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Diastereoselective Synthesis of Tetrahydrospiro[carbazole-1,3′-indolines] via an $InBr_3$-Catalyzed Domino Diels–Alder Reaction

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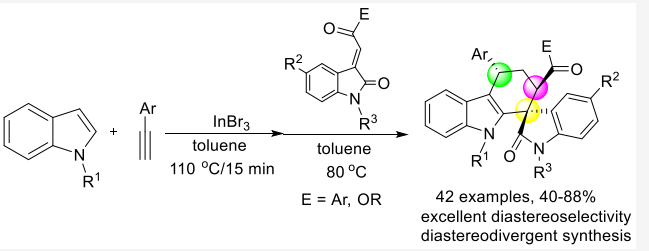
ABSTRACT: A simple $InBr_3$-catalyzed domino reaction of indoles, phenylacetylenes, and various 3-methyleneoxindolines in toluene is described. This reaction not only provided a convenient synthetic protocol for polysubstituted tetrahydrospiro[carbazole-1,3′-indolines] in good yields but also gave completely different diastereoisomers of the tetrahydrospiro[carbazole-1,3′-indolines] to that of the previously reported TfOH-catalyzed one-pot reaction of indoles, acetophenones, and 3-methyleneoxindolines. Additionally, the $InBr_3$-catalyzed reaction of the initially prepared 1,1′-bis(indolyl)phenylethanes with 3-phenacylideneoxindolines also gave the corresponding tetrahydrospiro[carbazole-1,3′-indolines] in good yields and with excellent diastereoselectivity. The reaction mechanism involved the sequential *in situ* generation of reactive dienophilic 3-alkenylindole, the Diels–Alder reaction, and the Lewis acid controlled diastereoisomerization process.



INTRODUCTION

Tetrahydrocarbazole and spirooxindoles scaffolds appear broadly in many biologically active compounds and functional materials.[1,2] Many tetrahydrocarbazole-containing molecules possess a wide range of biological activities such as DNA biosynthesis, Inhibitors in bacteria,[3a] treating potency cigarette smoke-induced acute lung injury in patients[3b] and anxiolytic activity (Figure 1).[3c] The tetrahydrocarbazole derivatives also

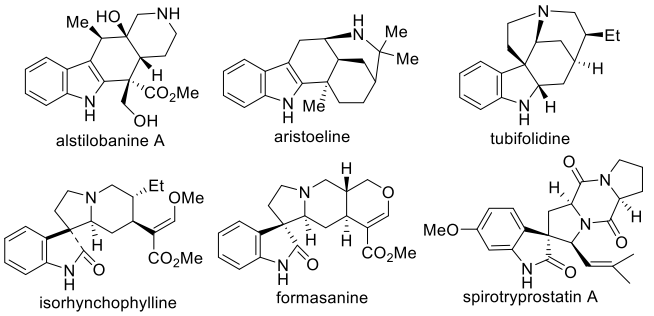


Figure 1. Representative natural products containing tetrahydrocarbazole or spirooxindole scaffolds

show significant inhibitory activity against *Mycobacterium tuberculosis* and are thus of interest as potential new lead compounds for anti-TB active drugs.[3d,f] Nowadays, various synthetic strategies for the preparation of tetrahydrocarbazole derivatives have been exploited.[4−8] Among these sophisticated synthetic methodologies for tetrahydrocarbazoles, the Diels–Alder reaction of 3-vinyl- or 2-vinylindoles with diverse dienophiles has been proven to be the most efficient strategy for the synthesis of many tetrahydrocarbazole derivatives.[9,10] In this respect, the domino reaction of the *in situ* generated 3-vinylindoles and its sequential Diels–Alder reaction showed many advantages such as avoiding time-consuming isolation of the intermediates, minimal waste generation, molecular diversity, and atom-economy. In recent years, many elegant synthetic methodologies with definite regio-, diastereo-, and enantio-control strategies based on the domino Diels–Alder reaction have been successfully developed.[11,12]

For the construction of diverse spiro-carbazole-oxindole systems, the Diels–Alder reaction of vinylindoles with reactive dienophilic 3-methyleneoxindoles has attracted great attention.[13−15] For example, Barbas and co-workers successfully developed C2-symmetric bisthiourea catalyzed Diels–Alder reaction of 3-vinylindolines with 3-methyleneindolinones for enantioselective construction of spiro[carbazole-1,3′-oxindolines] (eq 1 in Scheme 1).[13a] Recently, we found that TfOH catalyzed a one-pot reaction of indoles, acetophenones and 3-methyleneoxindolines in toluene afforded polysubstituted tetrahydrospiro[carbazole-1,3′-indolines] in satisfactory yields with high diastereoselectivity (eq 2 in Scheme 1).[16] For developing the synthetic applications of this efficient synthetic

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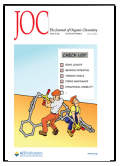

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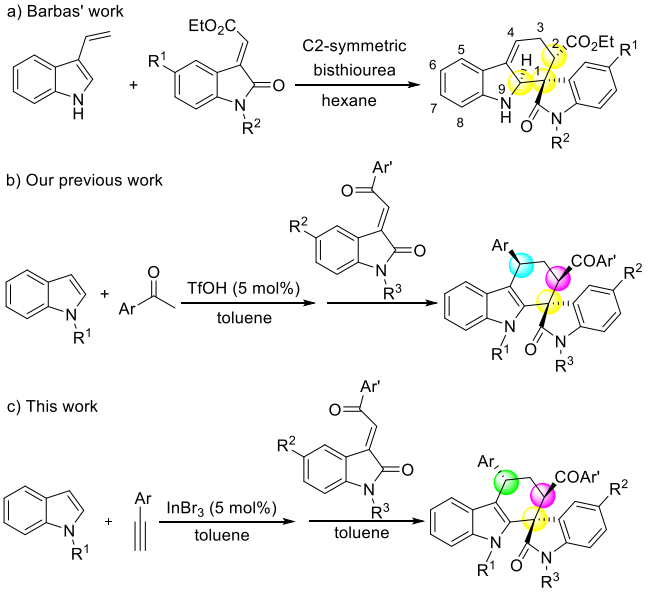
Scheme 1. Diastereoselective Synthesis of Polysubstituted Tetrahydrospiro[carbazole-1,3′-indolines]



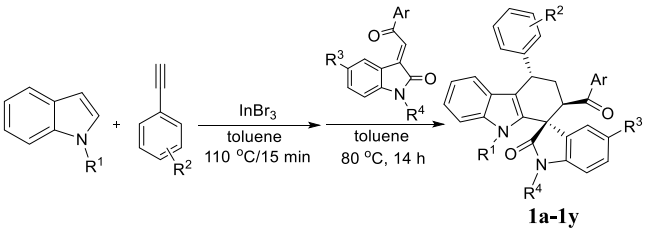
protocol, we noticed that the desired 3-alkenylindoles can also be easily obtained by indium nonafluorobutanesulfonate[17a] or indium tribromide[17b] catalyzed hydroarylation reaction of alkynes with indoles. Thus, the domino reaction of indoles, phenylacetylenes, and (*E*)-3-phenacylideneoxindoles was carried out in toluene in the presence of the readily available Lewis acid $InBr_3$. We found that polysubstituted tetrahydrospiro[carbazole-1,3′-indolines] with the definite configuration could be conveniently prepared in good yields (eq 3 in Scheme 1). This $InBr_3$-catalyzed domino reaction of indoles, phenylacetylenes, and various 3-methyleneoxindolines in toluene not only provided a convenient synthetic protocol for polysubstituted tetrahydrospiro[carbazole-1,3′-indolines] in good yields but also gave the completely different diastereoisomer of the tetrahydrospiro[carbazole-1,3′-indolines] to that of the corresponding TfOH catalyzed one-pot reaction of indoles, acetophenones, and 3-methyleneoxindolines. Herein we wish to reveal this very unprecedented result and the related reactions.

RESULTS AND DISCUSSION

It has been reported that $InBr_3$ catalyzed hydroarylation of alkynes with indoles leading to the synthesis of 3-vinylindoles in good to excellent yields.[17b] Therefore, a one-pot two-step reaction procedure was first employed. After the finishing of the reaction of phenylacetylene and *N*-methylindole in toluene in the presence of $InBr_3$ at 110 °C for 15 min, (*E*)-1-benzyl-5-methyl-3-(2-oxo-2-(4-methoxyphenylethylidene)indolin-2-one was introduced. The second-step reaction was carried out in 110 °C. After workup, the expected polysubstituted spiro[carbazole-1,3′-indoline] **1a** was obtained in a moderate yield. Then, the amount of acid catalyst, molar ratio of the three substrates, reaction temperature, and reaction time of the one-pot two-step reaction procedure were carefully screened. At last, we were pleased to find product **1a** can be obtained in 76% yield by carrying out the second-step reaction at 80 °C for 14 h. The TLC analysis showed that only one product was predominately formed in the reaction system.

With the feasible reaction conditions, the scope of the domino reaction was explored. Various (*E*)-3-phenacylideneoxindoles were employed in the one-pot two-step reaction. The results were summarized in Table 1. All reactions

Table 1. Synthesis of Spiro[carbazole-1,3′-indolines] 1a–1y[a]



1a-1y

entry	comp	R^1	R^2	R^3	R^4	Ar	yield (%)[b]
1	**1a**	Me	H	Me	Bn	*p*-$CH_3OC_6H_4$	76
2	**1b**	Me	H	Me	Bn	*p*-$CH_3C_6H_4$	75
3	**1c**	Me	H	Me	Bn	*p*-ClC_6H_4	68
4	**1d**	Me	H	Me	*n*-Bu	*p*-$CH_3C_6H_4$	54
5	**1e**	Me	H	Me	*n*-Bu	*p*-$CH_3OC_6H_4$	48
6	**1f**	Me	H	Cl	Bn	*p*-$CH_3C_6H_4$	88
7	**1g**	Me	H	H	Bn	*p*-$CH_3OC_6H_4$	76
8	**1h**	Me	H	F	Bn	C_6H_5	89
9	**1i**	Me	H	H	Bn	C_6H_5	65
10	**1j**	H	H	Me	Bn	*p*-ClC_6H_4	68
11	**1k**	H	H	H	Bn	*p*-$CH_3C_6H_4$	76
12	**1l**	H	H	H	Bn	*p*-$CH_3OC_6H_4$	69
13	**1m**	H	H	Cl	Bn	*p*-$CH_3OC_6H_4$	87
14	**1n**	H	H	Cl	Bn	*p*-$CH_3C_6H_4$	77
15	**1o**	H	H	Me	Bn	*p*-$CH_3C_6H_4$	76
16	**1p**	H	H	H	Bn	C_6H_5	68
17	**1q**	Me	*p*-Cl	Me	Bn	*p*-$CH_3C_6H_4$	70
18	**1r**	Me	*p*-Me	H	Bn	*p*-$CH_3C_6H_4$	69
19	**1s**	Me	*m*-Me	H	Bn	*p*-$CH_3C_6H_4$	71
20	**1t**	Me	*p*-OEt	H	Bn	*p*-$CH_3C_6H_4$	50
21	**1u**	Me	*o*-OMe	H	Bn	*p*-$CH_3C_6H_4$	62
22	**1v**	Me	*p*-Ph	H	Bn	*p*-$CH_3C_6H_4$	46
23	**1w**	Me	*p*-Br	H	Bn	*p*-$CH_3C_6H_4$	89
24	**1x**	Me	*p*-F	H	Bn	*p*-$CH_3C_6H_4$	72
25	**1y**	Me	*o*-F	H	Bn	*p*-$CH_3C_6H_4$	71

[a]Reaction conditions: indole (0.7 mmol), phenylacetylene (0.5 mmol), $InBr_3$(5 mol %), toluene (2.0 mL), 110 °C, 15 min; 3-phenacylideneoxindole (0.5 mmol), 80 °C, 14 h. [b]Isolated yields.

proceeded smoothly to give the expected tetrahydrospiro[carbazole-1,3′-indolines] **1a–1i** in moderate to good yields (entries 1–9). Besides 1-methylindole, indole itself also resulted in the spiro products **1j–1p** in good yields (entries 10–16). Additionally, the substituted phenylacetylenes also gave the spiro compounds **1q–1y** in satisfactory yields (entries 17–25). It should be pointed out that the known 1,1′-bis(indolyl)phenylethanes were also produced as a byproduct in very lower yields in some cases.[18] The structures of the obtained products **1a–1y** were fully characterized by various spectroscopies. Because there are three chiral centers in the newly formed cyclohexenyl ring, several diastereoisomers might be formed in the reaction. ^1H and ^{13}C NMR spectra clearly showed that there is only one diastereoisomer in the obtained products. The single-crystal structures of the compounds **1g** (Figure 2), **1h**, **1i**, and **1m** (Figure S1–S4)

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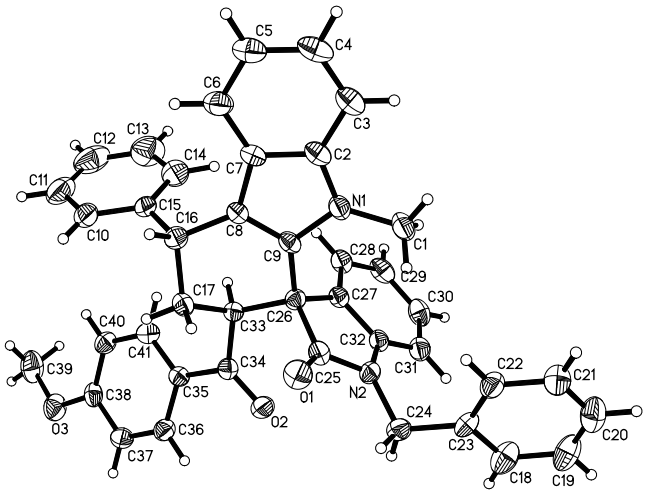


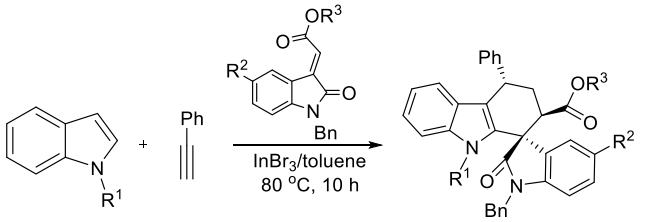
Figure 2. ORTEP drawing (30%) of the crystal structure of the compound **1g**.

were determined by the X-ray diffraction method, in which the 4-aryl group exists on the *trans*-position of the 2-benzoyl group and the 1-phenyl group of the oxindole moiety. It was well-known that the benzoyl group and the phenyl group of the oxindole moiety exist on the *cis*-position in the starting (*E*-)-3-phenacylideneoxindoles.[19] Thus, the relative configuration of these two groups was inversed in the reaction, which means that this reaction must have a diastereoisomerization process. Therefore, based on NMR spectra and single-crystal structures, the spiro compounds **1a**−**1y** were assigned as relative (1,2)-*cis*-(2,4)-*trans*-configuration. Comparing the relative configuration of tetrahydrospiro[carbazole-1,3′-indolines] **1a**−**1y** with that of our previously prepared similar spiro compounds (eq 2 in Scheme 1) by the TfOH-catalyzed a one-pot reaction of indoles, acetophenones, and 3-methyleneoxindolines in toluene,[16a] it is very interesting to find that only the configuration of the 4-aryl group is opposite, while the configurations of the 2-benzoyl group and the 1-phenyl group of the oxindole moiety are the same. Thus, these two reactions successfully provided efficient methods for the diastereoselective synthesis of polysubstituted tetrahydrospiro[carbazole-1,3′-indolines]. These two reactions complemented each other for the synthesis of the spiro compounds with a definite configuration.

With success in the reactions of 3-phenacylideneoxindoles, we turned our attention to another commonly used 3-methyleneoxindole. A couple of alkyl (*E*)-2-(2-oxoindolin-3-ylidene)acetates were employed in the one-pot reaction. The results are summarized in Table 2. The reactions usually resulted in the expected spiro compounds **2a**−**2g** in moderate yields. In each case, the byproducts 1,1′-bis(indolyl)-phenylethanes were also observed. All of the spiro products **2a**−**2g** were characterized by IR, HRMS, and ^{1}H and ^{13}C NMR spectroscopies. The single-crystal structure of compound **2f** (Figure 3) indicated that it has the same relative configuration as that of the spiro compounds **1g**, **1h**, **1i**, and **1m**, in which the 2-ethoxycarbonyl group stands on the *trans*-position of the 4-aryl group and the 1-phenyl group of the oxindole moiety. This result showed that this reaction has the same outcome as the stereochemistry.

In order to study the reaction mechanism, we tried to separate the expected key intermediate 3-vinylindole in the reaction. According to the previous report,[17b] $InBr_3$-catalyzed

Table 2. Synthesis of Spiro[carbazole-1,3′-indolines] 2a−2g[a]



2a-2g

entry	compd	R^1	R^2	OR^3	yield (%)[b]
1	**2a**	H	Cl	OMe	49
3	**2b**	H	H	OEt	48
4	**2c**	H	F	OEt	52
5	**2d**	H	Cl	OEt	50
6	**2e**	H	Me	OEt	46
7	**2f**	Me	Me	OEt	45
8	**2g**	Me	H	OEt	40

[a]Reaction conditions: indole (0.7 mmol), phenylacetylene (0.5 mmol), alkyl (*E*)-2-(2-oxoindolin-3-ylidene)acetate (0.5 mmol), toluene (2.0 mL), $InBr_3$ (5 mol %), 80 °C, 10 h. [b]Isolated yields.

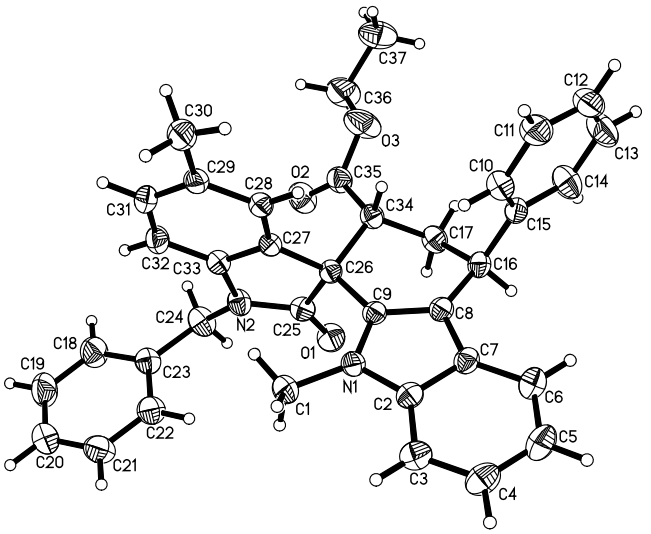


Figure 3. ORTEP drawing (30%) of the crystal structure of the compound **2f**.

hydroarylation of phenylacetylene with *N*-methylindole in toluene gave 1-methyl-3-(1-phenylvinyl)indole in a high yield. However, we could not isolate the desired 3-vinylindole in the reaction. From the $InBr_3$-catalyzed reaction of 1-methylindole with phenylacetylene in toluene, 1,1′-bis(indolyl)phenylethane can be isolated in 74% yield. We envisioned that 1,1′-bis(indolyl)phenylethane might be involved in the formation of spiro compounds. Thus, the reaction of the initially prepared 1,1′-bis(indolyl)phenylethanes with 3-phenacylideneoxindoles was investigated under similar reaction conditions. The results are summarized in Table 3. It can be seen that the same spiro compounds **1c**, **1e**, and **1r** were obtained in slightly higher yields (entries 1−3). Then, 1,1′-bis(indolyl)-phenylethanes **3a**−**3e** derived from *p*-MeO-, *p*-Et-, *p*-*n*-Pro-, *p*-*n*-Bu-, and *p*-NO_2-substituted phenylacetylenes were also employed in the reaction. The expected spiro compounds **4a**−

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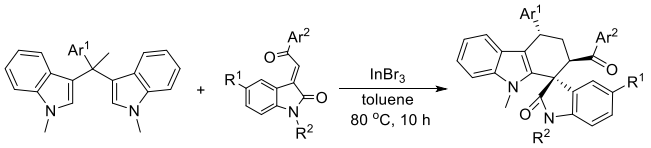
Table 3. Synthesis of Spiro[carbazole-1,3′-indoline]s 4a–4g[a]



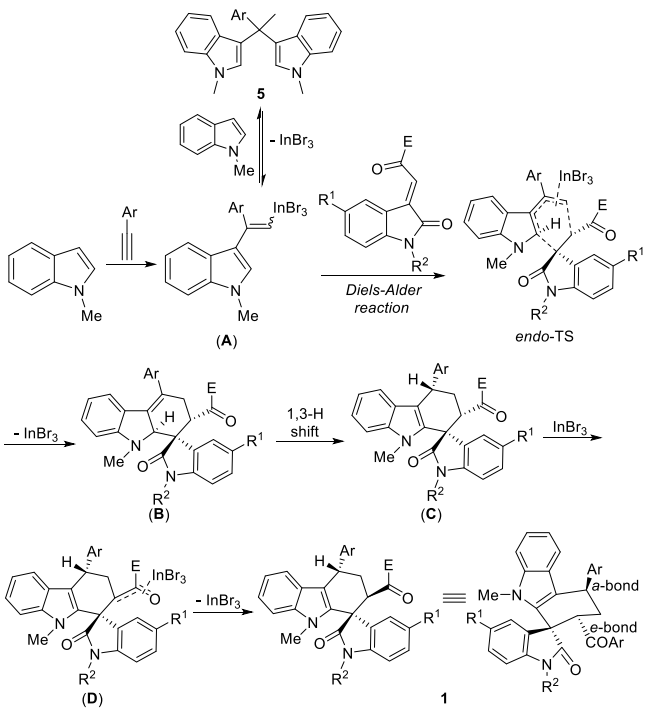
entry	comp	Ar^1	R^1	R^2	Ar^2	yield (%)[b]
1	**1c**	C_6H_5	Me	Bn	*p*-ClC_6H_4	79
2	**1e**	C_6H_5	Me	*n*-Bu	*p*-$MeOC_6H_4$	70
3	**1r**	*p*-MeC_6H_4	H	Bn	*p*-MeC_6H_4	78
4	**4a**	*p*-$MeOC_6H_4$	Me	Bn	*p*-ClC_6H_4	77
5	**4b**	*p*-EtC_6H_4	Me	Bn	*p*-ClC_6H_4	72
6	**4c**	*p*-EtC_6H_4	Cl	Bn	*p*-MeC_6H_4	45
7	**4d**	*p*-*n*-PrC_6H_4	Me	Bn	*p*-ClC_6H_4	77
8	**4e**	*p*-*n*-PrC_6H_4	H	Bn	*p*-$MeOC_6H_4$	79
9	**4f**	*p*-*n*-BuC_6H_4	Me	Bn	*p*-ClC_6H_4	74
10	**4g**	*p*-$NO_2C_6H_4$	Me	Bn	*p*-ClC_6H_4	50

[a]Reaction conditions: 1,1′-bis(indolyl)phenylethane (0.35 mmol), 3-phenacylideneoxindoline (0.35 mmol), toluene (2.0 mL), $InBr_3$ (5 mol %), 80 °C, 10 h. [b]Isolated yields.

4g were produced in satisfactory yields (entries 4–10). The structures of the obtained products **4a–4g** were all established by IR, HRMS, ^1H and ^{13}C NMR spectroscopies. These results not only showed that this reaction has a wide variety but also indicated that 1,1′-bis(indolyl)phenylethane was the key intermediate of the domino reaction.

For explaining the formation of the spiro compounds, a plausible reaction mechanism was brought forward in Scheme 2 on the basis of the obtained results and the previous reports.[16−19] At first, the $InBr_3$-catalyzed reaction of indole with phenylacetylene in toluene gave a $InBr_3$-coordinated 2-alkenylindole (**A**), which could react further with an excess indole to give the isolated 1,1′-bis(indolyl)phenylethane **3**. On the other hand, 1,1′-bis(indolyl)phenylethane **3** might lose an indolyl scaffold under the circumstance of $InBr_3$ to give 2-alkenylindole (**A**).[19b,19c] In fact, they were in the interchange equilibrium in the reaction system. Then, a Diels–Alder reaction of the intermediate (**A**) with 3-phenacylideneoxindole through the *endo*-transition state gave the cyclized intermediate (**B**), which in turn converted to the intermediate (**C**) by the *antarafacial* 1,3-H shift under the catalysis of $InBr_3$. At last, in the catalysis of $InBr_3$, the intermediate (**C**) converted to the more stable diastereoisomer **1** by the epimerization process of the intermediate (**D**). In this reaction process, the Lewis acid $InBr_3$ plays a crucial effect on the diastereoselectivity, which dynamically controlled the formation of the relatively unstable diastereoisomer (Ar on *a*-bond and ArCO on *e*-bonds). Alternatively, the strong Brønsted acid TfOH-catalyzed reaction of indole, acetophenone, and 3-methyleneoxindole to give the most thermodynamically stable diastereoisomer (both Ar and ArCO on *e*-bonds).[16a] DFT calculations showed that the free energy difference of the two diastereoisomers is 4.3 kcal/mol (Supporting Information).

Scheme 2. Plausible Reaction Mechanism



To support the reaction mechanism, some control experiments were carried out. At first, 3-(1-phenylvinyl)indole was initially prepared from the reaction of 3-acetylindole with phenylmagnesium bromide according to the published method.[20] The further reaction with 3-phenacylideneoxindole carried out in the presence of $InBr_3$ gave the spiro compound **1k** in 85% yield (Scheme 3). Second, Diels–Alder reaction of 3-(1-phenylvinyl)indole with 3-phenacylideneoxindole in toluene at 80 °C for 15 h gave the expected intermediate **B1** in 86% yield, which was in turn converted to the spiro compound **1n** in 80% yield by heating in toluene in the presence of $InBr_3$. These results not only clearly showed that 3-alkenylindole token part in the reaction process, but also suggested that $InBr_3$ actually controlled the outcome of the stereochemistry. When the above-obtained tetrahydrospiro-[carbazole-1,3′-indolines] **1b** and **1c** were treated with HOTf in toluene at 80 °C for 30 min. Instead of the formation of the spiro compounds with the conversion of the relative configuration, it was surprised to find that the spiro skeleton was decomposed to give the oxindole-substituted carbazole derivatives **5a** and **5b** in 78% and 81% yields, respectively (Scheme 3). The chemical structures of the carbazoles were confirmed by determining the single-crystal structure **5a** (Figure S6).[16b] It should be pointed out that the spiro compound **5a**, which was previously prepared from the TfOH-catalyzed one-pot reaction of *N*-methylindole, acetophenone, and 3-methyleneoxindoline in toluene, and a plausible formation mechanism was also rationally proposed in our recent work.[16b] On the other hand, it could not be converted to the spiro compound **1n** in toluene in the presence of $InBr_3$. These results indicated that the two diastereoisomers could not be interchanged in the reaction system. Additionally, we tried to dehydrogenated tetrahydrospiro[carbazole-1,3′-indolines] by oxidation with 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) in EtOH or MeCN; complicated mixtures were obtained. These results showed that the obtained spiro compounds were sensitive to the reaction conditions. At last, for industrial applications, the gram-scale reactions were conducted. The spiro compound **1j** could be successfully prepared in 54% yield. It was a little lower than the previous yields in the microscale reactions.

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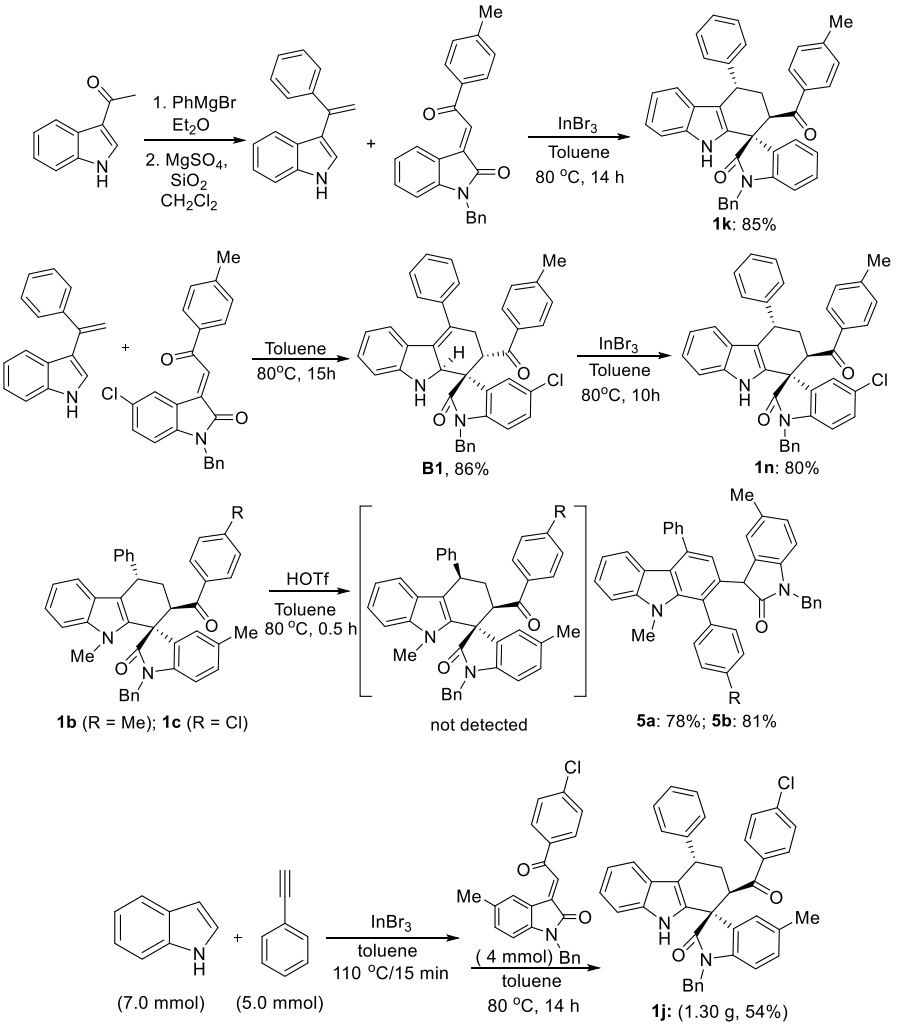
Scheme 3. Control and Gram-Scale Experiments



■ CONCLUSIONS

In summary, we have investigated the $InBr_3$-catalyzed domino reaction of indoles, phenylacetylenes, and 3-methyleneoxindolines. This one-pot two-step reaction successfully provided an efficient synthetic protocol for functionalized tetrahydrospiro[carbazole-1,3′-indolines] in good yields and with high diastereoselectivity. More importantly, this reaction selectively afforded tetrahydrospiro[carbazole-1,3′-indolines] with a different configuration to that of the known reaction. The relative configuration of the spiro compounds was confirmed by the determination of several single-crystal structures. The stereochemistry of the reaction was clearly elucidated. The advantages of this reaction including easily available starting materials, relatively mild conditions, excellent diastereoselectivity, and wide functional group tolerance, which enabled this reaction, might find potential applications in synthetic and medicinal chemistry.

■ EXPERIMENTAL SECTION

Unless noted, the commercial reagents and solvents were used without further purification. 1,1′-Bis(indolyl)phenylethanes[18a] and (*E*)-3-methyleneoxindoles[18b,c] were prepared by the published methods. Melting points were recorded with a micromelting point apparatus and are uncorrected. IR spectra were recorded using a Bruker Tensor 27 spectrometer (KBr disc). The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Varian 400 spectrometer at 400 or 100 MHz. High-resolution mass spectra (HRMS) were recorded in ESI mode using a MicroTOF mass spectrometer. Single-crystal X-ray data were collected with a Bruker Smart APEX-2 CCD diffractometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were monitored by observation under UV light (254 and 365 nm).

1. General Procedure for the Preparation of Tetrahydrospiro[carbazole-1,3′-indolines] 1a−1y. In a 10 mL Shleck tube were added indole (0.7 mmol, 1.4 equiv), phenylacetylene (0.5 mmol, 1.0 equiv), indium bromide (0.025 mmol, 0.05 equiv), and toluene (2.0 mL). The mixture was heated at 110 °C by an oil bath for 15 min. Then, (*E*)-3-phenacylideneoxindole (0.5 mmol, 1.0 equiv) was added, and the solution was heated at 80 °C by an oil bath for 14 h. After removing the solvent, the residue was subjected to column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:20) to afford the desired products **1a−1y**.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-methoxybenzoyl)-9-methyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1a**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 242 mg, 76%, mp 140−142 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.46−7.35 (m, 7H), 7.32−7.30 (m, 1H), 7.26−7.25 (m, 1H), 7.19−7.14 (m, 2H), 7.14−7.08 (m, 2H), 7.00−6.95 (m, 2H), 6.81 (s, 1H), 6.76−6.74 (m, 1H), 6.57−6.55 (m, 2H), 5.33 (d, J = 15.6 Hz, 1H), 4.90 (d, J = 14.8 Hz, 1H), 4.76 (d, J = 4.4 Hz, 1H), 4.36 (d, J = 12.4 Hz, 1H), 3.75 (s, 3H), 3.67−3.59 (m, 1H), 2.83 (s, 3H), 2.22−2.19 (m, 1H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.7, 176.9, 163.3, 144.4, 142.3, 138.3, 136.6, 134.7,

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132.2, 131.1, 130.6, 129.2, 128.7, 128.6, 128.5, 128.4, 128.1, 127.8, 126.6, 126.0, 123.4, 122.1, 119.2, 113.9, 113.5, 109.0, 108.8, 55.4, 49.9, 49.5, 45.1, 37.7, 33.0, 29.5, 21.1; IR (KBr) υ 3697, 3325, 3056, 3024, 1714, 1678, 1599, 1574, 1494, 1467, 1363, 1337, 1262, 1229, 1180, 1165, 1120, 1078, 1026, 986, 930, 876, 840, 810, 775 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{36}N_2NaO_3^+$ ([M + Na]$^+$) 639.2618, found 639.2610.

rel-(1S,2R,4S)-1′-Benzyl-5′,9-dimethyl-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1b**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 233 mg, 75%, mp 224−226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.46−7.42 (m, 2H), 7.39−7.34 (m, 5H), 7.31−7.30 (m, 1H), 7.26−7.25 (m, 1H), 7.18−7.12 (m, 2H), 7.03−7.01 (m, 2H), 6.98−6.95 (m, 2H), 6.90−6.88 (m, 2H), 6.81 (s, 1H), 6.76−6.74 (m, 1H), 5.33 (d, J = 15.2 Hz, 1H), 4.90 (d, J = 15.6 Hz, 1H), 4.76 (d, J = 11.2 Hz, 1H), 3.62 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.84 (s, 3H), 2.27 (s, 3H), 2.24−2.21 (m, 1H), 2.16 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.8, 176.9, 144.3, 143.8, 142.3, 138.3, 136.6, 134.7, 132.5, 132.2, 131.1, 129.3, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 127.7, 126.7, 126.0, 123.5, 122.2, 119.3, 114.0, 109.1, 108.9, 50.1, 49.5, 45.2, 37.7, 32.9, 29.5, 21.5, 21.1; IR (KBr) υ 3699, 3056, 3026, 1715, 1683, 1602, 1495, 1468, 1436, 1364, 1336, 1290, 1232, 1184, 1127, 1076, 1028, 985, 934, 851, 816, 791 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{36}N_2NaO_2^+$ ([M + Na]$^+$) 623.2669, found 623.2672.

rel-(1S,2R,4S)-1′-Benzyl-2-(4-chlorobenzoyl)-5′,9-dimethyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1c**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 218 mg, 68%, mp 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.47−7.43 (m, 2H), 7.39−7.35 (m, 5H), 7.32−7.30 (m, 1H), 7.28−7.27 (m, 1H), 7.19−7.12 (m, 2H), 7.07−7.05 (m, 2H), 7.02−6.97 (m, 4H), 6.80−6.75 (m, 2H), 5.30 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.77 (d, J = 4.4 Hz, 1H), 4.34 (d, J = 12.4 Hz, 1H), 3.63 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.84 (s, 3H), 2.17−2.16 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 176.5, 144.3, 142.2, 139.4, 138.3, 136.4, 134.4, 133.3, 132.3, 130.8, 129.7, 129.4, 128.8, 128.7, 128.6, 128.5, 128.4, 127.7, 126.7, 125.9, 123.3, 122.2, 119.3, 119.2, 113.8, 109.1, 108.8, 50.0, 49.4, 45.1, 37.7, 32.7, 29.5, 21.1; IR (KBr) υ 3702, 3059, 1707, 1688, 1589, 1494, 1469, 1434, 1401, 1367, 1336, 1292, 1201, 1183, 1092, 1013, 987, 929, 875, 842, 814, 763 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{33}ClN_2NaO_2^+$ ([M + Na]$^+$) 643.2123, found 643.2124.

rel-(1S,2R,4S)-1′-Butyl-5′,9-dimethyl-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1d**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 159 mg, 54%, mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.42 (m, 2H), 7.39−7.35 (m, 3H), 7.25−7.24 (m, 1H), 7.17−7.16 (m, 2H), 7.05−7.03 (m, 1H), 7.00−6.96 (m, 3H), 6.88−6.86 (m, 2H), 6.81−6.78 (m, 2H), 4.74 (d, J = 4.8 Hz, 1H), 4.35 (d, J = 12 Hz, 1H), 3.97−3.82 (m, 2H), 3.57 (td, J_1 = 13.2 Hz, J_2 = 5.2 Hz, 1H), 3.00 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 1.93−1.82 (m, 2H), 1.53−1.51 (m, 1H), 1.04 (t, J = 7.6 Hz, 3H), 0.89−0.83 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.6, 176.4, 144.4, 143.6, 142.6, 138.3, 134.8, 132.6, 131.8, 131.2, 129.2, 129.0, 128.6, 128.5, 128.4, 126.6, 126.0, 123.5, 122.1, 119.2, 113.9, 108.8, 108.2, 49.9, 49.4, 40.6, 37.7, 32.8, 29.4, 29.3, 21.5, 21.1, 20.7, 13.9; IR (KBr) υ 3693, 3025, 1711, 1687. 1604, 1495, 1467, 1366, 1341, 1294, 1229, 1192, 1168, 1115, 1013, 982, 929, 849, 814, 771 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{39}H_{38}N_2NaO_2^+$ ([M + Na]$^+$) 589.2825, found 589.2813.

rel-(1S,2R,4S)-1′-Butyl-2-(4-methoxybenzoyl)-5′,9-dimethyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1e**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 145 mg, 48%, mp 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.37 (m, 5H), 7.25−7.16 (m, 3H), 7.08−7.03 (m, 3H), 6.99−6.98 (m, 1H), 6.81−6.78 (m, 2H), 6.55−6.54 (m, 2H), 4.74 (s, 1H), 4.34−4.31 (m, 1H), 3.93−3.88 (m, 2H), 3.75 (s, 3H), 3.62−3.56 (m, 1H), 3.01 (s, 3H), 2.21 (s, 3H), 2.21−2.16 (m, 1H), 1.89−1.85 (m, 2H), 1.06−1.02 (m, 3H), 0.86−0.84 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 176.4, 163.1, 144.4, 142.6, 138.3, 134.8, 131.8, 131.2, 130.5, 129.2, 128.6, 128.5, 128.2, 126.5, 126.0, 123.5, 122.1, 119.2, 113.9, 113.4, 108.7, 108.2, 55.3, 49.8, 49.4, 40.6, 37.7, 32.9, 29.4, 29.3, 21.1, 20.6, 13.8; IR (KBr) υ 3695, 3055, 1710, 1680, 1599, 1495, 1465, 1366, 1342, 1308, 1262, 1228, 1192, 1163, 1115, 1031, 984, 929, 838, 816, 772 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{39}H_{38}N_2NaO_3^+$ ([M + Na]$^+$) 605.2775, found 605.2760.

rel-(1S,2R,4S)-1′-Benzyl-5′-chloro-9-methyl-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1f**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 282 mg, 88%, mp 223−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.57 (m, 2H), 7.47−7.43 (m, 2H), 7.40−7.30 (m, 6H), 7.25−7.25 (m, 1H), 7.21−7.14 (m, 3H), 7.01−6.99 (m, 4H), 6.92−6.90 (m, 2H), 6.80−6.78 (m, 1H), 5.35 (d, J = 15.2 Hz, 1H), 4.90 (d, J = 15.2 Hz, 1H), 4.77 (d, J = 4.4 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 3.60 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.88 (s, 3H), 2.28 (s, 3H), 2.28−2.23 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.6, 176.5, 144.1, 144.0, 143.3, 138.3, 136.0, 133.6, 132.9, 132.2, 129.2, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 127.9, 126.8, 125.9, 123.1, 122.5, 119.4, 119.3, 114.5, 110.2, 108.9, 50.4, 49.5, 45.3, 37.6, 32.8, 29.6, 21.5; IR (KBr) υ 3696, 3029, 1721, 1681, 1605, 1484, 1429, 1364, 1332, 1269, 1230, 1212, 1188, 1168, 1122, 1077, 1027, 985, 926, 874, 847, 818 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{33}ClN_2NaO_2^+$ ([M + Na]$^+$) 643.2123, found 643.2129.

rel-(1S,2R,4S)-1′-Benzyl-2-(4-methoxybenzoyl)-9-methyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1g**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 237 mg, 76%, mp 183−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.44−7.31 (m, 8H), 7.29−7.26 (m, 1H), 7.19−7.12 (m, 3H), 7.09−7.04 (m, 3H), 7.01−6.97 (m, 1H), 6.92−6.86 (m, 2H), 6.56−6.54 (m, 2H), 6.36 (d, J = 15.6 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.77 (d, J = 4.8 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 3.75 (s, 3H), 3.62 (td, J_1 = 12.4 Hz, J_2 = 4.8 Hz, 1H), 2.84 (s, 3H), 2.20 (d, J = 13.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.8, 176.9, 163.3, 144.6, 144.4, 138.3, 136.5, 134.5, 131.1, 130.5, 128.9, 128.8, 128.6, 128.4, 128.1, 127.8, 126.6, 126.0, 122.7, 122.6, 122.2, 119.2, 114.1, 113.5, 109.3, 108.9, 55.4, 50.00, 49.4, 45.2, 37.7, 33.0, 29.5; IR (KBr) υ 3690, 3054, 3026, 1724, 1677, 1600, 1571, 1510, 1487, 1466, 1420, 1359, 1337, 1294, 1267, 1225, 1184, 1167, 1111, 1076, 1031, 985, 907, 876, 840, 804, 776, 753 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{34}N_2NaO_3^+$ ([M + Na]$^+$) 625.2462, found 625.2450.

rel-(1S,2R,4S)-2-Benzoyl-1′-benzyl-5′-fluoro-9-methyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1h**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 272 mg, 89%, mp 143−145 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58−7.58 (m, 2H), 7.43−7.33 (m, 9H), 7.27−7.26 (m, 1H), 7.19−7.10 (m, 6H), 7.00−7.00 (m, 1H), 6.87−6.86 (m, 1H), 6.79−6.79 (m, 2H), 5.35 (d, J = 15.0 Hz, 1H), 4.91 (d, J = 15.0 Hz, 1H), 4.78 (s, 1H), 4.39 (d, J = 12.0 Hz, 1H), 3.62−3.58 (m, 1H), 2.90 (s, 3H), 2.24 (d, J = 13.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.0, 176.5, 159.1 (d, J = 240.8 Hz), 144.0, 140.7, 138.4, 136.1, 134.8, 133.6, 133.1, 132.7 (d, J = 7.3 Hz), 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 126.7, 125.9, 122.5, 119.4, 119.3, 115.3 (d, J = 20.0 Hz), 114.2, 110.8 (d, J = 24.6 Hz), 109.9 (d, J = 7.8 Hz), 108.9, 50.3, 49.8, 45.3, 37.6, 32.6, 29.5; IR (KBr) υ 3697, 3058, 1718, 1687, 1597, 1490, 1470, 1447, 1368, 1332, 1267, 1225, 1201, 1165, 1077, 1025, 986, 969, 937, 873, 847, 815, 791 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{31}FN_2NaO_2^+$ ([M + Na]$^+$) 613.2262, found 613.2253.

rel-(1S,2R,4S)-2-Benzoyl-1′-benzyl-9-methyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1i**): ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 193 mg, 65%, mp 217−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.60 (m, 2H), 7.44−7.25 (m, 10H), 7.19−7.14 (m, 3H), 7.12−7.05 (m, 5H), 7.01−6.97 (m, 1H), 6.92−6.89 (m, 2H), 5.35 (d, J = 15.2 Hz, 1H), 4.93 (d, J = 15.2 Hz, 1H), 4.78 (d, J = 4.8 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 3.60 (td, J_1 = 12.8 Hz, J_2 = 5.2 Hz, 1H), 2.85 (s, 3H), 2.27 (d, J = 13.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.2, 176.8, 144.6, 144.3, 138.4, 136.5, 135.0, 134.4, 133.0, 131.0, 129.0, 128.8, 128.6, 128.4, 128.3, 128.2, 127.8, 126.7, 126.0, 122.7, 122.3, 119.2, 119.1, 114.1, 109.3, 108.9, 50.2, 49.4, 45.2, 37.7, 32.7,

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29.5.; IR (KBr) υ 3056, 3027, 1718, 1682, 1608, 1484, 1465, 1369, 1340, 1296, 1267, 1217, 1187, 1169, 1105, 1078, 1028, 984, 952, 924, 907, 869, 834, 790 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{32}N_2NaO_2^+$ ([M + Na]$^+$) 595.2356, found 595.2349.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-chlorobenzoyl)-5′-methyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1j**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 213 mg, 68%, mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 2H), 7.48−7.44 (m, 2H), 7.40−7.36 (m, 5H), 7.33−7.26 (m, 2H), 7.17−7.15 (m, 3H), 7.12−7.12 (m, 4H), 7.02−6.99 (m, 2H), 6.77−6.75 (m, 2H), 5.25 (d, J = 15.6 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.76 (d, J = 5.2 Hz, 1H), 4.35 (d, J = 11.6 Hz, 1H), 3.84 (td, J_1 = 12.8 Hz, J_2 = 5.6 Hz, 1H), 2.31 (d, J = 13.6 Hz, 1H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 197.1, 177.1, 177.0, 144.1, 141.5, 139.5, 136.7, 136.6, 134.1, 133.0, 132.3, 130.6, 129.9, 129.5, 128.7, 128.5, 128.4, 127.9, 127.8, 126.9, 123.3, 122.6, 119.8, 119.4, 113.1, 110.9, 109.4, 48.9, 48.2, 44.5, 37.4, 33.3, 21.1; IR (KBr) υ 3698, 3439, 3323, 3058, 3026, 1713, 1589, 1495, 1454, 1400, 1342, 1288, 1210, 1185, 1092, 1027, 1011, 991, 928, 873, 840, 809, 779 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{31}ClN_2NaO_2^+$ ([M + Na]$^+$) 629.1966, found 629.1977.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1k**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 226 mg, 76%, mp 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.55 (m, 2H), 7.45−7.27 (m, 8H), 7.24−7.09 (m, 7H), 7.03−6.98 (m, 2H), 6.94−6.86 (m, 4H), 5.32 (d, J = 15.6 Hz, 1H), 4.90 (d, J = 15.6 Hz, 1H), 4.76 (d, J = 4.8 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 3.80 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.36 (d, J = 13.6 Hz, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.0, 177.4, 144.2, 144.0, 143.9, 136.8, 136.6, 134.1, 132.2, 130.8, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 127.9, 127.7, 127.0, 126.7, 122.7, 122.5, 119.8, 119.4, 113.4, 110.9, 109.6, 49.0, 48.23, 44.5, 37.5, 33.4, 21.5; IR (KBr) υ 3697, 3459, 3323, 3056, 3028, 1710, 1684, 1607, 1489, 1455, 1346, 1290, 1229, 1210, 1176, 1116, 1078, 1030, 994, 900, 869, 825 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{32}N_2NaO_2^+$ ([M + Na]$^+$) 595.2356, found 595.2362.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-methoxybenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1l**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 210 mg, 69%, mp 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.55 (m, 2H), 7.45−7.27 (m, 9H), 7.21−7.10 (m, 6H), 7.04−6.98 (m, 2H), 6.93−6.86 (m, 2H), 6.61−6.59 (m, 2H), 5.32 (d, J = 15.6 Hz, 1H), 4.91 (d, J = 15.6 Hz, 1H), 4.76 (d, J = 4.8 Hz, 1H), 4.42 (d, J = 12.4 Hz, 1H), 3.82 (d, J = 4.8 Hz, 1H), 3.77 (s, 3H), 2.35 (d, J = 13.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 177.4, 163.3, 144.3, 144.0, 136.8, 136.6, 134.1, 130.9, 130.7, 129.0, 128.8, 128.6, 128.4, 127.9, 127.7, 127.6, 127.0, 126.7, 122.6, 122.5, 119.7, 119.4, 113.5, 113.3, 110.9, 109.5, 55.4, 49.0, 48.1, 44.4, 37.5, 33.6; IR (KBr) υ 3618, 3256, 3058, 1696, 1678, 1602, 1573, 1510, 1490, 1456, 1359, 1291, 1262, 1230, 1170, 1115, 1078, 1029, 991, 955, 902, 869, 840, 808 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{32}N_2NaO_3^+$ ([M + Na]$^+$) 611.2305, found 611.2314.

*rel-(1S,2R,4S)-1′-Benzyl-5′-chloro-2-(4-methoxybenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1m**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 280 mg, 87%, mp 270−272 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.47−7.43 (m, 2H), 7.40−7.30 (m, 6H), 7.25 (s, 1H), 7.19−7.11 (m, 6H), 7.02−6.99 (m, 1H), 6.96 (s, 1H), 6.78−6.76 (m, 1H), 6.63−6.61 (m, 2H), 5.27 (d, J = 15.2 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.75 (d, J = 4.8 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 3.86−3.81 (m, 1H), 3.78 (s, 3H), 2.37 (d, J = 13.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.8, 176.9, 163.5, 144.0, 142.6, 136.8, 136.1, 133.3, 132.7, 130.8, 129.0, 128.9, 128.7, 128.4, 127.9, 127.8, 127.7, 127.5, 126.9, 126.8, 123.1, 122.8, 119.9, 119.5, 113.7, 111.0, 110.6, 55.4, 49.2, 48.4, 44.5, 37.4, 33.6; IR (KBr) υ 3695, 3300, 3063, 1703, 1677, 1599, 1511, 1485, 1454, 1349, 1310, 1264, 1229, 1168, 1117, 1076, 1025, 991, 922, 840, 817 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{31}ClN_2NaO_3^+$ ([M + Na]$^+$) 645.1915, found 645.1899.

*rel-(1S,2R,4S)-1′-Benzyl-5′-chloro-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1n**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 242 mg, 77%, mp 168−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.52 (m, 2H), 7.48−7.44 (m, 2H), 7.41−7.37 (m, 3H), 7.35−7.28 (m, 4H), 7.20−7.15 (m, 4H), 7.11−7.09 (m, 2H), 7.03−6.99 (m, 1H), 6.97−6.95 (m, 3H), 6.80−6.78 (m, 1H), 5.29 (d, J = 15.2 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.75 (d, J = 4.8 Hz, 1H), 4.37 (d, J = 11.6 Hz, 1H), 3.80 (td, J_1 = 12.8 Hz, J_2 = 5.2 Hz, 1H), 2.38 (d, J = 13.6 Hz, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.9, 176.9, 144.2, 144.0, 142.6, 136.8, 136.1, 133.2, 132.7, 131.9, 129.2, 129.0, 128.9, 128.7, 128.6, 128.4, 127.9, 127.8, 126.8, 123.1, 122.8, 120.0, 119.5, 113.6, 111.0, 110.6, 49.2, 48.5, 44.5, 37.4, 33.5, 21.6, 21.5; IR (KBr) υ 3623, 3437, 3269, 3059, 1703, 1681, 1606, 1486, 1454, 1430, 1342, 1290, 1229, 1210, 1175, 1118, 1076, 1027, 994, 916, 869, 841, 812 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{40}H_{31}ClN_2NaO_2^+$ ([M + Na]$^+$) 629.1966, found 629.1974.

*rel-(1S,2R,4S)-1′-Benzyl-5′-methyl-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1o**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 231 mg, 76%, mp 262−264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 2H), 7.47−7.43 (m, 2H), 7.39−7.36 (m, 4H), 7.32−7.30 (m, 1H), 7.29−7.27 (m, 1H), 7.17−7.11 (m, 5H), 7.01−6.93 (m, 4H), 6.78−6.74 (m, 2H), 5.29 (d, J = 15.6 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.75 (d, J = 4.2 Hz, 1H), 4.40 (d, J = 12.4 Hz, 1H), 3.83 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.38−2.35 (m, 1H), 2.29 (s, 3H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.0, 177.3, 144.3, 143.9, 141.6, 136.8, 136.7, 134.3, 132.2, 132.1, 130.8, 129.4, 129.1, 128.8, 128.6, 128.5, 127.6, 127.5, 127.0, 126.7, 123.3, 122.5, 119.8, 119.4, 113.2, 110.9, 109.4, 49.1, 48.2, 44.5, 37.5, 33.5, 21.6, 21.1; IR (KBr) υ 3695, 3310, 3026, 1693, 1604, 1497, 1453, 1347, 1291, 1232, 1212, 1187, 1174, 1078, 1028, 993, 931, 875, 846, 827, 809, 770 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{34}N_2NaO_2^+$ ([M + Na]$^+$) 609.2512, found 609.2517.

*rel-(1S,2R,4S)-2-Benzoyl-1′-benzyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1p**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 197 mg, 68%, mp 157−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.45−7.28 (m, 9H), 7.21−7.10 (m, 8H), 7.05−6.98 (m, 2H), 6.94−6.87 (m, 2H), 5.31 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.76 (d, J = 4.8 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 3.80 (td, J_1 = 13.6 Hz, J_2 = 5.6 Hz, 1H), 2.36 (d, J = 13.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.4, 177.2, 144.2, 144.0, 136.8, 136.6, 134.7, 133.9, 133.1, 130.8, 129.0, 128.9, 128.6, 128.4, 128.3, 127.9, 127.7, 126.9, 126.7, 122.7, 122.6, 122.5, 119.8, 119.4, 113.4, 110.9, 109.6, 49.0, 48.3, 44.5, 37.4, 33.3; IR (KBr) υ 3077, 3020, 1710, 1678, 1600, 1468, 1465, 1369, 1338, 1299, 1266, 1221, 1177, 1109, 1104, 1069, 1022, 988, 985, 920, 906, 867, 839, 791 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{39}H_{30}N_2NaO_2^+$ ([M + Na]$^+$) 581.2199, found 581.2205.

*rel-(1S,2R,4S)-1′-Benzyl-4-(4-chlorophenyl)-5′,9-dimethyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1q**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 229 mg, 70%, mp 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.42−7.40 (m, 2H), 7.38−7.29 (m, 5H), 7.22−7.12 (m, 3H), 7.07−7.05 (m, 2H), 7.01−6.93 (m, 4H), 6.77−6.74 (m, 2H), 5.32 (d, J = 15.2 Hz, 1H), 4.89 (d, J = 15.2 Hz, 1H), 4.72 (d, J = 4.8 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 3.62 (td, J_1 = 13.2 Hz, J_2 = 5.2 Hz, 1H), 2.83 (s, 3H), 2.29 (s, 3H), 2.19−2.17 (m, 1H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.6, 176.6, 144.0, 142.9, 142.2, 138.3, 136.5, 134.7, 132.5, 132.4, 132.3, 130.8, 130.0, 129.3, 129.1, 128.7, 128.6, 128.4, 128.3, 127.7, 125.8, 123.3, 122.2, 119.4, 119.0, 113.4, 109.1, 108.9, 49.9, 49.4, 45.1, 37.1, 32.5, 29.5, 21.5, 21.1; IR(KBr)υ: 3699, 3028, 1712, 1686, 1603, 1497, 1468, 1437, 1363, 1335, 1289, 1231, 1184, 1128, 1081, 1031, 1012, 988, 934, 838, 818, 793 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{35}ClN_2NaO_2^+$ ([M + Na]$^+$) 657.2279, found 657.2287.

*rel-(1S,2R,4S)-1′-Benzyl-9-methyl-2-(4-methylbenzoyl)-4-(p-tolyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1r**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white

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solid, 214 mg, 69%, mp 205−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.38−7.35 (m, 2H), 7.32−7.23 (m, 5H), 7.17−7.10 (m, 4H), 7.07−6.96 (m, 4H), 6.89−6.85 (m, 4H), 5.36 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.73 (d, J = 4.0 Hz, 1H), 4.43 (d, J = 12.4 Hz, 1H), 3.57 (td, J_1 = 13.2 Hz, J_2 = 5.2 Hz, 1H), 2.84 (s, 3H), 2.43 (s, 3H), 2.34−2.18 (m, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.9, 176.9, 144.6, 143.8, 141.2, 138.3, 136.5, 136.1, 134.3, 132.5, 131.1, 129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.2, 127.7, 126.0, 122.7, 122.6, 122.2, 119.3, 119.2, 114.3, 109.3, 108.8, 50.2, 49.4, 45.1, 37.3, 32.9, 29.4, 21.5, 21.1; IR (KBr) υ 3700, 3029, 1716, 1683, 1605, 1488, 1466, 1362, 1338, 1293, 1266, 1230, 1209, 1186, 1169, 1110, 1078, 1015, 987, 903, 882, 843, 805, 773, 753 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{36}N_2NaO_2^+$ ([M + Na]$^+$) 623.2669, found 623.2672.

rel-(1S,2R,4S)-1′-Benzyl-9-methyl-2-(4-methylbenzoyl)-4-(m-tolyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1s):*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 221 mg, 71%, mp 182−183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.39−7.35 (m, 2H), 7.32−7.28 (m, 2H), 7.27−7.23 (m, 2H), 7.19−7.11 (m, 5H), 7.04−6.97 (m, 4H), 6.91−6.86 (m, 4H), 5.36 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.73 (d, J = 4.4 Hz, 1H), 4.45 (d, J = 16.0 Hz, 1H), 3.57 (td, J_1 = 12.0 Hz, J_2 = 5.6 Hz, 1H), 2.84 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H), 2.22−2.19 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.9, 176.9, 144.6, 144.2, 143.8, 138.3, 138.1, 136.5, 134.3, 132.5, 131.1, 129.4, 129.3, 129.0, 128.9, 128.8, 128.4, 127.7, 127.6, 127.4, 126.0, 125.6, 122.7, 122.6, 122.1, 119.3, 119.2, 114.2, 109.3, 108.8, 50.2, 49.34, 45.1, 37.7, 37.6, 32.9, 29.4, 21.6; IR (KBr) υ 3699, 3028, 1717, 1684, 1606, 1487, 1466, 1361, 1338, 1292, 1230, 1210, 1182, 1108, 1077, 1013, 987, 905, 886, 843, 830, 794, 770, 754 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{36}N_2NaO_2^+$ ([M + Na]$^+$) 623.2669, found 623.2672.

rel-(1S,2R,4S)-1′-Benzyl-4-(4-ethoxyphenyl)-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1t):*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 163 mg, 50%, mp 215−217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.39−7.35 (m, 2H), 7.32−7.27 (m, 3H), 7.18−7.01 (m, 6H), 7.04−6.98 (m, 2H), 6.96−6.85 (m, 6H), 5.36 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.6 Hz, 1H), 4.71 (d, J = 4.0 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H)„ 4.14−4.06 (m, 2H), 3.55 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.84 (s, 3H), 2.27 (s, 3H), 2.20 (d, J = 13.6 Hz, 1H), 1.46 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.0, 176.9, 157.8, 144.6, 143.8, 138.3, 136.5, 136.2, 134.2, 132.6, 131.1, 129.6, 129.1, 128.9, 128.8, 128.4, 127.8, 127.7, 126.0, 122.7, 122.6, 122.2, 119.3, 119.2, 114.5, 109.3, 108.8, 63.6, 50.2, 49.4, 45.2, 36.8, 32.9, 29.5, 21.5, 15.0; IR (KBr) υ 3056, 3030, 1713, 1680, 1608, 1509, 1483, 1362, 1336, 1297, 1247, 1185, 1168, 1115, 1079, 1046, 1013, 987, 922, 906, 873, 838, 810 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{43}H_{38}N_2NaO_3^+$ ([M + Na]$^+$) 653.2775, found 653.2781.

rel-(1S,2R,4R)-1′-Benzyl-4-(2-methoxyphenyl)-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1u):*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 198 mg, 62%, mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.60 (m, 2H), 7.39−7.35 (m, 3H), 7.32−7.27 (m, 2H), 7.17−7.12 (m, 3H), 7.10−6.85 (m, 11H), 5.38 (d, J = 15.2 Hz, 1H), 5.04 (d, J = 4.8 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.38 (d, J = 12.4 Hz, 1H), 3.86 (s, 3H), 3.43 (td, J_1 = 12.4 Hz, J_2 = 5.2 Hz, 1H), 2.84 (s, 3H), 2.33 (d, J = 13.6 Hz, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.0, 177.0, 157.5, 144.7, 143.7, 138.4, 136.6, 134.8, 132.7, 132.0, 131.4, 129.5, 129.0, 128.8, 128.5, 128.0, 127.8, 126.0, 122.8, 122.6, 122.2, 120.3, 119.3, 119.2, 114.6, 110.4, 109.2, 108.8, 55.5, 51.1, 49.5, 45.2, 32.3, 29.5, 27.0, 21.5; IR (KBr) υ 3432, 3056, 1716, 1682, 1606, 1486, 1463, 1363, 1338, 1290, 1238, 1170, 1111, 1077, 1029, 990, 901, 873, 842 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{36}N_2NaO_3^+$ ([M + Na]$^+$) 639.2618, found 639.2605.

rel-(1S,2R,4S)-4-([1,1′-Biphenyl]-4-yl)-1′-benzyl-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1v).*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 157 mg, 46%, mp 230−232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.65 (m, 4H), 7.62−7.60 (m, 2H), 7.53−7.44 (m, 4H), 7.40−7.36 (m, 3H), 7.33−7.30 (m, 2H), 7.20−7.13 (m, 3H), 7.08−7.00 (m, 4H), 6.92−6.84 (m, 4H), 5.37 (d, J = 15.2 Hz, 1H), 4.92 (d, J = 15.2 Hz, 1H), 4.81 (d, J = 4.4 Hz, 1H), 4.47 (d, J = 12.4 Hz, 1H), 3.67−3.60 (m, 1H), 2.86 (s, 3H), 2.26−2.23 (m, 1H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.8, 176.9, 144.7, 143.9, 143.5, 141.0, 139.7, 138.4, 136.5, 134.5, 132.6, 131.1, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 127.8, 127.3, 127.2, 127.1, 126.0, 122.8, 122.7, 122.3, 119.4, 119.3, 114.1, 109.4, 108.9, 50.2, 49.4, 45.2, 37.5, 32.8, 29.5, 21.5; IR (KBr) υ 3453, 3026, 1711, 1682, 1605, 1482, 1464, 1339, 1225, 1161, 1077, 873, 841 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{47}H_{38}N_2NaO_2^+$ ([M + Na]$^+$) 685.2825, found 685.2815.

rel-(1S,2R,4S)-1′-Benzyl-4-(4-bromophenyl)-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1w):*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 305 mg, 89%, mp 191−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.54 (m, 4H), 7.39−7.35 (m, 2H), 7.32−7.28 (m, 1H), 7.24−7.12 (m, 6H), 7.05−6.98 (m, 4H), 6.94−6.85 (m, 4H), 5.35 (d, J = 15.6 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.71 (d, J = 4.4 Hz, 1H), 4.35 (d, J = 12.4 Hz, 1H), 3.60 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.84 (s, 3H), 2.29 (s, 3H), 2.16 (d, J = 13.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.6, 176.7, 144.6, 144.1, 143.5, 138.4, 136.5, 134.5, 132.6, 131.7, 130.9, 130.4, 129.2, 128.8, 128.5, 128.3, 127.8, 125.8, 122.8, 122.4, 120.5, 119.5, 119.1, 113.5, 109.4, 109.0, 50.0, 49.4, 45.2, 37.3, 32.5, 29.6, 21.6; IR (KBr) υ 3453, 3027, 1712, 1684, 1605, 1485, 1464, 1360, 1336, 1289, 1229, 1185, 1167, 1106, 1073, 1008, 985, 903, 880, 838, 792 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{33}BrN_2NaO_2^+$ ([M + Na]$^+$) 687.1618, found 687.1613.

rel-(1S,2R,4S)-1′-Benzyl-4-(4-fluorophenyl)-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1x):*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 225 mg, 72%, mp 256−258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.59 (m, 2H), 7.39−7.29 (m, 5H), 7.25−7.21 (m, 1H), 7.19−7.10 (m, 5H), 7.06−6.98 (m, 4H), 6.94−6.86 (m, 4H), 5.36 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.74 (d, J = 4.4 Hz, 1H), 4.39 (d, J = 12.4 Hz, 1H), 3.60 (td, J_1 = 12.8 Hz, J_2 = 5.2 Hz, 1H), 2.84 (s, 3H), 2.28 (s, 3H), 2.17 (d, J = 13.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.7, 176.7, 161.8 (d, J = 243.0 Hz), 144.6, 144.0, 140.1, 140.0, 138.4, 136.5, 134.4, 132.6, 130.1, 130.0, 129.1, 129.0, 128.8, 128.4, 128.3, 127.8, 125.9, 122.7, 122.6, 122.4, 119.2 (d, J = 27.3 Hz), 115.4 (d, J = 21.1 Hz), 113.9, 109.4, 109.0, 50.0, 49.3, 45.1, 37.0, 32.7, 29.5, 21.5; IR (KBr) υ 3440, 3029, 1714, 1682, 1604 1490, 1463, 1360, 1337, 1290, 1215, 1185, 1166, 1109, 1075, 1013, 985, 903, 879, 841 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{33}FN_2NaO_2^+$ ([M + Na]$^+$) 627.2418, found 627.2410.

rel-(1S,2R,4R)-1′-Benzyl-4-(2-fluorophenyl)-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one ***(1y):*** ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 219 mg, 71%, mp 194−196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.39−7.35 (m, 3H), 7.33−7.27 (m, 1H), 7.24−7.23 (m, 1H), 7.20−7.12 (m, 6H), 7.05−6.98 (m, 4H), 6.91−6.86 (m, 4H), 5.37 (d, J = 15.2 Hz, 1H), 5.03 (d, J = 4.8 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.39 (d, J = 11.2 Hz, 1H), 3.55 (td, J_1 = 13.6 Hz, J_2 = 5.6 Hz, 1H), 2.84 (s, 3H), 2.29−2.27 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.6, 176.7, 161.2 (d, J = 245 Hz), 144.6, 143.9, 138.3, 136.4, 134.9, 132.6, 131.2 (d, J = 14.4 Hz), 131.0, 130.1 (d, J = 4.2 Hz), 129.1, 129.0, 128.8, 128.5 (d, J = 8.0 Hz), 128.4, 128.2, 127.7, 125.7, 124.0 (d, J = 3.2 Hz), 122.6, 122.3, 119.4, 119.2 (d, J = 3.7 Hz), 119.0, 115.5 (d, J = 21.5 Hz), 113.0, 109.3, 108.9, 50.5, 49.3, 45.2, 31.7, 30.2, 29.5, 21.5; IR (KBr) υ 3429, 3029, 1724, 1684, 1606, 1485, 1465 1360, 1337, 1293, 1266, 1228, 1184, 1110, 1078, 1031 987, 905, 879, 838, 798 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{33}FN_2NaO_2^+$ ([M + Na]$^+$) 627.2418, found 627.2404.

2. General Procedure for the Preparation of Tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate 2a−2g. To a 10 mL Schlenk tube were added indole (0.6 mmol, 1.2 equiv), phenylacetylene (0.6 mmol, 1.2 equiv), alkyl (*E*)-2-(2-oxoindolin-3-ylidene) acetate (0.5 mmol, 1.0 equiv), indium bromide (0.025 mmol, 0.05 equiv), and toluene (2.0 mL). The mixture was heated at 80 °C by an oil bath for 10 h. After removing the solvent,

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the residue was subjected to column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:20) to afford the desired products **2a**−**2g**.

*rel-Methyl(1S,2R,4S)-1′-benzyl-5′-chloro-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2a**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 139 mg, 49%, mp 209−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.33 (m, 7H), 7.25−7.10 (m, 8H), 7.00−6.97 (m, 2H), 6.80−6.78 (m, 1H), 5.10 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.2 Hz, 1H), 4.68−4.48 (m, 1H), 3.65−3.59 (m, 1H), 3.45 (s, 3H), 3.39−3.39 (m, 1H), 2.45 (d, J = 13.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.1, 172.3, 144.1, 142.3, 136.8, 135.9, 133.0, 132.0, 129.1, 128.9, 128.6, 128.3, 128.2, 128.0, 127.8, 126.8, 126.5, 123.5, 122.9, 120.0, 119.6, 114.0, 110.9, 110.5, 52.1, 49.6, 44.7, 44.5, 36.6, 32.3; IR (KBr) υ 3354, 3035, 1742, 1614, 1449, 1339, 1283, 1266, 1169, 1063, 923, 850, 810, 756 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{34}H_{27}ClN_2NaO_3^+$ ([M + Na]$^+$) 569.1602, found 569.1599.

*rel-Ethyl(1S,2R,4S)-1′-benzyl-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2b**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 131 mg, 48%, mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2H), 7.36−7.27 (m, 6H), 7.25−7.23 (m, 2H), 7.14−7.07 (m, 4H), 7.04−7.00 (m, 1H), 6.97−6.94 (m, 1H), 6.91−6.89 (m, 1H), 5.15 (d, J = 15.2 Hz, 1H), 4.78 (d, J = 15.2 Hz, 1H), 4.69 (d, J = 5.6 Hz, 1H), 3.94−3.86 (m, 1H), 3.85−3.77 (m, 1H), 3.65 (td, J_1 = 12.8 Hz, J_2 = 5.6 Hz, 1H), 3.42 (d, J = 13.2 Hz, 1H), 2.42 (d, J = 13.2 Hz, 1H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4, 172.0, 144.5, 143.7, 136.8, 136.4, 132.9, 131.3, 129.0, 128.9, 128.5, 128.3, 128.0, 127.8, 127.0, 126.4, 123.2, 123.0, 122.6, 119.8, 119.5, 113.8, 110.9, 109.5, 60.8, 49.7, 44.8, 44.3, 36.8, 32.2, 13.8; IR (KBr) υ 3343, 3068, 1754, 1634, 1465, 1460, 1334, 1256, 1242, 1156, 1027, 922, 865, 845 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{35}H_{30}N_2NaO_3^+$ ([M + Na]$^+$) 549.2149, found 549.2146.

*rel-Ethyl(1S,2R,4S)-1′-benzyl-5′-fluoro-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2c**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 147 mg, 52%, mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.42 (m, 2H), 7.38−7.31 (m, 5H), 7.25−7.23 (m, 3H), 7.20−7.10 (m, 4H), 6.99−6.94 (m, 2H), 6.83−6.81 (m, 2H), 5.14 (d, J = 15.6 Hz, 1H), 4.77 (d, J = 15.6 Hz, 1H), 4.69 (d, J = 5.6 Hz, 1H), 3.98−3.90 (m, 1H), 3.88−3.80 (m, 1H), 3.62 (td, J_1 = 13.2 Hz, J_2 = 6.4 Hz, 1H), 3.36 (td, J_1 = 13.2 Hz, J_2 = 2.4 Hz, 1H), 2.45 (d, J = 13.2 Hz, 1H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 171.8, 159.3 (d, J = 240.8 Hz,), 144.2, 139.6, 139.5, 136.4 (d, J = 77.5 Hz), 133.1 (d, J = 77.0 Hz), 132.1, 128.9, 128.6, 128.2, 127.9, 126.8, 126.5, 122.8, 119.9, 119.6, 115.3 (d, J = 23.4 Hz), 114.0, 111.2 (d, J = 24.5 Hz), 110.9, 110.0 (d, J = 7.5 Hz), 61.0, 50.0, 44.7, 44.5, 36.6, 32.1, 29.7, 13.8; IR (KBr) υ 3340, 3066, 1730, 1617, 1488, 1449, 1340, 1266, 1243, 1176, 1065, 1030, 931, 865, 813 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{35}H_{29}FN_2NaO_3^+$ ([M + Na]$^+$) 567.2054, found 567.2054.

*rel-Ethyl(1S,2R,4S)-1′-benzyl-5′-chloro-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2d**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 145 mg, 50%, mp 123−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.41 (m, 2H), 7.37−7.28 (m, 6H), 7.24−7.10 (m, 7H), 7.02−6.96 (m, 2H), 6.82−6.80 (m, 1H), 5.15 (d, J = 15.2 Hz, 1H), 4.77 (d, J = 15.2 Hz, 1H), 4.68 (d, J = 5.2 Hz, 1H), 3.99−3.91 (m, 1H), 3.88−3.80 (m, 1H), 3.62 (td, J_1 = 13.2 Hz, J_2 = 6.0 Hz, 1H), 3.40−3.36 (m, 1H), 2.45 (d, J = 13.6 Hz, 1H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 171.8, 144.2, 142.2, 136.8, 135.9, 133.1, 132.0, 129.0, 128.9, 128.6, 128.3, 128.2, 128.0, 127.8, 126.8, 126.5, 123.6, 122.8, 119.9, 119.6, 114.1, 110.9, 110.4, 61.0, 49.7, 44.8, 44.4, 36.6, 32.1, 13.8; IR (KBr) υ 3628, 3333, 1728, 1607, 1485, 1453, 1430, 1337, 1294, 1174, 1108, 1076, 1050, 1026, 873, 812 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{35}H_{29}ClN_2NaO_3^+$ ([M + Na]$^+$) 583.1759, found 583.1753.

*rel-Ethyl(1S,2R,4S)-1′-benzyl-5′-methyl-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2e**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 129 mg, 46%, mp 230−232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.43 (m, 2H), 7.36−7.29 (m, 7H), 7.19−7.04 (m, 6H), 6.98−6.94 (m, 1H), 6.85 (s, 1H), 6.79−6.77 (m, 1H), 5.15 (d, J = 15.2 Hz, 1H), 4.76 (d, J = 15.6 Hz, 1H), 4.69 (d, J = 6.0 Hz, 1H), 3.97−3.89 (m, 1H), 3.86−3.80 (m, 1H), 3.66 (td, J_1 = 12.8 Hz, J_2 = 5.6 Hz, 1H), 3.40 (d, J = 13.6 Hz, 1H), 2.42 (d, J = 13.6 Hz, 1H), 2.25 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4, 172.0, 144.6, 141.2, 136.8, 136.5, 133.2, 132.5, 131.3, 129.3, 128.8, 128.5, 128.3, 127.9, 127.8, 127.0, 126.4, 123.9, 122.5, 119.7, 119.5, 113.6, 110.8, 109.2, 60.8, 49.6, 44.7, 44.3, 36.7, 32.2, 21.1, 13.8; IR (KBr) υ 3538, 3343, 1730, 1606, 1453, 1433, 1329, 1268, 1169, 1109, 1066, 1019, 869, 825 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{36}H_{32}N_2NaO_3^+$ ([M + Na]$^+$) 563.2305, found 563.2298.

*rel-Ethyl(1S,2R,4S)-1′-benzyl-5′,9-dimethyl-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2f**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 129 mg, 45%, mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.34−7.30 (m, 7H), 7.23−7.10 (m, 4H), 7.06−7.04 (m, 1H), 6.97−6.94 (m, 1H), 6.88 (s, 1H), 6.80−6.78 (m, 1H), 5.10 (d, J = 15.2 Hz, 1H), 4.80 (d, J = 15.2 Hz, 1H), 4.70 (d, J = 5.2 Hz, 1H), 3.80−3.76 (m, 2H), 3.50 (td, J_1 = 13.2 Hz, J_2 = 6.4 Hz, 1H), 3.29 (d, J = 13.2 Hz, 1H), 2.83 (s, 3H), 2.26 (s, 3H), 2.26−2.23 (m, 1H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.4, 171.7, 144.5, 141.5, 138.3, 136.2, 133.4, 132.6, 131.2, 129.2, 128.7, 128.5, 128.4, 128.4, 127.8, 126.3, 126.0, 124.2, 122.2, 119.4, 119.2, 114.3, 108.9, 108.8, 60.5, 50.1, 47.5, 44.8, 36.9, 31.6, 29.6, 21.1, 13.8; IR (KBr) υ 3333, 3058, 1727, 1614, 1491, 1450, 1340, 1293, 1267, 1168, 1077, 1027, 931, 864, 812 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{37}H_{34}N_2NaO_3^+$ ([M + Na]$^+$) 577.2462, found 577.2461.

*rel-Ethyl(1S,2R,4S)-1′-benzyl-9-methyl-2′-oxo-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indoline]-2-carboxylate (**2g**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 112 mg, 40%, mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2H), 7.34−7.29 (m, 7H), 7.25−7.25 (m, 2H), 7.19−7.10 (m, 4H), 7.05−7.01 (m, 1H), 6.97−6.90 (m, 2H), 5.13 (d, J = 15.2 Hz, 1H), 4.83 (d, J = 15.2 Hz, 1H), 4.71−4.70 (m, 1H), 3.78−3.75 (m, 2H), 3.53−3.49 (m, 1H), 3.32 (d, J = 12.4 Hz, 1H), 2.83 (s, 3H), 2.24 (d, J = 12.8 Hz, 1H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.4, 171.7, 144.4, 143.9, 138.3, 136.1, 133.5, 131.2, 129.0, 128.8, 128.4, 128.4, 128.3, 127.9, 126.3, 126.0, 123.5, 123.0, 122.2, 119.4, 119.2, 114.4, 109.1, 108.8, 60.5, 50.1, 47.6, 44.8, 36.9, 31.5, 29.5, 13.7; IR (KBr) υ 3438, 3293, 1777, 1605, 1460, 1444, 1320, 1270, 1177, 1109, 1056, 1020, 871, 830 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{36}H_{32}N_2NaO_3^+$ ([M + Na]$^+$) 563.2305, found 563.2308.

3. General Procedure for the Preparations of 1,1′-Bis(indolyl)phenylethanes. To a 10 mL Schlenk tube were added indole (1.5 mmol, 3.0 equiv), phenylacetylene (0.5 mmol, 1.0 equiv), indium bromide (0.025 mmol, 0.05 equiv), and toluene (2.0 mL). The mixture was heated at 90 °C by an oil bath for 3 h. After the solvent was removed, the residue was subjected to column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:60) as an eluent to afford compounds **3a**−**3e**.

*3,3′-(1-(4-Ethylphenyl)ethane-1,1-diyl)bis(1-methyl-1H-indole) (**3a**):* ethyl acetate and petroleum ether (v/v = 1:60) as the eluent, white solid, 170 mg, 82%, mp 204−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 5H), 7.26−7.24 (m, 1H), 7.17−7.13 (m, 2H), 7.07−7.05 (m, 2H), 6.93−6.89 (m, 2H), 6.48 (s, 2H), 3.66 (s, 6H), 2.62 (q, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.6, 141.3, 137.8, 128.0, 127.9, 127.2, 126.9, 123.5, 122.2, 121.0, 118.3, 109.1, 43.4, 32.6, 29.2, 28.3, 15.4; IR (KBr) υ 3427, 3060, 1925, 1694, 1594, 1510, 1468, 1335, 1246, 1207, 1142, 1081, 1002, 857, 805 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{28}H_{28}N_2Na^+$ ([M + Na]$^+$) 415.2145, found 415.2146.

*3,3′-(1-(4-Nitrophenyl)ethane-1,1-diyl)bis(1-methyl-1H-indole) (**3b**):* ethyl acetate and petroleum ether (v/v = 1:60) as the eluent, white solid, 108 mg, 50%, mp 242−243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.07 (m, 2H), 7.58−7.56 (m, 2H), 7.32−7.30 (m, 1H), 7.24−7.17 (m, 5H), 6.96−6.92 (m, 2H), 6.53 (s, 2H), 3.69 (s,

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6H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.1, 146.0, 137.8, 129.0, 128.0, 126.4, 123.1, 121.7, 121.4, 118.7, 109.4, 44.1, 32.7, 29.1; IR (KBr) υ 3688, 3053, 1909, 1736, 1614, 1539, 1468, 1364, 1325, 1244, 1204, 1128, 1084, 1049, 1013, 977, 920, 846, 805 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{26}H_{23}N_3NaO_2^+$ ([M + Na]$^+$) 432.1682, found 432.1682.

*3,3′-(1-(4-Butylphenyl)ethane-1,1-diyl)bis(1-methyl-1H-indole) (**3c**):* ethyl acetate and petroleum ether (v/v = 1:60) as the eluent, white solid, 174 mg, 79%, mp 159−160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 5H), 7.26−7.23 (m, 1H), 7.17−7.13 (m, 2H), 7.05−7.03 (m, 2H), 6.93−6.89 (m, 2H), 6.48 (s, 2H), 3.65 (s, 6H), 2.59−2.55 (m, 2H), 2.33 (s, 3H), 1.62−1.55 (m, 2H), 1.39−1.30 (m, 2H), 0.91 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.8, 140.2, 138.0, 128.2, 128.1, 127.9, 127.1, 123.7, 122.4, 121.2, 118.5, 109.3, 43.6, 35.4, 33.8, 32.7, 29.5, 22.7, 14.3; IR (KBr) υ 3434, 3064, 1955, 1696, 1569, 1510, 1445, 1336, 1220, 1203, 1114, 1003, 856, 803 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{30}H_{32}N_2Na^+$ ([M + Na]$^+$) 443.2458, found 443.2459.

*3,3′-(1-(4-Propylphenyl)ethane-1,1-diyl)bis(1-methyl-1H-indole) (**3d**):* ethyl acetate and petroleum ether (v/v = 1:60) as the eluent, white solid, 173 mg, 81%, mp 156−158 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 5H), 7.26−7.24 (m, 1H), 7.17−7.13 (m, 2H), 7.05−7.03 (m, 2H), 6.93−6.89 (m, 2H), 6.48 (s, 2H), 3.66 (s, 6H), 2.55 (t, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.65−1.60 (m, 2H), 0.94−0.91 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.6, 139.8, 137.8, 128.1, 127.9, 127.8, 126.9, 123.6, 122.3, 121.0, 118.3, 109.1, 43.4, 37.6, 32.6, 29.2, 24.5, 14.0; IR (KBr) υ 3455, 3056, 1924, 1665, 1575, 1510, 1494, 1383, 1274, 1224, 1142, 1043, 1032, 852, 832 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{29}H_{30}N_2Na^+$ ([M + Na]$^+$) 429.2301, found 429.2303.

*3,3′-(1-(4-Methoxyphenyl)ethane-1,1-diyl)bis(1-methyl-1H-indole) (**3e**):* ethyl acetate and petroleum ether (v/v = 1:60) as the eluent, white solid, 116 mg, 56%, mp 186−188 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 5H), 7.24 (s, 1H), 7.18−7.14 (m, 2H), 6.94−6.90 (m, 2H), 6.79−6.77 (m, 2H), 6.47 (s, 2H), 3.78 (s, 3H), 3.66 (s, 6H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4, 140.7, 137.8, 129.0, 128.0, 126.8, 123.6, 122.2, 121.0, 118.3, 113.0, 109.1, 55.1, 43.0, 32.6, 29.2; IR(KBr)υ: 3050, 2042, 1887, 1736, 1606, 1504, 1467, 1366, 1328, 1241, 1174, 1083, 1021, 835, 809 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{27}H_{26}N_2NaO^+$ ([M + Na]$^+$) 417.1937, found 417.1941.

4. General Procedure for the Preparation of Tetrahydrospiro[carbazole-1,3′-indolines] 4a−4g. To a 10 mL flask were added 1,1′-bis(indolyl)phenylethane (0.35 mmol, 1.0 equiv), (*E*)-3-phenacylideneoxindole (0.35 mmol, 1.0 equiv), indium bromide (0.018 mmol, 0.05 equiv), and toluene (3.0 mL). The mixture was heated at 80 °C by an oil bath for 10 h. After removing the solvent, the residue was subjected to column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:20) as an eluent to afford the desired products **1c**, **1e**, **1r**, and **4a−4g**.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-chlorobenzoyl)-4-(4-methoxyphenyl)-5′,9-dimethyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4a**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 181 mg, 77%, mp 213-215 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.38−7.35 (m, 2H), 7.32−7.27 (m, 4H), 7.19−7.17 (m, 2H), 7.09 (s, 4H), 7.01−6.97 (m, 4H), 6.79−6.75 (m, 2H), 5.29 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.73−4.72 (m, H), 4.34 (d, J = 12.0 Hz, 1H), 3.88 (s, 3H), 3.59 (td, J_1 = 12.8 Hz, J_2 = 5.2 Hz, 1H), 2.83 (s, 3H), 2.17 (s, 3H), 2.14 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.1, 176.6, 158.6, 142.3, 139.4, 138.3, 136.5, 136.2, 134.3, 133.4, 132.3, 130.9, 129.8, 129.6, 129.4, 128.8, 128.7, 128.4, 127.8, 126.0, 123.4, 122.3, 119.3, 119.2, 114.3, 114.0, 109.2, 108.9, 55.5, 50.2, 49.4, 45.2, 36.9, 32.9, 29.5, 21.1; IR (KBr) υ 3409, 3062, 1887, 1710, 1680, 1584, 1493, 1466, 1434, 1396, 1331, 1290, 1245, 1204, 1173, 1084, 1027, 982, 926, 873, 844, 807 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{35}ClN_2NaO_3^+$ ([M + Na]$^+$) 673.2228, found 673.2212.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-chlorobenzoyl)-5′,9-dimethyl-4-(4-propylphenyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4b**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 169 mg, 72%, mp 239−241 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.38−7.35 (m, 2H), 7.32−7.28 (m, 5H), 7.25 (s, 1H), 7.19−7.12 (m, 2H), 7.05−6.96 (m, 6H), 6.80 (s, 1H), 6.77−6.75 (m, 1H), 5.30 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.74 (d, J = 4.0 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 3.61 (td, J_1 = 12.8 Hz, J_2 = 5.2 Hz, 1H), 2.84 (s, 3H), 2.75 (dd, J_1 = 15.2 Hz, J_2 = 7.6 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 1H), 1.34 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.0, 176.6, 142.8, 142.3, 141.4, 139.3, 138.3, 136.5, 134.4, 133.4, 132.3, 130.9, 129.8, 129.4, 128.8, 128.6, 128.5, 128.4, 128.1, 127.7, 126.0, 123.4, 122.2, 119.3, 119.2, 114.2, 109.1, 108.8, 50.2, 49.4, 45.2, 37.4, 32.9, 29.5, 28.6, 21.1, 16.1; IR (KBr) υ: 3410, 3025, 1901, 1713, 1684, 1584, 1495, 1467, 1398, 1364, 1334, 1290, 1246, 1223, 1200, 1179, 1086, 1013, 988, 930, 873, 845, 809 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{43}H_{37}ClN_2NaO_2^+$ ([M + Na]$^+$) 671.2436, found 671.2419.

*rel-(1S,2R,4S)-1′-Benzyl-5′-chloro-4-(4-ethylphenyl)-9-methyl-2-(4-methylbenzoyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4c**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 105 mg, 45%, mp 264−266 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.39−7.36 (m, 2H), 7.33−7.32 (m, 1H), 7.29−7.27 (m, 4H), 7.26−7.25 (m, 1H), 7.18−7.13 (m, 3H), 7.02−6.99 (m, 4H), 6.90−6.88 (m, 2H), 6.79−6.77 (m, 1H), 5.34 (d, J = 15.2 Hz, 1H), 4.90 (d, J = 15.6 Hz, 1H), 4.74−4.73 (m, 1H), 4.36 (d, J = 12.4 Hz, 1H), 3.61−3.53 (m, 1H), 2.88 (s, 3H), 3.75 (dd, J_1 = 15.2 Hz, J_2 = 7.6 Hz, 2H), 2.28 (s, 3H), 2.23 (d, J = 12.0 Hz, 1H), 1.34 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.7, 176.5, 144.0, 143.3, 142.8, 141.1, 138.3, 136.0, 133.6, 133.0, 132.2, 129.1, 128.9, 128.8, 128.5, 128.4, 128.1, 127.9, 127.8, 125.9, 123.1, 122.4, 119.4, 114.6, 110.2, 108.9, 50.4, 49.5, 45.3, 37.3, 32.9, 29.6, 28.6, 21.6, 16.0; IR (KBr) υ 3428, 3058, 1721, 1675, 1603, 1481, 1429, 1360, 1322, 1228, 1186, 1160, 1119, 1075, 1016, 983, 918, 869, 843, 813 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{43}H_{37}ClN_2NaO_2^+$ ([M + Na]$^+$) 671.2436, found 671.2421.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-chlorbenzoyl)-5′,9-dimethyl-4-(4-propylphenyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4d**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 184 mg, 77%, mp 208−210 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.38−7.35 (m, 2H), 7.32−7.27 (m, 4H), 7.26−7.25 (m, 2H), 7.18−7.12 (m, 2H), 7.04 (s, 4H), 7.00−6.97 (m, 2H), 6.80 (s, 1H), 6.77−6.75 (m, 1H), 5.30 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.74 (d, J = 4.8 Hz, 1H), 4.36 (d, J = 12.4 Hz, 1H), 3.61 (td, J_1 = 12.4 Hz, J_2 = 5.2 Hz, 1H), 2.84 (s, 3H), 2.68 (t, J = 7.6 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 1H), 1.74 (td, J_1 = 14.8 Hz, J_2 = 7.6 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.0, 176.6, 142.2, 141.4, 141.2, 139.3, 138.3, 136.5, 134.4, 133.4, 132.3, 130.9, 129.8, 129.4, 128.8, 128.7, 128.6, 128.5, 128.4, 127.7, 126.0, 123.4, 122.2, 119.3, 119.2, 114.2, 109.1, 108.8, 50.2, 49.4, 45.2, 37.7, 37.4, 32.8, 29.5, 24.9, 21.1, 14.0; IR (KBr) υ 3419, 3025, 1903, 1718, 1683, 1585, 1494, 1468, 1431, 1398, 1367, 1334, 1291, 1248, 1222, 1200, 1177, 1087, 1013, 987, 929, 873, 844, 809 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{44}H_{39}ClN_2NaO_2^+$ ([M + Na]$^+$) 685.2592, found 685.2573.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-methoxybenzoyl)-9-methyl-4-(4-propylphenyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4e**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 184 mg, 79%, mp 121−123 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.39−7.35 (m, 2H), 7.32−7.28 (m, 2H), 7.25−7.21 (m, 4H), 7.18−7.13 (m, 3H), 7.10−7.04 (m, 3H), 7.00−6.96 (m, 1H), 6.91−6.85 (m, 2H), 6.55−6.53 (m, 2H), 5.36 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.74 (d, J = 4.4 Hz, 1H), 4.41 (d, J = 12.0 Hz, 1H), 3.74 (s, 3H), 3.59 (td, J_1 = 12.8 Hz, J_2 = 5.2 Hz, 1H), 2.84 (s, 3H), 2.68−2.64 (m, 2H), 2.18 (d, J = 13.2 Hz, 1H), 1.78−1.69 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.9, 177.0, 163.3, 144.7, 141.6, 141.0, 138.4, 136.6, 134.4, 131.2, 130.6, 128.9, 128.8, 128.7, 128.5, 128.4, 128.1, 127.8, 126.1, 122.8, 122.7, 122.2, 119.3, 119.2, 114.3, 113.5, 109.3, 108.9, 55.3, 50.1, 49.5, 45.2, 37.8, 37.4, 33.1, 29.5, 24.9, 14.0; IR (KBr) υ 3424, 3053, 1908, 1718, 1677, 1600, 1508, 1486, 1464, 1338, 1307, 1261, 1225, 1163, 1113, 1078, 1025, 986, 902, 873, 841, 802 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{44}H_{40}N_2NaO_3^+$ ([M + Na]$^+$) 667.2931, found 667.2922.

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*rel-(1S,2R,4S)-1′-Benzyl-4-(4-butylphenyl)-2-(4-chlorobenzoyl)-5′,9-dimethyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4f**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 181 mg, 74%, mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.38−7.35 (m, 2H), 7.32−7.27 (m, 4H), 7.25−7.24 (m, 2H), 7.19−7.12 (m, 2H), 7.04 (s, 4H), 7.01−6.99 (m, 2H), 6.80 (s, 1H), 6.77−6.75 (m, 1H), 5.30 (d, J = 15.2 Hz, 1H), 4.91 (d, J = 15.6 Hz, 1H), 4.74 (d, J = 4.4 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 3.61 (td, J_1 = 13.2 Hz, J_2 = 5.6 Hz, 1H), 2.83 (s, 3H), 2.72−2.68 (m, 2H), 2.18 (s, 3H), 2.14 (s, 1H), 1.73−1.66 (m, 2H), 1.46−1.41 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 176.6, 142.2, 141.4, 141.3, 139.3, 138.3 136.5, 134.4, 133.3, 132.3, 130.9, 129.7, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7, 126.0, 123.4, 122.2, 119.3, 119.2, 114.1, 109.1, 108.8, 50.1, 49.4, 45.1, 37.4, 35.4, 34.0, 32.8, 29.5, 22.5, 21.1, 14.0; IR (KBr) υ 3415, 3023, 1909, 1716, 1688, 1588, 1495, 1466, 1400, 1362, 1334, 1181, 1089, 1012, 987, 929, 877, 845, 810 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{45}H_{41}ClN_2NaO_2^+$ ([M + Na]$^+$) 699.2749, found 699.2737.

*rel-(1S,2R,4S)-1′-Benzyl-2-(4-chlorobenzoyl)-5′,9-dimethyl-4-(4-nitrophenyl)-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**4g**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, yellow solid, 120 mg, 50%, mp 252−254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32−8.30 (m, 2H), 7.57−7.55 (m, 4H), 7.39−7.29 (m, 3H), 7.22−7.10 (m, 4H), 7.08−7.06 (m, 3H), 7.03−6.98 (m, 2H), 6.78−6.75 (m, 2H), 5.26 (d, J = 15.6 Hz, 1H), 4.90 (d, J = 15.2 Hz, 1H), 4.84 (d, J = 5.2 Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 3.72 (td, J_1 = 13.6 Hz, J_2 = 6.0 Hz, 1H), 2.86 (s, 3H), 2.19 (s, 3H), 2.16 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 176.0, 152.2, 146.9, 142.1, 139.8, 138.4, 136.2, 134.5, 133.4, 132.6, 130.3, 129.7, 129.4, 129.3, 128.7, 128.3, 127.8, 125.5, 123.9, 123.2, 122.6, 119.7, 118.8, 112.4, 109.4, 109.1, 49.7, 49.4, 45.1, 37.6, 31.8, 29.6, 21.1; IR (KBr) υ 3445, 3027, 1712, 1689, 1591, 1518, 1495, 1470, 1399, 1343, 1184, 1091, 1012, 989, 931, 880, 854, 810 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{32}ClN_3NaO_4^+$ ([M + Na]$^+$) 688.1974, found 688.1973.

5. General Procedure for the Reactions of 3(9*H*-Carbazol-2-yl)indolin-2-ones 5a and 5b. To a 10 mL flask were added tetrahydrospiro[carbazole-1,3′-indolines] (0.35 mmol), toluene (3.0 mL), and TfOH (0.053 g), and the system was heated to 80 °C by an oil bath for 30 min. Upon completion, the solvent was removed at reduced pressure by rotatory evaporation, and the residue was subjected to column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:20) as an eluent to afford the desired products **5a**−**5b**.

*1-Benzyl-5-methyl-3-(9-methyl-4-phenyl-1-(p-tolyl)-9H-carbazol-2-yl)-1,3-dihydro-2H-inden-2-one (**5a**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 165 mg, 78%, mp 159−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.80 (m, 1H), 7.51−7.44 (m, 6H), 7.37−7.35 (m, 4H), 7.29−7.23 (m, 6H), 6.94−6.89 (m, 2H), 6.85 (s, 1H), 6.59−6.58 (m, 1H), 6.44 (s, 1H), 5.02−4.99 (m, 1H), 4.80−4.77 (m, 2H), 3.29 (s, 3H), 2.47 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.1, 142.4, 141.1, 141.0, 139.3, 137.7, 137.2, 136.3, 135.0, 134.3, 132.2, 132.1, 131.3, 130.8, 129.4, 129.2, 128.9, 128.7, 128.3, 128.1, 127.5, 127.4, 125.7, 125.5, 125.4, 122.2, 122.1, 119.7, 118.7, 108.6, 108.5, 48.9, 43.8, 32.2, 21.4, 21.0; IR (KBr) υ 3674, 3026, 1893, 1807, 1700, 1598, 1555, 1519, 1490, 1467, 1435, 1378, 1321, 1218, 1179, 1123, 1078, 1022, 1001, 982, 918, 892, 866, 826, 809, 788, 763 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{42}H_{34}N_2NaO^+$ ([M + Na]$^+$) 605.2563, found 605.2562.

*1-Benzyl-3-(1-(4-chlorophenyl)-9-methyl-4-phenyl-9H-carbazol-2-yl)-5-methyl-1,3-dihydro-2H-inden-2-one (**5b**):* ethyl acetate and petroleum ether (v/v = 1:20) as the eluent, white solid, 81%, mp 173−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.92 (m, 1H), 7.74−7.46 (m, 8H), 7.37−7.28 (m, 5H), 7.25−7.25 (m, 2H), 6.96−6.91 (m, 2H), 6.84 (s, 1H), 6.61−6.60 (m, 1H), 6.44−6.30 (m, 2H), 5.00 (d, J = 14.8 Hz, 1H), 4.79 (d, J = 15.6 Hz, 1H), 4.69 (s, 1H), 3.30−3.07 (m, 3H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7, 142.4, 141.1, 140.9, 139.1, 137.6, 136.7, 136.1, 134.2, 134.0, 133.9, 132.3, 132.2, 130.9, 129.3, 128.9, 128.8, 128.7, 128.3, 128.2, 127.6, 127.5, 127.3, 125.6, 125.4, 124.2, 122.2, 119.7, 118.9, 108.8, 108.6, 48.8, 43.8, 32.4, 21.0; IR (KBr) υ 3691, 3055, 3029, 1917, 1806, 1699, 1598, 1556, 1490, 1467, 1438, 1378, 1359, 1322, 1219, 1179, 1124, 1083, 1016, 1001, 984, 918, 866, 842, 829, 812, 764 cm^{-1}; MS (m/z) HRMS (ESI) calcd for $C_{41}H_{31}ClN_2NaO^+$ ([M + Na]$^+$) 625.2017, found 625.2007.

6. Synthesis of 3-(1-Phenylvinyl)-1*H*-indole and Its Diels−Alder Reaction. According to the reported method, under N_2, to a solution of phenylmagnesium bromide (25 mmol, 2.5 equiv) in dry Et_2O (40 mL) at 0 °C (ice bath) was added the Et_2O solution of 1-(1*H*-indol-3-yl)ethan-1-one (10 mmol, 1.0 equiv) dropwise. Then, the reaction mixture was warmed to 50 °C by an oil bath and stirred at the same temperature for 12 h. Upon completion, the reaction mixture was cooled to 0 °C by an ice bath. A saturated aqueous NH_4Cl solution (40 mL) was added dropwise. The organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was dissolved in CH_2Cl_2 (50 mL), to which was added anhydrous $MgSO_4$ (0.5 g per mmol of the substrate) followed by silica gel (200−300 mesh particle size, 0.5 g per mmol of the substrate). The mixture was then stirred at room temperature for 5 h, and the reaction progress was monitored by thin-layer chromatography. Upon completion, the reaction mixture was filtered and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by silica gel chromatography to afford the desired 3-(1-phenylvinyl)-1*H*-indole.

To a 50 mL flask were added 3-(1-phenylvinyl)-1*H*-indole (0.35 mmol, 1.0 equiv), (*E*)-1-benzyl-3-(2-oxo-2-(*p*-tolyl)ethylidene)-indolin-2-one (0.35 mmol, 1.0 equiv), $InBr_3$ (0.018 mmol, 0.05 equiv), and toluene (3 mL). The mixture was heated to 80 °C by an oil bath for 14 h. Upon completion, the solvent was removed. Then, the residue was purified by column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:20) as an eluent to afford the product *rel*-(1*S*,2*R*,4*S*)-1′-benzyl-2-(4-methylbenzoyl)-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (**1k**).

7. Procedure for the Gram-Scale Reaction of (1*S*,2*R*,4*S*)-1′-Benzyl-2-(4-clorobenzoyl)-5′-methyl-4-phenyl-2,3,4,9-tetrahydrospiro[carbazole-1,3′-indolin]-2′-one (1j). To a 40 mL Schlenk tube were added indole (7.0 mmol), phenylacetylene (5.0 mmol), indium bromide (0.125 mmol), and toluene (10.0 mL). The mixture was stirred at 110 °C by an oil bath for 15 min. Then, (*E*)-3-phenacylideneoxindoles (4.0 mmol) was added, and the solution was stirred at 80 °C by an oil bath for 16 h. After removing the solvent, the residue was subjected to column chromatography on silica gel with ethyl acetate and petroleum ether (v/v = 1:20) as an eluent to afford the desired product **1j** (1.30 g, 54%).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00103.

Experiment procedures and ^{1}H, ^{13}C NMR, and HRMS spectra (PDF)

Accession Codes

The crystallographic data of compounds **1g** (CCDC 2036202), **1h** (CCDC 2036203), **1i** (CCDC 2036204), **1m** (CCDC 2036205), **2f** (CCDC 2036206), and **5a** (CCDC 2036207) have been deposited at the Cambridge Crystallographic Database Center (http//www.ccdc.cam.ac.uk)

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Notes

The authors declare no competing financial interest.

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