yields, respectively. The diaryldiselenides with electron-donating (Me, OMe) and electron-withdrawing (F, Cl, CF_3) substituents at the *para*-position of the benzene ring afforded the desired products **4c**～**4g** in 53%～82% yields, showing that electron-rich diselenides (**4e**) provided the desired products in higher yields than electron-poor diselenides (**4g**). The substrate 1,2-bis(2,4,6-trimethylphenyl)diselane provided the desired product of **4h** in 76% yield, suggesting that the steric effect has no effect on this reaction. Additionally, 1,2-di(naphthalen-2-yl)diselane and 1,2-di(thiophen-2-yl)diselane were found to be good substrates for this transformation, giving the desired products **4i** and **4j** in 82% and 62% yields, respectively. Moreover, 1,2-dibenzyldiselane and 1,2-dimethyldiselane were suitable substrates, affording the desired products **4k** and **4l** in 60% and 45% yields, respectively.

Table 3 Substrate scope of diselenides[a]

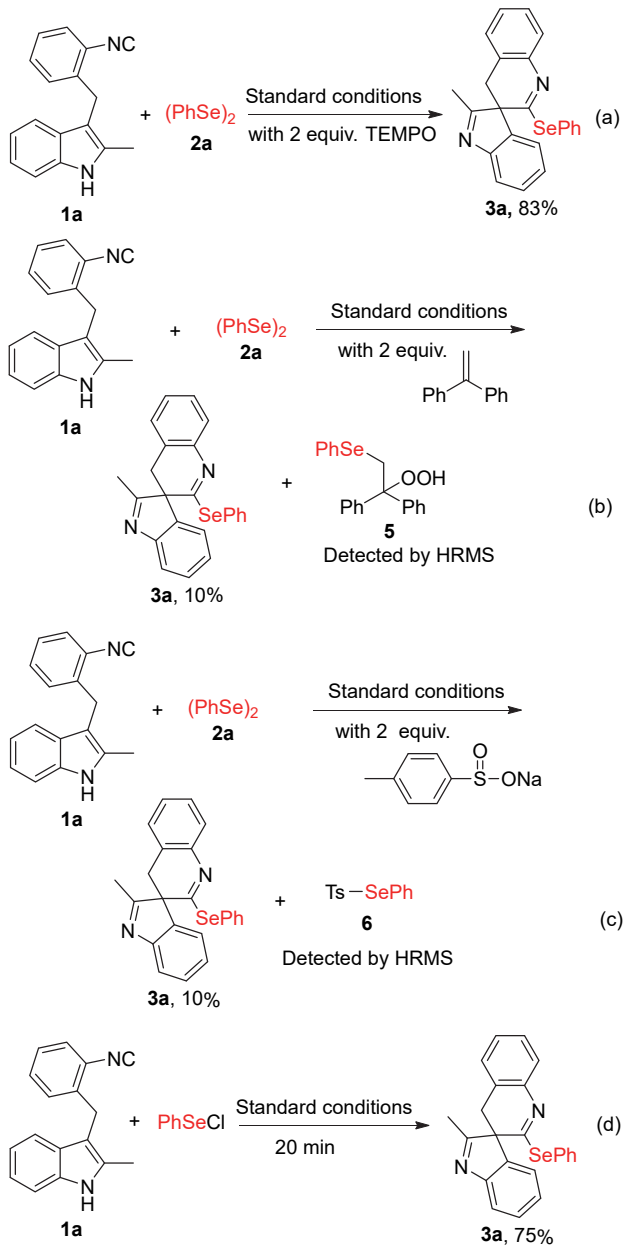




[a] Reaction conditions: **1** (0.2 mmol), diselenides **2** (0.1 mmol), TBHP (0.4 mmol), MeCN (2.0 mL), and 60 W white LEDs in N_2 at room temperature for 3 h. Isolated yield.

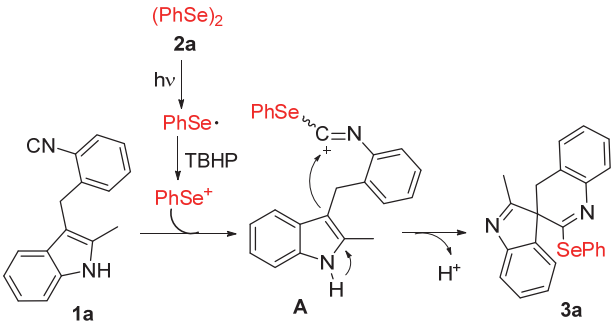
Control experiments were carried out to explore the possible reaction pathway as shown in Scheme 2. First, the reaction of **1a** and **2a** with 2.0 equiv. of TEMPO under the standard conditions afforded **3a** in 83% yield (Scheme 2a). The result of radical-inhibition experiment indicated that the reaction was prone to undergo a non-radical process. The reaction of **1a** and **2a** with 2.0 equiv. of ethene-1,1-diyldibenzene under the standard conditions provided **3a** in 10% yield and **5** (**5** was detected by

HRMS) (Scheme 2b). The reaction of **1a** and **2a** with 2.0 equiv. of sodium 4-methylbenzenesulfinate under the standard conditions gave **3a** in 10% yield with a trace amount of **6** (**6** was detected by HRMS). Moreover, most of the materials were recovered (Scheme 2c). In addition, **3a** was obtained in 75% yield when **1a** was reacted with PhSeCl under the standard condition for 20 min, suggesting that PhSe is a possible intermediate for the formation of **3a** (Scheme 2d). These results suggested that phenylselenyl free radicals were formed first under the irradiation of visible light, which would suffer oxidation by TBHP to afford phenylselenyl cation (PhSe).



Scheme 2 Control experiments for selenylative spirocyclization of **1a**

On the basis of the above controlled experiments and reported literatures,[15] a plausible mechanism for the formation of **3a** was proposed in Scheme 3. First, the irradiation of diphenyl diselenide (**2a**) produced phenylselenyl free radical, and phenylselenyl radical was oxidized to phenylselenyl cation (PhSe) by TBHP. Subsequently, the addition of PhSe to the isocyanide group of **1a** led to the formation of selenium ion **A**, which afforded the desired product **3a** through an electrophilic cyclization of **A** at the 3-position of the indole group.



Scheme 3 Possible pathways for the formation of **3a**

To explore the biological activities of these series of selenylated spiro[indole-3,3'-quinoline], the in vitro antitumor activities of compounds **3** and **4** were evaluated *via* MTT assays of T-24, MGC-803, and HeLa tumor cell lines. The commercial anticancer drug 5-fluorouracil (5-FU) was used as the positive control. The results showed that part of the compounds exhibited significant antitumor activities against the three tumor cell lines (MGC-803, HeLa, T-24). To our delight, compound **4d** exhibited potent inhibitory activity against T-24 cell lines with IC_{50} values of 8.4 μmol/L (Figure 2) and even demonstrated better cytotoxic activities than 5-FU.

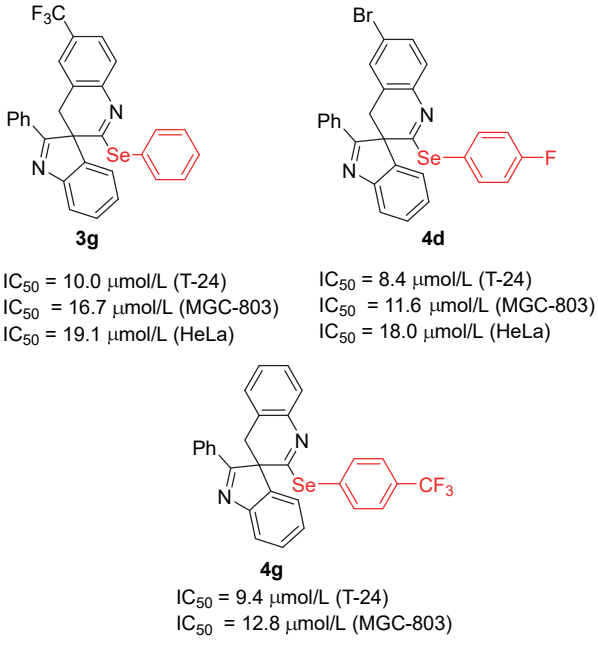
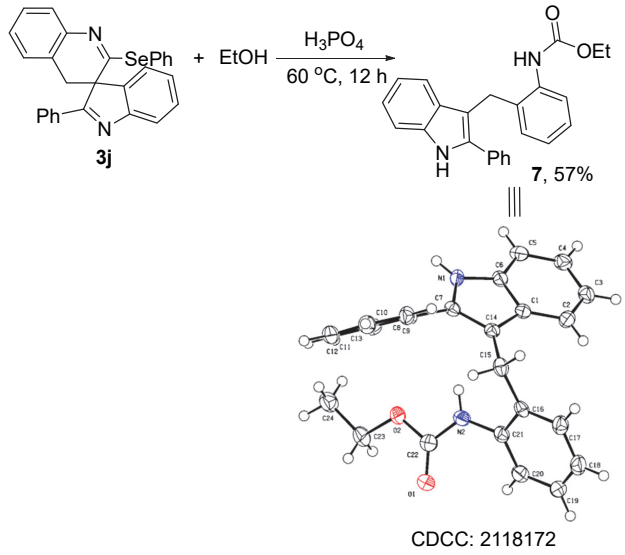


Figure 2 Anticancer activity of **3g**, **4d** and **4g**

Besides, we further investigated the transformations of the obtained **3j** using ethanol as nucleophile (Scheme 4).

To our delight, the reaction of **3j** and ethanol in the presence of H_3PO_4 (EtOH/H_3PO_4, V∶V=10∶1) at 60 ℃ for 12 h, and the desired products **7** were obtained via a nucleophilic substitution/aromatization cascade reaction in 57% yield.



Scheme 4 Synthetic application of **3j** to **5**

3 Conclusions

We have developed an efficient and metal-free visible-light-promoted isocyanide insertion protocol for the synthesis of selenylated spiro[indole-3,3'-quinoline] derivatives. This transformation is performed in mild conditions, without transition metal catalyst and photocatalyst, providing a rapid method to synthesize selenylated spiro[indole-3,3'-quinoline] derivatives. Further studies on the applications of selenylated spiro[indole-3,3'-quinoline] in drug design are currently ongoing in our laboratory.

4 Experimental section

4.1 General information

All manipulations were performed under an air atmosphere unless otherwise statement. Column chromatography was performed on silica gel (100～200, 300～400 mesh). NMR spectroscopy was performed on Bruker AV-400 or Bruker AV-600 instruments with $CDCl_3$. Chemical shifts for ^{1}H NMR spectra are reported as δ downfield from TMS (δ: 0.00). High resolution mass spectra (HRMS) were recorded on an Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI or APCI ionization source. LC-MS was obtained on an Agilent Technologies (6545 Q-TOF). Melting points were measured with a micro melting point apparatus. Unless stated otherwise, commercial reagents were used without further purification. The visible light catalytic reactions were performed in a photoreactor equipped with a 60 white LED lamp (manufacture by Jiadeng, Model number: CSDT, broadband source: 400～840 nm) in N_2 at room temperature, and the distance between lamp bulb with reaction test tube was 5 cm.

4.2 Typical procedure for the preparation of isocyanides

All isocyanides were prepared according to the reported procedure.[16] **1a** and **1j** have been reported, and the data of **1b**～**1i** and **1k**～**1p** are below.

3-(2-Isocyano-5-methoxybenzyl)-2-phenyl-1*H*-indole (**1b**): White solid (1.4 g, 80% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 131～132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.44～7.30 (m, 8H), 7.20～7.14 (m, 1H), 7.07 (t, J=7.4 Hz, 1H), 6.68～6.65 (m, 1H), 6.54 (d, J=2.6 Hz, 1H), 4.32 (s, 2H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 160.0, 139.6, 136.1, 136.0, 132.4, 129.1, 129.0, 128.0, 127.9, 127.7, 122.5, 120.0, 119.1, 115.1, 111.4, 110.9, 108.4, 55.3, 27.0. HRMS (ESI) calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$ 339.1942, found 339.1496.

3-(2-Isocyano-5-methylbenzyl)-2-phenyl-1*H*-indole (**1c**): White solid (1.2 g, 77% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 142～143 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.44～7.26 (m, 8H), 7.23～7.18 (m, 1H), 7.10～7.05 (m, 1H), 6.98 (d, J=7.9 Hz, 1H), 6.83 (s, 1H), 4.32 (s, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 139.8, 137.4, 136.1, 136.0, 132.5, 129.6, 129.2, 129.0, 128.0, 127.6, 127.5, 126.4, 122.5, 119.9, 119.2, 110.9, 108.6, 26.8, 21.4. HRMS (ESI) calcd for $C_{23}H_{18}N_2Na$ $[M+Na]^+$ 345.1362, found 345.1358.

3-(5-Fluoro-2-isocyanobenzyl)-2-phenyl-1*H*-indole (**1d**): White solid (1.1 g, 66% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 122～123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, J=12.3 Hz, 1H), 7.45～7.21 (m, 8H), 7.19～7.14 (m, 1H), 7.06～7.01 (m, 1H), 6.87～6.77 (m, 1H), 6.66～6.63 (m, 1H), 4.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 162.7 (d, J=251.2 Hz), 141.0 (d, J=8 Hz), 136.2 (d, J=38 Hz), 132.2, 129.1, 128.8, 128.5 (d, J=9 Hz), 128.1, 127.7, 122.7, 120.2, 119.0, 116.5 (d, J=12 Hz), 114.1 (d, J=23 Hz), 111.0, 107.6, 27.0. HRMS (ESI) calcd for $C_{22}H_{15}FN_2Na$ $[M+Na]^+$ 349.1111, found 349.1118.

3-(5-Chloro-2-isocyanobenzyl)-2-phenyl-1*H*-indole (**1e**): Yellow solid (1.3 g, 80% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 141～142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (s, 1H), 7.39～7.28 (m, 5H), 7.28～7.16 (m, 3H), 7.16～7.11 (m, 1H), 7.08～6.99 (m, 2H), 6.91 (d, J=1.9 Hz, 1H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 139.8, 136.3, 135.9, 135.6, 132.2, 129.3, 129.0, 128.8, 128.1, 127.7, 127.6, 127.2, 122.7, 120.1, 118.9, 111.0, 107.5, 26.9. HRMS (ESI) calcd for $C_{22}H_{16}ClN_2$ $[M+H]^+$ 343.0997, found 343.0997.

3-(5-Bromo-2-isocyanobenzyl)-2-phenyl-1*H*-indole (**1f**): White solid (1.5 g, 83% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 130～131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (s, 1H), 7.44 (d, J=7.5 Hz, 3H), 7.34 (t, J=7.4 Hz, 2H), 7.30～7.21 (m, 2H), 7.15 (d, J=7.4 Hz, 1H), 7.08～7.04 (m, 2H), 6.98～6.86 (m, 2H),

4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.9, 137.1, 136.2, 135.8, 134.1, 133.0, 128.9, 128.5, 128.2, 128.1, 127.9, 126.6, 126.2, 122.0, 119.7, 119.1, 110.9, 107.7, 29.5. HRMS (ESI) calcd for $C_{22}H_{16}BrN_2$ $[M+H]^+$ 387.0491, found 387.0465.

3-(2-Isocyano-5-(trifluoromethyl)benzyl)-2-phenyl-1*H*-indole (**1g**): Yellow solid (1.4 g, 78% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 89～90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.44～7.40 (m, 7H), 7.30～7.14 (m, 4H), 7.03 (t, J=7.3 Hz, 1H), 4.33 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 169.3, 139.0, 136.4, 135.9, 132.3, 131.2 (q, J=66.0 Hz), 129.0, 128.7, 128.2, 127.8, 127.1, 126.4 (q, J=6.0 Hz), 124.0 (q, J=6.0 Hz), 122.7, 120.2, 118.7, 111.1, 107.3, 26.9. HRMS (ESI) calcd for $C_{23}H_{16}F_3N_2$ $[M+H]^+$ 377.1260, found 377.1255.

3-(2-Isocyano-3,4-dimethylbenzyl)-2-phenyl-1*H*-indole (**1h**): White solid (1.2 g, 73% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 192～193 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 7.43～7.31 (m, 7H), 7.20～7.18 (m, 1H), 7.08～7.04 (m, 1H), 6.92 (d, J=7.9 Hz, 1H), 6.72 (d, J=7.9 Hz, 1H), 4.31 (s, 2H), 2.40 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 136.0, 136.0, 135.3, 135.0, 133.2, 132.5, 130.3, 129.2, 129.0, 127.9, 127.6, 125.9, 122.5, 119.9, 119.2, 110.9, 108.8, 27.2, 20.0, 15.6. HRMS (ESI) calcd for $C_{24}H_{21}N_2$ $[M+H]^+$ 337.1699, found 337.1702.

3-(5-Bromo-2-isocyanobenzyl)-2-phenyl-1*H*-indole (**1i**): White solid (1.5 g, 80% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 155～156 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (s, 1H), 7.40～7.35 (m, 5H), 7.33～7.25 (m, 3H), 7.19～7.16 (m, 2H), 7.09 (s, 1H), 7.04 (t, J=7.5 Hz, 1H), 4.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 139.9, 136.3, 135.9, 132.3, 130.2, 129.1, 128.8, 128.2, 127.9, 127.7, 123.8, 122.8, 120.2, 118.9, 111.0, 107.6, 26.9. HRMS (ESI) calcd for $C_{22}H_{15}BrN_2Na$ $[M+Na]^+$ 409.0311, found 409.0321.

2-(4-Fluorophenyl)-3-(2-isocyanobenzyl)-1*H*-indole (**1k**): White solid (1.1 g, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 122～123 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 7.40～7.33 (d, J=40.7 Hz, 5H), 7.26～7.03 (m, 7H), 4.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 162.6 (d, J=249.2 Hz), 137.4, 135.9, 135.2, 129.5, 129.4, 129.1, 128.9, 128.6 (d, J=3.1 Hz), 126.9 (d, J=22.4 Hz), 126.1, 126.0, 122.6, 120.1, 119.1, 116.2 (d, J=21.8 Hz), 110.9, 108.5, 26.8. HRMS (ESI) calcd for $C_{22}H_{16}FN_2$ $[M+H]^+$ 327.1292, found 372.1291.

2-(4-Chlorophenyl)-3-(2-isocyanobenzyl)-1*H*-indole (**1l**): White solid (1.3 g, 75% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 146～147 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 7.42～7.30 (m, 7H), 7.22～7.12 (m, 3H), 7.08 (t, J=7.5 Hz, 1H), 6.99 (d, J=7.6 Hz, 1H), 4.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 137.3, 136.0, 134.9, 134.0, 130.8, 129.5, 129.2, 129.1, 129.0, 128.8, 126.9, 126.7, 122.9, 120.2, 119.2, 111.0, 108.9, 26.8. HRMS (ESI) calcd for $C_{22}H_{16}ClN_2$ $[M+H]^+$ 343.0997, found 343.0996.

3-(2-Isocyanobenzyl)-5-methyl-2-phenyl-1*H*-indole (**1m**): White solid (1.1 g, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 131～132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (s, 1H), 7.37～7.22 (m, 7H), 7.16～7.09 (m, 2H), 7.04 (s, 1H), 6.97 (dd, J=7.0, 6.2 Hz, 2H), 4.25 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 136.7, 135.3, 133.3, 131.5, 128.5, 128.4, 128.3, 128.2, 128.0, 126.9, 126.5, 125.7, 125.6, 123.2, 109.6, 106.9, 25.8, 20.5. HRMS (ESI) calcd for $C_{23}H_{19}N_2$ $[M+H]^+$ 323.1543, found 323.1541.

5-Bromo-3-(2-isocyanobenzyl)-2-phenyl-1*H*-indole (**1n**): White solid (1.2 g, 65% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 154～155 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 7.38～7.28 (m, 7H), 7.23 (d, J=1.1 Hz, 2H), 7.18～7.11 (m, 2H), 6.95～6.90 (m, 1H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 137.5, 137.1, 134.6, 131.9, 130.9, 129.6, 129.1, 129.0, 128.4, 127.7, 127.0, 126.8, 125.5, 121.6, 113.2, 112.4, 108.0, 26.8. HRMS (ESI) calcd for $C_{22}H_{15}BrN_2Na$ $[M+Na]^+$ 409.0311, found 409.0312.

3-(2-Isocyanobenzyl)-1*H*-indole (**1o**): White solid (0.7 g, 60% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 55～56 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.41 (d, J=7.5 Hz, 1H), 7.32～7.22 (m, 2H), 7.17～7.06 (m, 4H), 6.99 (t, J=6.2 Hz, 1H), 6.91 (s, 1H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 137.6, 136.3, 129.9, 129.3, 127.1, 126.9, 126.7, 123.0, 122.1, 119.5, 118.9, 112.6, 111.2, 27.9. HRMS (ESI) calcd for $C_{16}H_{13}N_2$ $[M+H]^+$ 233.1073, found 233.1066.

3-(5-Bromo-2-isocyanobenzyl)-1-methyl-2-phenyl-1*H*-indole (**1p**): Yellow solid (0.36 g, 90% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), m.p. 124～125 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38～7.27 (m, 5H), 7.24～7.20 (m, 2H), 7.20～7.15 (m, 2H), 7.07 (d, J=8.4 Hz, 1H), 7.05～7.00 (m, 2H), 4.07 (s, 2H), 3.55 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.8, 139.3, 138.5, 136.2, 131.4, 130.2, 129.3, 128.9, 127.6, 127.5, 126.8, 126.3, 122.5, 121.1, 118.8, 117.8, 108.6, 107.0, 30.0, 25.8. HRMS (ESI) calcd for $C_{23}H_{17}BrN_2Na$ $[M+Na]^+$ 423.0467, found 423.0460.

4.3 Typical procedure for the preparation of diselenides

Diphenyl diselenide, 1,2-dibenzyldiselane and 1,2-dimethyldiselane were purchased commercially and used without further purification. Other diselenides were prepared according to the reported procedure.[17]

4.4 Typical procedure for the preparation of compounds **3** and **4**

To a solution of 3-(2-isocyanobenzyl)-2-methyl-1*H*-indole **1** (0.2 mmol), diselenides **2** (0.1 mmol) and MeCN (2 mL), degassing with N_2 and four evacuation/backfill cycles with N_2, was added TBHP (0.4 mmol). The mixture was stirred at room temperature under 60 W white LEDs. The progress of the reaction was monitored by thin-layer chromatography (TLC). After the reaction was completed, The mixture was quenched with water (3 mL), and

extracted with EtOAc (5 mL×3). The resulting orange solution was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2) yielding the desired products of **3** and **4**.

2-Methyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3a**): Yellow liquid (66.9 mg, 83% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=5∶1), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60～7.62 (m, 1H), 7.51～7.43 (m, 3H), 7.33～7.24 (m, 6H), 7.15～7.12 (m, 2H), 7.07 (d, *J*=6.9 Hz, 1H), 3.29 (d, *J*=16.4 Hz, 1H), 2.89 (d, *J*=16.4 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 180.2, 165.8, 155.8, 143.2, 139.7, 135.8, 129.6, 128.9, 128.5, 128.2, 127.7, 127.1, 126.8, 126.1, 126.1, 124.3, 123.5, 120.4, 64.9, 33.8, 17.8. HRMS (ESI) calcd for $C_{23}H_{19}N_2Se$ $[M+H]^+$ 403.0713, found 403.0710.

6'-Methoxy-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro-[indole-3,3'-quinoline] (**3b**): White solid (72.1 mg, 73% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1), m.p. 172～173 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.25～7.98 (m, 2H), 7.67 (d, *J*=7.7 Hz, 1H), 7.40 (s, 3H), 7.33 (t, *J*=7.5 Hz, 1H), 7.28 (d, *J*=7.2 Hz, 2H), 7.18 (t, *J*=7.1 Hz, 1H), 7.14 (t, *J*=7.3 Hz, 2H), 7.09 (d, *J*=8.6 Hz, 1H), 6.98 (t, *J*=7.4 Hz, 1H), 6.80 (d, *J*=7.4 Hz, 1H), 6.71～6.69 (m, 1H), 6.42 (s, 1H), 3.68 (s, 1H), 3.64 (s, 3H), 2.43 (d, *J*=16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.6, 162.2, 158.4, 154.1, 140.6, 137.1, 135.5, 131.2, 131.2, 129.6, 129.9, 128.8, 128.6, 128.3, 127.6, 127.2, 126.4, 125.6, 121.8, 121.5, 113.9, 112.5, 63.9, 55.3, 35.7. HRMS (ESI) calcd for $C_{29}H_{23}N_2OSe$ $[M+H]^+$ 495.0970, found 495.0983.

6'-Methyl-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3c**): White solid (66.9 mg, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1), m.p. 104～105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (m, 2H), 7.71 (d, *J*=7.7 Hz, 1H), 7.48～7.41 (m, 3H), 7.36 (td, *J*=7.7, 1.0 Hz, 1H), 7.33～7.26 (m, 2H), 7.23～7.15 (m, 3H), 7.07 (d, *J*=7.9 Hz, 1H), 7.04～6.96 (m, 2H), 6.80 (d, *J*=7.4 Hz, 1H), 6.71 (s, 1H), 3.69 (d, *J*=16.4 Hz, 1H), 2.47 (d, *J*=16.4 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.7, 164.3, 140.9, 140.4, 137.2, 135.6, 131.4, 131.0, 129.8, 129.5, 128.9, 128.8, 128.7, 128.6, 128.4, 127.1, 126.5, 126.3, 123.8, 121.9, 121.5, 64.2, 35.5, 21.2. HRMS (ESI) calcd for $C_{29}H_{23}N_2Se$ $[M+H]^+$ 479.1021, found 479.1025.

6'-Fluoro-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3d**): White solid (75.2 mg, 78% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1), m.p. 215～216 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.15 (d, *J*=6.1 Hz, 2H), 7.70 (d, *J*=7.6 Hz, 1H), 7.44 (d, *J*=6.2 Hz, 3H), 7.37 (t, *J*=7.5 Hz, 1H), 7.30 (d, *J*=7.3 Hz, 2H), 7.24 (t, *J*=7.0 Hz, 1H), 7.20～7.17 (m, 2H), 7.13～7.11 (m, 1H), 7.02 (t, *J*=7.4 Hz, 1H), 6.89 (t, *J*=7.4 Hz, 1H), 6.78 (d, *J*=7.4 Hz, 1H), 6.63 (d, *J*=7.2 Hz, 1H), 3.68 (d, *J*=16.6 Hz, 1H), 2.50 (d, *J*=16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 165.4 (d, *J*=2.0 Hz), 162.1 (d, *J*=246.0 Hz), 154.1, 140.2, 139.4 (d, *J*=3.0 Hz), 135.7, 131.4, 131.1, 129.6, 128.9, 128.7, 128.6, 127.9 (d, *J*=9.0 Hz), 126.8, 126.6, 126.3 (d, *J*=9.0 Hz), 121.7 (d, *J*=3.0 Hz), 115.2 (d, *J*=23.0 Hz), 114.6 (d, *J*=22.2 Hz), 63.5, 35.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.9. HRMS (ESI) calcd for $C_{28}H_{20}FN_2Se$ $[M+H]^+$ 483.0770, found 483.0785.

6'-Chloro-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3e**): White solid (69.7 mg, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1), m.p. 153～154 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.14 (d, *J*=5.7 Hz, 2H), 7.70 (d, *J*=7.7 Hz, 1H), 7.43 (s, 3H), 7.37 (t, *J*=7.5 Hz, 1H), 7.29 (d, *J*=7.3 Hz, 2H), 7.24～7.15 (m, 4H), 7.07 (d, *J*=8.4 Hz, 1H), 7.01 (t, *J*=7.4 Hz, 1H), 6.88 (s, 1H), 6.77 (d, *J*=7.4 Hz, 1H), 3.65 (d, *J*=16.6 Hz, 1H), 2.47 (d, *J*=16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.1, 167.1, 154.0, 141.5, 140.1, 135.7, 132.2, 131.4, 131.0, 129.7, 129.6, 128.9, 128.7, 128.6, 128.2, 128.2, 127.6, 126.7, 126.6, 125.9, 121.8, 121.7, 63.6, 35.1. HRMS (ESI) calcd for $C_{28}H_{20}ClN_2Se$ $[M+H]^+$ 499.0475, found 499.0481.

6'-Bromo-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3f**): White liquid (75.9 mg, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1), m.p. 175～176 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.14 (s, 2H), 7.71 (s, 1H), 7.57～7.14 (m, 9H), 7.03 (s, 2H), 6.78 (s, 1H), 3.65 (d, *J*=15.3 Hz, 1H), 2.47 (d, *J*=15.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.1, 167.3, 153.9, 141.9, 140.0, 135.7, 131.4, 131.2, 131.1, 130.9, 129.7, 129.6, 128.9, 128.7, 128.6, 127.9, 126.6, 126.2, 121.7, 121.7, 120.2, 63.6, 35.0. HRMS (ESI) calcd for $C_{28}H_{20}BrN_2Se$ $[M+H]^+$ 542.9970, found 542.9967.

2-Phenyl-2'-(phenylselanyl)-6'-(trifluoromethyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3g**): White solid (74.5 mg, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1), m.p. 189～190 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.21～8.10 (m, 2H), 7.73 (d, *J*=7.7 Hz, 1H), 7.52～7.43 (m, 4H), 7.40 (t, *J*=7.4 Hz, 1H), 7.33 (d, *J*=7.1 Hz, 2H), 7.28 (t, *J*=7.3 Hz, 1H), 7.24～7.21 (m, 3H), 7.18 (s, 1H), 7.04 (t, *J*=7.4 Hz, 1H), 6.74 (d, *J*=7.4 Hz, 1H), 3.72 (d, *J*=16.6 Hz, 1H), 2.60 (d, *J*=16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.0, 170.5, 154.1, 145.4, 140.0, 135.9, 131.5, 130.9, 129.8, 129.7, 129.1, 128.9, 128.8, 127.5 (q, *J*=205.7 Hz), 126.7, 126.6, 125.3 (q, *J*=4.3 Hz), 125.0, 121.9, 121.7, 63.8, 35.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.3. HRMS (ESI) calcd for $C_{29}H_{20}F_3N_2Se$ $[M+H]^+$ 533.0738, found 533.0757.

7',8'-Dimethyl-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro-[indole-3,3'-quinoline] (**3h**): White liquid (66.9 mg, 68% yield), R_f=0.5 (petroleum ether/ethyl acetate, *V*∶*V*=10∶1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.19～8.17 (m, 2H), 7.71 (d, *J*=7.7 Hz, 1H), 7.44～7.40 (m, 3H), 7.36～7.33 (m, 3H), 7.25～7.23 (m, 3H), 6.97 (t, *J*=7.5 Hz, 1H), 6.83 (d, *J*=7.4 Hz, 1H), 6.73 (d, *J*=7.4 Hz, 1H), 6.61 (d, *J*=7.4 Hz, 1H), 3.65 (d, *J*=16.3 Hz, 1H), 2.46 (d, *J*=16.3 Hz, 1H), 2.17 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.9, 164.5, 154.0, 140.7, 140.4, 137.0, 136.2, 133.3, 131.3, 131.2, 129.7, 129.3, 128.8, 128.6, 128.5,

127.9, 127.3, 126.4, 125.0, 121.9, 121.5, 121.4, 64.1, 35.7, 20.2, 12.7. HRMS (ESI) calcd for $C_{30}H_{25}N_2Se$ $[M+H]^+$ 493.1177, found 493.1189.

5'-Bromo-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3i**): White liquid (86.7 mg, 80% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.23～7.98 (m, 2H), 7.67 (d, J=7.7 Hz, 1H), 7.41～7.33 (m, 3H), 7.31～7.29 (m, 1H), 7.29～7.24 (m, 2H), 7.23～7.21 (m, 1H), 7.19～7.14 (m, 1H), 7.12 (t, J=7.3 Hz, 2H), 7.06～7.04 (m, 1H), 7.01～6.91 (m, 2H), 6.77 (d, J=7.4 Hz, 1H), 3.41 (d, J=17.3 Hz, 1H), 2.86 (d, J=17.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.0, 167.6, 153.9, 144.1, 140.5, 135.7, 131.3, 130.9, 129.6, 129.5, 128.9, 128.8, 128.7, 128.6, 126.7, 126.5, 125.7, 124.3, 124.2, 121.7, 121.4, 63.8, 35.2. HRMS (ESI) calcd for $C_{28}H_{20}BrN_2Se$ $[M+H]^+$ 542.9970, found 542.9986.

2-Phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3j**): White solid (74.3 mg, 80% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 218～219 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21～8.19 (m, 2H), 7.72 (d, J=7.7 Hz, 1H), 7.50～7.42 (m, 3H), 7.39～7.35 (m, 1H), 7.34～7.28 (m, 2H), 7.25～7.16 (m, 5H), 7.08 (td, J=7.3, 1.3 Hz, 1H), 7.04～6.98 (m, 1H), 6.91 (d, J=7.3 Hz, 1H), 6.77 (d, J=7.3 Hz, 1H), 3.72 (d, J=16.4 Hz, 1H), 2.54 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.5, 166.1, 154.1, 143.0, 140.4, 135.7, 131.3, 131.2, 129.7, 129.5, 128.9, 128.7, 128.5, 128.2, 128.1, 127.2, 127.0, 126.5, 124.2, 121.8, 121.6, 64.2, 35.4. HRMS (ESI) calcd for $C_{28}H_{21}N_2Se$ $[M+H]^+$ 465.0864, found 465.0886.

2-(4-Fluorophenyl)-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3k**): White solid (67.4 mg, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 157～158 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.25 (dd, J=8.8, 5.4 Hz, 2H), 7.75 (d, J=7.7 Hz, 1H), 7.43 (t, J=7.7 Hz, 1H), 7.39 (d, J=7.0 Hz, 2H), 7.33～7.22 (m, 5H), 7.19 (t, J=8.6 Hz, 2H), 7.14 (t, J=7.4, 1H), 7.07 (t, J=7.3 Hz, 1H), 6.98 (d, J=7.3 Hz, 1H), 6.84 (d, J=7.4 Hz, 1H), 3.71 (d, J=16.4 Hz, 1H), 2.60 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.3, 165.8, 164.6 (d, J=252.0 Hz), 153.9, 142.9, 140.3, 135.7, 131.9 (d, J=9.0 Hz), 129.5, 128.9, 128.6, 128.2 (d, J=4.0 Hz), 127.5 (d, J=3.0 Hz), 127.2, 126.8, 126.5 126.6 (d, J=5.0 Hz), 124.0, 121.7 (d, J=25.0 Hz), 115.9 (d, J=21.0 Hz), 64.1, 35.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −107.7. HRMS (ESI) calcd for $C_{28}H_{20}FN_2Se$ $[M+H]^+$ 483.0770, found 483.0780.

2-(4-Chlorophenyl)-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3l**): White solid (78.7 mg, 79% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 172～173 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.18 (d, J=8.5 Hz, 2H), 7.76 (d, J=7.7 Hz, 1H), 7.47 (d, J=8.5 Hz, 2H), 7.43 (t, J=7.5 Hz, 1H), 7.38 (d, J=7.2 Hz, 2H), 7.32～7.22 (m, 5H), 7.14 (t, J=7.3 Hz, 1H), 7.07 (t, J=7.4 Hz, 1H), 6.97 (d, J=7.3 Hz, 1H), 6.84 (d, J=7.5 Hz, 1H), 3.70 (d, J=16.4 Hz, 1H), 2.58 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.3, 165.6, 153.9, 142.9, 140.3, 137.5, 135.7, 130.8, 129.7, 129.5, 129.0, 128.9, 128.6, 128.2, 128.2, 127.3, 126.7, 126.7, 126.4, 123.9, 121.8, 121.7, 64.1, 35.2. HRMS (ESI) calcd for $C_{28}H_{20}ClN_2Se$ $[M+H]^+$ 499.0475, found 499.0485.

5-Methyl-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3m**): White solid (59.3 mg, 70% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 188～189 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.27 (s, 2H), 7.70 (s, 1H), 7.54 (s, 3H), 7.46 (s, 2H), 7.32 (s, 6H), 7.19 (s, 1H), 7.03 (s, 1H), 6.70 (s, 1H), 3.81 (d, J=15.3 Hz, 1H), 2.66 (d, J=15.3 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.6, 166.2, 151.9, 142.9, 140.8, 136.6, 135.6, 131.3, 131.0, 130.2, 129.5, 128.8, 128.6, 128.4, 128.2, 128.0, 127.2, 127.0, 126.5, 124.1, 122.4, 121.2, 63.9, 35.2, 21.5. HRMS (ESI) calcd for $C_{29}H_{23}N_2Se$ $[M+H]^+$ 479.1021, found 479.1031.

5-Bromo-2-phenyl-2'-(phenylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**3n**): White solid (82.4 mg, 76% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 181～182 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.15 (d, J=7.0 Hz, 2H), 7.54 (d, J=8.2 Hz, 1H), 7.50～7.36 (m, 4H), 7.33 (d, J=7.2 Hz, 2H), 7.27～7.11 (m, 5H), 7.08 (t, J=7.1 Hz, 1H), 6.90 (d, J=7.1 Hz, 1H), 6.85 (s, 1H), 3.69 (d, J=16.5 Hz, 1H), 2.51 (d, J=16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 164.6, 153.1, 142.6, 142.3, 135.7, 132.7, 131.5, 130.8, 129.7, 128.9, 128.7, 128.6, 128.4, 128.2, 127.5, 126.7, 126.6, 124.9, 123.4, 122.9, 119.9, 64.3, 35.2. HRMS (ESI) calcd for $C_{28}H_{20}BrN_2Se$ $[M+H]^+$ 542.9970, found 542.9986.

2-Methyl-2'-(*o*-tolylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**4a**): Yellow liquid (68.2 mg, 82% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=7.7 Hz, 1H), 7.47 (d, J=7.5 Hz, 1H), 7.39～7.34 (m, 1H), 7.24～7.19 (m, 2H), 7.17～7.13 (m, 3H), 7.07～6.97 (m, 4H), 3.17 (d, J=16.3 Hz, 1H), 2.84 (d, J=16.3 Hz, 1H), 2.22 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 180.3, 165.2, 155.6, 143.4, 142.6, 139.8, 137.4, 130.1, 129.5, 128.1, 127.8, 127.7, 126.7, 126.3, 126.1, 126.0, 124.2, 123.5, 120.4, 64.8, 33.8, 22.5, 17.9. HRMS (ESI) calcd for $C_{24}H_{21}N_2Se$ $[M+H]^+$ 417.0864, found 417.0879.

2'-((3-Fluorophenyl)selanyl)-2-methyl-4'H-spiro[indole-3,3'-quinoline] (**4b**): Yellow liquid (64.7 mg, 77% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=7.7 Hz, 1H), 7.41～7.37 (m, 1H), 7.24～7.16 (m, 6H), 7.13～7.06 (m, 2H), 7.04～6.95 (m, 2H), 3.26 (d, J=16.4 Hz, 1H), 2.83 (d, J=16.4 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 180.1, 165.1, 162.3 (d, J=248.0 Hz), 155.8, 143.1, 139.5, 131.2 (d, J=4.0 Hz), 130.0 (d, J=8.0 Hz), 129.8, 128.6 (d, J=8.0 Hz), 128.3, 127.8, 127.1, 126.2, 124.3, 123.6, 122.6 (d, J=22.0 Hz), 120.5, 115.7 (d, J=21.0 Hz), 64.9, 33.8, 17.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.1. HRMS (ESI) calcd for $C_{23}H_{18}FN_2Se$ $[M+H]^+$ 421.0614, found 421.0630.

2-Methyl-2'-(*p*-tolylselanyl)-4'*H*-spiro[indole-3,3'-qui-

noline] (**4c**): Yellow liquid (68.2 mg, 82% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=5∶1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, J=7.7 Hz, 1H), 7.39～7.34 (m, 1H), 7.29 (d, J=8.0 Hz, 2H), 7.19～7.14 (m, 3H), 7.10～7.01 (m, 4H), 6.99 (d, J=7.2 Hz, 1H), 3.20 (d, J=16.3 Hz, 1H), 2.81 (d, J=16.3 Hz, 1H), 2.28 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 180.3, 166.1, 155.7, 143.3, 139.8, 138.6, 135.8, 132.2, 129.8, 129.5, 128.1, 127.7, 126.8, 126.1, 126.1, 124.3, 123.5, 123.4, 120.4, 64.9, 33.8, 21.3, 17.8. HRMS (ESI) calcd for $C_{24}H_{21}N_2Se$ $[M+H]^+$ 417.0864, found 417.0879.

5-Bromo-2'-((4-fluorophenyl)selanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4d**): White solid (87.4 mg, 78% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 195～196 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.13 (d, J=6.9 Hz, 2H), 7.54 (d, J=8.2 Hz, 1H), 7.50～7.37 (m, 4H), 7.29～7.27 (m, 2H), 7.22 (t, J=7.6 Hz, 1H), 7.17～7.14 (m, 1H), 7.08 (t, J=7.3 Hz, 1H), 7.02～6.88 (m, 3H), 6.83 (s, 1H), 3.68 (d, J=16.6 Hz, 1H), 2.51 (d, J=16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.9, 164.6, 164.1 (d, J=247.5 Hz), 153.0, 142.4 (d, J=21.1 Hz), 138.0 (d, J=8.2 Hz), 132.7, 131.6, 130.8, 129.7, 128.7, 128.3 (d, J=16.3 Hz), 127.6, 126.7, 124.9, 123.4, 122.9, 121.1 (d, J=3.4 Hz), 119.9, 116.2 (d, J=21.6 Hz), 64.2, 35.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.0. HRMS (ESI) calcd for $C_{28}H_{19}BrFN_2Se$ $[M+H]^+$ 560.9875, found 560.9875.

2'-((4-Methoxyphenyl)selanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4e**): White solid (70.2 mg, 71% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 203～204 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.25 (s, 2H), 7.77 (s, 1H), 7.52 (s, 3H), 7.44 (s, 1H), 7.28～7.26 (m, 4H), 7.14 (s, 1H), 7.07 (s, 1H), 6.98 (s, 1H), 6.83～6.79 (m, 3H), 3.80 (s, 3H), 3.76 (s, 1H), 2.58 (d, J=16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.6, 166.9, 160.0, 154.0, 143.1, 140.5, 137.5, 131.2, 129.7, 129.4, 128.6, 128.2, 128.1, 127.1, 126.5, 126.4, 124.2, 121.8, 121.6, 117.2, 114.6, 64.1, 55.3, 35.5. HRMS (ESI) calcd for $C_{29}H_{23}N_2OSe$ $[M+H]^+$ 495.0970, found 495.0975.

2'-((4-Chlorophenyl)selanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4f**): White solid (81.7 mg, 82% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 215～216 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.23 (s, 2H), 7.78 (s, 1H), 7.55～7.40 (m, 4H), 7.32～7.31 (m, 3H), 7.26～7.25 (m, 3H), 7.17 (s, 1H), 7.08 (s, 1H), 7.00 (s, 1H), 6.83 (s, 1H), 3.79 (d, J=16.4 Hz, 1H), 2.63 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.4, 165.6, 154.1, 142.9, 140.3, 137.0, 134.9, 131.4, 131.1, 129.6, 129.6, 129.1, 128.7, 128.3, 128.2, 127.4, 126.6, 126.5, 125.1, 124.2, 121.8, 121.7, 64.1, 35.3. HRMS (ESI) calcd for $C_{28}H_{20}ClN_2Se$ $[M+H]^+$ 499.0475, found 499.0486.

2-Phenyl-2'-((4-(trifluoromethyl)phenyl)selanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**4g**): White solid (56.4 mg, 53% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 148～149 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.24～8.11 (m, 2H), 7.71 (d, J=7.7 Hz, 1H), 7.53～7.40 (m, 7H), 7.37 (t, J=7.6 Hz, 1H), 7.25 (t, J=7.6 Hz, 1H), 7.17 (s, 1H), 7.10 (t, J=7.4 Hz, 1H), 7.00 (t, J=7.5 Hz, 1H), 6.93 (d, J=7.3 Hz, 1H), 6.77 (d, J=7.5 Hz, 1H), 3.73 (d, J=16.5 Hz, 1H), 2.57 (d, J=16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 164.9, 154.1, 142.8, 140.2, 135.6, 132.0, 131.5, 131.1, 130.4 (q, J=32.5 Hz), 129.7, 129.7, 128.8, 128.4, 128.3, 127.6, 126.7, 126.6, 125.6 (q, J=3.6 Hz), 124.2, 122.4 (q, J=272.2 Hz), 121.8, 121.8, 64.2, 35.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.8. HRMS (ESI) calcd for $C_{29}H_{20}F_3N_2Se$ $[M+H]^+$ 533.0738 , found 533.0748.

2'-(Mesitylselanyl)-2-phenyl-4'H-spiro[indole-3,3'-quinoline] (**4h**): White solid (76.9 mg, 76% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 203～204 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.36 (s, 2H), 7.85 (d, J=7.6 Hz, 1H), 7.57 (s, 3H), 7.47 (t, J=7.5 Hz, 1H), 7.29 (t, J=7.3 Hz, 1H), 7.20 (d, J=7.6 Hz, 1H), 7.15 (t, J=7.2 Hz, 1H), 7.08 (t, J=7.4 Hz, 1H), 7.00 (d, J=7.1 Hz, 1H), 6.97 (s, 2H), 6.81 (d, J=7.4 Hz, 1H), 3.82 (d, J=16.3 Hz, 1H), 2.61 (d, J=16.3 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 165.1, 153.9, 143.5, 143.3, 140.5, 139.1, 131.3, 131.2, 129.9, 129.3, 128.5, 128.4, 128.1, 128.0, 126.6, 126.4, 126.2, 125.1, 124.0, 121.7, 121.6, 64.0, 35.4, 23.6, 21.1. HRMS (ESI) calcd for $C_{31}H_{27}N_2Se$ $[M+H]^+$ 507.1334, found 507.1355.

2'-(Naphthalen-1-ylselanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4i**): White solid (84.3 mg, 82% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 192～193 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.22 (s, 2H), 7.87 (s, 1H), 7.78～7.69 (m, 2H), 7.65 (s, 2H), 7.48～7.40 (m, 6H), 7.32 (d, J=7.6 Hz, 1H), 7.18 (s, 2H), 7.12 (d, J=6.8 Hz, 1H), 7.09～6.99 (m, 2H), 6.92 (s, 1H), 6.81 (s, 1H), 3.74 (d, J=16.3 Hz, 1H), 2.56 (d, J=16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.5, 166.2, 154.1, 143.0, 140.4, 135.1, 133.7, 132.9, 132.6, 131.3, 131.2, 129.7, 129.5, 128.7, 128.2, 128.1, 128.1, 127.8, 127.7, 127.2, 126.7, 126.5, 126.5, 126.2, 124.6, 124.2, 121.8, 121.7, 64.2, 35.4. HRMS (ESI) calcd for $C_{32}H_{23}N_2Se$ $[M+H]^+$ 515.1021, found 515.1045.

2-Phenyl-2'-(thiophen-2-ylselanyl)-4'*H*-spiro[indole-3,3'-quinoline] (**4j**): White solid (59.2 mg, 62% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 194～195 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.16 (d, J=6.7 Hz, 2H), 7.71 (d, J=7.6 Hz, 1H), 7.45～7.41 (m, 4H), 7.37 (t, J=7.5 Hz, 1H), 7.24 (d, J=4.1 Hz, 2H), 7.11～7.07 (m, 1H), 7.01 (t, J=7.4 Hz, 1H), 6.95～6.90 (m, 3H), 6.77 (d, J=7.5 Hz, 1H), 3.69 (d, J=16.4 Hz, 1H), 2.55 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 165.9, 142.9, 140.0, 136.5, 132.3, 131.5, 131.0, 129.7, 129.6, 128.8, 128.2, 128.2, 127.5, 127.4, 126.7, 124.1, 122.0, 121.6, 120.3, 63.8, 35.6. HRMS (ESI) calcd for $C_{26}H_{19}N_2SSe$ $[M+H]^+$ 471.0429, found 471.0434.

2'-(Benzylselanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4k**): White solid (60.0 mg, 60% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 136～

137 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J=7.1 Hz, 2H), 7.72 (d, J=7.6 Hz, 1H), 7.53 (d, J=7.6 Hz, 1H), 7.49～7.28 (m, 5H), 7.26～7.06 (m, 6H), 7.01～6.96 (m, 2H), 6.72 (d, J=7.3 Hz, 1H), 4.34 (s, 2H), 3.74 (d, J=16.4 Hz, 1H), 2.59 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.7, 165.5, 153.8, 143.0, 140.4, 138.6, 131.1, 129.7, 129.3, 129.1, 128.5, 128.4, 128.3, 128.2, 126.9, 126.7, 126.3, 126.0, 124.3, 121.7, 121.4, 64.2, 35.2, 29.5. HRMS (ESI) calcd for $C_{29}H_{22}N_2SeNa$ $[M+Na]^+$ 501.0840, found 501.0841.

2'-(Methylselanyl)-2-phenyl-4'*H*-spiro[indole-3,3'-quinoline] (**4l**): White solid (36.2 mg, 45% yield), R_f=0.5 (petroleum ether/ethyl acetate, V∶V=10∶1), m.p. 142～143 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.11 (s, 2H), 7.67 (d, J=7.1 Hz, 1H), 7.58～7.19 (m, 6H), 7.08 (s, 1H), 6.92 (d, J=7.5 Hz, 2H), 6.70 (d, J=6.7 Hz, 1H), 3.68 (d, J=16.3 Hz, 1H), 2.48 (d, J=16.3 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.9, 165.9, 153.7, 143.0, 140.8, 131.1, 131.1, 129.8, 129.3, 128.5, 128.3, 128.2, 126.8, 126.4, 126.0, 124.1, 121.7, 121.4, 77.3, 77.0, 76.7, 64.1, 35.1, 5.9. HRMS (ESI) calcd for $C_{23}H_{19}N_2Se$ $[M+H]^+$ 403.0708, found 403.0717.

4.5 Typical procedure for the preparation of compounds 7

A solution of **3j** (0.2 mmol), EtOH/H_3PO_4 (V∶V=10∶1, 2 mL) in a 10 mL test tube was stirred at 60 ℃ for 12 h under the air atmosphere. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was quenched with water (3 mL) and extracted with EtOAc (5 mL×3). The resulting orange solution was dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash column chromatography (R_f=0.5, petroleum ether/ethyl acetate, V∶V=5∶1) to give ethyl (2-((2-phenyl-1*H*-indol-3-yl)methyl)phenyl)carbamate (**7**) as white solid in 57% (42.2 mg) yield. m.p. 119～120 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.37 (s, 1H), 9.06 (s, 1H), 7.54～7.49 (m, 2H), 7.43 (dt, J=8.6, 6.2 Hz, 4H), 7.34 (t, J=7.3 Hz, 1H), 7.25 (d, J=7.9 Hz, 1H), 7.18～7.08 (m, 2H), 6.98～6.93 (m, 2H), 6.80 (d, J=7.7 Hz, 1H), 4.16 (s, 2H), 4.12 (q, J=7.1 Hz, 2H), 1.24 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 155.1, 136.7, 136.5, 135.7, 133.0, 129.5, 129.2, 128.5, 127.8, 127.8, 126.5, 125.5, 122.2, 119.4, 119.1, 111.7, 109.2, 60.7, 25.9, 15.1. HRMS (ESI) calcd for $C_{24}H_{23}N_2O_2$ 371.1754, found 371.1733.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **1**, **3** and **4**, **7**, crystallographic data for **3b** and **7**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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(Lu, Y.)

