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Note

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Construction of Bispirooxindole Heterocycles *via* Palladium-Catalyzed Ring-Opening Formal [3+2]-Cycloaddition of Spirovinylcyclopropyl Oxindole and 3-Oxindole Derivatives

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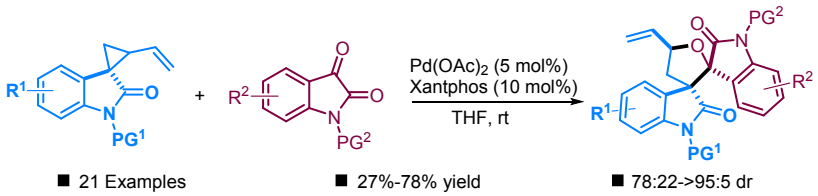
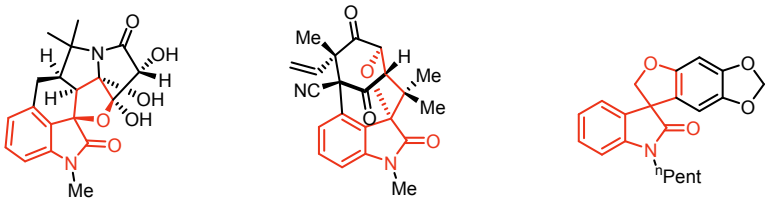
Abstract: A palladium-catalyzed ring-opening *oxo*-formal [3+2]-cycloaddition reaction of novel donor-acceptor spirovinylcyclopropyl oxindole with 3-oxindole is discribed. The developed protocol provides a facile access to *oxo*-bispirooxindole derivatives in good yields (up to 82% yield) with excellent diastereoselectivities (up to 20:1 *dr*).



Spirooxindoles are ubiquitious moieties found in a broad range of natural alkaloids and pharmaceuticals (Scheme 1).[1] These spirocyclic compounds, especially *oxo*-spirooxindoles, have been proven to possess interesting biological activities and attracted increasing synthetic attention over the last decade.[2] For instance, aspergilline A demonstrates an activity against tobacco mosaic virus and an antitumor activity, which was first isolated from fungus *Aspergillus versicolor*.[2a] XEN 907 is a novel pentacyclic spirooxindole showing excellent activities of sodium channel blockers.[2b] Not surprisingly,

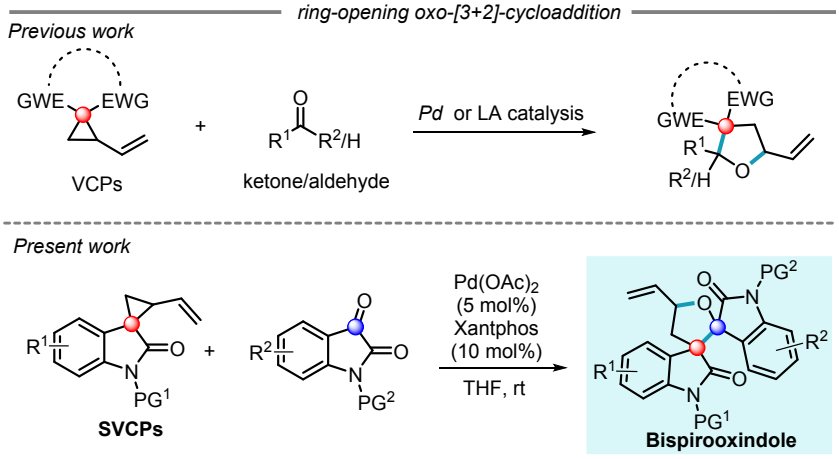
considerable synthetic efforts have been devoted to constructing this type of spirocyclic oxindole systems and varuious strategies including Diels-Alder cycloaddition,[3] [3+2]-cycloaddition[4] and cascade [3+2]-annulation reactions[5] have been established. Despite the emergence of these elegant approaches, exploiting new strategy for the stereoselective construction of spirooxindole derivatives is still highly desirable.[6]



Scheme 1 Examples of pharmaceuticals and natural products containing spirooxindole scafford.

Recently, vinyl cyclopropanes (VCPs) have emerged as a new family of "three-carbon-atom" synthons for the construction of cyclic compounds.[7] These versatile synthons can generate three-carbon dipoles efficiently by releasing the inherent strain energy of donor–acceptor (D-A) cyclopropanes in the presence of Pd(0) or Lewis acid.[8-9] To date, various dipolarophiles such as olefins,[10] aldehydes/ketones,[11] imines[12] and alkynes[13] have been used as the reaction partner to construct five-membered cyclic compounds with VCPs *via* [3+2]-cycloaddition/annulation processes. On the basis of Tsuji's pioneering work[14], many efforts have been directed toward the development of new pathways for the construction of five, six or seven-membered cyclic systems *via* [3+2], [3+3] or [4+3]-cycloaddition/annulation.[7, 15] Kerr[16], Johnson[17] and Shi[11] developed the protocols for the synthesis of five-membered *oxo*-heterocycles respectively. More recently, spirovinylcycpropanes (SVCPs) derived from meldrum's acid and 1,3-indanedione have been employed in the ring-opening [3+2]-reactions to assemble diverse spirocycles.[18] We envisaged that 3-oxindole-derived SVCPs could be employed as the precursor to proceed the ring-opening

[3+2]-reactions with carbonyl scaffold to rapidly access polycyclic spirooxindoles. Herein, we describe a practical palladium-catalyzed protocol to construct dispirooxindole frameworks in good yields and excellent diastereoselectivities *via oxo*-formal [3+2]-cycloaddition of novel spirovinylcyclopropyl oxindole with 3-oxindole derivatives (Scheme 2).

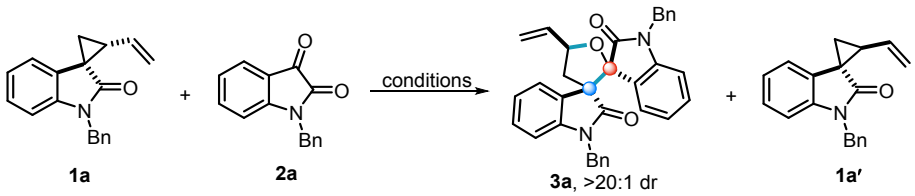


Scheme 2 Synthetic profiles of ring-opening *oxo*-formal [3+2]-cycloaddition of vinylcyclopropane derivatives.

To evaluate the viability of this designed approach to the bispirooxindole scaffold, we initially investigated a model reaction of spirovinylcylopropyl oxindole **1a** with 3-oxindole (**2a**) in the presence of palladium catalysts. To our delight, in the presence of 5 mol% of $Pd(PPh_3)_4$, the desired cycloaddition reaction proceeded smoothly in toluene, delivering bispirooxindole **3a** in 38% yield with >20:1 diastereoselectivity within 6 hours (Table1, entry 1). Then, a variety of phosphine ligands were screened (Table 1, entries 2-4), in which Xantphos afforded the highest yield for bispirooxindole **3a** (55%) and >20:1 dr. Chiral phosphine ligand *S*-BINAP was also tested. Unfortunately, only trace amount of cycloaddition product **3a** was observed though spirocyclopropane **1a** was completely consumed. It is worth noting that spirovinylpropanyl oxindole **1a** was converted into its diastereomer **1a'** in the presence of DPPP, *S*-BINAP, $Pd(PPh_3)_4$ as well as Xantphos without adding isatin derivative **2a**. Then, various palladium salts

were examined and $Pd(OAc)_2$ was proven the optimum catalyst (Table 1, entry 4 *vs* entries 5-7). Subsequently, with the use of $Pd(OAc)_2$/Xantphos as the catalyst, other solvents such as dichloromethane, MeCN, tetrahydrofuran, dioxane, DMF, methanol and toluene were also examined, and tetrahydrofuran (THF) gave the best result in terms of yield (entry 14 *vs* entries 8-13). Accordingly, we decided to manipulate the ratio between spirocyclopropane **1a** and isatin **2a** to further improve the yield of bipspirooxindole derivative **3a**. Unfortunately, the yield of the product was unable to be obviously increased upon varying the amount of spirocyclopropane **1a** or isatin derivative **2a** (Table1, entries 15-17). Finally, introducing the additive including *p*-nitrobenzoic acid and *N,N*-diisopropylethylamine hardly impacted the chemical yield (entries 18-19). Therefore, the optimal reaction conditions were established: using $Pd(OAc)_2$/Xantphos as the catalyst and THF as the solvent to perform the title reaction at room temperature (Table1, entry 14).

Table1 Optimization of the formal [3+2]-cycloaddition of isatin derivative and spirovinylcyclopropanyl oxindole.[a]



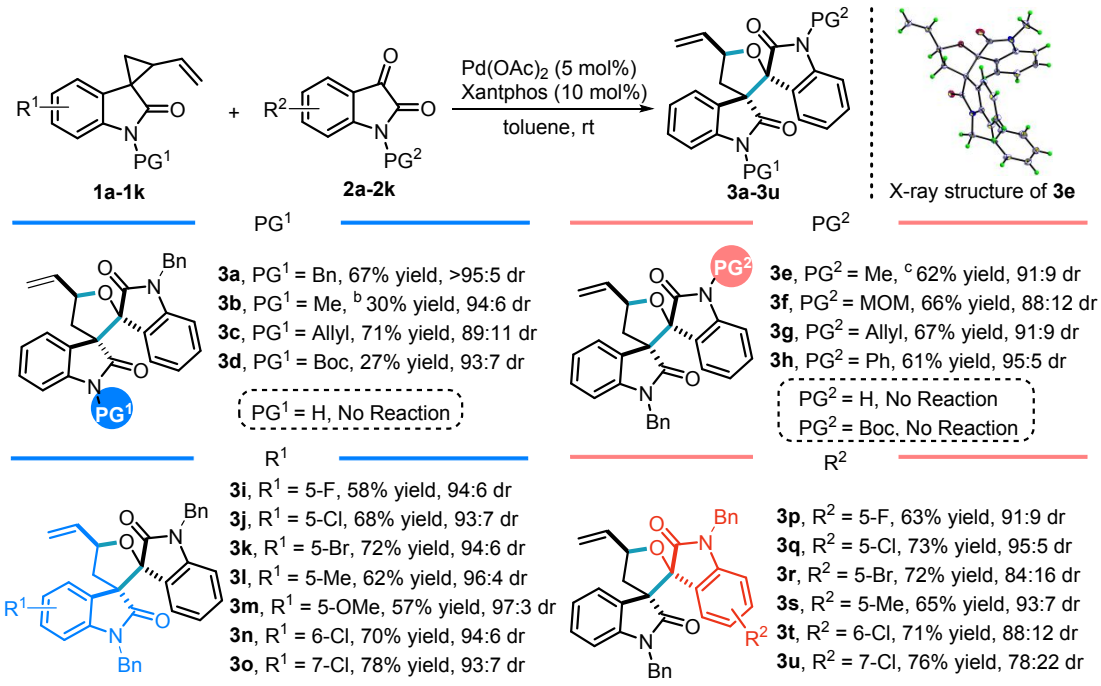
entry	Pd catatlyst	L	solvent	time (h)	yield (%)[b]
1	$Pd(PPh_3)_4$	-	DCE	6	38
2	$Pd(OAc)_2$	DPPP	DCE	24	18
3	$Pd(OAc)_2$	*S*-BINAP	DCE	24	Trace
4	$Pd(OAc)_2$	Xantphos	DCE	6	55
5	$PdCl_2$	Xantphos	DCE	24	-
6	$(PPh_3)_2PdCl_2$	Xantphos	DCE	24	-
7	$Pd_2(dba)_3$	Xantphos	DCE	8	38
8	$Pd(OAc)_2$	Xantphos	CH_2Cl_2	3	57
9	$Pd(OAc)_2$	Xantphos	Toluene	3	52
10	$Pd(OAc)_2$	Xantphos	MeCN	16	48
11	$Pd(OAc)_2$	Xantphos	DMF	12	38

12	$Pd(OAc)_2$	Xantphos	MeOH	12	43
13	$Pd(OAc)_2$	Xantphos	Dioxane	3	63
14	**$Pd(OAc)_2$**	**Xantphos**	**THF**	**3**	**67**
15[c]	$Pd(OAc)_2$	Xantphos	THF	3	68
16[d]	$Pd(OAc)_2$	Xantphos	THF	3	55
17[e]	$Pd(OAc)_2$	Xantphos	THF	3	61
18[f]	$Pd(OAc)_2$	Xantphos	THF	5	55
19[g]	$Pd(OAc)_2$	Xantphos	THF	5	52

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (5 mol%), ligand (10 mol%), solvent (1.0 mL), rt, 3-24 h. [b] Isolated yield. [c] The ratio of **1a**:**2a** = 1:1.5. [d] The ratio of **1a**:**2a** = 1:1. [e] The ra tio of **1a**:**2a** = 1.2:1. [f] 20 mol% of DIPEA was added. [g] 20 mol% of PNBA was added. DCE = 1,2-Dic hloroethane. DIPEA = *N,N*-Diisopropylethylamine. PNBA = *p*-Nitrobenzoic acid.

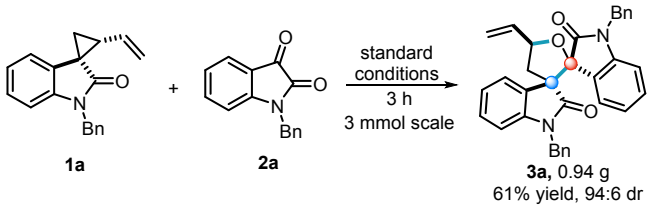
Under the optimized experimental conditions, various substituted isatin derivatives **2** and SVCPs **1** were examined. Firstly, we tested the reactivity of *N*-protected SVCPs as well as unsubstituted SVPCs for the ring-opening [3+2]-reaction. The results revealed that the substitution pattern was crucial for the reaction (Table 2, **3a-3d**). Benzyl protected SVCPs led to best results in terms of yield and diastereoselectivity (67% yield and >20:1 dr), and no desired product was obtained when unsubstituted SVPC was used (Table 2, **3a**). A variety of isatin derivatives were next investigated. In the case of isatin and *N*-Boc isatin, dispirooxindole derivative **3** was unaccessible. On the contrary, the SVCP bearing an electron-donating group such as Benzyl, MOM, Methyl and phenyl group gave moderate to good yields (**3e-3h**). It can be rationalized that the electronic density on nitrogen atom in SVCP and isatins would remarkably affect its reactivity. To explore the influence of the substituents on the reactivity of SVCPs, a series of substituted SVCPs at C5, C6 and C7 position were investigated. In most cases, the corresponding cycloaddition products were obtained in good yields and excellent diastereoselectivities (**3i-3o**). We next turned our attention to evaluate the reactivities of diversely substituted *N*-benzyl isatins in this reaction. The results reveals that various substituted *N*-Benzyl isatins were found to be suitable reaction partners (**3p-3u**). Notably, the *dr* was slightly eroded with the C6/C7 substitution (**3q** *vs* **3t** & **3u**). .

Table 2 Substrate Scope of the title reaction.[a]



[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (5 mol%), Xantphos (10 mol%), THF (1.0 mL), rt, 3 h. [b] **1b'** was used. [c] **1a'** was used.

To evaluate the practicability of the above methodology, a gram scale experiment was perf ormed on 3 mmol scale under the standard conditions (Scheme 3). To our delight, the reactio n worked well and the desired bispirooxindole **3a** was obtained in 61% yield with excellent diastereoselectivity (94:6 dr).

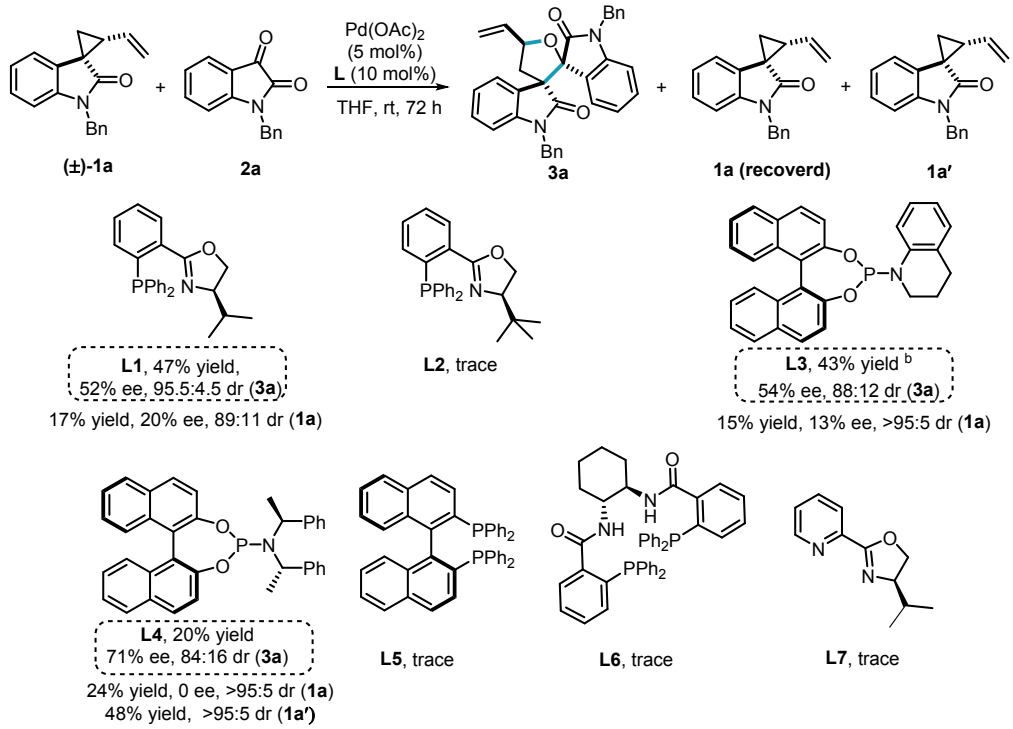


Scheme 3 Gram scale experiment for the synthesis of bispirooxindole **3a**

Besides, we also preliminarily exploited the title reaction in an asymmetric fashion. Pleasingl y, the ^{i}PrPHOX *P,N*-ligand **L1** gave bispirooxindole **3a** in moderate yield (47%) with moderate enantioselectivity (52% ee) and excellent dr (95.5:4.5), with revoverying **1a** in 17% yield and 20% ee with 89:11 dr, which verified the feasibility of chiral induction in this process (Table

3). Phosphoramidite ligand **L3** also gave comparable yield (43%) and enantioselectivity with a slightly lower dr (88:12), however, SVCP **1a** was recovered with lower yield and ee value. Ph osphoramidite ligand **L4,** an efficiemt ligand in the palladium catalytic system, was also tested. Unfortunately, bispirooxindole **3a** was obtained in a lower yield (20%) with a good enantiosele ctivity (71% ee). Meanwhile, the unreacted **1a** was recovered in 24% yield in a racemic form. Additionally, other ligands including *t*BuPHOX (**L2**), *S*-BINAP (**L5**), Trost's ligand (**L6**) and *i*P rOX (**L7**) only gave trace amount of bispirooxindole **3a** and SVCP diastereomer **1a'** was solel y separated.

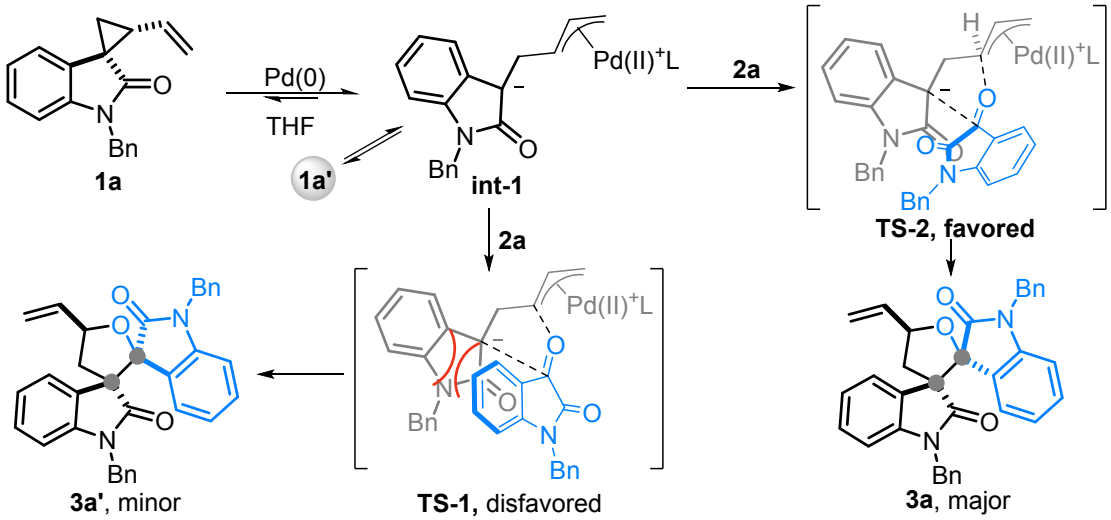
Table 3 Asymmetric ring-opening formal [3+2]-cycloaddition of SVCP and *N*-benzyl oxindole.[a]



[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Pd(OAc)_2$ (5 mol%), ligand (10 mol%), toluene (1.0 mL), rt, 72 h; [b] The reaction time was 6 h.

Based on the obtained results and relevant reports, we proposed a plausible mechanism as shown in Scheme 4. Initially, a Pd-stabilized zwitterionic 1,3-dipole intermediate **int-1** was formed through the palladium-catalyzed ring-opening of SVPC **1a**. Subsequently, intermediate **int-1** and *N*-benzyl isatin **2a** proceeded the formal [3+2] cycloaddition *via* transition state **TS-1** or **TS-2**. It's worth noting that the

intermediate **int-1** could be converted into the thermodynamically stable diastereomer **1a'** *via* an intermolecular cyclization in the absence of suitable dipolarophiles in the reaction system. The ^{1}H NMR monitoring experiments showed that the *dr* of **1a** and **1a'** reached to 38:62 after 3 hours under the standard conditions. Presumably, the severe steric repulsion between two phenyl moieties in transition state **TS-1** led to the formation of dipsirooxindole **3a'** as the minor diastereomer. On the contrary, the favored transition state **TS-2** generated spirooxindole **3a** as the major diastereomer.



Scheme 4 Proposed reaction pathway

In summary, we have developed a facile palladium-catalyzed ring-opening formal [3+2] cycloaddition of novel spirovinylcyclopropyl oxindole with *N*-protected 3-oxindoles, affording *oxo*-bispirooxindole in good yields with excellent diastereoselectivities under mild reaction conditions. This work would broaden the synthetic utility of spirovinylcyclopropanes as verstaile building blocks in the construction of polycyclic spirooxindole systems.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C

NMR data were collected at 75 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. . Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh). All solvents and commercially available reagents were either purified *via* literature procedures or used without further purification. The *N*-protected isatin derivatives were synthesized according to the references.[19]

General procedure for the synthesis of spirovinylcyclopropanyl oxindole 1a-1c, 1f-1l. To a solution of *N*-protected isatin derivative (20 mmol) in methanol (0.1 M) was added hydrazine hydrate (80% aqueous, 3.1 mL, 50 mmol, 2.5 equiv.). The mixture was refluxed for 2 h. Then methanol was removed and the resulting residue was extracted twice with EtOAc and washed with brine. The combined organic phases was dried and concentrated to afford the crude product 2-oxindole derivative, which was used in the next step without further purification. To a solution of 2-oxindole derivative in anhydrous THF was added NaH (2.0 g, 50 mmol, 2.5 equiv., 60% dispersion in mineral oil). The mixture was stirred at room temperature for 5 min and then 1,4-dibromo-2-butene (4.3 g, 20 mmol, 1.0 equiv.) was added to it. The reaction mixture was stirred at room temperature for 10 min before water (10 mL) was added to quench the excess NaH. The residue was extracted with twice with EtOAc and washed with brine. The organic phase was dried and concentrated *in vacuo.* The resulting residue was purified by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford spirovinylcyclopropyl

oxindole **1**.

1′-Benzyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1a**: White solid (2.6 g, 9.4 mmol, 47% yield over two steps); m.p. 97-99 °C; IR (KBr) ν 3078, 2928, 1691, 1617, 1460, 1367, 1178, 906, 754cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.35 (m, 5H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.06-7.08 (m, 1H), 6.94-6.99 (m, 2H), 6.11-6.23 (m, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 11.4 Hz, 1H), 2.68 (q, *J* = 8.7 Hz, 1H), 4.96 (s, 2H), 2 .12 (dd, *J* = 8.7, 4.5 Hz, 1H), 1.87 (dd, *J* = 7.8, 4.5 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 174.8, 142.4, 136.2, 134.0, 130.4, 128.7, 127.5, 127.3, 126.7, 122.0, 118.0, 116.9, 108.9, 44.0, 37.5, 33.7, 24.9; HRMS (TOF-ES+) m/z: calcd for $C_{19}H_{17}NNaO$ $[M+Na]^+$ 298.1208, found 298.1193.

1′-Methyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1b**: White solid (1.5 g, 7.6 mmol, 38% yield over two steps); m.p. 78-80 °C; IR (KBr) ν 3089, 2935, 1694, 1617, 1494, 1425, 1335, 1253, 1133, 906, 814 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 9.0 Hz, 1H), 6.88 (t, *J* = 8.4 Hz, 2H), 6.21-6.34 (m, 1H), 5.26 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.14 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.29 (s, 3H), 2.51 (q, *J* = 8.7 Hz, 1H), 1.92-2.01 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 174.6, 143.0, 134.1, 130.4, 126.8, 122.0, 117.9, 116.7, 37.1, 33.7, 26.5, 24.6; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}NONa$ 222.0895, found 222.0885.

1′-Allyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1c**: White solid (1.3 g, 5.8 mmol, 29% yield over two steps); m.p. 54-58 °C; IR (KBr) ν 2990, 1701, 1611, 1481, 1462, 1362, 1187, 993, 811, 749cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24 (td, *J* = 7.5, 0.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.86-6.91 (m, 2H), 6.27 (td, *J* = 17.1, 9.9 Hz, 1H), 5.52-5.94 (m, 1H), 5.22-5.53 (m, 3H), 5.14 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.42-4.44 (m, 2H), 2.53 (q, *J* = 8.4 Hz, 1H), 1.94-2.03 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 174.5, 142.5, 134.0, 131.9, 130.4, 126.7, 122.0, 118.0, 117.5, 116.8, 108.8, 42.7,

37.4, 33.6, 24.8; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{15}H_{15}NONa$ 248.1051, found 248.1041.

1′-Benzyl--5′-fluoro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1f**: White solid (1.8 g, 6.0 mmol, 30% yield over two steps); m.p. 79-81 °C; IR (KBr) ν 3071, 2993, 1699, 1602, 1484, 1362, 1160, 1008, 923,774 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.25-7.37 (m, 5H), 6.83 (dt, *J* = 8.7, 2.7 Hz, 1H), 6.60-6.69 (m, 2H), 6.24-6.36 (m, 1H), 5.31(dd, *J* = 17.1, 1.5 Hz, 1H), 5.20 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.98 (t, *J* = 16.5 Hz, 2H), 2.54 (d, *J* = 8.7 Hz, 1H), 2 .10 (dd, *J* = 7.8, 4.8 Hz, 1H), 1.99 (dd, *J* = 9.0, 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.5, 159.2 (d, J_{C-F} = 239 Hz), 138.2, 135.9, 133.6, 132.2 (d, J_{C-F} = 9 Hz), 128.8, 127.6, 127.3, 117.3, 112.8 (d, J_{C-F} = 23 Hz), 109.3 (d, J_{C-F} = 8 Hz), 106.3 (d, J_{C-F} = 25.5 Hz), 44.2, 37.9, 34.1 (d, J_{C-F} = 2 Hz), 25.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}NOFNa$ 316.1114, found 316.1110.

1′-Benzyl-5′-chloro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1g**: White solid (1.7 g, 5 mmol, 27% yield over two steps); m.p. 79-80 °C; IR (KBr) ν 3053, 2918, 1701, 1485, 1367, 1280, 1178, 1006, 799, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.25-7.37 (m, 5H), 7.10 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.23-6.35 (m, 1H), 5.31(dd, *J* = 17.1, 1.5 Hz, 1H), 5.20 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.98 (dd, *J* = 17.4, 15.9 Hz, 2H), 2.56 (q, *J* = 8.4 Hz, 1H), 2 .10 (dd, *J* = 8.1, 4.8 Hz, 1H), 2.01 (dd, *J* = 8.7, 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.3, 140.9, 135.8, 133.5, 132.2, 128.8, 127.7, 127.6, 127.3, 126.5, 118.6, 117.4, 109.7, 44.1, 37.9, 33.7, 25.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}NOClNa$ 332.0818, found 332.0809.

1′-Benzyl-5′-bromo-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1h**: White solid (1.3 g, 3.6 mmol, 18% yield over two steps); m.p. 89-91 °C; IR (KBr) ν 3077, 2940, 1691, 1604, 1482, 1367, 1073, 986, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.33 (m, 6H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.22-6.34 (m, 1H), 5.31(dd, *J* = 17.1, 1.2 Hz, 1H), 5.20 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.97 (dd,

J = 18.0, 15.9 Hz, 1H), 2.56 (q, *J* = 8.7 Hz, 1H), 2 .09 (dd, *J* = 7.9, 4.9 Hz, 1H), 2.01 (dd, *J* = 8.8, 4.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.2, 141.3, 135.7, 133.5, 132.6, 129.4, 128.8, 127.7, 127.2, 121.3, 117.5, 114.8, 110.2, 44.1, 37.9, 33.6, 25.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}NOBrNa$ 376.0313, found 376.0312.

1′-Benzyl-5′-methyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1i**: White solid (2.2 g, 7.6 mmol, 38% yield over two steps); m.p. 76-78 °C; IR (KBr) ν 3097, 2983, 1676, 1597, 1494, 1372, 1178, 991, 879, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25-7.36 (m, 5H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.66-6.70 (m, 2H), 6.27-6.39 (m, 1H), 5.29 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.99 (t, *J* = 16.5 Hz, 1H), 2.54 (dd, *J* = 17.1, 8.7 Hz, 1H), 2.33 (s, 3H), 2.06 (dd, *J* = 7.8, 4.7 Hz, 1H), 1.98 (dd, *J* = 8.7, 4.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.8, 140.1, 136.3, 134.2, 131.7, 130.5, 128.7, 127.5, 127.3, 127.0, 118.9, 116.8, 108.6, 44.0, 37.4, 33.7, 24.8, 21.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{20}H_{19}NONa$ 312.1364, found 312.1360.

1′-Benzyl-5′-methoxyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1j**: White solid (1.3 g, 4.3 mmol, 22% yield over two steps); m.p. 99-101 °C; IR (KBr) ν 2920, 2828, 1694, 1494, 1372, 1233, 1170, 1028, 919, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27-7.34 (m, 5H), 6.65-6.71 (m, 2H), 6.49-6.50 (m, 1H), 6.28-6.40 (m, 1H), 5.31 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.98 (t, *J* = 16.2 Hz, 1H), 3.78 (s, 3H), 2.54 (q, *J* = 8.7 Hz, 1H), 2.08 (dd, *J* = 7.5, 4.5 Hz, 1H), 1.98 (dd, *J* = 8.7, 4.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.6, 155.9, 136.3, 136.0, 134.1, 131.8, 128.7, 127.5, 127.3, 116.9, 110.9, 109.2, 105.7, 55.8, 44.1, 37.7, 34.0, 24.9; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{20}H_{19}NO_2Na$ 328.1313, found 328.1299.

1′-Benzyl-6′-chloro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1k**: White solid (1.5 g, 4.9 mmol, 24% yield over two steps); m.p. 90-92 °C; IR (KBr) ν 3027, 2928, 1701, 1614, 1370, 1253, 1175, 1121,

1068, 998 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.26-7.38 (m, 5H), 6.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.75-6.78 (m, 2H), 6.28 (m, 1H), 5.30 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.96 (s, 2H), 2.54 (q, *J* = 8.7 Hz, 1H), 2.08 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.00 (dd, *J* = 8.7, 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 174.7, 143.5, 135.7, 133.6, 132.4, 128.9, 127.7, 127.3, 121.9, 118.9, 117.3, 109.4, 44.1, 37.7, 33.5, 25.0; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}NOClNa$ 332.0818, found 332.0812.

1′-Benzyl-7′-chloro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1l**: White solid (1.1 g, 3.7 mmol, 18% yield over two steps); m.p. 101-103 °C; IR (KBr) ν 3077, 3029, 2958, 1701, 1609, 1455, 1360, 1168, 1013, 909, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.12-7.35 (m, 5H), 7.13 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.22-6.34 (m, 1H), 5.44 (dd, *J* = 19.8, 16.2 Hz, 2H), 5.31 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.20 (dd, *J* = 10.2, 1.5 Hz, 1H), 2.56 (q, *J* = 8.7 Hz, 1H), 2.12 (dd, *J* = 8.1, 4.8 Hz, 1H), 2.03 (dd, *J* = 8.7, 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 175.2, 138.3, 137.9, 133.6, 129.2, 128.5, 127.1, 126.6, 122.9, 117.5, 116.4, 115.3, 45.0, 38.6, 33.6, 25.5; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}NOClNa$ 332.0818, found 332.0811.

General procedure for the synthesis of diastereomer SVCP 1a' and 1b'. To a solution of SVCP (0.2 mmol) in toluene (2 mL) were added $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and Xantphos (11.5 mg, 0.02 mmol). The mixture was stirred at room temperature for 12 h. Then the solvent was removed and purified by column chromatography to afford diasteriomer **1a'** or **1b'**.

1′-Benzyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1a'**: White solid (34.7 mg, 0.13 mmol, 63% yield); m.p. 95-96 °C; IR (KBr) ν 3075, 2944, 1781, 1660, 1443, 1380, 1133, 964 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.29-7.36 (m, 5H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.98-7.05 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.84-5.96 (m, 1H), 5.41 (d, *J* = 17.1 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.03 (dd, *J* = 23.4,

15.6 Hz, 2H), 2.75 (q, *J* = 8.1 Hz, 1H), 2 .18 (dd, *J* = 9.0, 4.5 Hz, 1H), 1.75 (dd, *J* = 7.2, 4.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.3, 143.2, 136.2, 133.4, 128.8, 127.6, 127.4, 126.8, 121.7, 121.1, 118.9, 109.1, 44.2, 36.6, 33.2, 23.3; HRMS (TOF-ES+) m/z: calcd for $C_{19}H_{17}NNaO$ $[M+Na]^+$ 298.1208, found 298.1211.

1′-Methyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one **1b**': White solid (26.3 mg, 13.2 mmol, 66% yield); m.p. 76-78 °C; IR (KBr) ν 3088, 2992, 1733, 1662, 1490, 1356, 1278, 1108, 975 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26-7.31 (m, 1H), 7.04 (dt, *J* = 7.5, 0.9 Hz, 1H), 6.94 (t, *J* = 8.1 Hz, 1H), 5.79-5.39 (m, 1H), 5.33-5.39 (m, 1H), 5.23-5.27 (m, 1H), 3.31 (s, 3H), 2.64 (dd, *J* = 16.5, 7.8 Hz, 1H), 2.08 (dd, *J* = 8.7, 4.5 Hz, 1H), 1.68 (dd, *J* = 7.5, 4.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.1, 144.1, 133.5, 127.5, 126.8, 121.6, 120.9, 118.7, 108.1, 35.4, 33.3, 26.6, 23.0; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}NONa$ 222.0895, found 222.0893.

Experimental procedure for the synthesis of 1′-*t*-butyloxycarbonyl-2-vinylspiro[cyclopropane- 1,3′ -indolin]-2′-one (1d) and 1′-*H*-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (1e). To a solution of 2-nitrobenzoic methylester (3.0 g, 15.4 mmol) in anhydours THF was add NaH (1.8 g, 46.2 mmol, 3.0 equiv., 60% dispersion in mineral oil) in small portions. The mixture was stirred at room temperature for 10 min, then 1,4-dibromo-2-butene (1.0 equiv.) was added. The reaction mixture was refluxed for 6 h and water (10 mL) was added. The resulting mixture was extracted with EtOAc (100 mL×2) and washed with brine (100 mL×2). The combined organic layers was dried, concentrated to yield methyl 2-vinyl-1-phenylcyclopropane carboxylate, which was then used in the next step without further purification. To a solution of methyl 2-vinyl-1-phenylcyclopropane carboxylate in AcOH (30 mL) was added Zn dust (5.0 g, 77 mmol, 5 equiv.) in small portions. The reaction mixture was stirred at room temperature for 30 min and EtOAc (100 mL) was added. The mixture was extracted with EtOAc (100

mL×2) and washed with saturated $NaHCO_3$. The combined organic layers was dried, concentrated and purified by flash column chromatography with PE:EtOAc = 9:1-5:1 to afford spirovinylcyclopropyl oxindole **1e** as a white solid (1.1 g, 6.2 mmol, 40% yield over two steps). m.p. 132-134 °C; IR (KBr) ν 3084, 2851, 1798, 1619, 1474, 1357, 1310, 1196, 1195, 990, 742 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.98 (s, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.96-7.06 (m, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.26 (dt, *J* = 17.2, 9.9 Hz, 1H), 5.28 (d, *J* = 17.1 Hz, 3H), 5.16 (d, *J* = 10.2 Hz, 1H), 2.53 (dd, *J* = 17.1, 8.7 Hz, 1H), 1.95-2.03 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.4, 140.2, 133.8, 130.9, 126.8, 122.0, 118.3, 116.9, 109.4, 37.6, 33.9, 24.8; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{12}H_{11}NONa$ 208.0738, found 208.0731.

To a solution of spirovinylcyclopropyl oxindole (1.0 g, 5.4 mmol) in THF was added DMAP (65.9 mg, 0.54 mmol, 0.1 equiv.) and Boc_2O (1.4 g, 6.5 mmol, 1.2 equiv.) respectively. The reaction mixture was stirred at room temperature for 12 h and the solvent was removed. Then, 3N HCl (10 mL) was added and the mixture was extracted with EA (50 mL×2) and washed with brine (100 mL). the combined organic layers was dried, concentrated and purified by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford spirovinylcyclopropyl oxindole **1d** as a white solid (1.1 g, 3.8 mmol, 61% yield). m.p. 113-115 °C; IR (KBr) ν 3080, 2980, 2930, 1756, 1611, 1467, 1370, 1245, 1150, 998, 846 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.26-7.28 (m, 1H), 7.15-7.18 (m, 1H), 6.84 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.15-6.27 (m, 1H), 5.28 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.2, 1.5 Hz, 1H), 2.50 (q, *J* = 8.7 Hz, 1H), 2.02-2.07 (m, 1H), 1.94-1.96 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ173.0, 149.4, 139.2, 133.3, 127.0, 124.2, 117.7, 114.9, 84.2, 39.5, 34.1, 28.1, 26.3; HRMS (TOF-ES+) m/z: calcd for $C_{17}H_{19}NNaO_3$ $[M+Na]^+$ 308.1263, found 308.1255.

General experimental procedure for the synthesis of bispirooxindole 3. To a solution of SVCP **1**

(0.15 mmol) and isatin derivative **2** (0.1 mmol) in THF (1 mL) was added palladium salt (5 mol%) and ligand (10 mol%). The mixture was stirred at room temperature for the given time. Then the solvent was removed and purified by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford bispirooxindole **3**.

The gram scale experiment for the synthesis of bispirooxindole **3a** was performed with SVCP **1** (4.5 mmol) and *N*-benzyl isatin **2a** (0.3 mmol) in THF (30 mL) under the standard conditions. The desired product **3a** was obtained in 61% yield with 94:6 dr (0.94 g).

5'-Vinyl-1''-benzyl-1-benzyl-dispiro[indoline-3,2'-furan-3',3''-indolin]-2,2''-dione (**3a)**: White solid. (34.3 mg, 0.067 mmol, 67% yield); m.p. 190-193 °C; IR (KBr) ν 3060, 2916, 1709, 1607, 1465, 1367, 1178, 1078, 1028, 998, 762 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.40 (d, J = 7.5 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.13-7.23 (m, 8H), 7.02-7.07 (m, 4H), 6.89 (t, J = 7.2 Hz, 2H), 6.66 (d, J = 7.8 Hz, 2H), 6.23-6.35 (m, 1H), 5.39-5.52 (m, 2H), 5.25 (d, J = 10.5 Hz, 1H), 4.90 (t, J = 15.6 Hz, 2H), 4.69 (dd, J = 15.9, 9.3 Hz, 2H), 3.10 (dd, J = 12.3, 10.2 Hz, 1H), 2.63 (dd, J = 12.6, 6.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.5, 176.0, 143.6, 143.6, 139.4, 136.0, 135.9, 130.9, 129.6, 129.0, 129.0, 127.8, 127.7, 127.6, 126.2, 124.7, 124.4, 123.7, 123.3, 123.1, 118.1, 110.0, 109.8, 86.9, 82.4, 60.4, 43.2, 43.1, 31.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{28}N_2O_3Na$ 535.1998, found 535.1990.

5'-Vinyl-1''-methyl-1-benzyl-dispiro[indoline-3,2'-furan-3',3''-indolin]-2,2''-dione (**3b)**: White solid. (13.1 mg, 0.03 mmol, 30% yield); m.p. 230-233 °C; IR (KBr) ν 3065, 2943, 1719, 1609, 1465, 1345, 1175, 1073, 1028, 934, 752 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.72 (d, J = 6.9 Hz, 1H), 7.21-7.35 (m, 7H), 7.03 (d, J = 7.5 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.50-6.58 (m, 4H), 5.36-5.45 (m, 2H), 5.25 (d, J = 9.6 Hz, 1H), 5.02 (d, J = 15.9 Hz, 1H), 4.61 (d, J = 15.9 Hz, 1H), 3.26 (d, J = 10.8 Hz, 1H), 2.97 (s, 3H), 2.38 (dd, J = 12.0, 6.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz) δ 175.6, 172.5, 143.8,

143.2,139.7, 136.4, 130.8, 129.6, 129.4, 129.0, 127.8, 125.9, 125.5, 123.6, 122.7, 121.8, 118.4, 109.5, 109.3, 87.4, 82.8, 61.2, 43.3, 26.6; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1676.

5'-Vinyl-1"-allyl-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3c)**: White solid. (32.8 mg, 0.071 mmol, 71% yield); m.p. 137-140 °C; IR (KBr) ν 2925, 1721, 1696, 1609, 1465, 1362, 1175, 1111, 996, 983, 924, 762 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.36 (d, J = 7.2 Hz, 1H), 7.13-7.30 (m, 6H), 7.03-7.05 (m, 2H), 6.92 (q, J = 7.2 Hz, 2H), 6.76 (d, J = 7.8 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 6.22-6.34 (m, 1H), 5.54-5.66 (m, 1H), 5.36-5.49 (m, 1H), 5.23 (d, J = 10.2 Hz, 1H), 4.98 (d, J = 10.2 Hz, 1H), 4.88 (d, J = 15.9 Hz, 1H), 4.75 (d, J = 17.4 Hz, 1H), 4.65 (d, J = 15.9 Hz, 1H), 4.37 (dd, J = 6.5, 4.5 Hz, 1H), 4.07 (dd, J = 16.8, 5.4 Hz, 1H), 3.08 (dd, J = 12.6, 10.2 Hz, 1H), 2.57 (dd, J = 12.6, 6.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.4, 175.7, 143.6, 139.5, 135.9, 131.8, 131.0, 129.6, 129.0, 127.8, 127.7, 126.2, 124.6, 124.2, 123.6, 123.1, 118.1, 117.5, 109.9, 109.7, 86.9, 82.4, 60.3, 43.2, 41.8; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{30}H_{26}N_2O_3Na$ 485.1841, found 485.1838.

5'-Vinyl-1"-tert-butoxycarbonyl-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3d)**: White solid. (14.1 mg, 0.027 mmol, 27% yield); m.p. 161-163 °C; IR (KBr) ν 2923, 1761, 1731, 1607, 1465, 1365, 1295, 1145, 981, 919, 838, 744 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.56 (d, J = 8.1 Hz, 1H), 7.29-7.36 (m, 3H), 7.17-7.21 (m, 4H), 7.07 (t, J = 7.8 Hz, 1H), 6.90 – 6.99 (m, 3H), 6.60 (d, J = 7.8 Hz, 1H), 6.24-6.36 (m, 1H), 5.38-5.46 (m, 2H), 5.24 (d, J = 10.2 Hz, 1H), 4.87 (d, J = 15.9 Hz, 1H), 4.57 (d, J = 15.9 Hz, 1H), 3.04 (dd, J = 12.6, 9.9 Hz, 1H), 2.75 (dd, J = 12.6, 6.0 Hz, 1H), 1.55 (s, 9H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz) δ 175.5, 174.6, 148.6, 143.6, 140.0, 139.42, 135.7, 131.4, 129.9, 129.0, 127.8, 127.5, 125.4, 125.1, 124.7, 123.2, 123.0, 122.7, 118.4, 114.7, 110.2, 87.8, 84.3, 83.1, 60.8, 43.2, 28.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{32}H_{30}N_2O_5Na$ 545.2052, found

545.2049.

5'-Vinyl-1"-benzyl-1-methyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3e)**: White solid. (27.0 mg, 0.062 mmol, 62% yield); m.p. 229-231 °C; IR (KBr) ν 2928, 1706, 1604, 1465, 1357, 1235, 1175, 998, 929, 757, 707 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.35 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.8 Hz, 2H), 7.15-7.22 (m, 3H), 7.12 (t, J = 7.8 Hz, 1H), 6.89-7.00 (m, 4H), 6.83 (d, J = 7.8 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 6.21-6.33 (m, 1H), 5.36-5.48 (m, 2H), 5.22 (d, J = 10.8 Hz, 1H), 4.94 (d, J = 15.9 Hz, 1H), 4.66 (d, J = 15.9 Hz, 1H), 3.04 (dd, J = 12.3, 9.9 Hz, 1H), 2.97 (s, 3H), 2.57 (dd, J = 12.6, 6.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.7, 176.4, 144.1, 143.3, 138.7, 135.1, 130.1, 129.1, 128.6, 127.4, 126.9, 126.2, 124.4, 124.3, 123.9, 123.2, 122.6, 117.8, 109.1, 108.1, 87.2, 82.8, 60.8, 43.4, 40.1, 25.8; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1673.

5'-Vinyl-1"-benzyl-1-methoxymethyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3f)**: White solid. (30.7 mg, 0.066 mmol, 66% yield); m.p. 170-173 °C; IR (KBr) ν 3013, 2931, 1706, 1609, 1460, 1360, 1220, 1175, 1098, 919, 769 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.35 (d, J = 7.5 Hz, 1H), 7.27-7.31 (m, 2H), 7.15-7.22 (m, 3H), 7.13 (t, J = 7.7 Hz, 1H), 7.00-7.03 (m, 2H), 6.90-6.98 (m, 3H), 6.61 (d, J = 7.8 Hz, 1H), 6.21 -6.33 (m, 1H), 5.36-5.48 (m, 2H), 5.22 (d, J = 10.7 Hz, 1H), 4.94 (d, J = 16.0 Hz, 1H), 4.66 (d, J = 15.9 Hz, 1H), 3.04 (dd, J = 12.4, 9.9 Hz, 1H), 2.97 (s, 3H), 2.57 (dd, J = 12.5, 6.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 177.2, 176.4, 143.5, 142.7, 138.6, 135.0, 130.4, 129.2, 128.7, 127.4, 126.9, 126.5, 124.7, 124.0, 123.8, 123.7, 122.6, 117.9, 109.6, 109.2, 87.4, 82.8, 72.0, 60.8, 56.5, 43.5, 40.3; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{29}H_{26}N_2O_4Na$ 489.1790, found 489.1791.

5'-Vinyl-1"-benzyl-1-allyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3g)**: White solid. (30.1

mg, 0.067 mmol, 67% yield); m.p. 169-171 °C; IR (KBr) ν 3073, 2921, 1709, 1612, 1465, 1360, 1180, 1118, 991, 933, 754 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.38 (d, J = 7.4 Hz, 1H), 7.11-7.29 (m, 7H), 7.01-7.03 (m, 2H), 6.89-6.97 (m, 2H), 6.74 (d, J = 7.8 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 6.21-6.32 (m, 1H), 5.53-5.58 (m, 1H), 5.37-5.50 (m, 2H), 5.23 (d, J = 10.3 Hz, 1H), 4.90-5.02 (m, 2H), 4.81 (d, J = 17.2 Hz, 1H), 4.68 (d, J = 15.9 Hz, 1H), 4.33 (dd, J = 16.4, 4.3 Hz, 1H), 4.03 (dd, J = 16.4, 5.2 Hz, 1H), 3.05 (dd, J = 12.3, 10.5 Hz, 1H), 2.60 (dd, J = 12.5, 5.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.2, 176.0, 143.5, 139.4, 136.0, 131.6, 130.9, 129.6, 128.9, 127.7, 127.5, 126.1, 124.6, 124.3, 123.7, 123.2, 123.0, 118.1, 117.9, 109.9, 109.7, 86.8, 82.3, 60.5, 43.0, 42.0; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{30}H_{26}N_2O_3Na$ 485.1841, found 485.1839.

5'-Vinyl-1''-benzyl-1-phenyl-dispiro[indoline-3,2'-furan-3',3''-indolin]-2,2''-dione (**3h)**: White solid. (30.3 mg, 0.061 mmol, 61% yield); m.p. 205-208 °C; IR (KBr) ν 3060, 2918, 1709, 1592, 1489, 1360, 1185, 1116, 1073, 939, 747 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.45-7.57 (m, 4H), 7.33 (d, J = 7.4 Hz, 1H), 7.17-7.22 (m, 5H), 7.12 (d, J = 7.5 Hz, 2H), 6.95-7.03 (m, 4H), 6.68 (d, J = 7.8 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 6.22-6.34 (m, 1H), 5.40-5.57 (m, 2H), 5.24 (d, J = 10.3 Hz, 1H), 4.94 (d, J = 15.9 Hz, 1H), 4.70 (d, J = 15.9 Hz, 1H), 3.01-3.08 (m, 1H), 2.64 (dd, J = 12.6, 5.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.4, 176.1, 144.2, 143.5, 138.7, 135.1, 133.8, 130.1, 129.6, 129.3, 128.7, 128.4, 127.4, 126.9, 126.4, 124.8, 124.1, 123.7, 122.7, 118.0, 109.2, 87.4, 83.1, 61.3, 43.6, 39.8; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{33}H_{26}N_2O_3Na$ 521.1841, found 521.1835.

5'-Vinyl-1''-benzyl-5''-flouro-1-benzyl-dispiro[indoline-3,2'-furan-3',3''-indolin]-2,2''-dione (**3i)**: White solid. (30.7 mg, 0.06 mmol, 58% yield); m.p. 148-150 °C; IR (KBr) ν 3063, 2918, 1711, 1612, 1494, 1460, 1170, 1118, 1023, 757, 697 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.41 (d, J = 7.5 Hz, 1H), 7.20-7.22 (m, 7H), 7.02-7.10 (m, 6H), 6.92 (t, J = 7.8 Hz, 1H), 6.65-6.69 (m, 2H), 6.20-6.32 (m, 1H),

5.40-5.52 (m, 2H), 5.25 (d, J = 10.2 Hz, 1H), 4.91-5.00 (m, 2H), 4.68 (t, J = 15.3 Hz, 2H), 3.05-3.12 (m, 1H), 2.68 (dd, J = 12.6, 6.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.3, 175.9, 158.7 (d, $J_{C\text{-}F}$ = 238 Hz), 143.6, 139.8, 139.2, 135.8, 131.1, 129.0, 127.9, 127.8, 127.6, 127.3, 126.3, 125.6, 125.5, 124.1, 123.5, 118.3, 116.1 (d, $J_{C\text{-}F}$ = 24 Hz), 112.8 (d, $J_{C\text{-}F}$ = 26 Hz), 110.8 (d, $J_{C\text{-}F}$ = 8 Hz), 110.2, 86.9, 82.5, 60.6, 43.2, 31.4, 22.5, 14.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}N_2O_3FNa$ 553.1903, found 553.1898.

5'-Vinyl-1"-benzyl-5"-chloro-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3j**): White solid. (37.1 mg, 0.068 mmol, 68% yield); m.p. 157-159 °C; IR (KBr) ν 3065, 3023, 2908, 1711, 1614, 1482, 1345, 1180, 1066, 991, 749, 694 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.39 (d, J = 7.8 Hz, 1H), 7.27-7.34 (m, 2H), 7.18-7.24 (m, 7H), 6.99-7.04 (m, 4H), 6.91 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 6.20-6.32 (m, 1H), 5.40-5.52 (m, 2H), 5.25 (d, J = 11.1 Hz, 1H), 5.03 (d, J = 15.9 Hz, 1H), 4.94 (d, J = 16.2 Hz, 1H), 4.71 (d, J = 15.9 Hz, 1H), 4.60 (d, J = 15.9 Hz, 1H), 3.10 (dd, J = 12.6, 10.2 Hz, 1H), 2.70 (dd, J = 12.6, 6.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.5, 176.1, 143.7, 142.0, 138.5, 134.9, 134.6, 130.4, 129.1, 128.8, 128.8, 128.5, 127.6, 127.5, 127.0, 126.8, 126.4, 125.8, 125.5, 124.2, 123.3, 118.1, 110.2, 109.5, 87.1, 82.8, 60.7, 44.0, 43.6, 40.4; HRMS (TOF-ES+) m/z: $[M+K]^+$ calcd for $C_{34}H_{27}N_2O_3ClK$ 585.1347, found 585.1343.

5'-Vinyl-1"-benzyl-5"-bromo-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3k**): White solid. (42.5 mg, 0.072 mmol, 72% yield); m.p. 182-185 °C; IR (KBr) ν 2945, 2910, 1711, 1649, 1485, 1347, 1185, 1068, 988, 806 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.47-7.48 (m, 1H), 7.37-7.43 (m, 2H), 7.18-7.25 (m, 7H), 6.99-7.05 (m, 4H), 6.90 (t, J = 7.5 Hz, 1H), 6.64 (dd, J = 11.1, 8.7 Hz, 2H), 6.20-6.32 (m, 1H), 5.40-5.52 (m, 2H), 5.25 (d, J = 10.5 Hz, 1H), 5.03 (d, J = 15.9 Hz, 1H), 4.94 (d, J = 15.9 Hz, 1H), 4.70 (d, J = 15.9 Hz, 1H), 4.60 (d, J = 15.9 Hz, 1H), 3.10 (dd, J = 12.6, 10.2 Hz, 1H),

2.70 (dd, J = 12.6, 5.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.5, 176.0, 143.6, 142.5, 138.4, 134.9, 134.6, 132.1, 130.4, 128.9, 128.8, 128.2, 127.6, 126.9, 126.9, 126.8, 126.3, 126.2, 124.2, 123.3, 118.2, 115.9, 110.7, 109.5, 87.1, 82.9, 60.7, 44.0, 43.6, 40.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}N_2O_3BrNa$ 613.1103, found 613.1099.

5'-Vinyl-1"-benzyl-5"-methyl-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3l)**: White solid. (32.6 mg, 0.062 mmol, 62% yield); m.p. 170-173 °C; IR (KBr) ν 3035, 2921, 1704, 1609, 1492, 1357, 1173, 1076, 1026, 806, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (d, J = 7.5 Hz, 1H), 7.28-7.30 (m, 1H), 7.07-7.20 (m, 7H), 6.83-6.92 (m, 6H), 6.41-6.50 (m, 1H), 6.35-6.39 (m, 2H), 5.68 (dd, J = 15.3, 9.3 Hz, 1H), 5.46 (d, J = 17.1 Hz, 1H), 5.30 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 16.2 Hz, 1H), 5.03 (d, J = 15.9 Hz, 1H), 4.61 (d, J = 16.2 Hz, 1H), 4.42 (d, J = 16.2 Hz, 1H), 3.28 (dd, J = 12.6, 10.2 Hz, 1H), 2.60 (dd, J = 12.6, 6.0 Hz, 1H), 2.09 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.9, 176.6, 143.7, 141.1, 138.7, 135.2, 135.0, 132.6, 130.2, 129.3, 128.6, 127.3(3), 127.2(5), 126.9, 126.4, 125.8, 124.6, 124.0, 123.2, 117.9, 109.3, 109.0, 87.3, 82.9, 60.8, 43.7, 43.5, 40.4, 21.0; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{35}H_{30}N_2O_3Na$ 549.2154, found 549.2161.

5'-Vinyl-1"-benzyl-5"-methoxyl-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3m)**: White solid. (30.9 mg, 0.057 mmol, 57% yield); m.p. 177-180 °C; IR (KBr) ν 3030, 2955, 2916, 2841, 1696, 1609, 1494, 1435, 1350, 1302, 1193, 929 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.42 (d, J = 7.5 Hz, 1H), 7.17-7.21 (m, 7H), 6.88-7.04 (m, 6H), 6.75 (dd, J = 8.6, 2.4 Hz, 1H), 6.60 (t, J = 7.3 Hz, 2H), 6.21-6.33 (m, 1H), 5.39-5.52 (m, 2H), 5.24 (d, J = 10.4 Hz, 1H), 4.98 (d, J = 16.2 Hz, 1H), 4.89 (d, J = 15.9 Hz, 1H), 4.67 (t, J = 16.6 Hz, 2H), 3.54 (s, 3H), 3.08 (dd, J = 12.3, 10.1 Hz, 1H), 2.63 (dd, J = 12.5, 6.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.5, 175.8, 155.9, 143.7, 139.4, 136.8, 136.1, 135.8, 131.0, 129.0, 128.9, 127.8, 127.7, 127.5, 127.2, 126.3, 125.0, 124.4, 123.4, 118.1, 113.9,

112.0, 110.3, 110.1, 87.1, 82.4, 60.6, 55.6, 43.2, 43.1; HRMS (TOF-ES+) m/z: $[M+K]^+$ calcd for $C_{35}H_{30}N_2O_4K$ 581.1843, found 581.1841.

5'-Vinyl-1"-benzyl-6"-chloro-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3n)**: White solid. (38.2 mg, 0.07 mmol, 70% yield); m.p. 170-172 °C; IR (KBr) ν 3038, 2921, 1704, 1607, 1492, 1357, 1173, 1073, 811, 756, 692 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.36 (d, J = 7.5 Hz, 1H), 7.22-7.26 (m, 8H), 7.02-7.06 (m, 4H), 6.87-6.92 (m, 2H), 6.78 (s, 1H), 6.72 (d, J = 7.8 Hz, 1H), 6.21-6.33 (m, 1H), 5.39-5.52 (m, 2H), 5.25 (d, J = 9.9 Hz, 1H), 4.86-4.95 (m, 2H), 4.71 (t, J = 13.8 Hz, 2H), 3.03-3.10 (m, 1H), 2.66 (dd, J = 12.3, 5.7 Hz,1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.4, 176.0, 145.1, 143.5, 139.6, 135.9, 135.7, 134.2, 131.1, 129.0, 128.9, 127.9, 127.8, 127.6, 126.1, 124.2, 123.4, 122.8, 122.6, 118.2, 110.1, 110.0, 86.9, 82.4, 60.2, 43.2, 43.1; HRMS (TOF-ES+) m/z: $[M+K]^+$ calcd for $C_{34}H_{27}N_2O_3ClK$ 585.1347, found 585.1355.

5'-Vinyl-1"-benzyl-7"-chloro-1-benzyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3o)**: White solid. (42.5 mg, 0.078 mmol, 78% yield); m.p. 170-172 °C; IR (KBr) ν 3035, 2916, 1714, 1612, 1457, 1345, 1138, 1076, 727, 692 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.34 (d, J = 7.2 Hz, 1H), 7.20-7.26 (m, 8H), 7.08-7.10 (m, 2H), 6.84-6.96 (m, 4H), 6.75 (d, J = 7.8 Hz, 1H), 6.23-6.35 (m, 1H), 5.39-5.50 (m, 2H), 5.25 (d, J = 10.8 Hz, 1H), 5.14 (s, 2H), 4.88 (d, J = 15.6 Hz, 1H), 4.69 (d, J = 15.6 Hz, 1H), 3.09 (dd, J = 12.6, 10.2 Hz, 1H), 2.73 (dd, J = 12.6, 6.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.9, 176.7, 143.5, 139.6, 138.4, 137.1, 135.0, 131.7, 130.4, 128.7, 128.5, 127.5, 127.0, 126.9, 126.8, 126.5, 126.2, 124.1, 123.7, 123.6, 123.5, 118.1, 115.1, 109.2, 87.1, 82.7, 60.2, 44.8, 43.8, 40.8; HRMS (TOF-ES+) m/z: $[M+ Na]^+$ calcd for $C_{34}H_{27}N_2O_3ClNa$ 569.1608, found 569.1600.

5'-Vinyl-1"-benzyl-1-benzyl-5-flouro-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3p)**: White solid. (33.4 mg, 0.063 mmol, 63% yield); m.p. 181-183 °C; IR (KBr) ν 2933, 2514, 1709, 1609, 1492,

1340, 1175, 1028, 884, 752, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45 -7.47 (m, 1H), 7.41 (dd, *J* = 8.1, 2.7 Hz, 1H), 7.12-7.23 (m, 7H), 6.98-7.01 (m, 2H), 6.87-6.91 (m, 3H), 6.79 (dt, *J* = 8.7, 2.7 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.37-6.49 (m, 1H), 6.30 (dd, *J* = 8.6, 4.1 Hz, 1H), 5.65-5.73 (m, 1H), 5.47 (d, *J* = 17.2 Hz, 1H), 5.31 (dd, *J* = 10.1, 1.0 Hz, 1H), 5.05 (dd, *J* = 19.5, 16.0 Hz, 2H), 4.64 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 16.0 Hz, 1H), 3.30 (dd, *J* = 12.7, 10.0 Hz, 1H), 2.60 (dd, *J* = 12.7, 5.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.6, 176.3, 159.2 (d, J_{C-F} = 241 Hz), 143.5, 139.5, 139.4, 138.4, 135.0, 134.6, 129.2, 128.7(4), 128.7(0), 127.6, 127.5, 126.9, 126.4, 126.3, 125.0, 123.6, 123.1, 118.2, 116.5 (d, J_{C-F} = 23 Hz), 114.7 (d, J_{C-F} = 26 Hz), 109.9 (d, J_{C-F} = 8 Hz), 87.0, 83.0, 60.9, 43.9, 43.6, 40.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}N_2O_3FNa$ 553.1903, found 553.1897.

5'-Vinyl-1"-benzyl-1-benzyl-5-chloro-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3q)**: White solid. (39.9 mg, 0.073 mmol, 73% yield); m.p. 181-184 °C; IR (KBr) ν 3063, 2921, 1714, 1607, 1485, 1357, 1128, 1028, 816, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.66 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.07-7.25 (m, 8H), 6.99-7.02(m, 2H), 6.85-6.90 (m, 3H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.36-6.48 (m, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 5.66-5.74 (m, 1H), 5.47 (d, *J* = 17.1 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.15 (d, *J* = 15.8 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.60 (d, *J* = 15.8 Hz, 1H), 4.49 (d, *J* = 16.0 Hz, 1H), 3.29 (dd, *J* = 12.6, 10.0 Hz, 1H), 2.60 (dd, *J* = 12.7, 5.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.4, 176.2, 143.5, 142.1, 138.4, 135.0, 134.5, 130.2, 129.2, 128.9, 128.8, 128.7, 127.6, 126.8(9), 126.8(5), 126.5, 124.9, 123.5, 123.1, 118.2, 110.3, 109.4, 86.8, 83.0, 60.9, 43.9, 43.7, 40.4; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}N_2O_3ClNa$ 569.1608, found 569.1601.

5'-Vinyl-1"-benzyl-1-benzyl-5-bromo-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3r)**: White solid. (42.5 mg, 0.072 mmol, 72% yield); m.p. 190-193 °C; IR (KBr) ν 2921, 2851, 1724, 1709, 1607, 1484, 1357, 1175, 1033, 946, 814, 752 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.55 (d, *J* = 2.1 Hz,

1H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.15-7.30 (m, 8H), 7.00-7.03 (m, 4H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.63-6.68 (m, 2H), 6.20-6.32 (m, 1H), 5.41-5.53 (m, 2H), 5.26 (d, *J* = 10.7 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 15.9 Hz, 1H), 4.68 (d, *J* = 16.2 Hz, 1H), 4.61 (d, *J* = 15.9 Hz, 2H), 3.05 (dd, *J* = 12.4, 10.1 Hz, 1H), 2.68 (dd, *J* = 12.6, 5.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.2, 175.8, 143.5, 143.0, 139.1, 135.9, 135.5, 133.7, 129.8, 129.1, 129.0, 127.9, 127.8, 127.7, 127.3 ,127.0, 124.6, 123.4, 118.5, 115.4, 112.2, 110.0, 86.4, 82.6, 60.8, 43.2, 43.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}N_2O_3BrNa$ 613.1103, found 613.1103.

5'-Vinyl-1"-benzyl-1-benzyl-5-methyl-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3s)**: White solid. (34.2 mg, 0.065 mmol, 65% yield); m.p. 185-188 °C; IR (KBr) ν 2928, 1714, 1694, 1604, 1492, 1437, 1352, 1180, 1071, 1031, 971, 813 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44-7.48 (m, 2H), 7.08-7.24 (m, 7H), 6.84-6.92 (m, 6H), 6.40-6.52 (m, 2H), 6.30 (d, *J* = 8.1 Hz, 1H), 5.65-5.73 (m, 1H), 5.46 (d, *J* = 17.1 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.20 (d, *J* = 16.1 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.52 (dd, *J* = 16.2, 12.3 Hz, 2H), 3.31 (dd, *J* = 12.6, 10.0 Hz, 1H), 2.60 (dd, *J* = 12.6, 6.0 Hz, 1H), 2.11 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 176.8, 176.6, 143.6, 141.2, 138.8, 135.1, 132.9, 130.5, 129.0, 128.7, 128.6, 127.3, 127.1, 127.0, 126.5, 125.0, 124.6, 124.0, 122.9, 117.7, 109.2, 109.0, 87.3, 82.8, 60.9, 43.8, 43.4, 40.3, 20.9; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{35}H_{30}N_2O_3Na$ 549.2154, found 549.2137.

5'-Vinyl-1"-benzyl-1-benzyl-6-chloro-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3t)**: White solid. (38.7 mg, 0.071 mmol, 71% yield); m.p. 181-184 °C; IR (KBr) ν 3028, 2935, 1726, 1709, 1612, 1427, 1370, 1248, 1185, 1071, 939, 816 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.35 (d, *J* = 8.1 Hz, 1H), 7.15-7.28 (m, 8H), 7.01-7.03 (m, 4H), 6.86-6.92 (m, 2H), 6.80 (s, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.21-6.32 (m, 1H), 5.39-5.50 (m, 2H), 5.25 (d, *J* = 9.9 Hz, 1H), 4.95 (d, *J* = 15.9 Hz, 1H), 4.87 (d, *J* =

16.2 Hz, 1H), 4.71 (d, *J* = 15.9 Hz, 1H), 3.01-3.09 (m, 1H), 2.65 (dd, *J* = 12.3, 5.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz) δ 176.6, 175.9, 145.1, 143.6, 139.2, 136.0, 135.5, 135.4, 129.8, 129.1, 128.9, 128.0, 127.8, 127.7, 127.6, 124.6, 123.4, 123.3, 123.2, 123.1, 118.3, 110.3, 109.9, 86.5, 82.6, 60.5, 43.3, 43.0; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}N_2O_3ClNa$ 569.1608, found 569.1609.

5'-Vinyl-1"-benzyl-1-benzyl-7-chloro-dispiro[indoline-3,2'-furan-3',3"-indolin]-2,2"-dione (**3u)**: White solid. (41.5 mg, 0.076 mmol, 76% yield); m.p. 170-173 °C; IR (KBr) ν 3030, 2925, 1726, 1711, 1609, 1450, 1347, 1165, 1135, 1073, 946, 756 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.18-7.23 (m, 8H), 7.03-7.06 (m, 2H), 6.85-6.98 (m, 4H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.20-6.31 (m, 1H), 5.40-5.56 (m, 2H), 5.25 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 4.5 Hz, 1H), 4.94 (d, *J* = 15.9 Hz, 1H), 4.94 (d, *J* = 15.6 Hz, 1H), 3.02-3.09 (m, 1H), 2.66 (dd, *J* = 12.6, 5.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz) δ 177.4, 175.8, 143.5, 139.5, 139.1, 137.3, 136.0, 133.3, 129.9, 129.0, 128.9, 127.8, 127.7, 127.6, 127.4, 126.2, 125.4, 124.8, 124.6, 123.3, 118.4, 114.6, 110.0, 86.2, 82.7, 60.7, 44.8, 43.1; HRMS (TOF-ES+) m/z: $[M+Na]^+$ calcd for $C_{34}H_{27}ClN_2O_3Na$ 569.1608, found 569.1609.

Experimental procedure for the asymmetric formal [3+2]-cycloaddition reaction.

To a solution of SVCP **1a** (0.15 mmol) and isatin **2a** (0.1 mmol) in tuluene was added $Pd(OAc)_2$ (5 mol%) and ligand (10 mol%). The mixture was stirred at room temperature for 6-72 h. Then the solvent was removed and purified by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford bispirooxindole **3a** as a white solid. (10.2 mg, 0.020 mmol, 20% yield, 71% ee, 84:16 dr); $[\alpha]_D^{20}$= -58.6 (c = 0.01 in CH_2Cl_2); HPLC analysis: (CHIRALCEL IG, 30% *i*-propanol/hexane, 0.8 mL/min, UV: 254 nm), t_R = 16.5 min (major), 27.9 min (minor). The unreacted SVCP **1a** was recoverd *via* flash column chromatography (eluting with PE:EtOAc = 19:1-9:1). (7.0 mg, 0.026 mmol, 17% yield, 20%

ee, 89:11 dr); $[\alpha]_D^{20}$= +34.2 (c = 0.01 in CH_2Cl_2); HPLC analysis: (CHIRALCEL AD-H, 20% *i*-propanol/hexane, 1 mL/min, UV: 254 nm), t_R = 20.8 min (major), 25.5 min (minor).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxxx

^{1}H NMR, ^{13}C NMR spectra for all new compounds; NOE spectra for **1b** and **1b'**; HPLC of **1a** and **3a**; X-ray structures of **1g** and **3e**.

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Notes

The authors declare no competing financial interest.

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