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Graphical Abstract

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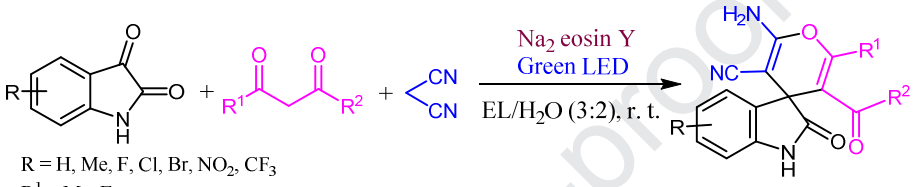

Eosin Y-catalyzed one-pot synthesis of spiro[4*H*-pyran-oxindole] under visible light irradiation

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Abstract—An efficient and simple synthetic approach has been developed for the preparation of biologically interesting spiro[oxindole-3,4'-(4'*H*-pyran)] derivatives via visible light-mediated one-pot, three-component reaction of isatins, 1,3-dicarbonyl compounds and malononitrile by using an inexpensive organic dye, Na_2 eosin Y, as the photocatalyst in aqueous ethyl lactate at ambient temperature. The substrate scope of this three-component reaction is expanded to linear 1,3-dicarbonyl compounds as viable starting materials.

Keywords:
Spiro[4*H*-pyran-oxindole]
Linear 1,3-dicarbonyl compounds
Multicomponent reaction
Eosin Y
Visible light

1. Introduction

In recent years, the use of light as a rich, readily available and almost inexhaustible source of clean energy in green organic synthesis has attracted considerable attention. Visible light-promoted organic reactions have enormous advantages such as low cost, safety, environmental friendliness, good compatibility with functional groups and wide substrate suitability [1-7]. In addition, multicomponent reactions (MCRs) have become useful synthetic tools for the preparation of novel and structurally diverse compounds in which at least three different starting materials join through covalent bonds in a single operation to form multiple bond with high efficiency, atomic economy and low synthesis cost [8-10]. Therefore, the exploration of practical and eco-friendly visible light-promoted MCRs is highly desirable in green and sustainable chemistry [11-12].

Spirooxindoles are versatile structural motifs and they are found in many natural products or synthetic compounds with important biological or pharmacological activities [13]. Due to their increased structural complexity and important biological activities, significant attention has been focused on the efficient and selective construction of various spirooxindole frameworks [14]. In very years, some complex spirooxindoles have been assembled, such as spirooxindole-fused thiazolidine (compound A) [15], spirooxindole-dihydroquinazolinone (compound **B**) [16], spirooxindole pyrrolone (compound **C**) [17], bridged *O*,*O*-ketals with spirooxindole skeleton (compound **D**) [18], spirooxindole-fused thiaindan (compound **E**) [19], spirooxindole-urazole (compound **F**) [20], as listed in the Figure 1.

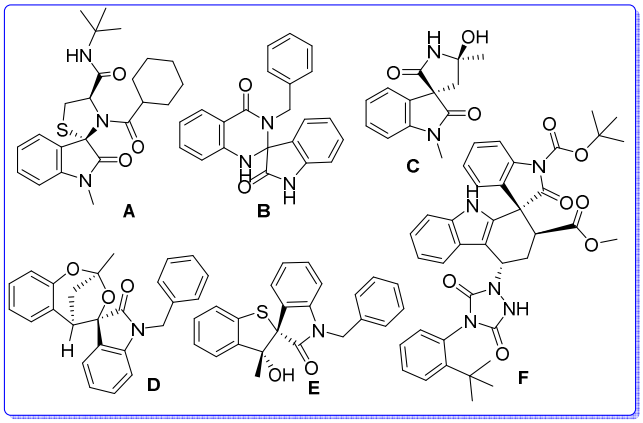

Figure 1. Selected representative compounds containing spirooxindole frameworks

Spiro[4*H*-pyran-oxindole] derivatives, which belong to the spirooxindole family of compounds, exhibit various biological activities such as anticancer, antifungal, and antibacterial, antioxidant, spasmolytic, diuretic, and anti-anaphylactic properties [21]. Because of the importance of such compounds, enormous effort has been made to synthesize these spiro compounds. Although many strategies have been developed for the

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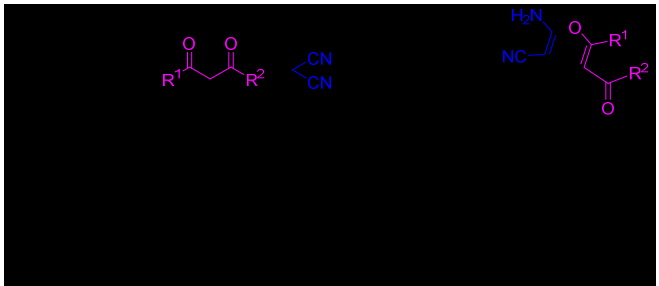
preparation of spiro[4*H*-pyran-oxindole], the classical method is by reaction of isatins with active methylene compounds and malononitrile in the presence of various catalysts such as sodium stearate [22], L-proline [23], L-proline-melamine [24], $C_4(DABCO\text{-}SO_3H)_2{\cdot}4Cl$ [25], trisodium citrate dehydrate [26], basic ionic liquid [27-28], hexamethylenetetramine [29], triethylamine [30-31], borax [32], α-amylase [33], or barium (*S*)-prolinate [34] (Scheme 1a). While such methods have facilitated the synthesis of spiro[4*H*-pyran-oxindole], they showed varying grades of success as well as limitations such as high temperature, longer reaction time, poor substrate scope, low yields, use of toxic solvents, or complex catalyst preparation. Thus, the development of more efficient, economical and general method for the synthesis of such important compounds is highly desirable.

In the past few years, ruthenium and iridium complexes are the most commonly used photocatalysts in organic photosynthesis [35-36] Although these complexes have excellent catalytic properties, they are expensive, unstable, and potentially toxic. Recently, eosin Y, a metal-free and readily available organic dye, has been widely used as an attractive alternative to transition metal complexes in various visible-light promoted organic transformations because it is usually relatively cheap and less toxic [37]. Inspired by aforementioned findings and as a part of our ongoing research in the field of green chemistry [38], herein, we report the visible light-mediated one-pot, three-component reaction of isatins, linear 1,3-dicarbonyl compounds and malononitrile for the synthesis of spiro[oxindole-3,4'-(4'*H*-pyran)] derivatives by using Na_2 eosin Y as a photocatalyst in aqueous ethyl lactate (EL) at room temperature (Scheme 1b). The reaction is a fruitful one-pot approach under highly effective, mild and facile reaction conditions.



Scheme 1 Different strategies for the synthesis of spiro[oxindole-3,4'-(4'*H*-pyran)] compounds

2. Results and discussion

To commence our studies, three-component reaction of isatin, malononitrile and ethyl acetoacetate was chosen as a model reaction for the optimization of the reaction conditions (Table 1). When the model reaction was performed in water-ethyl lactate at room temperature under white light emitting diode (LED) irradiation at ambient temperature, no desired product **4a** was formed, and only two component product of isatin and malononitrile, 2-(2-oxoindolin-3-ylidene)malononitrile (**I**), was detected. In order to promote this reaction, various organic photocatalysts including rose bengal, rhodamine B, riboflavin, basic fuchsine, erythrosin B, rhodamine 6G, alizarin, fluorescein, sodium anthraquinone sulfonate, xanthene, perylene, phenanthrenequinone, acenaphthenequinone, 9*H*-xanthen-9-one, 9-fluorenone, and Na_2 eosin Y (Figure 2) were examined under the same conditions. We are pleased to find this three-component reaction can be proceed and the corresponding product **4a** was obtained in 40–90% yields (Table 1, entries 2–17). These results indicated that Na_2 eosin Y exhibited the best performance for this reaction (entry 17). Besides organic photocatalysts, semiconductor materials such as mesoporous graphitic carbon nitride (g-C_3N_4) [39] and CdS [40] were also tested, which delivered **4a** in 52% and 78% yields, respectively (Table 1, entries 18 and 19).

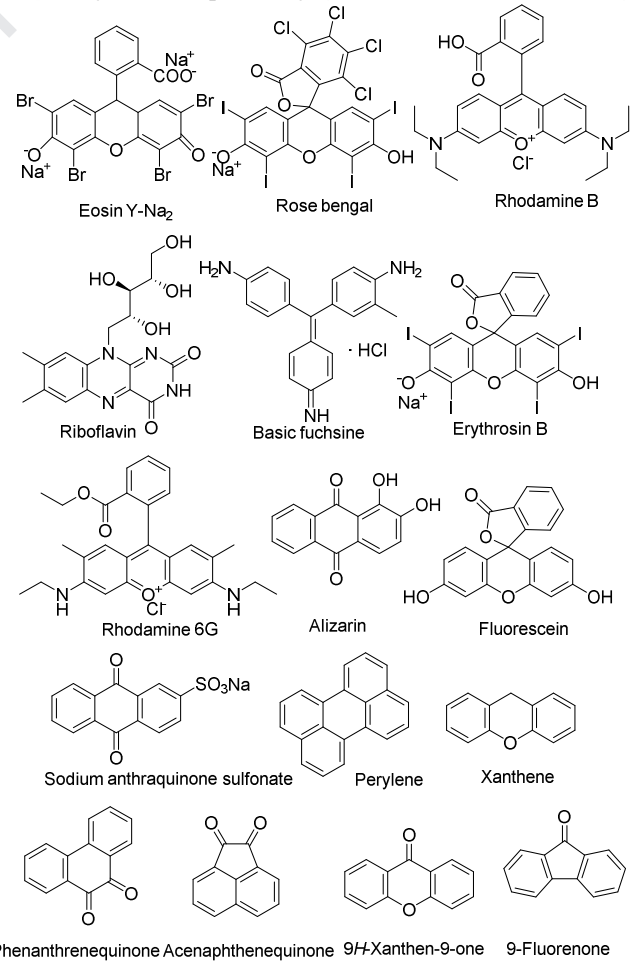
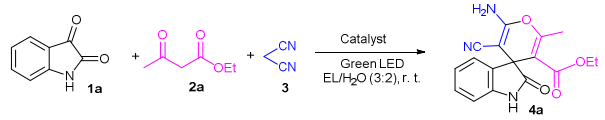


Figure 2 Photocatalysts tested in this study

Table 1

Catalyst Screen for the Reaction of Isatin, Ethyl Acetoacetate and Malononitrile[a]



Entry	Phocatalyst	Time (h)	Yield (%)[b]
1	no	12	0
2	Rose bengal	4	76
3	Rhodamine B	4	75
4	Riboflavin	4	72
5	Basic fuchsine	4	65
6	Erythrosin B	4	40
7	Rhodamine 6G	4	68
8	Alizarin	4	70
9	Fluorescein	4	72
10	Sodium anthraquinone sulfonate	4	65
11	Xanthene	4	38
12	Perylene	4	39
13	Phenanthrenequinone	4	48
14	Acenaphthenequinone	4	52
15	9*H*-Xanthen-9-one	4	51
16	9-Fluorenone	4	36
17	Na_2 eosin Y	4	90
18[c]	g-C_3N_4	4	52
19	CdS	4	78

[a] Reaction condition: isatin (1 mmol), malononitrile (1 mmol) and ethyl acetoacetate (1 mmol) in EL/H_2O (3:2, 2 ml), catalyst (2 mol%), room temperature, 10 W white LED.

[b] Isolated yield.

[c] 20 mg.

Table 2

Further optimization of the reaction conditions for the synthesis of **4a**[a]

Entry	Light Source	Time (h)	Yield (%)[b]
1	White light	$CHCl_3$	10
2	White light	CH_3CN	16
3	White light	THF	29
4	White light	DMF	31
5	White light	EtOAc	74
6	White light	CH_3OH	75
7	White light	H_2O	76
8	White light	EtOH	80
9	White light	EL	81
10	White light	EtOH:H_2O (1:1)	86
11	White light	EtOH:H_2O (2:1)	83
12	White light	EL:H_2O (1:1)	90
13	White light	EL:H_2O (2:1)	85
14	White light	EL:H_2O (1:2)	80
15	White light	EL:H_2O (3:2)	90
16	Green light	EL:H_2O (3:2)	94
17	Blue light	EL:H_2O (3:2)	88
18	Ultraviolet light	EL:H_2O (3:2)	90
19	no	EL:H_2O (3:2)	trace
20[c]	Green light	EL:H_2O (3:2)	79
21[d]	Green light	EL:H_2O (3:2)	85

[a] Reaction condition: isatin (1 mmol), malononitrile (1 mmol) and ethyl acetoacetate (1 mmol) in solvent (2 ml), Na_2 eosin Y (2 mol%), room temperature.

b Isolated yield.

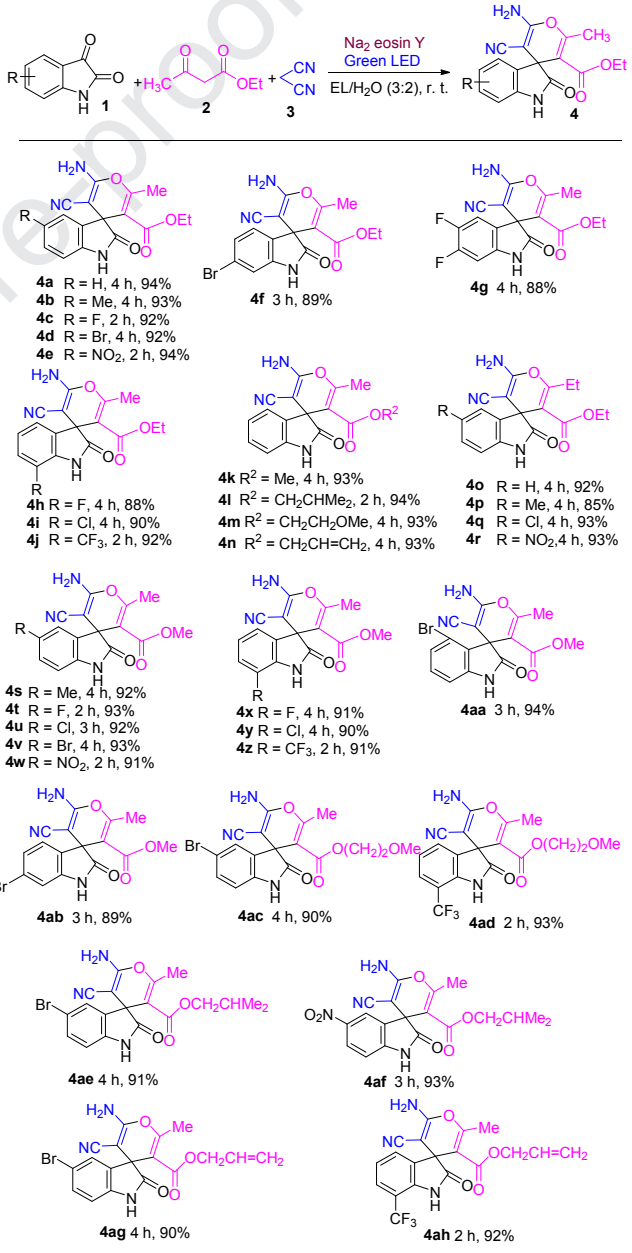
[c] 0.5 mol% Na_2 eosin Y.

[d] 1 mol% Na_2 eosin Y.

A screening of solvents revealed that ethyl lactate (EL) was the best solvent for this transformation. Other solvents, such as $CHCl_3$, CH_3CN, THF, DMF, EtOAc, CH_3OH resulted in lower yields (Table 2, entries 1–6). Further study found that the EL/H_2O solvent system was better for improving the yield of the corresponding product. Its ratio of 3:1 was found suitable for this three-component reaction, giving the expected product in 90% yield (entry 15). The screening with different light sources revealed that green light slightly increased the yield (entry 16). A control experiment showed that only a trace of the product **4a** was detected in the absence of light source (entry 19). The yield was decreased to 79% by using 0.5 mol% Na_2 eosin Y (Table 1, entry 20). These results imply that eosin Y and visible light are essential for the successful formation of product **4a**.

Table 3.

Synthesis of spiro[oxindole-3,4'-(4'*H*-pyran)] compounds from various isatins and β-keto ester[a]



[a] Reaction condition: isatin (1 mmol), β-keto esters (1 mmol) and malononitrile (1 mmol) in EL/H_2O (3:2, 2 ml), Na_2 eosin Y (2 mol%), 10 W green LED, room temperature, isolated yields.

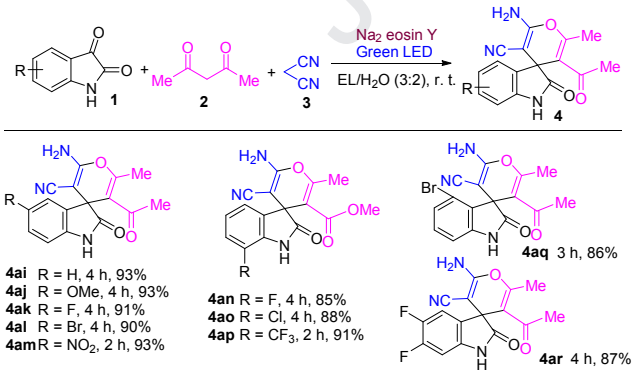
Under the established reaction conditions (Table 2, entry 16), the substrate scope of this three-component reaction was investigated. First, the reactivity of different isatins with ethyl acetoacetate and malononitrile was explored. As illustrated in Table 3, isatins containing electron-donating or electron-withdrawing groups on the aryl ring were able to undergo the three-component reaction. The position and electronic properties of substituents on the isatin skeleton have no apparent effect on the reaction and furnished the desired products **4** in high to excellent yields. Gratifyingly, the halogen substituted isatins are well tolerated in the transformation, which would offer the potential for further molecular complexity via post-functionalization.

Subsequently, we further examined the reactivity of 1,3-dicarbonyl compounds. The results show β-ketoesters with different ester groups such as methyl acetoacetate, isobutyl 3-oxobutanoate, 2-methoxyethyl acetoacetate, allyl acetoacetate all reacted smoothly under the standard conditions, furnishing the corresponding products in excellent yields. Methyl 3-oxopentanoate underwent the desired reaction, rendering the corresponding products **4o-4r** effectively.

In addition, the present method was equally effective for acetylacetone and led to the desired products in high yields (Table 4). In order to further extend the scope of the reaction, 1,3-diphenylpropane-1,3-dione was also employed in this transformation; however, the expected product was not isolated.

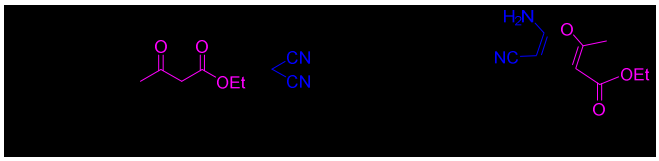
Table 4.

Synthesis of spiro[oxindole-3,4'-(4'*H*-pyran)] compounds from various isatins and acetylacetone [a]



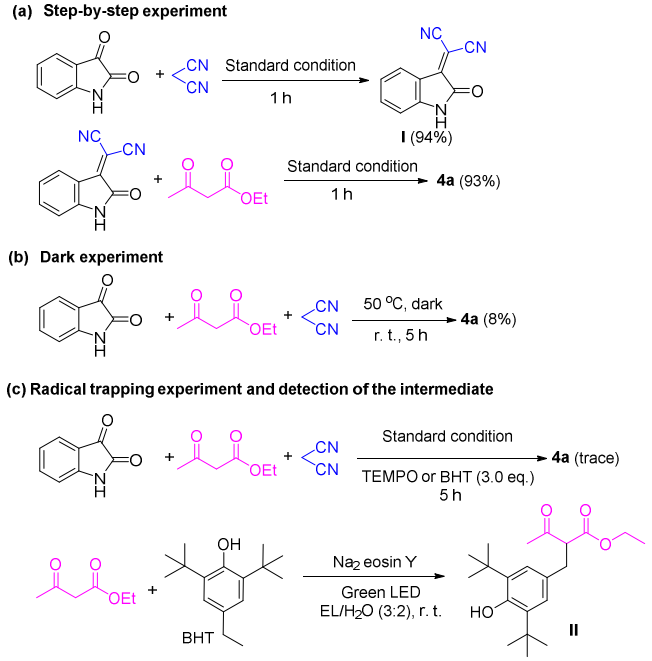
[a] Reaction condition: isatin (1 mmol), acetylacetone (1 mmol) and malononitrile (1 mmol) in EL/H_2O (3:2, 2 ml), Na_2 eosin Y (2 mol%), 10 W green LED, room temperature, isolated yields.

Furthermore, to demonstrate the scalability of this visible light-promoted three-component reaction, we carried out the model reaction on the gram scale. When the reaction was conducted at a 10 mmol scale, the desired product **4a** was generated in 93% yield (3.02 g), which is comparable with the performance of the 1.0 mmol scale reaction (Scheme 2).



Scheme 2 Large-scale synthesis of product **4a**

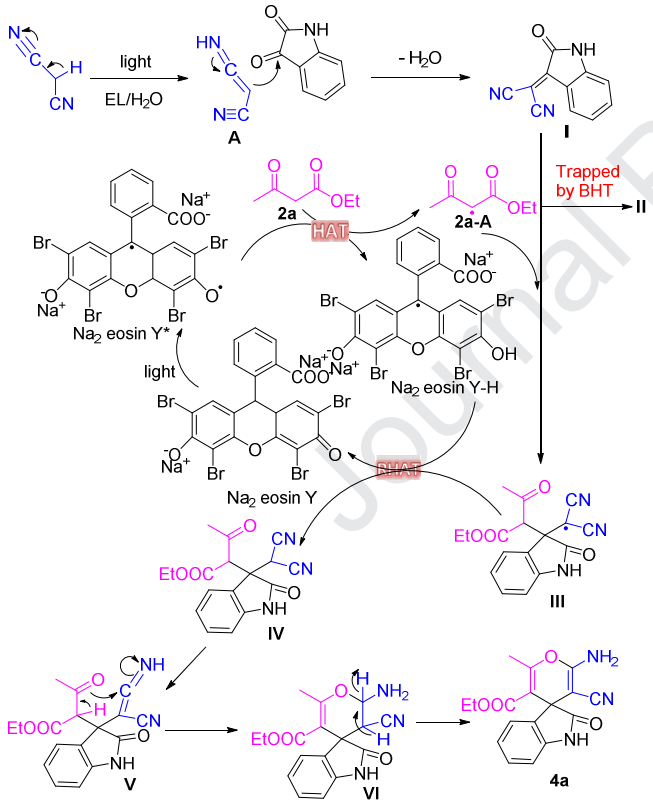
To elucidate the possible reaction mechanism, some preliminary studies were carried out. The Knoevenagel condensation of isatin with malononitrile took place in standard condition with the elimination of water to give the corresponding 2-(2-oxoindolin-3-ylidene)malononitrile (**I**) in 94% yield. Carrying out the reaction of **I** with ethyl acetoacetate generated the expected product **4a** in 93% yield (Scheme 3, a). Moreover, when the reaction was heated at 50 °C in the dark, product **4a** was obtained in very low yield (Scheme 3, b). In addition, this three-component reaction was completely suppressed in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger. The reaction did not work in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 3, c). Meanwhile, we found that the BHT-trapped product **II** could be separated and identified by IR, MNR and MS spectra. These results support the hypothesis that radical pathway is likely involved in the current reaction.



Scheme 3 Control reaction experiments

On the basis of these experimental results, a plausible reaction mechanism is proposed as shown in Scheme 4. According to previous report about the Knoevenagel

reaction [41], malononitrile undergoes tautomerization in the presence of aqueous ethyl lactate to give **A**. After this, Knoevenagel condensation of **A** and isatin occurs with the elimination of one molecule of water to give the intermediate **I**. In this step, visible light may exert a partial effect by applying additional energy to speed up the reaction. According to literature reports [42], eosin Y-derived photoexcited states can serve as direct hydrogen atom transfer (HAT) catalysts in the activation of C-H bonds. The formation of a α-carbonyl carbon radical **2a-A** is promoted by visible light activated Na_2 eosin Y* through a HAT process. The derived carbon radical **2a-A** is subsequently trapped by an electron deficient 2-(2-oxoindolin-3-ylidene)malononitrile (**I**) to form radical adduct **III**. A reverse hydrogen atom transfer (RHAT) process between eosin Na_2 Y-H and radical adduct **III** occurs to regenerate ground-state Na_2 eosin Y and the intermediate **IV**. Subsequently, the intermediate **IV** is further subjected to intramolecular cyclization to form the desired product **4a**.



Scheme 4 Proposed plausible mechanism

3. Conclusion

In summary, we have developed a simple and mild method for the preparation of spiro[oxindole-3,4'-(4'*H*-pyran)] derivatives via visible light-promoted one-pot, three-component reaction of isatins, linear 1,3-dicarbonyl compounds and malononitrile. The reaction proceeds smoothly in the presence of commercially available and inexpensive Na_2 eosin Y in aqueous ethyl lactate at room temperature under green LED irradiation under an air atmosphere, generating the desired products in high to excellent yields. This new approach meets the requirements of green chemistry and opens up a new way to develop more sustainable multicomponent reaction under visible light irradiation for constructing biological and synthetic important molecules. Detailed mechanisms and applications for this transformation are currently being studied in our laboratory.

4. Experimental

4.1 General information

All solvents and reagents were purchased from commercial suppliers and were used without further purification. Melting points were measured on X-5 apparatus and were uncorrected. The IR spectra were obtained on a Thermo Fisher is50 spectrometer using KBr pellets in the range of 400-4000 cm^{-1}. The ^1H NMR and ^{13}C NMR spectra were recorded on a Zhongke Niujin AS 400 spectrometer using TMS as internal standard. The mass spectra were performed on a 3200 Qtrap instrument with an ESI source. High resolution mass spectra (HR-MS) were measured on a Brukter Impact II instrument using ESI source. The WP-VLH-1020 photoreactor from Xi'an WATTECS experimental equipment co. LTD was used for the irradiation experiment.

*4.2 General Procedure for synthesis of spiro[oxindole-3,4'-(4'H-pyran)] (**4**)*

In a 15 mL quartz tube equipped with a magnetic stirrer bar, isatin (1 mmol), 1,3-dicarbonyl compound (1 mmol), malononitrile (1 mmol), and Na_2 eosin Y (0.02 mmol) were added successively in ethyl lactate/water (3:1, 2 mL). The reaction tube was exposed to green LED (520–525 nm, 10 W) irradiation at a distance of approximately 3 mm from bottom of the tube (SI, Figure S1) at room temperature in air with stirring for an appropriate time. The reaction progress was monitored by TLC. Upon completion, water was added to the mixture and the solid precipitate was filtered and washed with ethanol to obtain the desired pure product.

4.2.1 Ethyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4a)

White solid (305.5 mg, 94% yield); m.p.: 272-273 °C (lit. 270-272 °C [22]); IR (KBr): 3381, 3134, 2190, 1722, 1675, 1618, 1596, 1470, 1416, 1381, 1329, 1288, 1212, 1134, 1072, 755 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 7.22 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.18 (s, 2H), 7.08 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.79 (m, 2H), 2.34 (s, 3H), 0.81 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.1, 165.0, 159.4, 159.0, 142.6, 135.0, 129.0, 123.9, 122.3, 118.0, 109.8, 105.1, 60.7, 57.0, 49.4, 19.1, 13.5 ppm; ESI-MS: m/z = 325 $(M + H)^+$.

4.2.2 Ethyl 2'-amino-3'-cyano-5,6'-dimethyl-2-

oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4b)

White solid (315.3 mg, 93% yield); m.p.: 292-293 °C; IR (KBr): 3375, 3116, 2978, 2928, 2187, 1724, 1678, 1628, 1592, 1392, 1374, 1287, 1211, 1152, 1073, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 7.12 (s, 2H), 7.02 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.87 (s, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 3.95–3.59 (m, 2H), 2.31 (s, 3H), 2.22 (s, 3H), 0.80 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.1, 165.0, 159.34, 159.0, 140.1, 135.2, 131.1, 129.3, 124.4, 118.0, 109.5, 105.2, 60.7, 57.2, 49.5, 21.1, 19.0, 13.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}N_3O_4Na$, 362.1117; found, 362.1109.

4.2.3 Ethyl 2'-amino-3'-cyano-5-fluoro-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4c)

White solid (315.7 mg, 92% yield); m.p.: 265-266 °C (lit. 264-266 °C [24]); IR (KBr): 3280, 3161, 2193, 1731, 1699, 1680, 1631, 1599, 1482, 1416, 1381, 1315, 1290, 1215, 1122, 1089, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.21 (s, 2H), 7.07–6.95 (m, 2H), 6.78 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.94–3.63 (m, 2H), 2.33 (s, 3H), 0.82 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.1, 164.9, 159.4, 158.7 (d, $^1J_{CF}$ = 235.1 Hz), 157.5, 138.8, 136.8 (d, $^3J_{CF}$ = 7.4 Hz), 117.8, 115.2 (d, $^2J_{CF}$ = 25.5 Hz), 104.4, 60.8, 56.5, 50.0, 19.3, 13.6 ppm; ESI-MS: m/z = 343 $(M + H)^+$.

4.2.4 Ethyl 2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4d)

White solid (370.8 mg, 92% yield); m.p.: 259-260 °C (lit. 257-259 °C [24]); IR (KBr): 3379, 3189, 2207, 1715, 1652, 1615, 1596, 1472, 1417, 1380, 1282, 1223, 1137, 1073, 747, 687, 575 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.58 (s, 1H), 7.40 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.27 (s, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.85 (m, 2H), 2.37 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.7, 164.8, 160.0, 159.4, 141.9, 137.7, 131.8, 126.7, 117.9, 113.9, 111.8, 104.2, 60.9, 56.4, 49.7, 19.2, 13.5 ppm; ESI-MS: m/z = 403 $(M + H)^+$.

4.2.5 Ethyl 2'-amino-3'-cyano-6'-methyl-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4e)

White solid (347.8 mg, 94% yield); m.p.: 245-246 °C (lit. 245-247 °C [24]); IR (KBr): 3300, 3130, 2205, 1721, 1667, 1626, 1591, 1480, 1457, 1379, 1362, 1282, 1224, 1129, 1081, 757 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.19 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.04 (d, *J* = 2.4 Hz, 1H), 7.36 (s, 2H), 7.03 (d, *J* = 8.8 Hz, 1H), 3.95–3.71 (m, 2H), 2.38 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.6, 164.7, 161.0, 159.5, 149.1, 142.9, 136.5, 126.5, 119.6, 117.7, 110.1, 103.5, 61.1, 55.7, 49.7, 19.4, 13.6 ppm; ESI-MS: m/z = 370 $(M + H)^+$.

4.2.6 Ethyl 2'-amino-6-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4f)

White solid (358.7 mg, 89% yield); m.p.: 284-285 °C; IR (KBr): 3265, 3153, 2194, 1705, 1670, 1607, 1476, 1415, 1378, 1363, 1288, 1222, 1132, 1071, 742, 679, 644 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.60 (s, 1H), 7.27 (s, 2H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 4.08–3.61 (m, 2H), 2.35 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.9, 164.8, 159.7, 159.4, 144.3, 134.5, 125.8, 125.0, 121.5, 117.8, 112.6, 104.4, 60.9, 56.3, 49.3, 19.1, 13.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{14}BrN_3O_4Na$, 426.0065; found, 426.0072.

4.2.7 Ethyl 2'-amino-3'-cyano-5,6-difluoro-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4g)

White solid (317.7 mg, 88% yield); m.p.: 284-285 °C; IR (KBr): 3376, 3141, 2184, 1729, 1678, 1632, 1591, 1511, 1465, 1378, 1331, 1290, 1137, 1089, 1070, 778 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.56 (s, 1H), 7.34 (dd, *J* = 10.0, 8.0 Hz, 1H), 7.25 (s, 2H), 6.85 (dd, *J* = 10.4, 6.8 Hz, 1H), 4.01–3.63 (m, 2H), 2.33 (s, 3H), 0.87 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.2, 164.8, 159.9, 159.4, 151.2 (dd, $J_{CF=}$248.2, 13.7 Hz), 147.1 (dd, $J_{CF=}$237.6, 13.4 Hz), 139.2 (d, $^3J_{CF}$ = 10.0 Hz), 131.2, 117.8, 113 (dd, $J_{CF=}$14.6, 3.5 Hz), 104.1, 99.7, 60.9, 56.3, 49.6, 19.2, 13.7 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{13}F_2N_3O_4Na$, 384.0772; found, 384.0766.

4.2.8 Ethyl 2'-amino-3'-cyano-7-fluoro-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4h)

White solid (301.8 mg, 88% yield); m.p.: >300 °C; IR (KBr): 3321, 3194, 2199, 1730, 1717, 1680, 1651, 1604, 1491, 1473, 1415, 1378, 1330, 1289, 1207, 1145, 1078, 741 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.27 (s, 2H), 7.17–7.12 (m, 1H), 7.00–6.96 (m, 2H), 3.98–3.64 (m, 2H), 2.36 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.9, 164.5, 159.6, 159.4, 146.7 (d, $^1J_{CF}$ = 240.7 Hz), 138.0, 129.6 (d, $^3J_{CF}$ = 12.4 Hz), 123.3 (d, $^4J_{CF}$ = 4.1 Hz), 120.0, 117.8, 116.0 (d, $^2J_{CF}$ = 22.5 Hz), 104.6, 60.8, 56.5, 49.8, 19.2, 13.4 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{14}FN_3O_4Na$, 366.0866; found, 366.0870.

4.2.9 Ethyl 2'-amino-7-chloro-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4i)

White solid (323.1 mg, 90% yield); m.p.: >300 °C; IR (KBr): 3378, 3193, 2199, 1728, 1677, 1625, 1605, 1478, 1416, 1286, 1213, 1127, 1078, 765, 743 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.89 (s, 1H), 7.28 (s, 2H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 6.99 (t, *J* = 7.6, 1H), 4.09–3.61 (m, 2H), 2.36 (s, 3H), 0.83 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.1, 164.8, 159.7, 159.40, 140.4, 136.9, 129.0, 123.7, 122.6, 117.8, 114.2, 104.6, 60.9, 56.4, 50.3, 19.2, 13.4 ppm; HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{17}H_{14}ClN_3O_4K$, 398.0310; found, 398.0306.

4.2.10 Ethyl 2'-amino-3'-cyano-6'-methyl-2-oxo-7-(trifluoromethyl)spiro[indoline-3,4'-pyran]-5'-carboxylate (4j)

White solid (361.6 mg, 92% yield); m.p.: 265-266 °C; IR (KBr): 3302, 3178, 2197, 1731, 1674, 1622, 1487, 1459,

1382, 1336, 1315, 1293, 1219, 1170, 1142, 1083, 751 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.93 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.30 (s, 2H), 7.13 (t, *J* = 8.4 Hz, 1H), 4.02–3.57 (m, 2H), 2.36 (s, 3H), 0.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.6, 164.7, 160.3, 159.5, 140.0, 137.1, 125.5, 122.6, 124.1 (q, $^1J_{CF}$ = 270.2 Hz), 117.6, 111.1 (q, $^2J_{CF}$ = 22.6 Hz), 104.1, 60.9, 56.2, 48.7, 19.2, 13.2 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{14}F_3N_3O_4Na$, 416.0834; found, 416.0839.

4.2.11 Methyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4k)

White solid (289.2 mg, 93% yield); m.p.: 244-245 °C(lit. 245-247 °C [25]); IR (KBr): 3390, 3307, 3195, 2199, 1715, 1621, 1586, 1487, 1416, 1379, 1268, 1095, 1076, 762, 618 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 7.28–7.11 (m, 3H), 7.12–7.01 (m, 1H), 7.05–6.90 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.36 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.0, 165.6, 159.4, 158.9, 142.4, 134.9, 129.1, 123.8, 122.4, 118.0, 109.8, 105.3, 56.9, 51.9, 49.5, 19.3 ppm; ESI-MS: m/z = 311 $(M + H)^+$.

4.2.12 Isobutyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4l)

White solid (331.8 mg, 94% yield); m.p.: 232-234 °C; IR (KBr): 3208, 3096, 2968, 2920, 2873, 2230, 1724, 1713, 1653, 1472, 1407, 1365, 1283, 1220, 1127, 754 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.59–7.55 (m, 1H), 7.16–7.11 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.85 (d, *J* = 6.4 Hz, 2H), 3.61 (s, 2H), 2.18 (s, 3H), 1.91–1.83 (m, 1H), 0.89 (d, *J* = 2.8 Hz, 3H), 0.87 (d, *J* = 2.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.6, 167.7, 166.2, 164.2, 151.1, 147.0, 143.6, 138.2, 126.3, 123.4, 119.1, 113.5, 112.0, 81.1, 70.7, 50.0, 27.7, 19.3 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{19}N_3O_4Na$, 376.1273; found, 376.1280.

4.2.13 2-Methoxyethyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4m)

Yellow solid (330.2 mg, 93% yield); m.p.: 179-181 °C (lit. 179-181 °C [29]); IR (KBr): 3304, 3189, 2197, 1682, 1652, 1622, 1558, 1472, 1417, 1378, 1288, 1211, 1134, 1072, 753 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 7.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.15 (s, 2H), 7.06–6.99 (m, 1H), 6.94–6.90 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.04–3.68 (m, 2H), 3.20–3.12 (m, 2H), 3.12 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.9, 165.1, 159.2, 142.6, 134.9, 129.0, 123.8, 122.3, 117.9, 109.9, 105.2, 69.5, 63.8, 58.4, 57.1, 49.5, 19.4 ppm; ESI-MS: m/z = 355 $(M + H)^+$.

4.2.14 Allyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4n)

White solid (313.4 mg, 93% yield); m.p.: 242-244 °C; IR (KBr): 3298, 3185, 2197, 1732, 1682, 1635, 1623, 1603, 1473, 1410, 1377, 1331, 1284, 1212, 1131, 1091, 753 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 7.21 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.18 (s, 2H), 7.12–7.04 (m, 1H), 6.97–6.93 (m, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.56–5.46 (m, 1H), 5.18–4.87 (m, 2H), 4.32–4.30 (m, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.0, 164.8, 159.4, 159.2, 142.5, 134.9, 132.0, 129.0, 123.9, 122.3, 118.4, 117.9, 109.9, 105.1, 65.4, 57.0, 49.5, 19.2 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{15}N_3O_4Na$, 360.0960; found, 360.0951.

4.2.15 Ethyl 2'-amino-3'-cyano-6'-ethyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4o)

White solid (311.9 mg, 92% yield); m.p.: 222-223 °C; IR (KBr): 3389, 3177, 2197, 1712, 1682, 1600, 1405, 1364, 1224, 1149, 1081, 752 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.32–7.12 (m, 3H), 7.10–7.03 (m, 1H), 6.98–6.94 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.86–3.69 (m, 2H), 2.75–2.62 (m, 2H), 1.20 (t, *J* = 6.8 Hz, 3H), 0.81 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.0, 164.8, 163.0, 159.7, 142.6, 134.9, 129.1, 123.8, 122.4, 118.0, 109.8, 104.7, 60.8, 56.8, 49.4, 25.4, 13.5, 12.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}N_3O_4Na$, 362.1117; found, 362.1122.

4.2.16 Ethyl 2'-amino-3'-cyano-6'-ethyl-5-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4p)

White solid (300.1 mg, 85% yield); m.p.: 247-249 °C; IR (KBr): 3389, 3198, 2200, 1709, 1667, 1625, 1583, 1493, 1409, 1305, 1203, 1100, 1064, 734 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 1H), 7.16 (s, 2H), 7.07–6.96 (m, 1H), 6.87 (s, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 3.84–3.76 (m, 2H), 2.85–2.60 (m, 2H), 2.25 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.0, 164.9, 163.0, 159.6, 140.1, 135.1, 131.2, 129.3, 124.3, 118.0, 109.6, 104.7, 60.8, 57.0, 49.4, 25.4, 21.2, 13.5, 12.1 ppm; HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{19}H_{19}N_3O_4K$, 392.1013; found, 392.1007.

4.2.17 Ethyl 2'-amino-5-chloro-3'-cyano-6'-ethyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4q)

White solid (346.9 mg, 93% yield); m.p.: 250-251 °C; IR (KBr): 3390, 3188, 2200, 1713, 1620, 1584, 1476, 1413, 1340, 1283, 1212, 1174, 1072, 825 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.32–7.23 (m, 3H), 7.18 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.91–3.72 (m, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.8, 164.7, 163.9, 159.7, 141.5, 137.2, 129.0, 126.3, 123.9, 117.9, 111.3, 103.8, 60.93, 6.2, 49.7, 25.5, 13.4, 12.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{16}ClN_3O_4Na$, 396.0727; found, 396.0718.

4.2.18 Ethyl 2'-amino-3'-cyano-6'-ethyl-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4r)

Brown solid (357.1 mg, 93% yield); m.p.: 258-259 °C; IR (KBr): 3399, 3188, 2196, 1716, 1668, 1626, 1528, 1455, 1416, 1363, 1341, 1279, 1212, 1138, 1082, 752 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H), 8.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.41 (s, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 3.88–3.82 (m, 2H), 2.83–2.71 (m, 2H),

1.22 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.6, 164.9, 164.5, 159.8, 149.1, 142.9, 136.3, 126.6, 119.5, 117.7, 110.1, 103.1, 61.2, 55.5, 49.6, 25.7, 13.4, 11.9 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{18}H_{16}N_4O_6Na$, 407.0968; found, 407.0972.

4.2.19 Methyl 2'-amino-3'-cyano-5,6'-dimethyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4s)

White solid (299.0 mg, 92% yield); m.p.: 289-290 °C; IR (KBr): 3387, 3148, 2188, 1724, 1674, 1626, 1604, 1418, 1375, 1290, 1100, 809, 792, 567 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 1H), 7.15 (s, 2H), 7.03–6.95 (m, 1H), 6.92–6.85 (m, 1H), 6.70 (d, J = 7.6 Hz, 1H), 3.38 (s, 3H), 2.34 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.0, 165.6, 159.3, 159.0, 139.9, 135.1, 131.1, 129.3, 124.4, 118.0, 109.5, 105.4, 57.2, 51.9, 49.6, 21.1, 19.3 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{17}H_{15}N_3O_4Na$, 348.0960; found, 348.0954.

4.2.20 Methyl 2'-amino-3'-cyano-5-fluoro-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4t)

White solid (306.0 mg, 93% yield); m.p.: 254-255 °C; IR (KBr): 3391, 3159, 2191, 1727, 1674, 1606, 1489, 1418, 1377, 1381, 1291, 1091, 800, 604 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 7.25 (s, 2H), 7.11–6.98 (m, 2H), 6.82–6.80 (m, 1H), 3.41 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.1, 165.5, 159.6 (d, $^1J_{CF}$ = 236.0 Hz), 157.5, 138.6, 136.8 (d, $^3J_{CF}$ = 7.5 Hz), 117.8, 115.3 (d, $^2J_{CF}$ = 23.1 Hz), 111.8, 110.6, 110.5, 104.7, 56.5, 52.0, 50.1, 19.5 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{16}H_{12}FN_3O_4Na$, 352.0710; found, 352.0702.

4.2.21 Methyl 2'-amino-5-chloro-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4u)

White solid (317.4 mg, 92% yield); m.p.: 280-281 °C (lit. >260 °C [30]); IR (KBr): 3378, 3291, 3154, 2190, 1728, 1674, 1604, 1479, 1375, 1290, 1175, 1107, 1083, 689 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.58 (s, 1H), 7.33–7.18 (m, 4H), 6.84 (d, J = 8.0 Hz, 1H), 3.43 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.8, 165.5, 160.0, 159.5, 141.3, 137.2, 128.9, 126.3, 124.0, 117.8, 111.2, 104.5, 56.4, 52.1, 49.9, 19.5 ppm; ESI-MS: m/z = 345 (M + H)$^+$.

4.2.22 Methyl 2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4v)

White solid (361.8 mg, 93% yield); m.p.: 242-243 °C (lit. 240-242 °C [32]); IR (KBr): 3377, 3168, 2202, 1716, 1670, 1616, 1591, 1475, 1416, 1378, 1385, 1219, 1176, 1136, 1079, 747 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.58 (s, 1H), 7.38 (dd, J = 8.0, 2.0 Hz, 1H), 7.35–7.20 (m, 3H), 6.79 (d, J = 8.4 Hz, 1H), 3.42 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.7, 165.5, 160.0, 159.4, 141.7, 137.6, 131.8, 126.7, 117.8, 113.9, 111.8, 104.4, 56.4, 52.0, 49.8, 19.7 ppm; ESI-MS: m/z = 389 (M + H)$^+$.

4.2.23 Methyl 2'-amino-3'-cyano-6'-methyl-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4w)

White solid (324.0 mg, 91% yield); m.p.: 256-257 °C; IR (KBr): 3308, 3171, 2189, 1727, 1673, 1626, 1606, 1480, 1456, 1338, 1193, 840, 787 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.21 (dd, J = 8.6, 2.4 Hz, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.40 (s, 2H), 7.06 (d, J = 8.4 Hz, 1H), 3.44 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.6, 165.4, 160.9, 159.5, 148.9, 142.9, 136.4, 126.5, 119.5, 117.6, 110.0, 103.8, 55.6, 52.2, 49.8, 19.7 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{16}H_{12}N_4O_6Na$, 379.0655; found, 379.0661.

4.2.24 Methyl 2'-amino-3'-cyano-7-fluoro-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4x)

Yellow solid (299.4 mg, 91% yield); m.p.: 248-249 °C; IR (KBr): 3335, 3184, 2192, 1733, 1678, 1635, 1540, 1416, 1381, 1379, 1267, 1215, 1158, 1073, 650 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.29 (s, 2H), 7.16–7.12 (m, 1H), 7.04–6.93 (m, 2H), 3.42 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.8, 165.5, 159.5, 159.4, 146.6 (d, $^1J_{CF}$ = 240.7 Hz), 137.9, 129.4 (d, $^3J_{CF}$ = 12.4 Hz), 123.3 (d, $^4J_{CF}$ = 4.0 Hz), 119.9, 117.8, 116.1 (d, $^2J_{CF}$ = 17.3 Hz), 104.9, 56.5, 52.0, 49.9, 19.3 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{16}H_{12}FN_3O_4Na$, 352.0710; found, 352.0716.

4.2.25 Methyl 2'-amino-7-chloro-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4y)

White solid (310.5 mg, 90% yield); m.p.: 261-262 °C; IR (KBr): 3395, 3301, 2192, 1733, 1683, 1618, 1598, 1473, 1412, 1380, 1327, 1225, 1194, 1124, 1070, 740 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 7.33–7.24 (m, 3H), 7.08 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 3.42 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.0, 165.5, 159.6, 159.4, 140.2, 136.8, 129.1, 123.7, 122.6, 117.8, 114.1, 104.9, 56.4, 52.1, 50.5, 19.5 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{16}H_{12}ClN_3O_4Na$, 368.0414; found, 368.0426.

4.2.26 Methyl 2'-amino-3'-cyano-6'-methyl-2-oxo-7-(trifluoromethyl)spiro[indoline-3,4'-pyran]-5'-carboxylate (4z)

White solid (344.9 mg, 91% yield); m.p.: 246-247 °C; IR (KBr): 3352, 3190, 2202, 1716, 1682, 1623, 1603, 1456, 1337, 1122, 1097, 809, 739 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.31 (s, 2H), 7.12 (t, J = 7.6 Hz, 1H), 3.36 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.5, 165.4, 160.1, 159.5, 139.9, 136.9, 126.7 (d, $^1J_{CF}$ = 241.6 Hz), 122.8, 117.6, 111.3 (d, $^2J_{CF}$ = 32.5 Hz), 104.6, 56.5, 56.1, 52.0, 48.8, 19.5 ppm; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{17}H_{12}F_3N_3O_4Na$, 402.0678; found, 402.0685.

4.2.27 Methyl 2'-amino-4-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4aa)

White solid (365.7 mg, 94% yield); m.p.: >300 °C; IR (KBr): 3427, 3308, 3184, 2198, 1704, 1672, 1606, 1446, 1416, 1326, 1171, 1219, 1171, 1073, 907, 655 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.69 (s, 1H), 7.28 (s, 2H), 7.20–7.06 (m, 2H), 6.85 (dd, J = 7.2, 1.2 Hz, 1H), 3.45 (s,

3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.2, 165.4, 160.6, 160.2, 144.6, 131.5, 131.0, 125.8, 118.8, 117.7, 109.4, 103.3, 54.3, 52.1, 51.4, 19.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}BrN_3O_4Na$, 411.9909; found, 411.9908.

4.2.28 Methyl 2'-amino-6-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4ab)

White solid (346.2 mg, 89% yield); m.p.: 286-287 °C; IR (KBr): 3388, 3307, 3191, 2199, 1716, 1673, 1586, 1435, 1416, 1321, 1285, 1187, 1074, 911, 632 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 7.30 (s, 2H), 7.18 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 3.46 (s, 3H), 2.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.9, 165.5, 159.6, 159.4, 144.1, 134.4, 125.7, 125.0, 121.5, 117.8, 112.6, 104.7, 56.3, 52.1, 49.4, 19.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}BrN_3O_4Na$, 411.9909; found, 411.9903.

4.2.29 2-Methoxyethyl 2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4ac)

Brown solid (389.7 mg, 90% yield); m.p.: 220-221 °C (lit. 221-222 °C [29]); IR (KBr): 3292, 2196, 1670, 1474, 1376, 1289, 1086, 974, 746, 627 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.35 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.23 (s, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.03–3.80 (m, 2H), 3.23 (t, *J* = 4.8 Hz, 2H), 3.13 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.6, 165.0, 160.3, 159.3, 141.8, 137.6, 131.7, 126.7, 117.8, 113.9, 111.9, 104.2, 69.6, 64.0, 58.4, 56.5, 49.7, 19.4 ppm; ESI-MS: m/z = 433 $(M + H)^+$.

4.2.30 2-Methoxyethyl 2'-amino-3'-cyano-6'-methyl-2-oxo-7-(trifluoromethyl)spiro[indoline-3,4'-pyran]-5'-carboxylate (4ad)

White solid (393.4 mg, 93% yield); m.p.: 190-191 °C; IR (KBr): 3171, 2205, 1735, 1672, 1623, 1604, 1489, 1377, 1279, 1217, 1132, 1073, 769 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.30 (s, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 3.98–3.83 (m, 2H), 3.27–3.14 (m, 2H), 3.08 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.4, 164.8, 160.4, 159.4, 139.9, 137.0, 124.2 (q, $^1J_{CF}$ = 270.6 Hz), 122.6, 117.6, 111.4 (q, $^2J_{CF}$ = 32.5 Hz), 104.3, 69.4, 63.9, 58.4, 56.3, 48.7, 19.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}F_3N_3O_5Na$, 446.0940; found, 446.0936.

4.2.31 Isobutyl 2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4ae)

Yellow solid (392.2 mg, 91% yield); m.p.: 245-246 °C; IR (KBr): 3313, 3198, 2207, 1706, 1652, 1617, 1593, 1474, 1417, 1378, 1298, 1222, 1135, 1068, 777, 688 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.38 (dd, *J* = 8.4, 3.2 Hz, 1H), 7.33 (d, *J* = 2.8 Hz, 1H), 7.26 (s, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.70–3.56 (m, 2H), 2.38 (s, 3H), 3.67–3.58 (m, 1H), 0.72 (d, *J* = 6.4 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.6, 165.1, 160.3, 159.3, 141.7, 137.8, 126.6, 117.8, 114.0, 111.9, 104.1, 71.1, 56.6, 49.7, 27.4, 19.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}BrN_3O_4Na$, 454.0378; found, 454.0385.

4.2.32 Isobutyl 2'-amino-3'-cyano-6'-methyl-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4af)

White solid (370.1 mg, 93% yield); m.p.: 270-271 °C; IR (KBr): 3305, 3187, 2192, 1723, 1674, 1630, 1584, 1480, 1377, 1346, 1293, 1213, 1133, 1076, 754 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.21 (s, 1H), 8.21 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.38 (s, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 3.68–3.59 (m, 2H), 2.43 (s, 3H), 1.61–1.59 (m, 1H), 0.72 (d, *J* = 6.4 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.5, 164.9, 161.1, 159.4, 148.9, 143.0, 136.5, 126.6, 119.7, 117.6, 110.1, 103.4, 71.3, 55.8, 49.6, 27.4, 19.1, 14.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_4O_6Na$, 421.1124; found, 421.1120.

4.2.33 Allyl 2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (4ag)

Yellow solid (373.5 mg, 90% yield); m.p.: 259-260 °C (lit. >265 °C [31]); IR (KBr): 3314, 3203, 2204, 1720, 1653, 1617, 1592, 1476, 1414, 1380, 1280, 1220, 1138, 1066, 742 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.54 (s, 1H), 7.35 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.25 (s, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.60–5.50 (m, 1H), 5.14–4.91 (m, 2H), 4.34–4.32 (m, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.6, 164.6, 160.3, 159.3, 141.8, 137.6, 132.0, 126.8, 118.6, 117.8, 113.9, 111.9, 104.2, 65.5, 56.5, 49.7, 19.6 ppm; ESI-MS: m/z = 415 $(M + H)^+$.

4.2.34 Allyl 2'-amino-3'-cyano-6'-methyl-2-oxo-7-(trifluoromethyl)spiro[indoline-3,4'-pyran]-5'-carboxylate (4ah).

White solid (372.6 mg, 92% yield); m.p.: 262-263 °C; IR (KBr): 3306, 3176, 2194, 1733, 1674, 1636, 1620, 1600, 1487, 1417, 1384, 1315, 1199, 1138, 1080, 708 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.31 (s, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 5.41–5.51 (m, 1H), 5.05–4.91 (m, 2H), 4.38–4.18 (m, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.5, 164.5, 160.5, 159.4, 139.9, 137.0, 131.7, 124.1 (q, $^1J_{CF}$ = 270.4 Hz), 122.6, 118.9, 117.6, 111.0 (q, $^2J_{CF}$ = 32.5 Hz), 104.2, 65.6, 56.3, 48.7, 19.4 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{14}F_3N_3O_4Na$, 428.0834; found, 428.0840.

4.2.35 3'-Acetyl-6'-amino-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4ai)

White solid (274.4 mg, 93% yield); m.p.: 247-248 °C (lit. 242-243 °C [29]); IR (KBr): 3345, 3118, 2188, 1709, 1681, 1653, 1619, 1605, 1481, 1467, 1377, 1319, 1258, 1211, 1120, 1051, 768 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.38 (s, 1H), 7.15 (m, 1H), 7.11 (s, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.92 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 2.28 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.0, 179.0, 159.7, 156.6, 142.5, 134.6, 129.0, 123.8,

122.3, 118.0, 115.3, 110.0, 57.2, 49.9, 31.7, 19.8 ppm; ESI-MS: m/z = 295 $(M + H)^+$.

4.2.36 3'-Acetyl-6'-amino-5-methoxy-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4aj)

White solid (295.8 mg, 91% yield); m.p.: 278-279 °C (lit. 276-277 °C [33]); IR (KBr): 3257, 3176, 2193, 1697, 1653, 1592, 1492, 1466, 1437, 1418, 1378, 1297, 1155, 1055, 785 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.20 (s, 1H), 7.10 (s, 2H), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 3.67 (s, 3H), 2.28 (s, 3H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.0, 178.9, 159.7, 156.5, 155.5, 135.82, 135.8, 118.0, 115.2, 113.6, 110.3, 57.4, 55.9, 50.3, 31.8, 31.7, 19.8 ppm; ESI-MS: m/z = 325 $(M + H)^+$.

4.2.37 3'-Acetyl-6'-amino-5-fluoro-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4ak)

White solid (284.8 mg, 91% yield); m.p.: 298-300 °C (lit. 260 °C [34]); IR (KBr): 3284, 3140, 2196, 1705, 1687, 1651, 1628, 1605, 1487, 1456, 1405, 1384, 1357, 1265, 1220, 1153, 1082, 792, 624 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.38 (s, 1H), 7.18 (s, 2H), 7.03–6.90 (m, 2H), 6.76 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.7, 179.1, 159.6, 158.6 (d, $^1J_{CF}$ = 235.6 Hz), 157.7, 138.7, 136.6 (d, $^3J_{CF}$ = 7.6 Hz), 117.9, 115.2, 115.0, 111.4 (d, $^2J_{CF}$ = 23.4 Hz), 110.6, 56.8, 50.4, 31.9, 20.2 ppm; ESI-MS: m/z = 313 $(M + H)^+$.

4.2.38 3'-Acetyl-6'-amino-5-bromo-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4al)

White solid (335.7 mg, 90% yield); m.p.: 224-225°C (lit. 220-222 °C [32]); IR (KBr): 3356, 3235, 2192, 1703, 1653, 1617, 1593, 1478, 1419, 1378, 1300, 1215, 1175, 1053, 817, 605 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.20 (s, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.5, 178.7, 159.5, 158.6, 141.8, 137.6, 131.6, 126.3, 117.9, 114.9, 113.8, 111.7, 56.7, 50.1, 32.1, 20.2 ppm; ESI-MS: m/z = 373 $(M + H)^+$.

4.2.39 3'-Acetyl-6'-amino-2'-methyl-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4am)

White solid (316.2 mg, 93% yield); m.p.: >300 °C (lit. >300 °C [33]); IR (KBr): 3367, 3179, 2195, 1744, 1682, 1626, 1505, 1482, 1379, 1361, 1335, 1304, 1257, 1219, 1177, 1120, 1060, 988, 829 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.10 (s, 1H), 8.14 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.32 (s, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 2.43 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.4, 179.6, 160.1, 159.6, 149.1, 142.8, 136.5, 126.2, 119.1, 117.6, 114.7, 109.9, 56.1, 50.0, 32.2, 20.7 ppm; ESI-MS: m/z = 340 $(M + H)^+$.

4.2.40 3'-Acetyl-6'-amino-7-fluoro-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4an)

Yellow solid (266.1 mg, 85% yield); m.p.: >300 °C (lit. 265 °C [34]); IR (KBr): 3288, 3151, 2197, 1711, 1687, 1653, 1642, 1605, 1467, 1405, 1385, 1355, 1312, 1247, 1218, 1050, 780 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 7.20 (s, 2H), 7.10–7.05 (m, 1H), 6.96–6.86 (m, 2H), 2.34 (s, 3H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.7, 178.8, 159.6, 157.8, 146.3 (d, $^1J_{CF}$ = 240.8 Hz), 137.8, 129.5 (d, $^3J_{CF}$ = 12.4 Hz), 123.1 (d, $^4J_{CF}$ = 4.1 Hz), 119.7, 117.8, 116.0 (d, $^2J_{CF}$ = 16.1 Hz), 115.2, 56.8, 50.3, 32.0, 31.9, 20.2, 20.0 ppm; ESI-MS: m/z = 313 $(M + H)^+$.

4.2.41 3'-Acetyl-6'-amino-7-chloro-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4ao)

White solid (289.5 mg, 88% yield); m.p.: 278-279 °C (lit. 276-277 °C [33]); IR (KBr): 3285, 3168, 2193, 1725, 1671, 1644, 1620, 1601, 1475, 1418, 1379, 1362, 1303, 1220, 1166, 1062, 775 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 7.26 (d, *J* = 1.2 Hz, 1H), 7.24 (s, 2H), 7.04 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.74, 179.0, 159.6, 158.0, 140.3, 136.7, 128.9, 123.5, 122.3, 117.8, 115.2, 114.0, 56.7, 50.8, 32.1, 20.2 ppm; ESI-MS: m/z = 329 $(M + H)^+$.

4.2.42 3'-Acetyl-6'-amino-2'-methyl-2-oxo-7-(trifluoromethyl)spiro[indoline-3,4'-pyran]-5'-carbonitrile (4ap)

White solid (330.3 mg, 91% yield); m.p.: 283-285 °C; IR (KBr): 3348, 3187, 2192, 1732, 1674, 1650, 1624, 1602, 1488, 1418, 1380, 1317, 1299, 1219, 1116, 1061, 754 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.25 (s, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.6, 179.5, 159.6, 158.7, 140.0, 137.0, 127.5, 125.3, 124.2 (q, $^1J_{CF}$ = 270.2 Hz), 122.3, 117.7, 115.1, 110.7 (q, $^2J_{CF}$ = 32.5 Hz), 56.6, 49.1, 32.1, 20.4 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{12}F_3N_3O_3Na$, 386.0728; found, 386.0717.

4.2.43 3'-Acetyl-6'-amino-4-bromo-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4aq)

Yellow solid (320.8 mg, 86% yield); m.p.: >300 °C; IR (KBr): 3445, 3164, 2196, 1733, 1682, 1653, 1609, 1584, 1473, 1415, 1301, 1218, 1207, 1133, 1071, 630 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 2H), 7.07 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.82 (d, *J* = 6.4 Hz, 1H), 2.38 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.4, 178.2, 160.3, 158.9, 144.7, 131.4, 127.2, 125.6, 118.6, 117.7, 114.0, 109.3, 54.6, 51.7, 31.8, 20.3 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}N_3O_3Na$, 317.0776; found, 317.0764.

4.2.44 3'-Acetyl-6'-amino-5,6-difluoro-2'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carbonitrile (4ar)

White solid (288.0 mg, 87% yield); m.p.: 289-291 °C; IR (KBr): 3310, 3198, 2190, 1721, 1695, 1667, 1636, 1597, 1473, 1422, 1395, 1380, 1337, 1284, 1206, 1160, 1086, 775 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.25

(dd, *J* = 9.6, 8.0 Hz, 1H), 7.21 (s, 2H), 6.81 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.34 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.7, 179.2, 159.6, 158.2, 151.1 (dd, J_{CF} =242.6, 14.1 Hz), 147.1 (dd, J_{CF} =237.8, 13.3 Hz), 139.2 (d, $^3J_{CF}$ = 9.8 Hz), 131.0, 117.8, 114.9,113.6 (dd, J_{CF} =18.3, 7.1 Hz), 99.6, 56.5, 50.0, 32.1, 20.3 ppm; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{11}F_2N_3O_3Na$, 354.0666; found, 354.0672.

*4.3 Synthesis of intermediate **II***

A mixture of ethyl acetoacetate (1 mmol) and Na_2 eosin Y (0.02 mmol) in ethyl lactate/water (3:1, 2 mL) was taken in a reaction tube, radical inhibitor BHT (3.0 mmol) was added. The reaction tube was exposed to green LED (450–455 nm, 10 W) irradiation at room temperature in air with stirring for 5 h. Then, the reaction mixture was poured into H_2O (15 mL) and extracted with EtOAc ((3 × 20 mL). The combined organic layer was washed with brine (15 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude reaction mixture was purified by flash chromatography using ethyl acetate/hexane as an eluent to give intermediate **II**.

*4.3.1 Ethyl 2-(3,5-di-tert-butyl-4-hydroxybenzyl)-3-oxobutanoate (intermediate **II**) [43]*

Colorless oil (63.0 mg, 18% yield); IR (KBr): 2920, 1718, 1470, 1435, 1363, 1274, 1212, 1143, 1024, 883 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 2H), 5.08 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.73 (t, *J* = 7.6 Hz, 1H), 3.08 (d, *J* = 7.6 Hz, 2H), 2.19 (s, 3H), 1.41 (s, 18H), 1.19 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 187.5, 135.9, 128.7, 125.4, 125.2, 34.3, 30.4, 30.3, 29.8, 14.2 ppm; ESI-MS: m/z = 371 $(M + Na)^+$.

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- A pot, atom and step economy, three-component reaction has been developed.
- The use of an inexpensive organic dye, Na_2 eosin Y, as the photocatalyst, avoiding of any metal or acid catalysts.
- High yields and pure product formation at ambient temperature.
- Environmentally benign, simple, and highly efficient procedure with no purification needs.
- The use of light as a rich, readily available and almost inexhaustible source of clean energy.
- Wide range of substrates, good product diversity and easy scalability.
- No toxic and hazardous solvents are used.

Declaration of interests

☐ √ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The authors declare no competing financial interest.