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Iodine-Catalyzed Aerobic Oxidation of Spirovinylcyclopropyl Oxindoles to Form Spiro-1,2-dioxolanes Diastereoselectively

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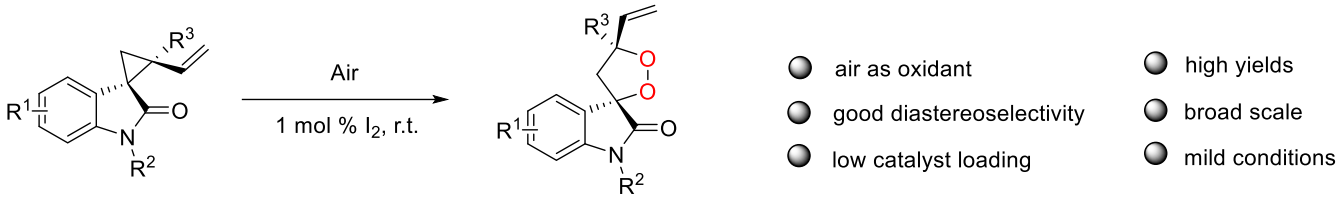


ABSTRACT: A novel method of iodine-catalyzed aerobic oxidation with spirovinylcyclopropyl oxindoles under mild conditions had been described. A series of spiro-1,2-dioxolanes were prepared in good to excellent yields and considerable diastereoselectivities. The new approach is operationally simple, scalable and tolerant of various functional groups.

1,2-Dioxolanes can be easily found in biologically active natural products and synthetic molecules (Figure 1).[1] For example, the mixture of plakortinic acids A and B isolated from the sponge-sponge symbiotic association shows cytotoxic activity on A2058 melanoma and DU-145 prostate cancer cells.[2a] 3-Alkoxy-1,2-dioxolanes exhibits promising levels of antimalarial activity against *Plasmodium falciparum*[2b] and endoperoxide triterpene derived from 11-keto-β-boswellic acid shows potent antitumor activity.[2c] Meanwhile, 1,2-dioxolane derivatives are also key building blocks in the synthesis of structurally complex targets, such as plakortone B[3a] and andavadoic acid.[3b]

Recently, the aerobic oxidation of donor–acceptor cyclopropanes, which have become important building blocks for constructing a wide range of carbo- and heterocyclic compounds,[4a] have been popular in the synthesis of 1,2-dioxolanes (Scheme 1). [4b-4e] The Mizuno's group reported that the photooxygenation of electron-rich 1,2-diarylcyclopropanes in the presence of 9,10-dicyanoanthracene (DCA) as a sensitizer in acetonitrile could afford *cis*- and *trans*-3,5-diaryl-l,2-dioxolanes in high yields.[5] And Shim's group showed that 2,2-diphenyl-2-vinylcyclopropane could yield 3,3-diphenyl-5-vinyl-l,2-dioxolane and benzophenone as the major products on the similarly co-sensitized photooxygenation.[6a] Feldman and co-workers widely explored the radical-mediated reaction of vinylcyclopropanes[6b] with oxygen in the presence of Ph_2Se_2 and AIBN to give l,2-dioxolanes in good yield and acceptable diastereoselectivity. [6c-6g] Then, Zhao and other researchers achieved the total synthesis of pharmaceutically active compounds via an asymmetric radical-mediated intermolecular Feldman oxygenation of vinylcyclopropanes.[7] In addition, Kulinkovich, Nguyen, Barnier and other researchers described that under UV irradiation or electrolysis conditions, several cyclopropanes with a strong electron-donating group combined with oxygen to furnish 1,2-dioxolanes.[8] Most of methods have modest stereoselectivity or poor stability of products, which severely restricts application in organic and pharmaceutical synthesis.[9] Besides, spirooxindole is a key structural motif in a broad range of natural alkaloids and biologically active molecules.[10] Therefore, a general protocol to synthesize stereoselective spiro-1,2-dioxolanes, especially the parallel combinations of 1,2-dioxolane and indolone motifs, would be highly desirable from the medicinal point of view. And molecular iodine[11] has emerged as an excellent catalyst, because of its high solubility in the reaction media, easy handling, low cost, and environmentally friendly nature in comparison to heavy metals. Heroin, we report a molecular iodine-catalyzed aerobic oxidation of spirovinylcyclopropyl oxindole for the synthesis of 5'-vinylspiro[indoline-3,3'-[1,2]dioxolane]-2-ones with exclusive stereoselectivity in high yields under mild conditions.

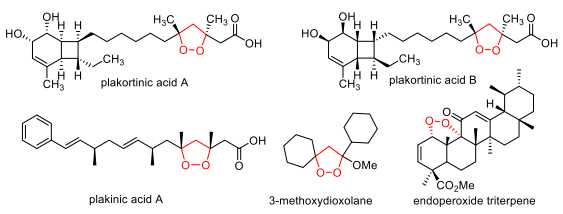
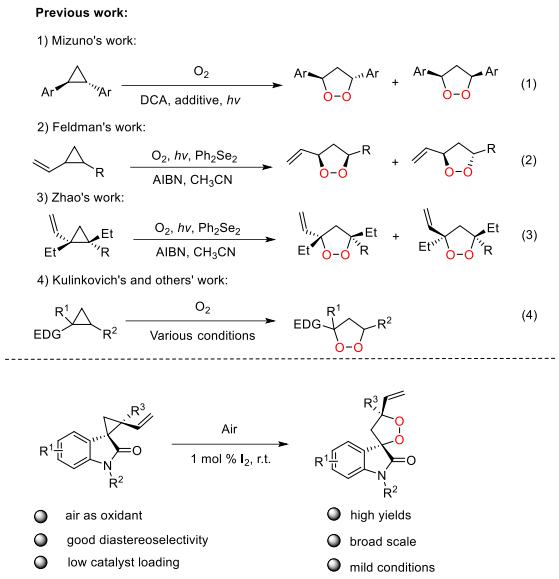


Figure 1. 1, 2-dioxolanes found in natural products and synthetic molecules

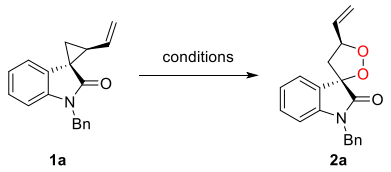
Scheme 1. Formal [3+2] Cycloaddition of Cyclopropanes with Oxygen



We initiated our investigation by subjecting *N*-benzyl spirovinylcyclopropyl oxindole **1a** with 5 mol % I_2 in toluene at room temperature under air atmosphere. The desired spiro-1,2-dioxolane **2a** could be obtained in a good diastereoselectivity while the yield was just 30% (Table 1, entry 1). The structure and stereochemistry of compound **2a** were characterized by a combination of NMR spectroscopy, high-resolution mass spectrometry (HRMS), and single-crystal X-ray diffraction.[15] To obtain satisfying yield of our desired compound, we then screened various amounts of this catalyst and solvents. The result indicated the amount of iodine had no apparent impact on diastereoselectivity but yield (entries 2-5). Among tested solvents, acetonitrile proved to be the best reaction solvent, giving **2a** in 91% yield with excellent diastereoselectivity (entries 6-14). Subsequently, we tried other iodine-containing catalysts. It showed that the corresponding product **2a** could be obtained only when adding 100% mol of SmI_2, but the reaction was hardly performed even if one of the above amounts (1%, 5%, 10% and 20%) of catalyst or 100% mol TEAI (tetra ethylammonium iodide) was added. (entries 15 and 16). In addition, when the reaction was run at 0 ℃, the target compound **2a** could be obtained in a favorable diastereoselectivity while the yield was just 39% (entry 17). However, the target product was not observed when the reaction was performed at reflux temperature (entry 18). Therefore, the reaction conditions identified in entry 14 were chosen as the standard conditions for further investigations.

With the optimal conditions in hand, we first studied the effect of substituents of nitrogen in spirovinylcyclopropyl oxindoles on the aerobic oxidation (Scheme 2). The introduction of alkyl substituents or phenyl at nitrogen position was tolerated and gave the corresponding products in good to excellent yield yields. However, the diastereoselectivities could be affected greatly, such as N-phenyl spirovinylcyclopropyl oxindole gave the target product in 75% yield and 70:30 diastereoselectivity. It is worth mentioning that, the target product 2e could also be obtained in 65% yield and a good diastereoselectivity (>95:5 dr), while the amount of catalyst was increased to 5% and the reaction time was slightly prolonged, which showed that the process was compatible for the containing carbon-carbon double bond substrates. Subsequently, the effects of aromatic ring

Table 1. Survey on Conditions for Formation of 2a[a]

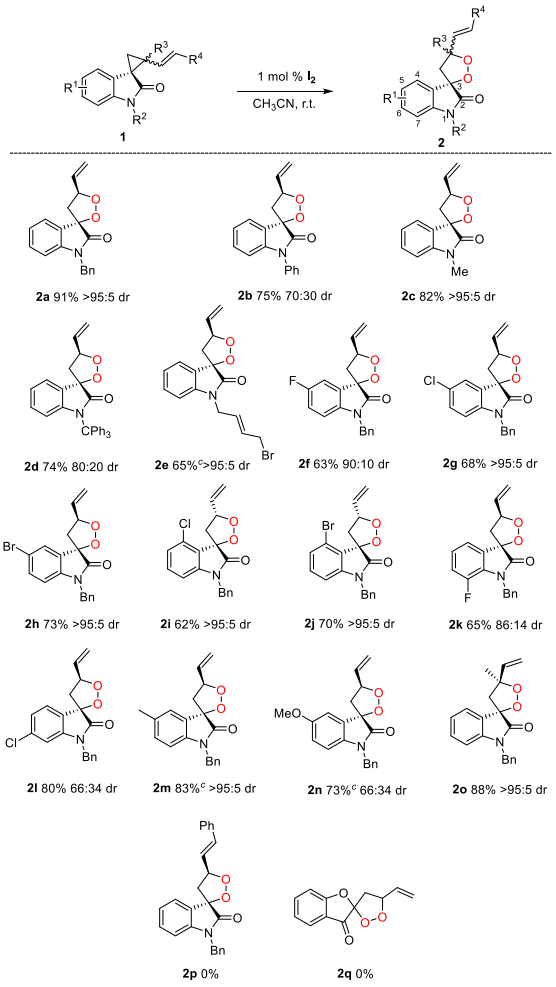


entry	catalyst	catalyst amount %	solvent	time	yield (%)	*dr*[b]
1	I_2	5	Toluene	2 h	30	>95 :5
2	I_2	20	Toluene	1 h	28	>95 :5
3	I_2	10	Toluene	1.5 h	37	>95 :5
4	I_2	1	Toluene	3.5 h	50	>95 :5
5	I_2	0.1	Toluene	7 d	23	>95 :5
6	I_2	1	DMF	7 d	NR[f]	--
7	I_2	1	DMSO	7 d	NR[f]	--
8	I_2	1	C_2H_5OH	3 d	trace	--
9	I_2	1	DCM	3.5 h	46	>95 :5
10	I_2	1	Et_2O	3 d	11	ND[g]
11	I_2	1	THF	3 d	22	ND[g]
12	I_2	1	Acetone	3.5 h	41	>95 :5
13	I_2	1	CH_3NO_2	3.5 h	38	>95 :5
14	I_2	1	CH_3CN	3.5 h	91	>95 :5
15	TEAI[e]	100	CH_3CN	7 d	NR[f]	--
16	SmI_2	100	CH_3CN	5 h	47	>95 :5
17[c]	I_2	1	CH_3CN	5 h	39	>95 :5
18[d]	I_2	1	CH_3CN	1 h	trace	--

[a]Typical conditions: **1a** (0.1 mmol), solvent (1.0 mL), rt, 1h-7d. [b]Determined through ^{1}H NMR spectroscopic analysis. [c]The reaction was performed at 0 °C. [d]The reaction was performed at reflux. [e]TEAI = Tetraethylammonium iodide. [f]NR = No Reaction. [g]ND = not determined.

substituents of spirovinylcyclopropyl oxindoles on the present reaction were examined. As shown in entries **2f-2j**, halogen substituents in C-4 and C-5 position could give excellent diaseteroselectivities (90:10 to >95:5 dr) and acceptable yields (62%-73%). And products **2k** and **2l** could be generated in relatively satisfying diaseteroselectivities (86:14 dr and 66:34 dr) and yields (65% and 80%).In addition, electron-donating groups located in C-5 position on benzene ring, such as methyl and methoxy, could give the desired products in satisfactory yields while a longer reaction time and 5 mol % loading of I_2 were required (**2m**, **2n**). It is worthy to note that the aerobic oxidation product **2o** could also be effectively formed using 1'-benzyl-2-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one as reactant partner. When R^4 was a phenyl group, the reaction became badly and a complex mixture was observed (**2p**). It indicated that the phenyl carried at the end of the double bond

Scheme 2. Substrate Scope[a]

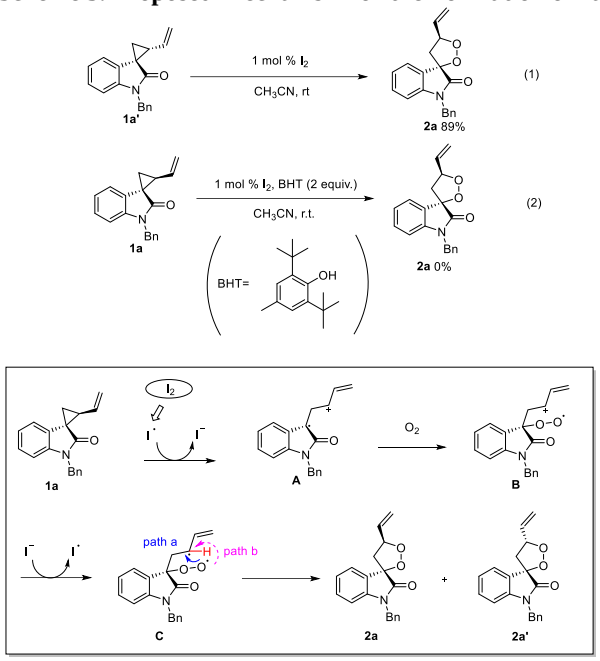


[a]Typical conditions: at room temperature, to a stirred solution of **1** (0.1 mmol) in CH_3CN (1.0 mL) was added 1 mol % I_2. [b]Determined through ^1H NMR spectroscopic analysis. [c]The amount of I_2 was 5 mol %.

might cause free radical transfer and destroy the stability of free radical intermediate C (Scheme 3). And we also tried spirocoumaranone to perform under the same condition, but the corresponding compound **2q** was not also obtained because of a complex mixture, suggesting that the cyclopropane with electron-donating group might hardly conduct this reaction. Besides, to compare the results against previous work, we also used to serveral simple vinyl cyclopropanes, such as (3-vinylcyclopropane-1,2-diyl)bis(phenylmethanone) but there was no reaction, which might indicate that spirovinylcyclopropyl oxindoles have a desirable activity on this reaction under the condition.

To understand this unique reaction pattern, we initially performed the reaction using the stereoisomer of **1a** (**1a'**) in place of **1a** and the target product **2a** was formed in 83% yield and excellent diastereoselectivity (1). Then the reaction was added butylated hydroxytoluene under the standard condition and found that it inhibited the progression of reaction completely (2).According to references and the above results, we proposed the reaction could proceed via a free radical process (Scheme 3).[12] Firstly, iodine radical[13] is generated in the solvent of acetonitrile and then produced the radical cation of **A** via a single-electron transfer step from **1a** to I^-. Subsequently, the attack of molecular dioxygen on the 1,3-radical cation **A** generates the

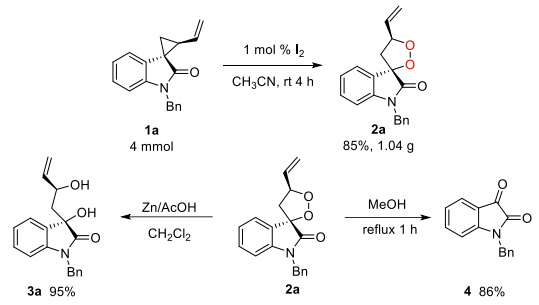
Scheme 3. Proposed Mechanism for the Formation of 2a



Condition[a]	Time	Yield
Dark	30 h	30%
Irradiation	3.5 h	88%

[a]General conditions: at room temperature, to a stirred solution of **1a** (0.1 mmol) in CH_3CN (1.0 mL) was added 1 mol % I_2.

Scheme 4. Scale-up Preparation and Synthetic Transformations of 2a



1,5-radical cation **B** and then undergoes a single-electron transfer from I^-. Finally, the corresponding compound **2a** and it's diastereomer **2a'** could be obtained from free radical intermediate **C** (via path a and b)**.** Besides, the result of control experiments under dark condition and with irradiation indicated iodine radical production rate might have influence on the reaction.

To demonstrate the synthetic potential of this catalytic system, the gram-scale preparation of highly functionalized **2a** was investigated. The reaction of 4 mmol of the starting material (**1a**) proceeded smoothly, delivering the corresponding product **2a** (1.04 g) in a yield of 85%, showing the reaction to be a practical tool for the synthesis of highly functionalized 1,2- dioxolanes (Scheme 4). When 1,2-dioxolane **2a** was treated with zinc metal in acetic acid, the O-O bond underwent reductive cleavage in high yield (95%) to afford 1,3-diol **3a**, which retained its original stereocenters set in the oxygenation reaction.[14a,14b] And hex-5-ene-1,3-diol fragment of **3a** has been reported to be used as intermediate directly during the synthesis of rugulactone, which can inhibit constitutive nuclear factor tor NF-$^{\kappa}$B activity in human lymphoma cell lines.[14c] In Addition, when **2a** was placed in the solvent of MeOH at reflux temperature, 1,2-dioxolane of

2a could be destroyed completely to convert back into **4** 1-benzylindoline-2,3-dione.

In conclusion, we have developed the first molecular iodine-catalyzed aerobic oxidation of spirovinylcyclopropyl oxindole. Various functional groups were well tolerated in the reaction affording the corresponding products in moderate to excellent yields and considerable diastereoselectivities (66:34 dr to >95:5 dr). More importantly, only a small amount of catalyst is required for this reaction to proceed smoothly, which means the less pollution to environment. In addition, the reaction could be scaled up without significant loss of yield, and the synthesized functionalized spiro-1,2-dioxolane could be further transformed into other promising diol compounds.

EXPERIMENTAL SECTION

General information. All reactions were performed in dry solvents and anhydrous conditions. DCM, THF, DMSO and MeCN etc. were freshly distilled over CaH_2 prior to use. All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.25mm SiliCycle silica gel plates and visualized under UV light. NMR spectra of the new product were recorded on Bruker Avance instrument (300 MHz, 400 MHz or 500 MHz for ^{1}H, 75 MHz, 101 MHz or 126 MHz for ^{13}C), calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for ^{1}H and ^{13}C NMR spectra respectively), calibrated to DMSO-d_6 as the internal reference (2.50 and 39.5 ppm for ^{1}H and ^{13}C NMR spectra respectively). ^{1}H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm) and multiplicity. The following abbreviations indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were taken on a Finnigan TSQ Quantum-MS instrument in the electron spray ionization (ESI). All of the spirovinylcyclopropanyl oxindoles (**1a**, **1c**, **1f**, **1g**, **1h**, **1l**, **1m**, **1n** and **1o**) were prepared according to literature procedures.[16] The rest of chemical reagents were obtained from commercial suppliers.

General Procedure for the substrates. (1b, 1d, 1e, 1i-1k)

Step 1: Experimental Procedure for the Synthesis of N-protected isatin derives.

1-Phenylindoline-2,3-dione: To a solution of isatin (4.41 g, 30 mmol) in DCE (150 ml) was added phenylboronic acid (5.49 g, 45 mmol), copper acetate (5.99 g, 30 mmol) and triethylamine (8.35 ml). The resulting mixture was stirred at room temperature for 1.5 h. After isatin was consumed thoroughly, reaction mixture was poured into water, extracted with EtOAc, washed by brine, combined organic layer dried over anhydrous $MgSO_4$, filtered, filtrate concentrated in vacuo to obtain crude product which was directly put to the next step without further purification.

*1-Tritylindoline-2,3-dione:*To a solution of isatin (4.41 g, 30 mmol) in DMF (150 ml) was added NaH (864 mg, 36 mmol, 60% dispersed in mineral oil) portion-wise during half hour at room temperature, stirred for 30 min, and triphenylmethyl bromide (11.64 g, 36 mmol) was added subsequently. The resulting mixture was stirred at room temperature for 2.5 h. After isatin was consumed thoroughly, reaction mixture was poured into sodium chloride solution, and yellow precipitate appeared. Filtration under reduced pressure, residue washed by water and dried by infrared lamp to obtain crude product which was directly put to the next step without further purification.

1-Benzyl isatin derive: To a solution of N-benzyl isatin derive (30 mmol) in DMF (120 ml) was added K_2CO_3 (72 mmol) and benzyl bromide (4.28 ml). The resulting mixture was stirred at room temperature overnight. After isatin derive was consumed thoroughly, reaction mixture was poured into 60 ml ice water and desired precipitate appeared. Filtration under reduced pressure, residue washed by water and dried by infrared lamp to obtain crude product N-protected isatin derive which was directly put to the next step without further purification.

Step2: General Procedure for Spirovinylcyclopropyl Oxindoles.

N-protected isatin derive (21 mmol) and hydrazine hydrate (30 ml) were added to a round bottomed flask in oil bath. Then, the resulting mixture was heated to reflux for 3 h, cooled to room temperature, extracted with EtOAc, combined organic layer dried over anhydrous $MgSO_4$, filtered, filtrate concentrated in vacuo and recrystallized from ethanol/water to obtain N-protected lindolin-2-one in 71% yield. Subsequently, to a solution of N-protected lindolin-2-one (15 mmol) in acetone (45 ml) was added 1,4-dibromobut-2-ene (4.51g, 21 mmol) and K_2CO_3 (6.22 g, 45 mmol) in oil bath. The resulting mixture was heated to reflux until the complete consumption of N-protected lindolin-2-one, cooled to room temperature, filtered, residue washed by ethyl acetate and combined organic layer washed by water and brine in sequence, dried over anhydrous Na_2SO_4, filtered, filtrate concentrated in vacuo and purified by flash chromatography on silica gel (eluent: petroleum ether - ethyl acetate = 30 : 1) to afford spirovinylcyclopropyl oxindole **1**.

(1S,2S)-1'-phenyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**1b)**. 1.02 g, 26% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 2H), 7.54 – 7.49 (m, 2H), 7.48 – 7.42 (m, 1H), 7.24 (td, *J* = 7.7, 1.3 Hz, 1H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.36 (ddd, *J* = 17.2, 10.4, 9.3 Hz, 1H), 5.35 (dd, *J* = 17.2, 1.8 Hz, 1H), 5.21 (dd, *J* = 10.4, 1.7 Hz, 1H), 2.65 (q, *J* = 8.6 Hz, 1H), 2.13 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.08 (dd, *J* = 8.8, 4.7 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, Chloroform-*d*) δ 174.1, 143.2, 135.0, 134.0, 130.3, 129.5, 127.8, 126.7, 126.6, 122.6, 118.2, 117.0, 109.2, 38.0, 33.8, 25.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}NO$ 262.1154; found 262.1157.

(1S,2R)-1'-trityl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**1d**). 1.67 g, 26% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 – 7.42 (m, 6H), 7.32 – 7.23 (m, 9H), 6.94 – 6.82 (m, 3H), 6.39 – 6.30 (m, 1H), 5.89 (ddd, *J* = 16.9, 10.3, 7.8 Hz, 1H), 5.40 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.28 (dd, *J* = 10.3, 1.6 Hz, 1H), 2.62 (q, *J* = 8.0 Hz, 1H), 2.02 (dd, *J* = 9.0, 4.4 Hz, 1H), 1.60 (d, *J* = 3.1 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 174.9, 148.3, 142.7, 134.6, 130.9, 129.2, 128.1, 127.1, 125.6, 122.0, 119.0, 117.3, 114.8, 74.2, 37.9, 34.4, 23.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}NO$ 428.1936; found 428.1940.

(1S,2S)-1'-((E)-4-bromobut-2-en-1-yl)-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**1e**). According to the step 2, isatin (4.41 g, 30 mmol) and hydrazine hydrate (42 ml) were added to a round-bottomed flask in oil bath under reflux temperature for 3 h. After work-up, indolin-2-one was obtained to the further step. Then, the solution of indolin-2-one (4.0 g, 30 mmol) in acetone (90 ml) was added 1,4-dibromobut-2-ene (19.25 g, 90 mmol) and K_2CO_3 (18.66 g, 135 mmol) to a round-bottomed flask in oil bath under reflux temperature until the complete consumption ofsubstrates. After work-up, the crude product was purified by flash chromatography on silica gel (eluent: petroleum ether - ethyl acetate = 30 : 1). 1.53 g, 16% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 (td, *J* = 7.7, 1.2 Hz, 1H),

7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.93 – 6.84 (m, 2H), 6.26 (ddd, *J* = 17.2, 10.3, 9.4 Hz, 1H), 6.02 – 5.75 (m, 2H), 5.27 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.7 Hz, 1H), 4.45 (dd, *J* = 5.2, 1.2 Hz, 2H), 3.98 – 3.90 (m, 2H), 2.54 (td, *J* = 9.0, 7.8 Hz, 1H), 2.06 – 1.92 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 174.4, 142.2, 133.9, 130.4, 129.3, 129.0, 126.8, 122.1, 118.1, 116.9, 108.6, 41.2, 37.4, 33.6, 31.4, 24.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}BrNO$ 318.0415; found 318.0420.

(1S,2R)-1'-benzyl-4'-chloro-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**1i**). 1.12 g, 24% yield. ^1H NMR (500 MHz, DMSO-d_6) δ 7.37 – 7.32 (m, 2H), 7.32 – 7.25 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 10.9, 8.0 Hz, 2H), 6.23 (dt, *J* = 17.2, 9.9 Hz, 1H), 5.40 (dd, *J* = 17.3, 1.8 Hz, 1H), 5.17 (dd, *J* = 10.4, 1.8 Hz, 1H), 4.99 (s, 2H), 3.31 (d, *J* = 8.7 Hz, 1H), 2.68 (dd, *J* = 8.8, 4.7 Hz, 1H), 1.87 (dd, *J* = 7.9, 4.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 173.4, 144.5, 136.7, 133.9, 129.1, 128.7, 128.0, 127.6, 126.6, 124.6, 123.4, 118.4, 108.7, 43.6, 34.7, 32.0, 21.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}ClNO$ 310.0920; found 310.0925.

(1S,2R)-1'-benzyl-4'-bromo-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**1j**). 1.54 g, 29% yield. ^1H NMR (500 MHz, DMSO-d_6) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.14 (dt, *J* = 15.7, 8.0 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.24 (dt, *J* = 17.2, 9.9 Hz, 1H), 5.40 (dd, *J* = 17.3, 1.8 Hz, 1H), 5.18 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.99 (d, *J* = 2.1 Hz, 2H), 3.37 (d, *J* = 9.0 Hz, 1H), 2.75 (dd, *J* = 8.9, 4.7 Hz, 1H), 1.83 (dd, *J* = 8.0, 4.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 173.4, 144.6, 136.7, 133.8, 129.2, 129.0, 127.9, 127.6, 126.6, 125.8, 118.5, 114.6, 109.2, 43.5, 35.3, 31.8, 21.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}BrNO$ 354.0415; found 354.0419.

(1S,2R)-1'-benzyl-7'-fluoro-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**1k**). 1.89 g, 43% yield. ^1H NMR (300 MHz, Chloroform-*d*) δ 7.34 (ddt, *J* = 18.6, 9.1, 4.8 Hz, 5H), 6.95 (dt, *J* = 8.2, 2.2 Hz, 2H), 6.74 (dt, *J* = 5.5, 2.4 Hz, 1H), 5.85 (dt, *J* = 17.8, 9.1 Hz, 1H), 5.41 (d, *J* = 16.8 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.25 – 5.09 (m, 2H), 2.75 (q, *J* = 8.2 Hz, 1H), 2.19 (dt, *J* = 6.6, 3.2 Hz, 1H), 1.75 (dt, *J* = 6.7, 3.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 176.0, 148.7, 146.8, 137.5, 133.0, 128.6, 127.6, 127.5, 122.2, 119.4, 116.9, 115.0, 114.9, 45.8, 36.4, 33.6, 23.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}FNO$ 294.1216; found 294.1219.

General Procedure for Synthesis of spiro-1,2-dioxolane. A mixture of 2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one **1a** (0.1 mmol) and 1 mol % I_2 (0.254 mg) in CH_3CN (1 mL) was placed in an oven-dried 25 mL eggplant type flask containing a magnetic stirrer (400 rpm/min) at room temperature for 10 h. Then, the solvent was removed, the product was purified through silica gel chromatography, eluting with petroleum ether/ethyl acetate (15:2~5:1) to give the desired products **2a**.

(3S,5'S)-1-benzyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2a**) 10 h. 27.9 mg, 91% yield. Yellow oil. IR (KBr, cm^{-1}) 3055, 2931, 2862, 1728, 1612, 1489, 1466, 1366, 1195, 949, 756, 733, 694. ^1H NMR (300 MHz, Chloroform-*d*) : δ 7.46 (dd, *J* = 7.4 Hz, 1.3 Hz, 1H), 7.36 – 7.22 (m, 6H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.21 – 6.05 (m, 1H), 5.55 (dt, *J* = 17.1, 1.0 Hz, 1H), 5.43 (dd, *J* = 10.3, 1.1 Hz, 1H), 5.16 (q, *J* = 7.4 Hz, 1H), 4.99 – 4.82 (dd, 2H), 3.04 (dd, *J* = 7.3, 1.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*): δ 174.1, 144.1, 133.0, 130.8, 126.3, 124.4, 123.4, 121.1, 108.7, 84.4, 84.1, 49.7, 26.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_3$ 308.1208; found 308.1210.

(3S,5'S)-1-phenyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2b**) 24 h. 22.0 mg, 75% yield. Yellow oil. IR (KBr, cm^{-1}) 3043, 2939, 2860, 1735, 1609, 1503, 1465, 1369, 1201, 757, 697. ^1H NMR (300 MHz, Chloroform-*d*): δ 7.55 (t, *J* = 6.7 Hz, 3H), 7.44 (d, J = 7.2 Hz, 3H), 7.38 – 7.26 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 6.6 Hz, 1H), 6.21 – 5.95 (m, 1H), 5.56 (dd, *J* = 17.2 Hz, 5.9 Hz, 1H), 5.44 (t, *J* = 9.6 Hz, 1H), 5.18 (q, J = 7.5 Hz, 1H), 3.44 – 2.74 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.5, 144.2, 133.9, 133.0, 130.7, 129.7, 128.3, 126.3, 124.9, 123.9, 121.0, 120.6, 110.0, 84.2, 83.2, 50.00. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}NO_3$ 294.1052; found 294.1057.

(3S,5'S)-1-methyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2c**) 3 h. 18.9 mg, 82% yield. Yellow oil. IR (KBr, cm^{-1}) 3046, 2947, 2931, 2850, 1733, 1610, 1502, 1464, 1451, 1379, 1278, 1080, 754, 703. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.16 – 6.09 (m, 1H), 5.53 (d, *J* = 17.2 Hz, 1H), 5.42 (d, *J* = 10.3 Hz, 1H), 5.13 (q, *J* = 7.5 Hz, 1H), 3.23 (s, 3H), 2.99 (qd, *J* = 12.4 Hz, 7.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 174.0, 144.1, 133.1, 130.8, 126.4, 124.4, 123.4, 120.9, 120.5, 108.6, 84.0, 49.8, 26.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}NO_3$ 232.0895; found 232.0899.

(3S,5'S)-1-trityl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2d**) 3 h. 34.0 mg, 74% yield. Yellow oil. IR (KBr, cm^{-1}) 3055, 2954, 2853, 1736, 1612, 1466, 1312, 1188, 748, 702. ^1H NMR (400 MHz, Chloroform-*d*): δ 7.52 – 7.46 (m, 6H), 7.44 – 7.40 (m, 1H), 7.32 – 7.23 (m, 9H), 7.03 – 6.96 (m, 2H), 6.33 – 6.28 (m, 1H), 6.10 – 5.98 (m, 1H), 5.50 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.2 Hz, 1H), 5.11 (q, *J* = 7.5 Hz, 1H), 2.94 (d, *J* = 7.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 174.8, 144.3, 141.8, 133.1, 129.3, 127.8, 127.0, 127.0, 124.1, 122.7, 120.9, 120.3, 116.2, 84.4, 83.4, 49.7, 48.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}NO_3$ 460.1834; found 460.1836.

(3S,5'S)-1-((E)-4-bromobut-2-en-1-yl)-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2e**) 7.5 h. 22.8 mg, 65% yield. Yellow oil. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.16 – 6.04 (m, 1H), 6.00 – 5.89 (m, 1H), 5.79 (dt, *J* = 15.4 Hz, 5.5 Hz, 1H), 5.54 (dd, *J* = 17.1 Hz, 5.2 Hz, 1H), 5.43 (dd, *J* = 10.3 Hz, 4.0 Hz, 1H), 5.21 (q, *J* = 6.8 Hz, 1H), 4.36 (d, *J* = 5.5 Hz, 2H), 3.94 (d, *J* = 7.2 Hz, 2H), 3.30 – 2.70 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.8, 143.1, 133.0, 130.8, 130.0, 127.9, 126.1, 124.7, 123.5, 121.0, 120.5, 109.4, 84.1, 49.7, 41.2, 31.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}BrNO_3$ 350.0314; found 350.0318.

(3S,5'S)-1-benzyl-5-fluoro-5'-vinylspiro[indoline-3,3'

[1,2]dioxolan]-2-one (**2f**) 5 h. 20.5 mg, 63% yield. Yellow oil. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.40 – 7.31 (m, 2H), 7.35 – 7.26 (m, 3H), 7.21 (dd, *J* = 7.5 Hz, 2.6 Hz, 1H), 6.96 (td, *J* = 8.8 Hz, 2.6 Hz, 1H), 6.65 (dd, *J* = 8.5 Hz, 4.0 Hz, 1H), 6.18 – 6.09 (m, 1H), 5.55 (dd, *J* = 16.4 Hz, 1.6 Hz, 1H), 5.44 (dt, *J* = 10.4 Hz, 0.8 Hz, 1H), 5.13 (q, *J* = 7.3 Hz, 1H), 4.98 – 4.82 (m, 2H), 3.05 (d, *J* = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.8, 160.5, 158.5, 134.9, 133.1, 129.0, 128.0, 127.3, 121.0, 117.0, 116.9, 112.7, 112.5, 110.4, 83.9, 50.0, 44.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}FNO_3$ 326.1114; found 326.1117.

(3S,5'S)-1-benzyl-5-chloro-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2g**) 5 h. 23.3 mg, 68% yield. Yellow oil. IR (KBr, cm^{-1}) 3086, 2924, 2854, 1728, 1612, 1481, 1435, 1342, 1265, 1172, 1072, 980, 935, 810, 740. ^1H NMR (500 MHz,

Chloroform-*d*): δ 7.47 (d, *J* = 2.2 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.34 – 7.29 (m, 3H), 7.25 (dd, *J* = 8.3 Hz, 2.2 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 6.19 – 6.12 (m, 1H), 5.57 (d, *J* = 17.1 Hz, 1H), 5.46 (d, *J* = 10.3 Hz, 1H), 5.16 (q, *J* = 7.3 Hz, 1H), 4.91 (q, *J* = 15.7 Hz, 2H), 3.06 (d, *J* = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.6, 141.6, 134.8, 133.0, 130.5, 129.0, 128.9, 128.2, 128.0, 127.3, 125.1, 121.0, 110.8, 84.2, 84.0, 49.9, 44.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}ClNO_3$ 342.0819; found 342.0821.

(3S,5'S)-1-benzyl-5-bromo-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2h**) 5 h. 28.2 mg, 73% yield. Yellow oil. ^1H NMR (300 MHz, Chloroform-*d*): δ 7.58 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.26 (m, 6H), 6.60 (dd, *J* = 8.3 Hz, 2.2 Hz, 1H), 6.18 – 6.06 (m, 1H), 5.55 (d, *J* = 17.1 Hz, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 5.14 (q, *J* = 7.8 Hz, 1H), 5.00 – 4.77 (m, 2H), 3.04 (d, *J* = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.5, 142.1, 134.7, 133.4, 133.0, 129.0, 128.6, 128.0, 127.8, 127.3, 121.1, 116.0, 111.2, 84.1, 84.0, 49.9, 44.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}BrNO_3$ 386.0314; found 386.0319.

(3S,5'R)-1-benzyl-4-chloro-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2i**) 4.5 h. 21.2 mg, 62% yield. Yellow oil. IR (KBr, cm^{-1}) 3055, 2939, 2856, 1720, 1612, 1496, 1465, 1373, 1350, 1265, 1087, 948, 756, 686. ^1H NMR (400 MHz, Chloroform-*d*): δ 7.39 – 7.26 (m, 5H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.04 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.64 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.01 (ddd, *J* = 17.2, 10.2, 7.7 Hz, 1H), 5.58 (dt, *J* = 17.1, 1.0 Hz, 1H), 5.47 – 5.37 (m, 2H), 4.89 (s, 2H), 3.34 (dd, *J* = 12.3, 9.3 Hz, 1H), 3.03 (dd, *J* = 12.3, 5.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, Chloroform-*d*): δ 173.9, 144.9, 134.8, 132.0, 131.9, 131.8, 129.0, 128.0, 127.3, 124.7, 122.0, 121.7, 108.3, 85.3, 83.9, 47.4, 44.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}ClNO_3$ 342.0819; found 342.0820.

(3S,5'R)-1-benzyl-4-bromo-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2j**) 1 h. 27.0 mg, 70% yield. Yellow oil. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.38 – 7.26 (m, 5H), 7.22 (dd, *J* = 8.2 Hz, 0.9 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.68 (dd, *J* = 7.9 Hz, 0.9 Hz, 1H), 6.06 – 5.98 (m, 1H), 5.59 (dt, *J* = 17.3 Hz, 1.0 Hz, 1H), 5.50 – 5.41 (m, 2H), 4.89 (d, *J* = 2.4 Hz, 2H), 3.41 (dd, *J* = 12.3 Hz, 9.6 Hz, 1H), 2.97 (dd, *J* = 12.3 Hz, 5.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.5, 142.1, 134.7, 133.5, 132.9, 129.0, 128.6, 128.0, 127.8, 127.3, 121.1, 116.0, 111.21, 84.1, 84.0, 49.9, 44.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}BrNO_3$ 386.0314; found 386.0318.

(3S,5'S)-1-benzyl-7-fluoro-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2k**) 4 h. 21.1 mg, 65% yield. Yellow oil. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.40 – 7.34 (m, 5H), 7.28 (dd, *J* = 5.4 Hz, 3.2 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.19 – 6.12 (m, 1H), 5.56 (dt, *J* = 17.1 Hz, 1.0 Hz, 1H), 5.45 (d, *J* = 10.3 Hz, 1H), 5.15 (q, *J* = 7.3 Hz, 1H), 5.10 – 5.04 (m, 2H), 3.04 (d, *J* = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 173.8, 160.5, 158.5, 134.9, 133.1, 129.0, 128.0, 127.3, 121.0, 117.0, 116.8, 112.8, 112.5, 110.4, 83.9, 50.0, 44.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}FNO_3$ 326.1114; found 326.1116.

(3S,5'S)-1-benzyl-6-chloro-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2l**) 4 h. 27.4 mg, 80% yield. Yellow oil. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.39 (td, *J* = 7.9 Hz, 6.2 Hz, 3H), 7.33 (tt, *J* = 6.9 Hz, 2.8 Hz, 3H), 7.09 (dt, *J* = 7.9 Hz, 1.6 Hz, 1H), 6.75 (dd, *J* = 3.3 Hz, 1.8 Hz, 1H), 6.04 – 5.97 (m, 1H), 5.61 – 5.53 (m, 1H), 5.49 – 5.44 (m, 1H), 5.24 (q, *J* = 7.2 Hz, 1H), 4.96 – 4.84 (m, 2H), 3.36 – 2.67 (m, 2H); $^{13}C\{1H\}$ NMR (75 MHz, Chloroform-d): δ 173.9, 144.9, 134.8, 132.0, 131.9, 131.8, 129.0, 128.0, 127.3, 124.7, 122.0, 121.7, 108.3, 85.3, 83.9, 47.4, 44.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}ClNO_3$ 342.0819; found 342.0823.

(3S,5'S)-1-benzyl-5-methyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2m**) 24 h. 26.6 mg, 83% yield. Yellow oil. ^1H NMR (300 MHz, Chloroform-*d*): δ 7.32 (d, *J* = 5.7 Hz, 6H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.62 (dd, *J* = 8.0 Hz, 2.1 Hz, 1H), 6.20 – 6.07 (m, 1H), 5.55 (d, *J* = 17.2 Hz, 1H), 5.43 (d, *J* = 10.3 Hz, 1H), 5.15 (q, *J* = 7.4 Hz, 1H), 4.97 – 4.81 (m, 2H), 3.10 – 2.96 (m, 2H), 2.33 (d, *J* = 2.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 174.2, 140.8, 135.4, 133.2, 133.1, 131.0, 128.9, 127.8, 127.3, 126.3, 125.3, 120.9, 109.5, 84.6, 84.1, 49.8, 44.0, 21.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}NO_3$ 322.1365; found 322.1368.

(3S,5'S)-1-benzyl-5-methoxy-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2n**) 48 h. 24.6 mg, 73% yield. Yellow oil. ^1H NMR (500 MHz, Chloroform-*d*): δ 7.37 – 7.29 (m, 5H), 7.10 (dd, *J* = 9.4, 2.6 Hz, 1H), 6.79 (ddd, *J* = 8.6, 4.1, 2.6 Hz, 1H), 6.64 (dd, *J* = 8.6, 3.3 Hz, 1H), 6.09 (dddd, *J* = 71.9, 17.2, 10.3, 7.3 Hz, 1H), 5.57 (ddt, *J* = 17.1, 15.9, 1.1 Hz, 1H), 5.49 – 5.41 (m, 1H), 5.25 (dq, *J* = 96.4, 7.2 Hz, 1H), 4.97 – 4.83 (m, 2H), 3.81 (s, 3H), 3.35 – 2.74 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 174.0, 156.6, 136.4, 135.3, 133.2, 133.0, 128.9, 127.8, 127.3, 120.9, 115.2, 111.7, 110.2, 84.0, 83.2, 55.9, 50.0, 44.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}NO_4$ 338.1314； found 338.1317.

(3S,5'S)-1-benzyl-5'-methyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one (**2o**) 24 h. 28.2 mg, 88% yield. Yellow oil. ^1H NMR (300 MHz, Chloroform-*d*): δ 7.48 (dd, *J* = 18.4, 7.4 Hz, 1H), 7.36 – 7.21 (m, 6H), 7.08 (dt, *J* = 12.9, 7.5 Hz, 1H), 6.72 (t, *J* = 6.9 Hz, 1H), 6.29 (ddd, *J* = 34.2, 17.8, 11.1 Hz, 1H), 5.52 (dd, *J* = 17.5, 3.1 Hz, 1H), 5.41 – 5.29 (m, 1H), 5.00 – 4.78 (m, 2H), 3.16 (dd, *J* = 40.1, 12.5 Hz, 1H), 2.86 (dd, *J* = 47.5, 12.9 Hz, 1H), 1.74 (d, *J* = 10.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 174.0, 143.4, 140.9, 139.6, 136.4, 131.2, 129.2, 127.7, 126.6, 125.5, 123.6, 115.6, 110.2, 87.3, 85.0, 54.0, 43.3, 23.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}NO_3$ 322.1365; found 322.1368.

Control Experiment. To a mixture of 1'-benzyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one **1a'** (27.54 mg, 0.1 mmol) in CH_3CN (1 mL) was added 1 mol % I_2 (0.254 mg). The resulting solution was stirred at room temperature until the complete consumption of **1a'**. After removal of solvent, the product was purified through silica gel to give the desired products **2a** in 89% yield. To a mixture of 1'-benzyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one **1a** (27.54 mg, 0.1 mmol) in CH_3CN (1 mL) was added by 1 mol % I_2 (0.254 mg) and BHT (44.1 mg, 2 e.q.). The resulting solution was stirred at room temperature. No desired product was obtained.

To a mixture of 1'-benzyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one **1a** (27.54 mg, 0.1 mmol) in CH_3CN (1 mL) was added 1 mol % I_2 (0.254 mg) under dark condition and with irradiation for 30 h and 3.5 h respectively. Then, the solvent was removed, the product was purified through silica gel chromatography, eluting with petroleum ether/ethyl acetate (15:2~5:1) to give the desired products **2a** in 30% and 88% yield respectively.

Scale-up Experiment. A mixture of 2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one **1a** (4 mmol) and 1 mol % I_2 (10.16 mg) in CH_3CN (40 mL) was placed in an oven-dried 100 mL eggplant type flask containing a magnetic stirrer (500 rpm/min) at room temperature for 4 h. Then, the solvent was removed, the product was purified through silica gel chromatography, eluting

with petroleum ether/ethyl acetate (15:2~5:1) to give the desired products **2a** (1.04 g, 85%).

Synthetic Transformations of 2a. To a mixture of (3S,5'S)-1-benzyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one **2a** (30.74 mg, 0.1 mmol) in MeOH (1 mL) was added sizeable stirrer. The resulting mixture was heated to reflux for 1 h. After removal of solvent, the product was purified through silica gel chromatography (eluent: petroleum ether - ethyl acetate = 5 : 1) to give the **4** 1-benzylindoline-2,3-dione in 86% yield.

To a mixture of (3S,5'S)-1-benzyl-5'-vinylspiro[indoline-3,3'-[1,2]dioxolan]-2-one **2a** (30.74 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) was added zinc powder (325 mg). The resulting mixture was cooled to 0 ºC and acetic acid (1 ml) was added dropwise slowly. Then this mixture was stirred at room temperature for 1.5 h. Filtration under reduced pressure, residue washed by CH_2Cl_2, combined organic layer dried over anhydrous Na_2SO_4, filtered, filtrate concentrated in vacuo and purified by flash chromatography on silica gel (eluent: petroleum ether - ethyl acetate = 3 : 1) to afford **3a** in 95% yield.

(S)-1-benzyl-3-hydroxy-3-((S)-2-hydroxybut-3-en-1-yl)indolin-2-one (**3a**) 29.4 mg, 95% yield. Colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*): δ 7.52 (dd, J = 7.4 Hz, 1.3 Hz, 1H), 7.36 – 7.24 (m, 6H), 7.11 (td, J = 7.6 Hz, 1.0 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.96 – 5.84 (m, 1H), 5.29 (dt, J = 17.2 Hz, 1.4 Hz, 1H), 5.14 (dt, J = 10.4 Hz, 1.3 Hz, 1H), 5.00 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 4.77 – 4.71 (m, 1H), 2.25 (dd, J = 14.7 Hz, 10.2 Hz, 1H), 1.97 (dd, J = 14.7 Hz, 2.9 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*): δ 178.0, 142.0, 140.0, 135.3, 130.5, 129.8, 128.9, 127.8, 127.3, 124.3, 123.3, 115.3, 109.8, 76.0, 69.6, 43.9, 43.5.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
^{1}H and ^{13}C NMR spectra of substrates and products (PDF); Crystallographic data for compound **2a** (CIF)

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Notes

The authors declare no competing financial interest.

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