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Solvent-Controlled, Tunable Domino Reaction of 3-Ylideneoxindoles with in Situ-Generated α-Aryldiazomethanes: A Facile Access to 3-Spirocyclopropyl-2-oxindole and Pyrazoloquinazolinone Scaffolds

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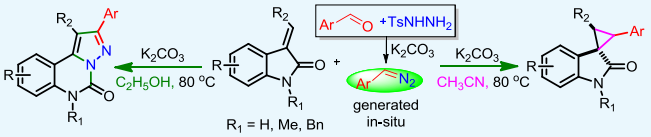
Supporting Information

ABSTRACT: A mild and efficient solvent-controlled, metal-free switchable 1,3-dipolar cycloaddition/ring contraction or ring expansion domino reaction of 3-ylideneoxindoles with in situ-generated α-aryldiazomethanes has been developed. This domino reaction provided a series of aryl-substituted 3-spirocyclopropyl-2-oxindoles and pyrazoloquinazolinones with excellent regio- and diastereoselectivity from common substrates under varying solvent conditions.



INTRODUCTION

Structurally complex scaffolds with extensive applications in the pharmaceutical industry have attracted the attention of the synthetic community to design and develop expeditious strategies toward their construction.[1] Among which, spirooxindole represents a ubiquitous skeleton and stands first with regard to its structural complexity and pharmacological utilities.[2,3] Particularly, 3-spirocyclopropyl-2-oxindole is a privileged scaffold, which is found in a plethora of natural products and pharmaceuticals that possess a wide spectrum of biological activities such as antitumor, anti-obesity, and antidiabetic.[4] As these scaffolds also inhibit enzymes such as HIV-1 non-nucleoside reverse transcriptase and kinase and arginine vasopressin hormone, they are useful in the treatment of congestive heart failure, hypertension, edema, and hyponatremia.[5] Considering these biological properties, numerous innovative synthetic approaches have evolved toward the stereoselective construction of spirooxindole scaffolds.[6−15]

3-Spirocyclopropyl-2-oxindoles can be traditionally synthesized in a straightforward, diastereoselective manner by treating oxindoles with bromonitroolefins.[7] They can also be obtained by reacting 3-ylidene-oxindoles with 1,2-dihaloalkanes,[8] diazo compounds under the catalysis of dirhodiumtetraacetate,[9] pyridinium salts in the presence of base,[10] ethyl diazoacetate,[11] or bromonitroalkyl derivatives in a Michael−alkylation cascade manner.[12] Alternatively, they can be constructed by the ring contraction of corresponding spiro-[pyrazolin-3,3-oxindoles], which are obtained by 1,3-dipolar cycloaddition of 3-ylidene-oxindoles with active diazo partners such as 2,2,2-trifluorodiazoethane,[13] α-diazocarbonyl compounds,[14] or the Bestmann Ohira reagent (Scheme 1).[15] However, the aforementioned strategies suffer from disadvantages such as lower yields; harsh reaction conditions; use of gaseous, toxic, and explosive CF_3CHN_2; and requirement of transition metal catalysts and active diazo partners. Considering these limitations, investigations for alternate approaches that avoid usage of expensive and explosive diazo compounds for the stereoselective synthesis of these scaffolds are still in great demand. Moreover, in spite of the advances being made, use of inactive α-aryldiazomethanes is rarely exploited in the cyclopropanation of 3-ylidene-oxindoles.

On the other hand, tremendous advances have been made in the field of switchable intermolecular domino reactions,[16] challenging yet desirable transformations that deliver different products from identical substrates through solvent regiodivergent procedures. Domino reactions have the advantage that minimal purification is required and are step- and atom-economical processes. In continuation of our interest in developing domino strategies toward the synthesis of bioactive scaffolds,[17] we wondered if we could construct 3-spirocyclopropyl-2-oxindole by trapping α-aryldiazomethanes (generated in situ from tosylhydrazide and aldehyde) with 3-ylidene-oxindoles via elimination of N_2 in a diastereoselective manner, an approach that has not been described. To realize our goal, initially 3-ylidene-oxindole **1a** was treated with tosylhydrazide

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Scheme 1. 1,3-Dipolar Cycloadditions of 3-Ylidene-oxindoles and α-Diazo Compounds for the Synthesis of 3-Spirocyclopropyl-2-oxindoles

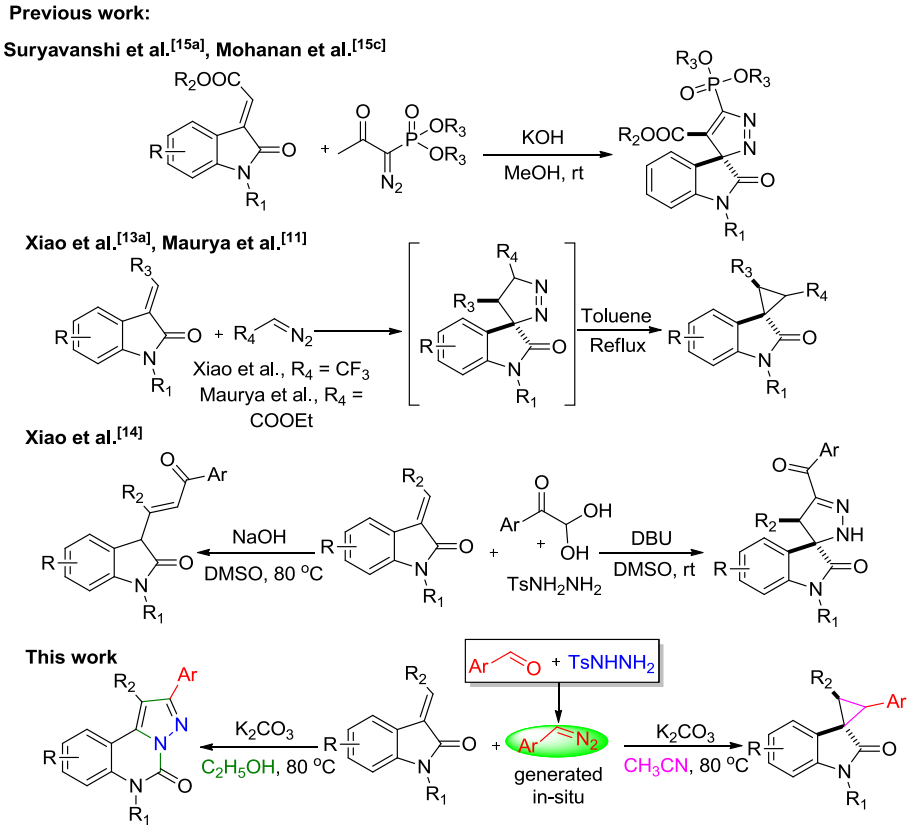
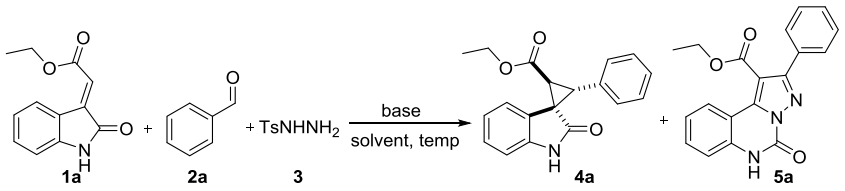


Table 1. Optimization of Reaction Conditions[a]



entry	base	solvent	temp (°C)	yield of **4a** (%)[b]	dr. of **4a**[c] (%)	yield of **5a** (%)[b]
1	K_2CO_3	CH_3CN	80	88	>95	
2	K_2CO_3	CH_2Cl_2	40	54	>95	
3	K_2CO_3	THF	60	63	>95	
4	K_2CO_3	toluene	100	50	>95	
5	DBU	CH_3CN	80	76	>95	
6	Et_3N	CH_3CN	80	72	>95	
7	Py	CH_3CN	80	66	>95	
8	Cs_2CO_3	CH_3CN	80	83	>95	
9	K_2CO_3	EtOH	80	<5		76
10	K_2CO_3	MeOH	65	<5		68
11	Cs_2CO_3	EtOH	80	<5		70
12	DBU	EtOH	80	<5		55
13	Et_3N	EtOH	80	<5		55
14	Py	EtOH	80	<5		50

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), **3** (0.5 mmol), base (1.0 mmol for entries 1−8 and 1.5 mmol for entries 9−14), and solvent (5 mL). [b]Isolated yields after column chromatography. [c]The dr. values were determined by ^{1}H NMR analysis.

3 and aldehyde **2a** for the anticipated cyclopropanation, and to our delight, 3-spirocyclopropyl-2-oxindole **4a** was obtained with high diastereoselectivity (>95) in 88% yield. Surprisingly, changing the reaction medium from CH_3CN to EtOH delivered pyrazoloquinazolinones **5** via the anticipated 1,3-dipolar cycloaddition, followed by an unexpected rearrangement. It is worth mentioning that pyrazoloquinazolinones are also quite interesting fused heterocyclic compounds with vast application in the pharmaceutical industry. They possess AMPA, Gly/NMDA, and KA receptor antagonistic and

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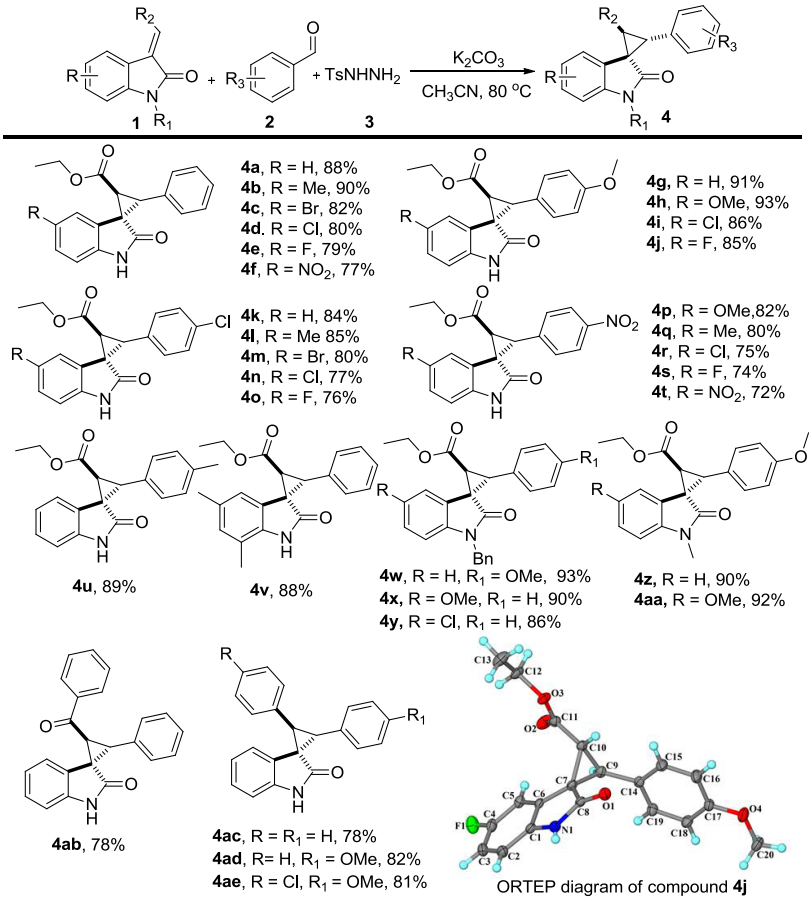
Table 2. Scope of the 1,3-Dipolar Cycloaddition/Ring Contraction Sequence Domino Reaction[a]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), **3** (0.5 mmol), K_2CO_3 (1.0 mmol), CH_3CN (5.0 mL); yields of isolated products.

benzodiazepine receptor agonistic activities and also inhibit phosphodiesterase 10A and vaccinia virus.[17] Herein, we wish to describe our unique observation of solvent-controlled switchable domino reaction between 3-ylidene-oxindoles and α-aryldiazomethanes, which deliver substituted 3-spirocyclopropyl-2-oxindole and pyrazoloquinazolinones.

RESULTS AND DISCUSSION

To investigate the envisioned strategy as shown in Table 1, we commenced our study by treating (*E*)-ethyl-2-(2-oxoindolin-3-ylidene)acetate with (diazomethyl)benzene, which was generated in situ from benzaldehyde and $TsNHNH_2$ in acetonitrile employing 2.0 equiv of K_2CO_3 in open air under refluxing temperature. As expected, 1,3-dipolar cycloaddition/ring contraction occurred smoothly and resulted 3-spirocyclopropyl-2-oxindole **4** (Table 1, entry 1) with excellent regio- and diastereoselectivity. The structure of the compound **4** was unambiguously confirmed by spectroscopic and X-ray crystallographic data. These interesting results encouraged us to investigate various parameters that increase the reaction efficiency. Changing the solvent from acetonitrile to other aprotic solvents such as CH_2Cl_2, tetrahydrofuran (THF), and toluene offered no improvement in the yield (Table 1, entries 2−4). Screening of various organic and inorganic bases such as DBU, Et_3N, pyridine, Cs_2CO_3, and K_2CO_3 revealed that K_2CO_3 was the best base of choice (Table 1, entries 5−8).

To our surprise, use of protic solvents such as EtOH offered an unexpected rearrangement, leading to generation of pyrazoloquinazolinones **5**. The structure of the compound was also confirmed by X-ray analysis. This stimulating result forced us to scrutinize the reaction parameters in detail. It is clear that EtOH is superior to MeOH, whereas K_2CO_3 appeared to be an optimal base even for this transformation (Table 1, entries 9−14).

With optimized reaction conditions established, the scope and generality of the regio- and diastereoselective 1,3-dipolar cycloaddition/ring contraction reaction to assemble a series of 3-spirocyclopropyl-2-oxindoles were explored first by varying the substitution pattern on both 2,3-oxindole and aldehyde partners. As summarized in Table 2, the electronic nature of substituents on 2,3-oxindole has only a marginal impact on the reaction efficiency. Accordingly, a series of 3-ylidene-oxindoles bearing electron-neutral, electron-donating (e.g., Me and OMe), and electron-withdrawing substituents (e.g., F, Cl, Br, and NO_2) on the aromatic ring reacted well with in situ-generated α-aryldiazomethanes and delivered corresponding products with good regio- and diastereoselectivity (Table 2, **4a−v**). It is pleasing to mention that phenacylidene and arylideneoxindoles were also well compatible with the transformation, providing corresponding products in good yields (Table 2, **4ab−ae**). In the next stage, we have also studied the reactivity of substrates by varying the substitution pattern on the phenacylidene and phenylidine moieties, which delivered corresponding products in moderate to good yields. Notably, the electronic nature of substituents on the aryl moiety of α-aryldiazomethane has discernible impact on the

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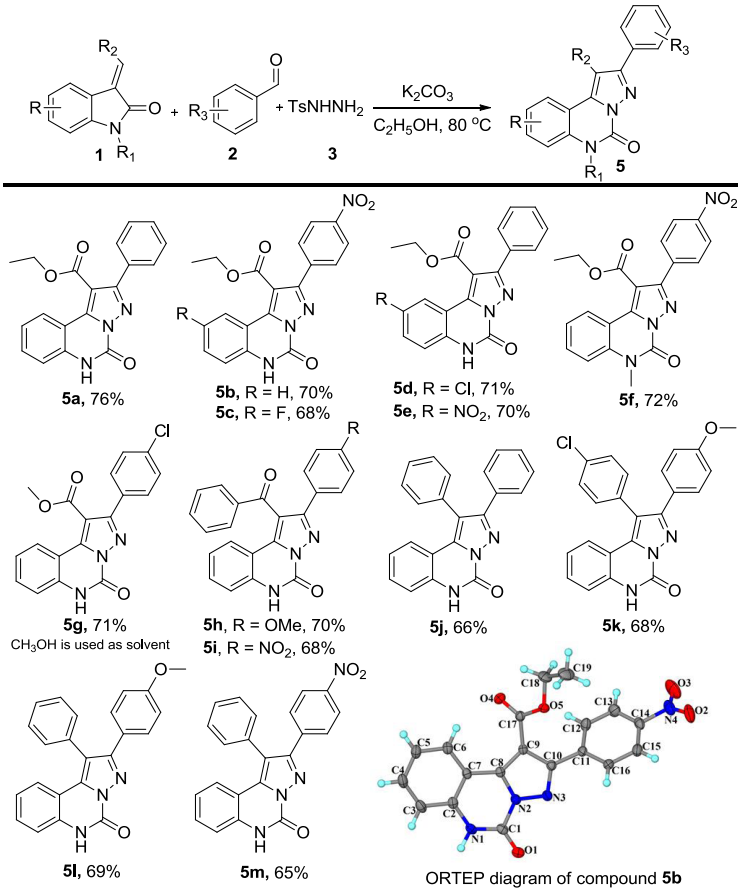
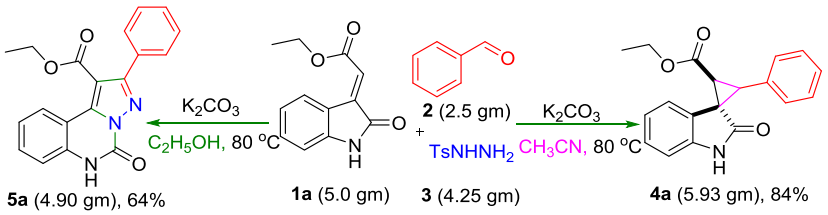
Table 3. Scope of the 1,3-Dipolar Cycloaddition/Ring Expansion Sequence Domino Reaction[a]



[a]Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), **3** (0.5 mmol), K_2CO_3 (1.5 mmol), CH_3OH (5.0 mL); yields of isolated products.

Scheme 2. Gram-Scale Synthesis of Compounds 4a and 5a



reaction efficacy, where electron-donating (e.g., Me and OMe) groups provided corresponding products in slightly better yields than the electron-withdrawing groups (e.g., Cl and NO_2). Furthermore, investigation on the effect of N-protecting groups such as -Me and -Bn revealed that even N-protected 3-ylidene-oxindoles could also be successfully involved in this transformation without altering the reaction efficacy (Table 2, **4w−z** and **4aa**).

Encouraged by these fruitful results, to explore our solvent-switchable domino reaction, we next turned to broaden the scope of pyrazoloquinazolinone construction from ethyl-2-(2-oxoindolin-3-ylidene)acetate and α-aryldiazomethane in the presence of protic solvents (Table 3). A broad range of 3-ylidene-oxindoles were converted into corresponding pyrazoloquinazolinones in moderate to good yields irrespective of substituents on the aromatic ring of 2,3-oxindole (Table 3, **5a−e**). Oxindole bearing various electron-donating and electron-withdrawing heteroatoms at the fifth position of the 2,3-oxindole ring are equally amenable for this rearrangement and delivered corresponding products in good yields. Comparable variation in the yields of the products was observed by changing the substitution pattern on the aromatic ring of the diazo partner. Similar to cyclopropanation, better yields were obtained with electron-donating substituents (Table 3, **5h**, **5k**, and **5l**) than with electron-withdrawing substituents (Table 3, **5b**, **5c**, **5f**, **5i**, and **5m**). It is worth mentioning that this rearrangement could also be successfully extended to even phenacylidene and phenylidineoxindoles to generate corresponding pyrazoloquinazolinones in moderate to good yields (Table 3, **5h−m**).

To further extend the synthetic feasibility of this reaction, a gram-scale reaction was performed under optimized reaction conditions by changing the solvent that delivered 3-spirocyclopropyl-2-oxindole (**4a**) and pyrazoloquinazolinone (**5a**) without affecting the reaction efficacy and diastereoselectivity, showing its potential for bulk-scale utility (Scheme 2).

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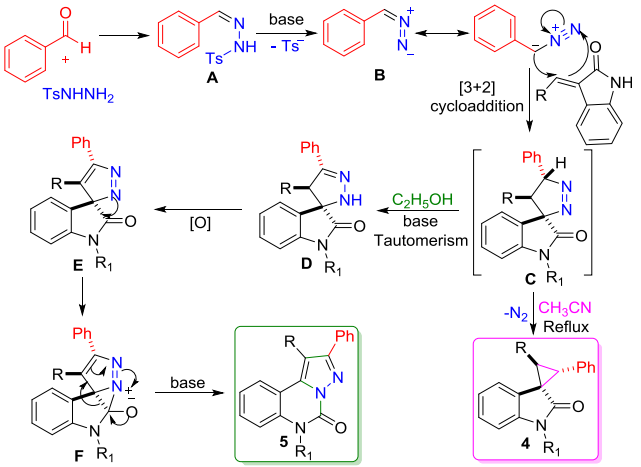
On the basis of literature[11−15] and our outcome, a plausible mechanism was proposed (Scheme 3). Initially, aldehyde

Scheme 3. Plausible Reaction Mechanism



reacts with $TsNHNH_2$ and generates corresponding hydrazone intermediate **A**, which subsequently converts to aryldiazomethane **B** in the presence of base by the elimination of tosyl group. A formal 1,3-dipolar cycloaddition of 3-ylideneoxindoles with aryldiazomethane **B** would afford intermediate **C**, which undergoes decomposition in an aprotic solvent under elevated temperatures to deliver 3-spirocyclopropyl-2-oxindole **4**. Moreover, it is also assumed that in the presence of protic solvent, intermediate **C** transforms into intermediate **D** by tautomerism, which may generate spiropyrazole-oxindole **E** by air oxidation.[15a,c] Intermediate **E** after spontaneous rearrangement delivers pyrazoloquinazolinones **5** via a ring-expanded intermediate **F**.[15d]

CONCLUSIONS

In summary, an attractive, switchable solvent-controlled product-selectivity domino reaction between 3-ylideneoxindoles and an in situ-generated α-aryldiazo compound has been developed for the synthesis of 3-spirocyclopropyl-2-oxindole and pyrazoloquinazolinones with high regio- and diastereoselectivity. Two types of domino reactions, i.e., 1,3-dipolar cycloaddition/ring contraction and unprecedented 1,3-dipolar cycloaddition/ring expansion reactions, were demonstrated by employing variable solvent conditions from identical substrates. Broad functional-group tolerance, absence of metals, and atom and step economy are the salient features of the developed protocol. Further investigations toward 1,3-dipolar cycloaddition reactions with methyleneindolinones and evaluation of biological activity for the synthesized scaffolds are currently underway.

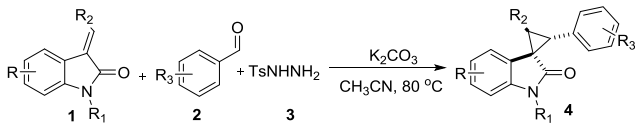
EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all reagents were used as received from commercial sources. All air- and moisture-sensitive reactions were conducted under a nitrogen or argon atmosphere using flame-dried or oven-dried glassware with magnetic stirring. Tetrahydrofuran (THF) was dried over Na with benzophenone and distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica plates (silica gel 60 F254, Merck) using UV-light, iodine, and *p*-anisaldehyde for visualization. Column chromatography was carried out using silica gel (60−120 mesh or 100−200 mesh) packed in glass columns. Technical-grade EtOAc and petroleum ether were used for column chromatography and were distilled prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Room temperature (r.t.) is 23−25 °C.

Materials. Commercial reagents were purchased from Merck, Alfa, Spectrochem, or TCI and used as received with the following exceptions. Tetrahydrofuran (THF), ethylene glycol dimethyl ether, toluene, and 1,4-dioxane were dried over Na with the benzophenone-ketyl intermediate as indicator. Dichloroethane and dichloromethane were distilled over CaH_2, and acetonitrile (CH_3CN) was distilled over P_2O_5. *N*,*N*-Dimethylformamide was distilled under reduced pressure. Other commercially available reagents and solvents were used without further purification.

Instrumentation. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or dimethyl sulfoxide (DMSO) as solvent on Bruker Avance 400, Inova Instruments, with 400, 300, and 500 MHz frequency spectrometers. The coupling constant J is given in hertz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$, δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR) and DMSO (^1H NMR: δ = 2.54 and ^{13}C NMR: δ = 39.52 ppm). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard or TMS (δ = 0.0) as the internal standard, and signal patterns are indicated as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q = quartet, qd = quartet of doublet, m = multiplet, br = broad, and tt = triplet of triplet. IR spectra were recorded on a Bruker infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a Waters-TOF spectrometer.

General Procedure for the Preparation of Spirocyclopropyloxindoles (4a−ae). 3-Ylideneoxindole **1** (0.50



mmol), arylaldehyde **2** (0.50 mmol), and $TsNHNH_2$ **3** (0.50 mmol) were stirred in 5.0 mL of CH_3CN at room temperature in a 10 mL Schlenk tube for 10 min. Then, to this solution was added K_2CO_3 (1.0 mmol) at the same temperature and the reaction mixture was stirred at refluxing temperature for 2 h. Upon the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with 10 mL of water and extracted with EtOAc (3 × 10 mL). The organic layers were combined and washed with brine and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to afford the desired product **4**.

Analytical Data for the Compounds 4a−ae. *Ethyl-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (4a).* Following the general procedure (80 °C for 2 h), compound **4a** was obtained after column chromatography (hexane/EtOAc 8:2) in 88% yield as a white solid. mp 182−183 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.32−7.18 (m, 6H), 7.02 (td, J = 7.6, 0.9 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H), 4.31−4.11 (m, 2H), 3.79 (d, J = 8.3 Hz, 1H), 3.35 (d, J = 8.3 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H)

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ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 168.2, 141.2, 133.4, 131.4, 130.6, 128.3, 127.8, 126.3, 122.7, 122.3, 109.9, 61.7, 39.6, 39.4, 37.3, 14.2 ppm. HRMS calcd for $C_{19}H_{18}O_3N$ $[M + H]^+$: 308.1281; found: 308.1289.

*Ethyl-5′-methyl-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4b**).* Following the general procedure (80 °C for 2 h), compound **4b** was obtained after column chromatography (hexane/EtOAc 8:2) in 90% yield as a creamy white solid. mp 230−232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.36−7.16 (m, 6H), 7.00 (dd, J = 7.9, 0.7 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 4.33−4.05 (m, 2H), 3.75 (d, J = 8.3 Hz, 1H), 3.33 (d, J = 8.3 Hz, 1H), 2.34 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 168.6, 138.9, 133.0, 131.6, 129.2, 128.1, 128.0, 127.5, 126.8, 123.4, 109.6, 61.6, 40.3, 40.0, 37.3, 21.4, 14.2 ppm. HRMS calcd for $C_{20}H_{20}O_3N$ $[M + H]^+$: 322.1437; found: 322.1435.

*Ethyl-5′-bromo-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4c**).* Following the general procedure (80 °C for 2 h), compound **4c** was obtained after column chromatography (hexane/EtOAc 8:2) in 82% yield as a white solid. mp 183−183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.37−7.21 (m, 6H), 6.64 (d, J = 8.3 Hz, 1H), 4.32−4.17 (m, 2H), 3.77 (d, J = 8.4 Hz, 1H), 3.35 (d, J = 8.4 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.33, 168.2, 140.2, 132.4, 130.4, 129.2, 128.8, 128.2, 127.7, 125.9, 114.9, 111.6, 61.8, 40.9, 39.8, 37.5, 14.2 ppm. HRMS calcd for $C_{19}H_{17}O_3NBr$ $[M + H]^+$: 386.0386; found: 386.0391.

*Ethyl-5′-chloro-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4d**).* Following the general procedure (80 °C for 2 h), compound **4d** was obtained after column chromatography (hexane/EtOAc 8:2) in 80% yield as a creamy white solid. mp 222−224 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.31−7.24 (m, 5H), 7.19 (dd, J = 8.3, 2.1 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 4.31−4.16 (m, 2H), 3.77 (d, J = 8.4 Hz, 1H), 3.35 (d, J = 8.4 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 168.22, 139.7, 132.4, 129.2, 128.4, 128.2, 127.7, 127.6, 127.6, 123.2, 110.7, 61.8, 40.9, 39.9, 37.5, 14.2 ppm. HRMS calcd for $C_{19}H_{17}O_3NCl$ $[M + H]^+$: 342.0891; found: 342.0890.

*Ethyl-5′-fluoro-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4e**).* Following the general procedure (80 °C for 2 h), compound **4e** was obtained after column chromatography (hexane/EtOAc 8:2) in 79% yield as a white solid. mp 186−189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.32−7.24 (m, 6H), 6.94−6.87 (m, 1H), 6.68 (dd, J = 8.5, 4.3 Hz, 1H), 4.31−4.15 (m, 2H), 3.75 (d, J = 8.3 Hz, 1H), 3.36 (d, J = 8.3 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 168.3, 158.8 (d, J = 239.1 Hz), 137.2, 132.5, 129.2, 128.2, 127.7, 114.0 (d, J = 23.8 Hz), 110.9 (d, J = 26.6 Hz), 110.3 (d, J = 8.2 Hz), 61.8, 40.9, 40.2, 37.4, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.37 ppm. HRMS calcd for $C_{19}H_{17}O_3NF$ $[M + H]^+$: 326.1187; found: 326.1184.

*Ethyl-5′-nitro-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4f**).* Following the general procedure (80 °C for 2 h), compound **4f** was obtained after column chromatography (hexane/EtOAc 8:2) in 77% yield as a light yellow solid. mp 168−170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.45 (d, J = 2.1 Hz, 1H), 8.20 (dd, J = 8.6, 2.2 Hz, 1H), 7.35−7.24 (m, 5H), 6.85 (d, J = 8.6 Hz, 1H), 4.26 (qq, J = 10.9, 7.2 Hz, 2H), 3.94 (d, J = 8.5 Hz, 1H), 3.42 (d, J = 8.5 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 167.8, 146.8, 143.3, 131.9, 129.2, 128.3, 128.0, 127.4, 124.6, 119.1, 109.7, 62.2, 41.4, 39.7, 38.0, 14.2 ppm. HRMS calcd for $C_{19}H_{17}O_5N_2$ $[M + H]^+$: 353.1132; found: 353.1137.

*Ethyl-3-(4-methoxyphenyl)-2′-oxospiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4g**).* Following the general procedure (80 °C for 2 h), compound **4g** was obtained after column chromatography (hexane/EtOAc 8:2) in 91% yield as a white solid. mp 210−212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 8.5 Hz, 3H), 7.02 (dd, J = 15.2, 7.6 Hz, 1H), 6.87−6.79 (m, 3H), 4.28−4.12 (m, 2H), 3.77 (s, 3H), 3.73 (d, J = 8.4 Hz, 1H), 3.32 (d, J = 8.3 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 168.6, 158.9, 141.2, 130.3, 127.5, 126.8, 124.8, 122.6, 122.1, 113.5, 109.8, 61.5, 55.2, 40.0, 37.5, 14.2 ppm. HRMS calcd for $C_{20}H_{20}O_4N$ $[M + H]^+$: 338.1387; found: 338.1388.

*Ethyl-5′-methoxy-3-(4-methoxyphenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4h**).* Following the general procedure (80 °C for 2 h), compound **4h** was obtained after column chromatography (hexane/EtOAc 8:2) in 93% yield as a light brown solid. mp 178−181 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 2.4 Hz, 1H), 6.84−6.81 (m, 2H), 6.78−6.71 (m, 2H), 4.27−4.14 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.69 (d, J = 8.3 Hz, 1H), 3.32 (d, J = 8.3 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 168.5, 158.9, 155.5, 134.8, 130.3, 128.1, 124.8, 113.5, 112.8, 110.2, 109.3, 61.6, 55.9, 55.2, 40.4, 40.3, 37.5, 14.2 ppm. HRMS calcd for $C_{21}H_{22}O_5N$ $[M + H]^+$: 368.1492; found: 368.1490.

*Ethyl-5′-chloro-3-(4-methoxyphenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4i**).* Following the general procedure (80 °C for 2 h), compound **4i** was obtained after column chromatography (hexane/EtOAc 8:2) in 86% yield as a brown solid. mp 180−182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.50 (d, J = 2.1 Hz, 1H), 7.22−7.16 (m, 3H), 6.81 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.3 Hz, 1H), 4.30−4.17 (m, 2H), 3.76 (s, 3H), 3.72 (d, J = 8.4 Hz, 1H), 3.32 (d, J = 8.4 Hz, 1H),1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 168.3, 159.1, 139.8, 130.3, 128.5, 127.6, 127.4, 124.4, 123.1, 113.6, 110.8, 61.8, 55.2, 40.6, 40.0, 37.7, 14.2 ppm. HRMS calcd for $C_{20}H_{19}O_4NCl$ $[M + H]^+$: 372.0997; found: 372.1000.

*Ethyl-5′-fluoro-3-(4-methoxyphenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4j**).* Following the general procedure (80 °C for 2 h), compound **4j** was obtained after column chromatography (hexane/EtOAc 8:2) in 85% yield as a brown solid. mp 168−171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.27 (dd, J = 8.9, 2.3 Hz, 1H), 7.20 (d, J = 8.6 Hz, 2H), 6.89 (td, J = 8.9, 2.3 Hz, 1H), 6.81 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 4.1 Hz, 1H), 4.22 (qq, J = 10.9, 7.1 Hz, 2H), 3.75 (s, 3H), 3.70 (d, J = 8.3 Hz, 1H), 3.32 (d, J = 8.3 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 168.4, 159.1 158.8 (d, J = 239.1 Hz), 137.1, 130.3, 128.4 (d, J = 9.5 Hz), 124.4, 113.8 (d, J = 23.5 Hz), 113.6, 110.8 (d, J = 26.4 Hz), 110.1 (d, J = 8.1 Hz), 61.7, 55.2, 40.6, 40.3, 37.6, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.26 ppm. HRMS calcd for $C_{20}H_{19}O_4NF$ $[M + H]^+$: 356.1293; found: 356.1292.

*Ethyl-3-(4-chlorophenyl)-2′-oxospiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4k**).* Following the general procedure (80 °C for 2 h), compound **4k** was obtained after column

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chromatography (hexane/EtOAc 8:2) in 84% yield as a white solid. mp 159−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.29−7.21 (m, 5H), 7.04 (td, J = 7.7, 1.0 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 4.28−4.12 (m, 2H), 3.73 (d, J = 8.2 Hz, 1H), 3.31 (d, J = 8.2 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 168.2, 141.2, 133.4, 131.4, 130.6, 128.3, 127.8, 126.3, 122.8, 122.3, 109.9, 61.7, 39.8, 39.4, 37.3, 14.2 ppm. HRMS calcd for $C_{19}H_{17}O_3NCl$ $[M + H]^+$: 342.0892; found: 342.0893

*Ethyl-3-(4-chlorophenyl)-5′-methyl-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4l**).* Following the general procedure (80 °C for 2 h), compound **4l** was obtained after column chromatography (hexane/EtOAc 8:2) in 85% yield as a light brown solid. mp 208−209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.29−7.20 (m, 5H), 7.03 (dd, J = 7.9, 0.8 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 4.29−4.13 (m, 2H), 3.69 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 8.2 Hz, 1H), 2.34 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 168.3, 138.9, 133.3, 131.8, 131.6, 130.6, 128.3, 128.2, 126.4, 123.3, 109.7, 61.7, 39.9, 39.4, 37.2, 21.3, 14.2 ppm. HRMS calcd for $C_{20}H_{19}O_3NCl$ $[M + H]^+$: 356.1048; found: 356.1051.

*Ethyl-5′-bromo-3-(4-chlorophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4m**).* Following the general procedure (80 °C for 2 h), compound **4m** was obtained after column chromatography (hexane/EtOAc 8:2) in 80% yield as a creamy white solid. mp 214−215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.62 (d, J = 1.8 Hz, 1H), 7.36 (dd, J = 8.3, 2.0 Hz, 1H), 7.28−7.18 (m, 4H), 6.62 (d, J = 8.3 Hz, 1H), 4.31−4.17 (m, 2H), 3.72 (d, J = 8.3 Hz, 1H), 3.30 (d, J = 8.3 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 167.9, 140.2, 133.6, 140.0, 130.7, 130.6, 128.4, 126.0, 115.1, 111.4, 62.0, 39.9, 39.7, 37.5, 14.2 ppm. HRMS calcd for $C_{19}H_{16}O_3NBrCl$ $[M + H]^+$: 419.9997; found: 419.9999.

*Ethyl-5′-chloro-3-(4-chlorophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4n**).* Following the general procedure (80 °C for 2 h), compound **4n** was obtained after column chromatography (hexane/EtOAc 8:2) in 77% yield as a creamy white solid. mp 206−208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.29−7.19 (m, 5H), 6.70 (d, J = 8.3 Hz, 1H), 4.32−4.16 (m, 2H), 3.72 (d, J = 8.3 Hz, 1H), 3.31 (d, J = 8.3 Hz, 1H), 1.31 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 168.0, 139.7, 133.6, 131.0, 130.6, 128.4, 128.0, 127.8, 123.3, 110.9, 62.0, 39.9, 39.8, 37.4, 14.2 ppm. HRMS calcd for $C_{19}H_{16}O_3NCl_2$ $[M + H]^+$: 376.0502; found: 376.0507.

*Ethyl-3-(4-chlorophenyl)-5′-fluoro-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4o**).* Following the general procedure (80 °C for 2 h), compound **4o** was obtained after column chromatography (hexane/EtOAc 8:2) in 76% yield as a creamy white solid. mp 149−151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.28−7.20 (m, 5H), 6.94 (td, J = 8.9, 2.6 Hz, 1H), 6.68 (dd, J = 8.5, 4.3 Hz, 1H), 4.31−4.15 (m, 2H), 3.70 (d, J = 8.3 Hz, 1H), 3.31 (d, J = 8.3 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 168.0, 158.9 (d, J = 239.5 Hz), 137.2, 133.6, 131.1, 130.6, 128.3, 127.9 (d, J = 9.3 Hz), 114.3 (d, J = 23.8 Hz), 110.9 (d, J = 26.7 Hz), 110.4 (d, J = 8.2 Hz), 61.9, 40.1, 39.9, 37.3, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.06 ppm. HRMS calcd for $C_{19}H_{16}O_3NClF$ $[M + H]^+$: 360.0797; found: 360.0800.

*Ethyl-5′-methoxy-3-(4-nitrophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4p**).* Following the general procedure (80 °C for 2 h), compound **4p** was obtained after column chromatography (hexane/EtOAc 7:3) in 82% yield as a brown solid. mp 192−195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.7 Hz, 2H), 7.98 (s, 1H), 7.48 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 2.1 Hz, 1H), 6.79 (dt, J = 16.2, 5.4 Hz, 2H), 4.30−4.17 (m, 2H), 3.81 (s, 3H), 3.78 (d, J = 8.2 Hz, 1H), 3.37 (d, J = 8.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 167.8, 155.8, 147.3, 140.6, 134.6, 130.2, 127.0, 123.3, 113.3, 110.4, 109.7, 62.0, 55.9, 40.3, 39.2, 37.1, 14.2 ppm. HRMS calcd for $C_{20}H_{19}O_6N_2$ $[M + H]^+$: 383.1238; found: 383.1241.

*Ethyl-5′-methyl-3-(4-nitrophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4q**).* Following the general procedure (80 °C for 2 h), compound **4q** was obtained after column chromatography (hexane/EtOAc 7:3) in 80% yield as a brown solid. mp 215−218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (bs, 1H), 8.14 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H), 7.05 (d, J = 7.9 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 4.31−4.16 (m, 2H), 3.78 (d, J = 8.2 Hz, 1H), 3.36 (d, J = 8.2 Hz, 1H), 2.35 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 167.8, 147.2, 140.7, 138.8, 132.1, 130.2, 128.6, 125.8, 123.5, 123.3, 109.8, 61.9, 40.1, 38.9, 37.1, 21.3, 14.2. HRMS calcd for $C_{20}H_{19}O_5N_2$ $[M + H]^+$: 367.1289; found: 367.1291.

*Ethyl-5′-chloro-3-(4-nitrophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4r**).* Following the general procedure (80 °C for 2 h), compound **4r** was obtained after column chromatography (hexane/EtOAc 7:3) in 75% yield as a brick red solid. mp 186−188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17−8.13 (m, 3H), 7.52 (d, J = 1.6 Hz, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7.27−7.23 (m, 1H), 6.82 (d, J = 8.3 Hz, 1H), 4.34−4.20 (m, 2H), 3.81 (d, J = 8.3 Hz, 1H), 3.39 (d, J = 8.3 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 167.5, 147.4, 140.0, 139.7, 130.2, 128.2, 128.1, 127.4, 123.4, 123.3, 110.9, 62.2, 39.9, 39.4, 37.3, 14.2 ppm. HRMS calcd for $C_{19}H_{16}O_5N_2Cl$ $[M + H]^+$: 387.0742; found: 387.0747.

*Ethyl-5′-fluoro-3-(4-nitrophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4s**).* Following the general procedure (80 °C for 2 h), compound **4s** was obtained after column chromatography (hexane/EtOAc 7:3) in 74% yield as a brown solid. mp 164−168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.16 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.29 (dd, J = 8.8, 2.5 Hz, 1H), 6.97 (td, J = 8.8, 2.6 Hz, 1H), 6.78 (dd, J = 8.5, 4.3 Hz, 1H), 4.32−4.18 (m, 2H), 3.79 (d, J = 8.3 Hz, 1H), 3.38 (d, J = 8.2 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 167.5, 147.4, 139.8 (d, J = 29.0 Hz), 130.2, 129.9, 128.2, 128.1, 127.4, 123.4, 123.3, 110.9, 62.1, 40.2, 39.4, 37.2, 14.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −119.49 ppm. HRMS calcd for $C_{19}H_{16}O_5N_2F$ $[M + H]^+$: 371.1038; found: 371.1041.

*Ethyl-5′-nitro-3-(4-nitrophenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4t**).* Following the general procedure (80 °C for 2 h), compound **4t** was obtained after column chromatography (hexane/EtOAc 7:3) in 72% yield as a brown solid. mp 255−258 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 2.1 Hz, 1H), 8.26 (dd, J = 8.7, 2.2 Hz, 2H), 8.19 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.6 Hz, 1H), 4.36−4.20 (m, 2H), 3.96 (d, J = 8.4 Hz, 1H), 3.47 (s, 1H), 1.32 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 167.2, 147.6, 146.5, 143.6, 139.2,

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130.2, 126.6, 125.1, 123.5, 119.4, 109.6, 62.5, 40.0, 39.6, 37.8, 14.2 ppm. HRMS calcd for $C_{19}H_{16}O_7N_3$ $[M + H]^+$: 398.0983; found: 398.0984.

*Ethyl-2′-oxo-3-(p-tolyl)spiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4u**).* Following the general procedure (80 °C for 2 h), compound **4u** was obtained after column chromatography (hexane/EtOAc 8:2) in 89% yield as a white solid. mp 188−191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (bs, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.17−7.09 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H), 6.96 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 4.22−4.03 (m, 2H), 3.68 (d, J = 8.3 Hz, 1H), 3.26 (d, J = 8.3 Hz, 1H), 2.23 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 172.9, 168.3, 142.7, 136.8, 130.3, 129.5, 129.0, 128.1, 126.8, 122.2, 121.7, 110.1, 61.7, 40.5, 39.3, 37.0, 21.2, 14.5 ppm. HRMS calcd for $C_{20}H_{20}O_3N$ $[M + H]^+$: 322.1438; found: 322.1436.

*Ethyl-5′,7′-dimethyl-2′-oxo-3-phenylspiro[cyclopropane-1,3′-indoline]-2-carboxylate (**4v**).* Following the general procedure (80 °C for 2 h), compound **4v** was obtained after column chromatography (hexane/EtOAc 8:2) in 88% yield as a white solid. mp 225−228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.32−7.19 (m, 6H), 6.83 (d, J = 0.6 Hz, 1H), 4.26−4.11 (m, 2H), 3.73 (d, J = 8.3 Hz, 1H), 3.34 (d, J = 8.3 Hz, 1H), 2.31 (s, 3H), 2.04 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 168.5, 138.0, 133.0, 131.4, 129.5, 129.2, 127.9, 127.4, 126.3, 120.6, 119.1, 61.5, 40.5, 40.2, 37.2, 21.3, 16.1, 14.2 ppm. HRMS calcd for $C_{21}H_{22}O_3N$ $[M + H]^+$: 336.1594; found: 336.1593.

*Ethyl-1′-benzyl-3-(4-methoxyphenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4w**).* Following the general procedure (80 °C for 2 h), compound **4w** was obtained after column chromatography (hexane/EtOAc 9:1) in 93% yield as a creamy white solid. mp 149−151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 1H), 7.31−7.14 (m, 8H), 7.02 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 7.8 Hz, 1H), 4.91 (d, J = 15.6 Hz, 1H), 4.82 (d, J = 15.6 Hz, 1H), 4.28−4.11 (m, 2H), 3.78 (s, 3H), 3.77 (d, J = 7.3 Hz, 1H), 3.42 (d, J = 8.3 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 168.7, 159.0, 143.1, 136.0, 130.3, 128.7, 127.6, 127.4, 126.4, 124.8, 122.5, 122.2, 113.5, 108.9, 61.5, 55.2, 44.1, 40.1, 39.8, 37.4, 14.2 ppm. HRMS calcd for $C_{27}H_{26}NO_4$ $[M + H]^+$: 428.1856; found: 428.1860.

*Ethyl-1′-benzyl-5′-methoxy-2′-oxo-3-phenylspiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4x**).* Following the general procedure (80 °C for 2 h), compound **4x** was obtained after column chromatography (hexane/EtOAc 9:1) in 90% yield as a creamy white solid. mp 148−149 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 4.3 Hz, 4H), 7.30−7.23 (m, 4H), 7.22−7.19 (m, 3H), 6.72 (dd, J = 8.5, 2.5 Hz, 1H), 6.67 (s, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.78 (d, J = 15.6 Hz, 1H), 4.29−4.16 (m, 2H), 3.79 (d, J = 8.3 Hz, 1H), 3.78 (s, 3H), 3.46 (d, J = 8.3 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 168.6, 155.7, 136.7, 136.1, 132.9, 129.2, 128.7, 128.1, 127.7, 127.6, 127.4, 112.5, 109.7, 109.3, 61.6, 55.9, 44.2, 40.7, 34.0, 37.1, 14.2 ppm. HRMS calcd for $C_{27}H_{25}NNaO_4$ $[M + H]^+$: 450.1681; found: 450.1673.

*Ethyl-1′-benzyl-5′-chloro-2′-oxo-3-phenylspiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4y**).* Following the general procedure (80 °C for 2 h), compound **4y** was obtained after column chromatography (hexane/EtOAc 9:1) in 86% yield as a light yellow solid. mp 150−152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.35−7.22 (m, 8H), 7.15 (dd, J = 13.6, 4.8 Hz, 3H), 6.68 (d, J = 8.4 Hz, 1H), 4.89 (d, J = 15.7 Hz, 1H), 4.78 (d, J = 15.7 Hz, 1H), 4.34−4.15 (m, 2H), 3.81 (d, J = 8.3 Hz, 1H), 3.48 (d, J = 8.3 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 168.4, 141.7, 135.6, 132.5, 129.2, 128.8, 128.2, 128.0, 127.9, 127.8, 127.8, 127.5, 127.4, 123.2, 109.8, 61.8, 44.2, 41.0, 39.6, 37.3, 14.2 ppm. HRMS calcd for $C_{26}H_{23}O_3NCl$ $[M + H]^+$: 432.1361; found: 432.1371.

*Ethyl-3-(4-methoxyphenyl)-1′-methyl-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4z**).* Following the general procedure (80 °C for 2 h), compound **4z** was obtained after column chromatography (hexane/EtOAc 9:1) in 90% yield as a white solid. mp 156−157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.4 Hz, 1H), 7.30 (td, J = 7.7, 0.9 Hz, 1H), 7.24 (d, J = 8.6 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 8.7 Hz, 2H), 4.26−4.10 (m, 2H), 3.78 (s, 3H), 3.74 (d, J = 8.3 Hz, 1H), 3.35 (d, J = 8.3 Hz, 1H), 3.18 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 168.6, 158.9, 144.1, 130.2, 127.6, 126.3, 124.7 122.4, 122.2, 113.5, 108.0, 61.5, 55.2, 39.8, 39.7, 37.5, 26.6, 14.2 ppm. HRMS calcd for $C_{21}H_{22}O_4N$ $[M + H]^+$: 352.1543; found: 352.1542.

*Ethyl-5′-methoxy-3-(4-methoxyphenyl)-2′-oxospiro-[cyclopropane-1,3′-indoline]-2-carboxylate (**4aa**).* Following the general procedure (80 °C for 2 h), compound **4aa** was obtained after column chromatography (hexane/EtOAc 9:1) in 92% yield as a white solid. mp 145−147 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 2.4 Hz, 1H), 6.85−6.81 (m, 3H), 6.77 (d, J = 8.5 Hz, 1H), 4.26−4.12 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 3.70 (d, J = 8.3 Hz, 1H), 3.35 (d, J = 8.3 Hz, 1H), 3.16 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 168.6, 158.9, 155.7, 137.7, 130.2, 127.6, 124.7, 113.5, 112.4, 109.6, 108.2, 61.5, 55.9, 55.2, 40.1, 39.9, 37.4, 26.7, 14.2 ppm. HRMS calcd for $C_{22}H_{24}O_5N$ $[M + H]^+$: 382.1649; found: 382.1666.

*2-Benzoyl-3-phenylspiro[cyclopropane-1,3′-indolin]-2′-one (**4ab**).* Following the general procedure (80 °C for 2 h), compound **4ab** was obtained after column chromatography (hexane/EtOAc 8:2) in 78% yield as a light yellow solid. mp 212−213 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.79 (s, 1H), 7.57−7.52 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.37−7.26 (m, 6H), 7.17 (td, J = 7.7, 1.1 Hz, 1H), 6.98 (td, J = 7.7, 0.9 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 4.29 (d, J = 8.3 Hz, 1H), 4.15 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 173.9, 140.9, 137.0, 133.7, 133.3, 129.3, 128.8, 128.5, 128.2, 127.6, 126.5, 122.4, 122.4, 109.8, 41.9, 41.3, 39.9 ppm. HRMS calcd for $C_{23}H_{18}O_2N$ $[M + H]^+$: 340.1332; found: 340.1344.

*2,3-Diphenylspiro[cyclopropane-1,3′-indolin]-2′-one (**4ac**).* Following the general procedure (80 °C for 2 h), compound **4ac** was obtained after column chromatography (hexane/EtOAc 8:2) in 78% yield as a creamy white solid. mp 213−218 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.41 (d, J = 7.4 Hz, 2H), 7.37−7.27 (m, 8H), 7.09 (td, J = 7.7, 1.0 Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 6.72 (dd, J = 7.6, 0.8 Hz, 1H), 6.06 (d, J = 7.5 Hz, 1H), 3.98 (d, J = 8.7 Hz, 1H), 3.59 (d, J = 8.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 141.0, 135.0, 134.6, 129.9, 129.4, 128.6, 128.2, 128.1, 127.7, 127.4, 126.6, 121.4, 120.9, 109.6, 42.6, 39.9, 39.8 ppm. HRMS calcd for $C_{22}H_{18}ON$ $[M + H]^+$: 312.1383; found: 312.1381.

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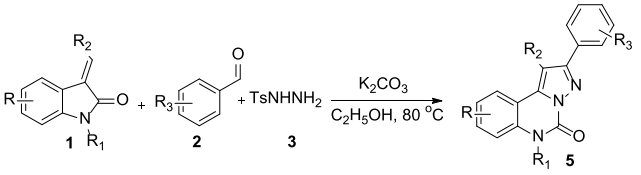
*2-(4-Methoxyphenyl)-3-phenylspiro[cyclopropane-1,3′-indolin]-2′-one (**4ad**).* Following the general procedure (80 °C for 2 h), compound **4ad** was obtained after column chromatography (hexane/EtOAc 8:2) in 82% yield as a creamy white solid. mp 188−191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.36−7.27 (m, 7H), 7.08 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.6 Hz, 2H), 6.81−6.76 (m, 1H), 6.70 (t, J = 7.6 Hz, 1H), 6.04 (d, J = 7.5 Hz, 1H), 3.94 (d, J = 8.7 Hz, 1H), 3.78 (s, 3H), 3.54 (d, J = 8.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 158.9, 140.9, 135.1, 130.4, 130.0, 128.6, 128.2, 127.6, 126.6, 126.5, 121.4, 120.8, 113.6, 109.6, 55.2, 42.3, 39.9, 39.9 ppm. HRMS calcd for $C_{23}H_{20}O_2N$ $[M + H]^+$: 342.1489; found: 342.1495.

*2-(4-Chlorophenyl)-3-(4-methoxyphenyl)spiro-[cyclopropane-1,3′-indolin]-2′-one (**4ae**).* Following the general procedure (80 °C for 2 h), compound **4ae** was obtained after column chromatography (hexane/EtOAc 8:2) in 81% yield as a creamy white solid. mp 200−202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.30 (d, J = 6.4 Hz, 4H), 7.21 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 7.5 Hz, 1H), 6.84 (dd, J = 15.7, 8.0 Hz, 3H), 6.76 (d, J = 7.5 Hz, 1H), 6.06 (d, J = 7.4 Hz, 1H), 3.87 (d, J = 8.5 Hz, 1H), 3.79 (s, 3H), 3.48 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 159.0, 140.8, 133.6, 133.5, 131.3, 130.3, 128.8, 127.8, 126.7, 126.1, 121.6, 120.8, 113.6, 109.6, 55.2, 42.4, 39.8, 39.0 ppm. HRMS calcd for $C_{23}H_{19}O_2NCl$ $[M + H]^+$: 376.1099; found: 376.1111.

General Procedure for the Preparation of Dihydropyrazoloquinazolones (5a−m). 3-Ylideneoxindole **1** (0.50



mmol), arylaldehyde **2** (0.50 mmol), and $TsNHNH_2$ **3** (93 mg, 0.50 mmol) were stirred in 5.0 mL of C_2H_5OH at room temperature in a 10 mL Schlenk tube for 10 min. Then, to this solution was added K_2CO_3 (1.50 mmol) at the same temperature and the reaction mixture was stirred at refluxing temperature for 2 h. Upon the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with 10 mL of water, and extracted with EtOAc (3 × 10 mL). The organic layers were combined and washed with brine and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to afford the desired product **5**.

Analytical Data for the Compounds 5a−m. *Ethyl-5-oxo-2-phenyl-5,6-dihydropyrazolo[1,5-c]quinazoline-1-carboxylate (**5a**).* Following the general procedure (80 °C for 2 h), compound **5a** was obtained after column chromatography (hexane/EtOAc 5:5) in 75% yield as a creamy white solid. mp 342−344 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 8.79 (d, J = 8.2 Hz, 1H), 7.71−7.64 (m, 2H), 7.56−7.50 (m, 2H), 7.45 (dd, J = 6.4, 3.6 Hz, 3H), 7.34 (t, J = 7.3 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 157.4, 146.1, 141.8, 134.4, 132.1, 131.7, 129.2, 129.1, 128.0, 126.3, 124.3, 116.6, 112.3, 109.9, 61.5, 13.7 ppm. HRMS calcd for $C_{19}H_{16}O_3N_3$ $[M + H]^+$: 334.1192; found: 334.1199.

*Ethyl-2-(4-nitrophenyl)-5-oxo-5,6-dihydropyrazolo[1,5-c]-quinazoline-1-carboxylate (**5b**).* Following the general procedure (80 °C for 2 h), compound **5b** was obtained after column chromatography (hexane/EtOAc 5:5) in 70% yield as a creamy white solid. mp 336−338 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 1H), 8.93 (d, J = 7.9 Hz, 1H), 8.33 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.51−7.36 (m, 2H), 4.32 (q, 6.8 Hz, 2H), 1.15 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 168.3, 159.0, 152.7, 149.2, 147.0, 144.0, 140.5, 136.6, 135.1, 131.0, 128.2, 127.8, 121.2, 116.5, 114.0, 66.2, 18.6 ppm. HRMS calcd for $C_{19}H_{15}O_5N_4$ $[M + H]^+$: 379.1037; found: 379.1039.

*Ethyl-9-fluoro-2-(4-nitrophenyl)-5-oxo-5,6-dihydropyrazolo[1,5-c]quinazoline-1-carboxylate (**5c**).* Following the general procedure (80 °C for 2 h), compound **5c** was obtained after column chromatography (hexane/EtOAc 5:5) in 68% yield as a creamy white solid. mp 230−235 °C. ^{1}H NMR (300 MHz, DMSO) δ 12.42 (s, 1H), 8.65 (dd, J = 10.5, 2.7 Hz, 1H), 8.37 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.63−7.49 (m, 1H), 7.44 (dd, J = 9.0, 5.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 162.4, 157.9, 155.5, 153.0, 147.1, 142.8, 140.7, 138.2, 131.9, 129.9, 122.7, 119.3, 119.0, 117.5, 117.4, 111.6, 111.5, 111.0, 110.7, 108.2, 60.8, 12.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0 ppm. HRMS calcd for $C_{19}H_{14}O_5N_4F$ $[M + H]^+$: 397.0943; found: 397.0968.

*Ethyl-9-chloro-5-oxo-2-phenyl-5,6-dihydropyrazolo[1,5-c]quinazoline-1-carboxylate (**5d**).* Following the general procedure (80 °C for 2 h), compound **5d** was obtained after column chromatography (hexane/EtOAc 5:5) in 71% yield as a creamy white solid. mp 345−348 °C. ^{1}H NMR (300 MHz, DMSO) δ 12.27 (bs, 1H), 8.61 (d, J = 7.4 Hz, 1H), 7.68−7.54 (m, 5H), 7.45−7.31 (m, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.10 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 164.2, 154.3, 144.2, 141.7, 136.0, 134.4, 132.2, 131.4, 131.0, 128.8, 125.8, 123.7, 116.6, 111.72, 108.7, 61.8, 14.0 ppm. HRMS calcd for $C_{19}H_{15}O_3N_3Cl$ $[M + H]^+$: 368.0797; found: 368.0798.

*Ethyl-9-nitro-5-oxo-2-phenyl-5,6-dihydropyrazolo[1,5-c]-quinazoline-1-carboxylate (**5e**).* Following the general procedure (80 °C for 2 h), compound **5e** was obtained after column chromatography (hexane/EtOAc 5:5) in 70% yield as a creamy white solid. mp 190−195 °C. ^{1}H NMR (300 MHz, DMSO) δ 12.48 (s, 1H), 9.03 (d, J = 2.1 Hz, 1H), 8.37 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.81 (dd, J = 8.8, 2.1 Hz, 1H), 7.36 (d, J = 8.8 Hz, 2H), 4.28 (tt, J = 11.7, 5.8 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO) δ 162.9, 153.7, 147.7, 143.3, 140.7, 138.7, 135.0, 134.4, 130.4, 130.2, 127.9, 123.3, 123.2, 118.2, 114.7, 61.4, 13.4 ppm. HRMS calcd for $C_{19}H_{15}N_4O_5$ $[M + H]^+$: 379.1037; found: 379.1025.

*Ethyl-6-methyl-2-(4-nitrophenyl)-5-oxo-5,6-dihydropyrazolo[1,5-c]quinazoline-1-carboxylate (**5f**).* Following the general procedure (80 °C for 2 h), compound **5f** was obtained after column chromatography (hexane/EtOAc 5:5) in 72% yield as a light yellow solid. mp 268−272 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.31 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 7.40−7.30 (m, 3H), 4.33 (q, J = 7.0 Hz, 2H), 2.45 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 168.3, 158.8, 152.7, 149.2, 146.9, 144.1, 138.3, 137.7, 135.1, 130.6, 127.8, 121.1, 116.3, 113.7, 66.2, 26.0, 18.6 ppm. HRMS calcd for $C_{20}H_{17}O_5N_4$ $[M + H]^+$: 393.1194; found: 393.1193.

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*Methyl-2-(4-chlorophenyl)-5-oxo-5,6-dihydropyrazolo-[1,5-c]quinazoline-1-carboxylate (**5g**).* Following the general procedure using MeOH as solvent instead of EtOH (65 °C for 2 h), compound **5g** was obtained after column chromatography (hexane/EtOAc 5:5) in 71% yield as a light brown solid. mp 324−326 °C. ^{1}H NMR (300 MHz, DMSO) δ 12.28 (s, 1H), 8.53 (d, J = 8.0 Hz, 1H), 7.69−7.54 (m, 5H), 7.44−7.31 (m, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (75 MHz, DMSO) δ 164.2, 153.45, 143.6, 141.2, 135.5, 133.9, 131.6, 130.8, 130.3, 128.4, 125.2, 123.2, 116.1, 111.2, 107.8, 52.2 ppm. HRMS calcd for $C_{18}H_{13}O_3N_3Cl$ $[M + H]^+$: 354.0640; found: 354.0655.

*1-Benzoyl-2-(4-methoxyphenyl)pyrazolo[1,5-c]-quinazolin-5(6H)-one (**5h**).* Following the general procedure (80 °C for 2 h), compound **5h** was obtained after column chromatography (hexane/EtOAc 5:5) in 70% yield as a creamy white solid. mp 380−382 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO) δ 12.36 (s, 1H), 10.15 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 7.87−7.73 (m, 3H), 7.58 (s, 1H), 7.51−7.36 (m, 5H), 7.24 (d, J = 7.0 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 199.27, 166.1, 164.9, 160.0, 149.5, 142.7, 141.6, 135.3, 135.1, 134.5, 134.4, 132.3, 131.3, 129.9, 128.6, 127.1, 125.7, 121.4, 119.3, 60.5 ppm. HRMS calcd for $C_{24}H_{18}O_3N_3$ $[M + H]^+$: 396.1348; found: 396.1362.

*1-Benzoyl-2-(4-nitrophenyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**5i**).* Following the general procedure (80 °C for 2 h), compound **5i** was obtained after column chromatography (hexane/EtOAc 5:5) in 68% yield as a creamy white solid. mp 370−372 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO) δ 12.07 (s, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.78 (t, J = 7.5 Hz, 3H), 7.62 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 7.39−7.25 (m, 5H), 7.01 (t, J = 7.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 192.6, 152.4, 147.9, 144.9, 140.6, 137.7, 137.1, 135.2, 134.5, 131.3, 129.8, 129.4, 129.0, 124.7, 123.6, 123.5, 116.6, 115.3, 111.7 ppm. HRMS calcd for $C_{23}H_{15}N_4O_4$ $[M + H]^+$: 411.1088; found: 411.1093.

*1,2-Diphenylpyrazolo[1,5-c]quinazolin-5(6H)-one (**5j**).* Following the general procedure (80 °C for 2 h), compound **5j** was obtained after column chromatography (hexane/EtOAc 5:5) in 66% yield as a creamy white solid. mp 340−342 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 7.59 (dd, J = 7.9, 1.5 Hz, 2H), 7.54−7.48 (m, 4H), 7.45−7.38 (m, 3H), 7.35 (d, J = 8.0 Hz, 1H), 7.31−7.25 (m, 3H), 7.01 (t, J = 7.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 158.4, 150.0, 142.3, 139.7, 137.5, 136.9, 135.5, 134.8, 134.2, 133.4, 133.4, 133.2, 133.0, 127.8, 127.7, 121.8, 121.1, 117.9 ppm. HRMS calcd for $C_{22}H_{16}ON_3$ $[M + H]^+$: 338.1288; found: 338.1307.

*1-(4-Chlorophenyl)-2-(4-methoxyphenyl)pyrazolo[1,5-c]-quinazolin-5(6H)-one (**5k**).* Following the general procedure (80 °C for 2 h), compound **5k** was obtained after column chromatography (hexane/EtOAc 5:5) in 68% yield as a creamy white solid. mp 360−362 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.94 (s, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.3 Hz, 3H), 7.37 (t, J = 8.8 Hz, 3H), 7.14 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 3.75 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO) δ 160.1, 153.1, 144.8, 137.7, 135.3, 133.8, 133.1, 132.0, 130.6, 130.0, 129.8, 124.5, 123.4, 122.8, 116.5, 115.4, 114.4, 112.9, 55.6 ppm. HRMS calcd for $C_{23}H_{17}O_2N_3Cl$ $[M + H]^+$: 402.1004; found: 402.1015.

*2-(4-Methoxyphenyl)-1-phenylpyrazolo[1,5-c]quinazolin-5(6H)-one (**5l**).* Following the general procedure (80 °C for 2 h), compound **5l** was obtained after column chromatography (hexane/EtOAc 5:5) in 69% yield as a creamy white solid. mp 310−312 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO) δ 11.61 (s, 1H), 7.53−7.48 (m, 2H), 7.27−7.16 (m, 8H), 6.94 (d, J = 8.6 Hz, 2H), 6.91−6.84 (m, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 164.3, 158.8, 150.3, 142.3, 139.5, 136.9, 136.6, 134.4, 133.3, 133.2, 132.8, 129.3, 127.9, 127.6, 121.5, 120.91, 119.5, 118.1, 60.0 ppm. HRMS calcd for $C_{23}H_{18}O_2N_3$ $[M + H]^+$: 368.1394; found: 368.1409.

*2-(4-Nitrophenyl)-1-phenylpyrazolo[1,5-c]quinazolin-5(6H)-one (**5m**).* Following the general procedure (80 °C for 2 h), compound **5m** was obtained after column chromatography (hexane/EtOAc 5:5) in 65% yield as a brown solid. mp 315−318 °C. ^{1}H NMR (300 MHz, DMSO) δ 12.08 (s, 1H), 8.19 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.59 (s, 2H), 7.54−7.41 (m, 3H), 7.37 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 151.1, 147.7, 144.6, 138.9, 138.2, 135.3, 132.2, 131.0, 130.8, 130.2, 129.4, 124.2, 123.4, 122.9, 117.5, 116.6, 113.0 ppm. HRMS calcd for $C_{22}H_{15}O_3N_4$ $[M + H]^+$: 383.1139; found: 383.1142.

*5′-(4-Methoxyphenyl)-4′-(p-tolyl)-2′,4′-dihydrospiro-[indoline-3,3′-pyrazol]-2-one (**D**).* ^{1}H NMR (400 MHz, DMSO) δ 10.31 (s, 1H), 7.90 (s, 1H), 7.46 (d, J = 8.7 Hz, 2H), 7.07−6.99 (m, 3H), 6.87 (dd, J = 15.2, 8.3 Hz, 4H), 6.73 (d, J = 7.7 Hz, 1H), 6.53 (t, J = 7.5 Hz, 1H), 6.18 (d, J = 7.4 Hz, 1H), 4.76 (s, 1H), 3.72 (s, 3H), 2.21 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ 179.8, 159.7, 151.5, 142.9, 136.8, 133.0, 129.5, 129.4, 129.2, 128.1, 127.2, 126.4, 125.5, 121.2, 114.3, 109.6, 73.7, 58.6, 55.6, 21.2 ppm. HRMS calcd for $C_{24}H_{22}O_2N_3$ [M + H]+: 384.1707; found: 384.5140.

*4′-(4-Chlorophenyl)-5′-(4-methoxyphenyl)-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (**D1**).* ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO) δ 10.04 (s, 1H), 7.72 (s, 1H), 7.48−7.41 (m, 3H), 7.14 (d, J = 8.6 Hz, 2H), 6.96 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 6.65 (dd, J = 11.5, 8.3 Hz, 2H), 6.50 (t, J = 7.5 Hz, 1H), 6.23 (d, J = 7.4 Hz, 1H), 4.63 (s, 1H), 3.64 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO) δ 184.6, 163.7, 155.2, 147.1, 138.3, 135.9, 135.1, 133.7, 133.21, 132.6, 131.5, 131.3, 131.1, 126.1, 118.7, 114.4, 79.2, 63.3, 59.9. ppm. HRMS calcd for $C_{23}H_{19}ClN_3O_2$ $[M + H]^+$: 404.1160; found: 404.5130.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental details and characterization data (PDF)

Crystallographic data (CIF)(CIF)

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Notes

The authors declare no competing financial interest.

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