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Synthesis of spiro[furan-3,3′-indolin]-2′-ones by PET-catalyzed [3+2] reactions of spiro[indoline-3,2′-oxiran]-2-ones with electron-rich olefins

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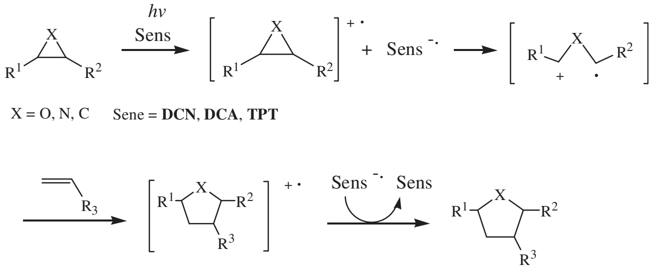
ABSTRACT

An efficient procedure for the synthesis of spiro[furan-3,3′-indolin]-2-ones and dispiro[cycloalkane-1,2′-furan-3′,3″-indolin]-2″-ones has been achieved in high yields and stereoselectivity by photoinduced electron transfer-catalyzed [3+2] reactions of substituted spiro[indoline-3,2′-oxiran]-2-ones with olefins. The reactions proceed by ring opening of spiro[indoline-3,2′-oxiran]-2-ones via C$_\beta$–O bond cleavage and subsequent cycloaddition with olefins by using 2,4,6-triphenylpyrylium tetarfluoroborate (**TPT**) as a sensitizer.

1. Introduction

Photoinduced electron transfer (PET) catalysis is an important tool in modern synthetic photochemistry.[1] Increasing research activity in PET processes has focused not only on mechanism but also in discovering new synthetically useful reactions. The advantages of the PET-catalyzed reactions over the classical photoreactions lie in the increase of reaction selectivity, reaction rate, and the yields of products. For example, the PET-catalyzed ring opening of oxiranes,[2] azirines,[3] aziridines,[4] and cyclopropanes[5] and subsequent intermolecular or intramolecular [3+2] reactions with alkenes or alkynes provided a more efficient route to synthesis of cyclic compounds than simple photolytic 1,3-diplar cycloaddition. In these reactions, the high active radical cations of oxiranes, azirines, aziridines, and cyclopropanes were first produced by photoinduced electron transfer from these compounds to excited oxidative photosensitizers like 1,4-dicyanophthalene (**DCN**), 9,10-dicyanoanthracene (**DCA**) or 2,4,6-triphenylpyrylium tetrafluoroborate (**TPT**) and the C–C bond cleavage of these three-membered cyclic radical cations occurred quickly to produce 1,3-radical cations, which could be captured by alkenes or alkynes to give the five-membered cyclic radical cations; after the back electron transfer from the photosensitizer radical anions to these five-membered cyclic radical cations, polysubstituted tetrahydrofuran, dihydropyrrole, pyrrolidine, and cyclopentane were formed (Scheme 1).



Scheme 1. PET-catalyzed [3+2] reactions of oxirane, azirine, aziridine, and cyclopropanes with olefins.

Recently, we reported a novel synthesis of polysubstituted tetrahydrofurans by PET-catalyzed [3+2] reactions of oxiranecarbonitriles with electron-rich olefins via **TPT**-sensitized C$_\beta$–O bond cleavage of oxiranecarbonitriles and subsequent [3+2] cycloaddition with olefins (Scheme 2),[6] which was much different from the reported **DCN** or **DCA** sensitized [3+2] cycloaddition of oxiranes with olefins via C–C bond cleavage of oxiranes.[2] In the reactions, the radical cations of oxiranes were first produced by electron transfer from oxiranes to excited **TPT**, the oxirane radical cations underwent C$_\beta$–O bond cleavage and subsequent [3+2] cycloaddition with olefins produced tetrahydrofuran radical cations, which finally accepted an electron from **TPT** radical afforded the products and regenerated **TPT** cation (Scheme 3).[6]

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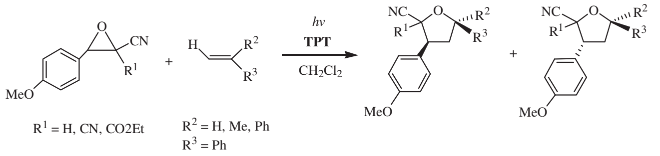
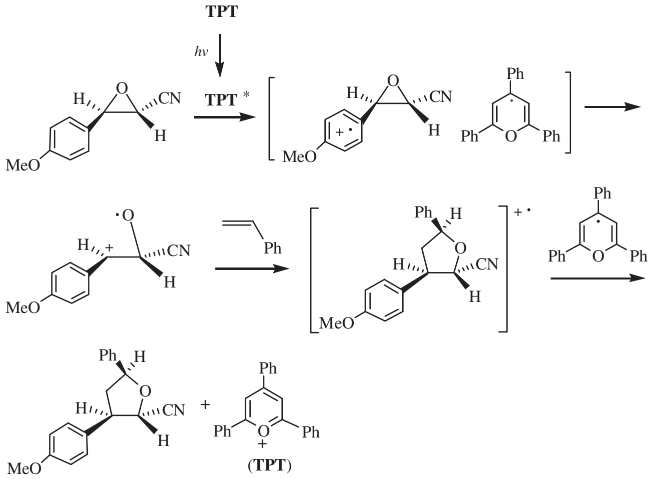
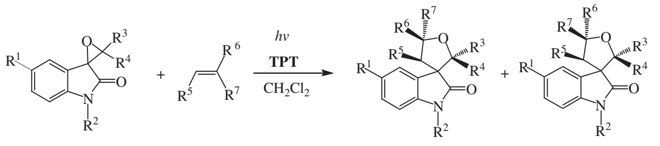


Scheme 2. **TPT**-catalyzed [3+2] reaction of oxiranes with olefins.



Scheme 3. Mechanism of **TPT**-catalyzed [3+2] reaction of oxirane with olefin.

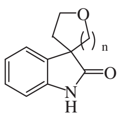
As a continuous investigation, we report in this paper an efficient synthesis of spiro[furan-2′,3-indolin]-2-ones (**3**) by the **TPT**-catalyzed [3+2] reactions of spiro[indoline-3,2′-oxiran]-2-ones (**1**) with electron-rich olefins (**2**) via **TPT**-sensitized C_β–O bond cleavage of spiro-oxiranes and subsequent [3+2] reactions with olefins (Scheme 4).



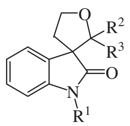
1 2 3 4

Scheme 4. **TPT**-catalyzed [3+2] reactions of spiro[indoline-3,2′-oxiran]-2-ones (**1**) with olefins.

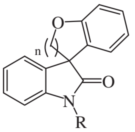
The heterocyclic spiro-oxindole framework is an important structural motif in biologically relevant compounds as natural products and pharmaceuticals.[7] 3-Azaspiro-oxindole derivatives are well-known and a number of synthetic methods have been developed for expedition of these structural frameworks.[8] 3-oxaspiro-oxindoles also possess some important biological activities. For example, **Ia**,**b** are used for progesterone receptor antagonists;[9a] **Ic** are used for treating hypertension of mammals;[9b] **IIa**,**b** are used for treatment and prevention of hypercholesterolemia, benign prostatic hyperplasia, pruritis, and cancer.[9c] but the reports for the preparation of the corresponding 3-oxaspiro-oxindole analogues are rare.[9,10] For example, Almendros recently reported the synthesis of dihydrospiro[furan-2′,3-indole]-2-ones by ruthenium, silver, and palladium-catalyzed carbonyl-addition/cyclization reaction of 2-indolinone-tethered homoallylic alcohols;[10a] Alcaide reported the synthesis of spiro[furan-3′,3-indole]-2-ones by indium-mediated Barbier-type carbonyl-allenylation reaction from isatin to give 3-hydroxy-3-allenyl-2-indolinones and subsequent palladium-catalyzed spirocyclization by α-allenols-cross coupling reaction;[10b] Ganguly reported the synthesis of spiro[furan-3′,3-indole]-2-ones by radical cyclization of *N*-(2-bromophenyl)3-furan-3-carboxyamide;[10c] Menéndez reported the synthesis of dihydrospiro[furan-3′,3-indole]-2′,2-diones by one-pot transformation of 3-(4-hydroxyalkyl)indoles under Swern conditions;[10d] Giorgi–Renault reported the synthesis of dihydrospiro[furan-3′,3-indole]-2′,2-diones by oxidative rearrangement of 3,4-dihydropyrano[3,4-*b*]indol-1-ones with *m*-chloroperbenzoic acid.[10e]



Ia-b



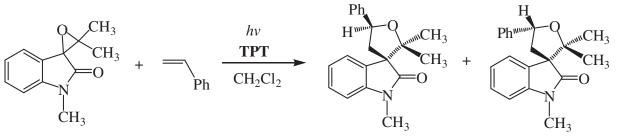
Ic



IIa-b

2. Results and discussion

We first examined the photoreaction of 3′,3′-dimethylspiro[indoline-3,2′-oxiran]-2-ones (**1a**) with styrene (**2a**) in the presence of different sensitizers, such as **TPT**, **DCA**, **DCN**, and chloranil. The deaerated anhydrous CH_2Cl_2 solutions of **1a** with **2a** and a catalytic amount of photosensitizers (5% equiv) were irradiated at λ≥350 nm at ambient temperature and the progress of the reaction was monitored by TLC chromatography at different interval. It was found that the reaction of **1a** and **2a** could afford the [3+2] products, 3,3-dimethylspiro[furan-3,3′-indolin]-2′-ones **3a** and **4a** (8:1), in high yields only under the catalysis of **TPT** and the reaction was completely regioselective as depicted in Scheme 5.



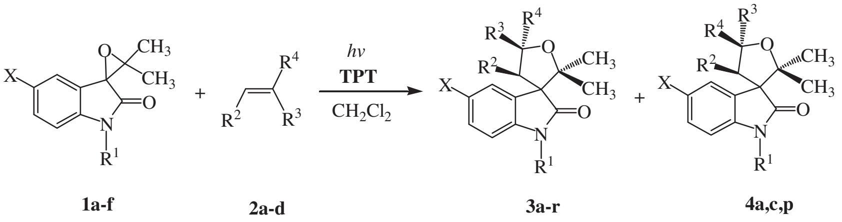
1a **2a** **3a** **4a**

Scheme 5. **TPT**-catalyzed [3+2] reaction of **1a** with **2a**.

But in the case of other sensitizers, such as **DCA**, **DCN**, and chloranil, the reaction was much slow and the products were complex. If the deaerated anhydrous CH_2Cl_2 solution of **1a** and **2a** was irradiated at λ≥350 nm in the absence of **TPT** for long time (48 h), no products were detected. Thus, the **TPT** as catalyst was not only more superior than other sensitizers but also necessary. Therefore **TPT** was selected as the sensitizer in the [3+2] reactions of spiro[indoline-3,2′-oxiran]-2-ones with olefins.

The photoreactions of 3′,3′-dimethylspiro[indoline-3,2′-oxiran]-2-ones (**1a**–**g**) with olefins (**2a**–**d**) were examined under the same conditions and the results were listed in Table 1. It could be found that the products obtained were only one stereoisomer in most cases, but for several reactions, such as **1a** or **1c** with **2a**; **1d** with **2b**, two stereoisomers were produced in different ratio. The two stereoisomers were easily separated by repeated thin plate chromatography. All these products **3a**–**r** and **4a**, **4c**, **4p** were characterized by ^{1}H, ^{13}C NMR spectroscopy, HRMS, and IR. The configurations of representative products **3a**, **4a**, **3j**, **3p**, **4p**, and **3r** were determined by NOESY as depicted in Fig. 1. The reciprocal interaction of H-5 and H-4′ was observed in **3a** in accord with the cis configuration of 5-phenyl group and 3′-carbonyl group in products **3a**; in contrast, no reciprocal interaction of H-5 and H-4′ was observed in **4a** in accord with the trans configuration of 5-phenyl group and 3′-carbonyl group in products **4a**. The reciprocal interactions of H-4 and H-5 with H-4′ were observed in **3j** in accord with the cis configuration of 5-phenyl group and 3′-carbonyl group in products **3j**. The reciprocal interaction of hydrogen atom in 5-methyl group and H-4′ was observed in **3p** in accord with the cis configuration of 5-phenyl group and 3′-carbonyl group in products **3p** in contrast, no

Table 1
Photochemical [3+2] reactions of oxiranes **1a–f** with **2a–d**[a]



Entry	Substrate							t (hr)	Convn. (%) [b]	Product	Yield[c] (**3**/**4**) (%)
		R^1	X		R^2	R^3	R^4				
1	**1a**	H	H	**2a**	H	Ph	H	10	90	**3a**, **4a**	79 (8:1)
2	**1b**	CH_3	H	**2a**	H	Ph	H	10	95	**3b**	93
3	**1c**	Ph	H	**2a**	H	Ph	H	5	100	**3c**, **4c**	97 (6:1)
4	**1a**	H	H	**2b**	H	Ph	CH_3	8	79	**3d**	90
5	**1b**	CH_3	H	**2b**	H	Ph	CH_3	8	93	**3e**	94
6	**1c**	Ph	H	**2b**	H	Ph	CH_3	5	100	**3f**	96
7	**1a**	H	H	**2c**	H	Ph	Ph	15	81	**3g**	89
8	**1b**	CH_3	H	**2c**	H	Ph	Ph	10	93	**3h**	82
9	**1c**	Ph	H	**2c**	H	Ph	Ph	10	100	**3i**	95
10	**1a**	H	H	**2d**	$C_6H_4CH_2$		H	15	82	**3j**	92
11	**1b**	CH_3	H	**2d**	$C_6H_4CH_2$		H	15	93	**3k**	90
12	**1c**	Ph	H	**2d**	$C_6H_4CH_2$		H	15	95	**3l**	88
13	**1d**	CH_3	Br	**2a**	H	Ph	H	10	68	**3m**	75
14	**1e**	CH_3	CH_3	**2b**	H	Ph	CH_3	8	93	**3n**	89
15	**1f**	CH_3	OCH_3	**2a**	H	Ph	CH_3	8	90	**3o**	85
16	**1d**	CH_3	Br	**2b**	H	Ph	CH_3	8	78	**3p**, **4p**	96 (8:1)
17	**1g**	CH_3	NO_2	**2a**	H	Ph	CH_3	36	12	—	—
18	**1f**	CH_3	CH_3	**2d**	$C_6H_4CH_2$		H	15	95	**3q**	93
19	**1d**	CH_3	Br	**2d**	$C_6H_4CH_2$		H	15	75	**3r**	91

[a] Compound **1a** (95 mg, 0.5 mmol), **2a** (78 mg, 0.75 mmol), and **TPT** (10 mg) were dissolved in 20 ml dry dichloromethane in a 25 ml reaction flask. The solution was deaerated by bubbling Ar for 30 min and then irradiated at $\lambda \geq 350$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature.

[b] Conversion was calculated on the basis of substrate **1a–f**.

[c] Yield of isolated products was based on consumed substrates **1a–f**.

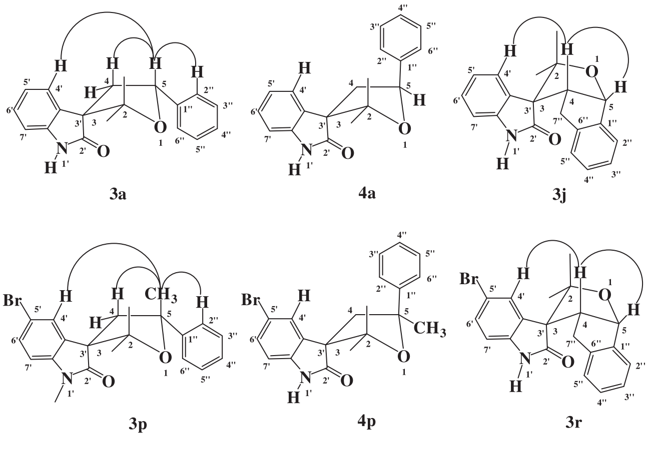


Fig. 1. NOESY correlations of **3a**, **4a**, **3j**, **3p**, **4p**, and **3r**.

reciprocal interaction of H-4′ with hydrogen atom in 5-methyl group were observed in **4p**. The NOESY correlations of **3r** was similar to that of **3j** and the structure of **3r** was also determined by the X-ray crystallography (Fig. 2),[11] which was consistent to the structure of **3r** determined by NOESY.

It should be noticed that the substituents on the oxoindole ring have some influences to the photoreaction efficiency of spiro[indoline-3,2′-oxiran]-2-ones. In comparison of the conversion of **1a–c** in photoreactions with **2a–d**, the reaction rates of **1a** (R^1=H), **1b** (R^1=Me), and **1c** (R^1=Ph) increase gradually. The photoreactions of **1c** with **2a–c** are nearly quantitative in shorter reaction time, but **1a** and **1b** need more time to complete the reactions. In addition, the electron-withdrawing groups X at 5′ position of indole ring, such as bromine atom in **1d** retard the photoreaction (entry 13, 16, and 19) and the nitro group in **1g** restrains the photoreaction at all (entry 17); but the electron-donating groups, such as methyl and methoxy groups in **1e,f** seemly have no great influence to the photoreactions (entry 14 and 15).

Then, we examined the photoreactions of oxiranes bearing an electron-withdrawing group, such as ethyl spiro[2-oxo-indoline-3,2′-oxiran]-3′-carboxylate (**1h**) and 3′-phenylspiro[indoline-3,2′-oxiran]-2-ones (**1i**), with olefins under the same conditions. Similar results were obtained for the reactions of 3′,3′-dimethylspiro [indoline-3,2′-oxiran]-2-one (**1h,i**) (Table 2), and the obtained 3-

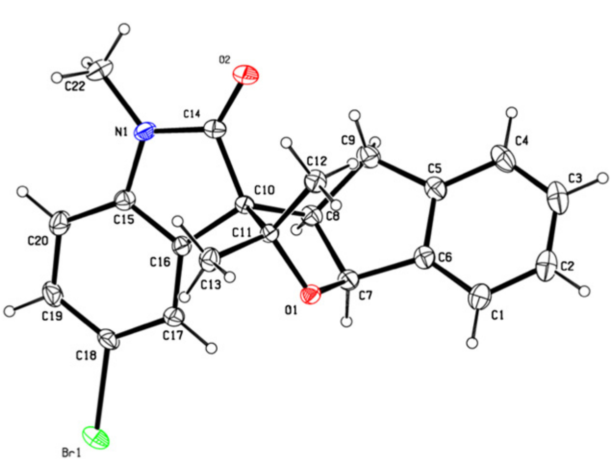
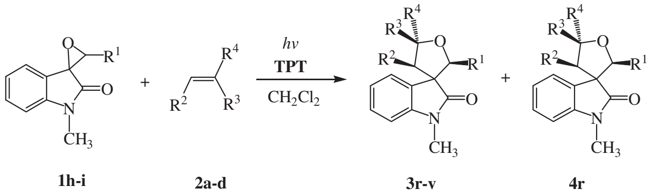


Fig. 2. X-ray crystal structure of **3r**.

Table 2
Photochemical [3+2] reactions of oxiranes **1h**,**i** with **2a**,**d**[a]



Entry	Substrate						t (hr)	Convn. (%) [b]	Product	Yield[c] (**3**/**4**) (%)
		R^1		R^2	R^3	R^4				
1	**1h**	COOEt	**2b**	H	Ph	CH_3	15	95	**3s**, **4s**	93 (6:1)
2	**1h**	COOEt	**2c**	H	Ph	Ph	15	85	**3t**	89
3	**1h**	COOEt	**2d**	$C_6H_4CH_2$	H		15	82	**3u**	81
4	**1i**	Ph	**2a**	H	Ph	CH_3	15	79	**3v**	92
5	**1i**	Ph	**2d**	$C_6H_4CH_2$	H		15	60	**3w**	90

[a] Compound **1h** (124 mg, 0.5 mmol), **2b** (89 mg, 0.75 mmol), and **TPT** (10 mg) were dissolved in 20 ml dry dichloromethane in a 25 ml reaction flask. The solution was deaerated by bubbling Ar for 30 min and then irradiated at $\lambda \geq 350$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature.
[b] Conversion was calculated on the basis of substrate **1h**,**i**.
[c] Yield of isolated products was based on consumed substrates **1h**,**i**.

oxaspiro-oxindoles (**3s**–**w**) were also derived from **TPT**-sensitized C_β–O bond cleavage of oxiranes and subsequent [3+2] reactions with olefins from the elucidation of ^1H, ^{13}C NMR spectroscopy and HRMS of all these products. The configurations of representative product **3s**, **4s**, and **3v** were determined by NOESY correlations and by the comparison with the NOESY correlations of substrates **1h**,**i**. It was found that the configurations of two substrates **1h**,**i** were different: no NOESY correlation was observed between H-2 and H-4′ in **1h**, but the NOESY correlation could be observed between H-2 and H-4′ in **1i**. On the other hand, it could be inferred that the configurations of C-2 in products **3s**–**w** were the same as those in the **1h**,**i** because only C_β–O bond cleavage in photoreaction and the configuration of C-2 had no change. Therefore, the configuration of **3s** and **4s** could be assigned by the reciprocal interaction of hydrogen atom in 5-methyl group with H-4′ as well as with H-2; the configuration of **3v** was assigned by the reciprocal interaction of hydrogen atom in 5-methyl group with H-2 and H-4′ as shown in Fig. 3.

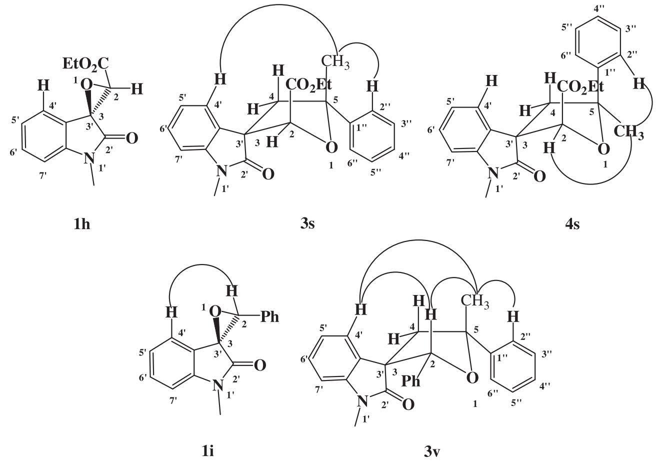
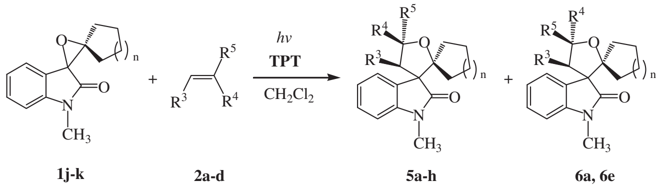


Fig. 3. NOESY correlations of the **1h**,**i** and **3s**, **4s**, **3v**.

It could be noticed from the Table 2 that the photoreactions of **1h**,**i** turn slow when two methyl groups in **1a**–**f** are replaced by ethoxycarbonyl group (**1h**) or phenyl group (**1i**). Much more time is needed to reach higher conversions, or the conversions decrease in the same irradiation time.

In order to synthesize dispiro-oxoindole compounds by the established **TPT**-sensitized [3+2] reactions, two dispiro-oxiranes (**1j**–**k**) were prepared and the **TPT**-sensitized photoreactions with olefins (**2a**–**d**) were carried out under the same conditions. The obtained dispiro oxoindoles **5a**–**h** were also derived from **TPT**-sensitized C_β–O bond cleavage of oxiranes and subsequent [3+2] cycloaddition with olefins from the elucidation of their ^1H, ^{13}C NMR spectroscopy, and HRMS (Table 3). The configurations of representative products **5a**, **6a**, and **5h** were determined by NOESY (Fig. 4).

Table 3
Photochemical [3+2] reactions of oxiranes **1j**,**k** with **2a**–**d**[a]



Entry	Substrate						t (hr)	Convn. (%) [b]	Product	Yield[c] (**5**/**6**) (%)
		n		R^3	R^4	R^5				
1	**1j**	1	**2a**	H	Ph	H	10	95	**5a**, **6a**	88 (5:1)
2	**1j**	1	**2b**	H	Ph	CH_3	10	94	**5b**	94
3	**1j**	1	**2c**	H	Ph	Ph	15	93	**5c**	69
4	**1j**	1	**2d**	$C_6H_4CH_2$		H	15	77	**5d**	64
5	**1k**	2	**2a**	H	Ph	H	8	100	**5e**, **6e**	92 (6:1)
6	**1k**	2	**2b**	H	Ph	CH_3	5	99	**5f**	82
7	**1k**	2	**2c**	H	Ph	Ph	10	98	**5g**	91
8	**1k**	2	**2d**	$C_6H_4CH_2$		H	15	95	**5h**	86

[a] Compound **1j** (115 mg, 0.5 mmol), **2a** (78 mg, 0.75 mmol), and **TPT** (10 mg) were dissolved in 20 ml dry dichloromethane in a 25 ml reaction flask. The solution was deaerated by bubbling Ar for 30 min and then irradiated at $\lambda \geq 350$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature.
[b] Conversion was calculated on the basis of substrate **1j**,**k**.
[c] Yield of isolated products was based on consumed substrates **1j**,**k**.

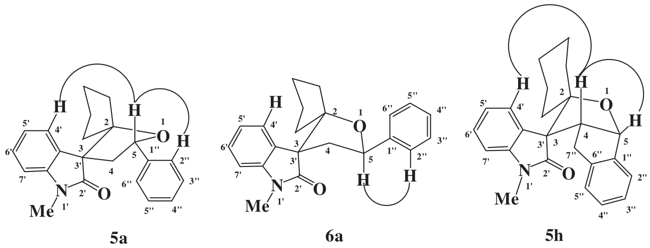


Fig. 4. NOESY correlations of the **5a**, **6a**, and **5h**.

It is found from Table 3 that the photoreaction efficiency of **1h**,**i** with olefins **2a**–**d** is much similar to that of **1b** in Table 1. The reactions of **1h**,**i** with **2a**,**b** are relatively easier than those with **2c**,**d**. The NOESY correlations of products **5a**, **6a**, and **5h** are also similar to those of **3a**, **4a**, and **3j**, thus the configurations of products **5a**, **6a**, and **5h** are also similar to those of **3a**, **4a**, and **3j**.

Since no reaction ever took place in the dark or in the absence of **TPT** with prolonged irradiation under the same conditions, the photoreaction of **1** and **2** might be rationalized as a PET-catalyzed non-synchronous cation radical [3+2] reaction, similarly to the **DCN**-sensitized [3+2] reactions of stilbene oxides[2] (Scheme 1). The photoreactions were first initiated by the photoinduced electron transfer from substrates **1a**–**f** and **1h**–**k** to excited **TPT** could be confirmed by the free energy change of electron transfer, ΔG, calculated by the Rehm–Weller equation ($\Delta G_{ET}=E_{1/2}^{ox}(D)-E_{1/2}^{red}(A)-\Delta E_{excit}+E_{coul}$[12]). The oxidative potentials of **1a**–**k** were determined by cyclic voltammetry technique, the reduction potential of excited **TPT** ($E_{TPT^*/TPT^{-\bullet}}^{red}=E_{1/2}^{red}+\Delta E_{excit}$) was 2.0 V versus SCE[1d] and the E_{coul} in dichloromethane was 0.13 V. The ΔGs calculated were listed in Table 4.

Table 4
The ΔG_{ET} of the photoinduced electron transfer (PET) between **TPT** and oxiranes **1a**–**k**

Entry	Substrate		E_p^{ox} (V)[a] versus SCE	ΔG_{ET} (V) versus SCE
		X		
1	**1a**	H	1.65	−0.23
2	**1b**	H	1.60	−0.27
3	**1c**	H	1.73	−0.14
4	**1d**	Br	1.78	−0.09
5	**1e**	CH_3	1.61	−0.26
6	**1f**	OCH_3	1.38	−0.49
7	**1g**	NO_2	2.12	0.25
8	**1h**	H	1.73	−0.14
9	**1i**	H	1.75	−0.12
10	**1j**	H	1.70	−0.17
11	**1k**	H	1.72	−0.15

[a] The oxidation potentials were measured by cyclic voltammetry using a 4 mm diameter glassy carbon disk electrode as working electrode, a platinum tab as the counter electrode, and a saturated calomel electrode as the reference electrode in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate.

It could be observed that the PET between **TPT** and **1a**–**f** and **1h**–**k** are thermodynamically feasible because ΔGs are negative except for **1g**. In comparison of the reactivity of **1b** and **1e**–**g** (entry 5 and 14–17 in Table 1) with the corresponding values of ΔG_{ET}, it can be found that the electron-withdrawing group Br atom and NO_2 at 5′ position of oxoindole ring make the ΔG_{ET} for PET between **TPT** and **1d** and **1g** increase as compared with the ΔG_{ET} between **TPT** and **1b**, and the reactivity of **1d** and **1g** with **2b** decease (entry 16 and 17 in Table 1). In fact, NO_2 lead the ΔG_{ET} for PET between **TPT** and **1g** become positive and no reaction took place. Differently, the electron-donating group, such as methyl and methoxy groups in **1e**,**f** make ΔG_{ET} for PET between **TPT** and **1e** or **1d** decrease, but the reactivity of **1e**,**f** with **2b** has no great change (entry 14 and 15 in Table 1) as compared with that of **1b**. On the other hand, since the oxidation potentials of **2a**–**d** (1.67–1.83 V vs SCE[13]) were close to those of **1a**–**d**, the electron transfer between excited **TPT** and **2a**–**d** was also possible. However, the cyclodimerization of **2a**–**d** catalyzed by **TPT** was very slow in comparison with the photoreactions of **1a**–**f** with **2a**–**d** under the same conditions. Thus it could be inferred that the great negative values of ΔG_{ET} do not correlate to great reactivity of substrates.

3. Conclusion

In conclusion, an efficient photochemical approach to the synthesis of spiro[furan-2′,3-indolin]-2-ones and dispiro[cycloalkane-1,2′-furan-3′,3″-indolin]-2″-ones in high yields and stereoselectivity has been established by 2,4,6-triphenylpyrylium tetrafluoroborate (**TPT**) catalyzed [3+2] reaction of spiro[indoline-3,2′-oxiran]-2-one with olefins under mild conditions in this work.

4. Experimental section

4.1. Experimental protocols

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200–300 mesh). Analytical TLC was performed with silica gel GF_{254} plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in parts per million using TMS as internal standard and spin–spin coupling constants (J) are given in hertz. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEXII47e spectrometer by ESI. The substrates **1a**–**g** and **5a**,**b** were prepared according to the reported procedures.[14]

4.2. General procedure for the photoreaction

Spiro[indoline-3,2′-oxiran]-2-one (**1a**) (95 mg, 0.5 mmol) and styrene (**2a**) (78 mg, 0.75 mmol) were dissolved in 50 ml anhydrous dichloromethane in a 50 ml reaction flask. The solution was deaerated by bubbling Ar for 30 min and then **TPT** (10 mg, 0.025 mmol) was added. The solution was irradiated at $\lambda \geq 350$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature until the complete conversion of the starting material. The progress of reaction was monitored by TLC at regular intervals. After the solvent was removed under reduced pressure, the residue was separated by column chromatography on silica gel eluted by hexane/acetone 20:1 (v/v) to afford product **3a** and **4a**. The two stereoisomers were further separated by preparative thin layer chromatography and purified by recrystalization to give pure **3a** and **4a**.

*4.2.1. 2,3-Dimethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3a**).* Pale yellow solid; mp: 156–157 °C; IR (KBr): 3251 (b), 3061, 3028, 2973, 2926, 1710 (s), 1618, 1470 (m), 1381, 1332 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.43 (s, 1H), 7.47 (d, J=7.6 Hz, 2H), 7.38 (t, J=7.6 Hz, 2H), 7.29 (d, J=6.8 Hz, 1H), 7.20 (d, J=7.6 Hz, 2H), 6.99–6.93 (m, 1H), 6.90 (d, J=8.4 Hz, 1H), 5.72 (t, J=8.4 Hz, 1H), 2.91 (dd, J=12.8, 7.2 Hz, 1H), 2.46 (dd, J=12.8, 8.4 Hz, 1H), 1.42 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 180.05, 143.17, 140.84, 130.15, 128.38, 128.38, 128.19, 127.11, 126.09, 125.44, 125.44, 122.10, 109.56, 84.78, 77.54, 61.29, 44.22, 27.34, 23.92; ESI-HRMS: m/z calcd for $C_{19}H_{19}NO_2+H^+$: 294.1489, found 294.1493.

*4.2.2. 2,2-Dimethyl-5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**4a**).* Yellow grease; IR (KBr): 3255 (b,) 3061, 3028, 2971, 2927, 1709 (s), 1620 (m), 1470 (m), 1363 (m), 1336 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_{3)}$ δ ppm 8.58 (s, 1H), 7.56 (d, J=7.6 Hz, 2H), 7.42 (d, J=7.6 Hz, 1H), 7.39–7.35 (m, 2H), 7.30–7.22 (m, 2H), 7.08 (dt, J=7.6, 0.8 Hz, 1H), 6.90 (d, J=7.6 Hz, 1H), 5.48 (t, J=8.0 Hz, 1H), 2.77 (dd, J=12.8, 8.8 Hz, 1H), 2.67–2.62 (m, 1H), 1.47 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 179.40, 142.83, 140.50, 131.38, 128.35, 128.35, 128.14, 127.35, 126.08, 126.08, 125.24, 122.25, 109.73, 85.36, 78.42, 61.04, 44.71, 25.87, 25.02; ESI-HRMS: m/z calcd for $C_{19}H_{19}NO_2+H^+$: 294.1489, found 294.1491.

*4.2.3. 1′,2,2-Trimethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3b**).* Yellow grease; IR (KBr): 3058, 3027, 2976, 2934, 1712 (s), 1610 (s), 1493 (m), 1469 (m), 1374 (m), 1350 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56 (d, J=7.6 Hz, 2H), 7.44 (d, J=7.6 Hz, 1H), 7.36 (t, J=7.6 Hz, 2H), 7.33–7.24 (m, 2H), 7.10 (t, J=7.6 Hz, 1H), 6.85 (d, J=7.6 Hz, 1H), 5.47 (t, J=8.4 Hz, 1H), 3.21 (s, 3H), 2.74 (dd, J=13.2, 9.2 Hz, 1H), 2.60 (dd, J=13.2, 8.0 Hz, 1H), 1.42 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.91, 143.29, 142.87, 130.79, 128.29, 128.29, 128.10, 127.25, 125.98, 125.98, 124.80, 122.21, 107.93, 85.22, 78.31, 60.53, 44.62, 26.28, 25.75, 24.97; ESI-HRMS: m/z calcd for $C_{20}H_{21}NO_2+H^+$: 308.1645, found 308.1642.

*4.2.4. 2,2-Dimethyl-1′,5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3c**).* Yellow grease; IR (KBr): 3056, 3027, 2945, 2859, 1710 (s), 1610 (m), 1492 (m), 1458 (m), 1373 (m), 1352 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55–7.48 (m, 4H), 7.43–7.37 (m, 5H), 7.31–7.25 (m, 2H), 7.19 (t, J=7.6 Hz, 1H), 7.03 (t, J=7.2 Hz, 1H), 6.80 (d, J=8.0 Hz, 1H), 5.77 (t, J=8.0 Hz, 1H), 3.00 (dd, J=12.8, 7.2 Hz, 1H), 2.53 (dd, J=12.8, 8.8 Hz, 1H), 1.47 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 177.36, 143.63, 143.15, 134.47, 129.61, 129.61, 129.55, 128.40, 128.40, 128.08, 128.08, 127.13, 126.68, 126.68, 125.48, 125.48, 125.35, 122.52, 109.13, 85.13, 77.73, 60.88, 44.42, 27.49, 23.97; ESI-HRMS: m/z calcd for $C_{25}H_{23}NO_2+H^+$: 370.1802, found 370.1799.

*4.2.5. 2,2-Dimethyl-1′,5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**4c**).* Yellow grease; IR (KBr): 3050, 3020, 2946, 2857, 1711 (s), 1608 (m), 1495 (m), 1452 (m), 1368 (m), 1357 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.61 (d, J=7.2 Hz, 2H), 7.52 (t, J=8.4 Hz,), 7.42–7.34 (m, 5H), 7.29–7.21 (m, 2H), 7.13 (t, J=7.6 Hz, 1H), 6.84 (d, J=8.0 Hz, 1H), 5.50 (t, J=8.0 Hz, 1H), 2.80 (m, 2H), 1.49 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 176.90, 143.46, 142.68, 134.54, 130.32, 129.61, 129.61, 128.35, 128.35, 128.08, 128.06, 127.38, 126.69, 126.69, 126.30, 126.30, 125.14, 122.64, 109.28, 85.73, 78.38, 60.72, 44.65, 25.40, 25.06; ESI-HRMS: m/z calcd for $C_{25}H_{23}NO_2+H^+$: 370.1802, found 370.1804.

*4.2.6. 2,2,5,-Trimethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3d**).* Pale yellow solid; mp: 236–238 °C; IR (KBr): 3285 (b), 3032, 2968, 2917, 1712 (s), 1608, 1457 (m), 1371, 1338 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.96 (s, 1H), 7.62 (d, J=7.2 Hz, 1H), 7.48 (d, J=7.6 Hz, 2H), 7.34 (t, J=7.6 Hz, 2H), 7.24–7.21 (m, 2H), 7.08 (t, J=7.6 Hz, 1H), 6.86 (d, J=8.0 Hz, 1H), 3.35 (d, J=13.2 Hz, 1H), 2.64 (d, J=12.8 Hz, 1H), 1.72 (s, 3H), 1.16 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 178.42, 151.26, 140.11, 132.68, 127.91, 127.87, 127.87, 126.17, 126.09, 124.74, 124.74, 122.12, 109.58, 86.04, 83.15, 61.80, 50.01, 34.21, 26.46, 25.66; ESI-HRMS: m/z calcd for $C_{20}H_{21}NO_2+H^+$: 308.1645, found 308.1648.

*4.2.7. l′,2,2,5-Tetramethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3e**).* Pale yellow solid; mp: 124–126 °C; IR (KBr): 3056, 2976, 2931, 1713 (s), 1610 (m), 1492 (m), 1469 (m), 1373 (m), 1347 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.64 (d, J=7.6 Hz, 1H), 7.47 (d, J=7.6 Hz, 2H), 7.35–7.29 (m, 3H), 7.20 (t, J=7.2 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 6.85 (d, J=7.6 Hz, 1H), 3.33 (d, J=12.8 Hz, 1H), 3.18 (s, 3H), 2.60 (d, J=13.2 Hz, 1H), 1.71 (s, 3H), 1.15 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 176.36, 151.24, 143.16, 132.11, 127.89, 127.83, 127.83, 126.12, 125.64, 124.68, 124.68, 122.05, 107.93, 85.90, 83.02, 61.37, 50.02, 34.16, 26.40, 26.38, 25.67; ESI-HRMS: m/z calcd for $C_{21}H_{23}NO_2+H^+$:322.1802, found 322.1806.

*4.2.8. 2,2,5-Trimethyl-l′,5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3f**).* Pale yellow solid; mp: 176–178 °C; IR (KBr): 3058, 3023, 2953, 2857, 1712 (s), 1605, 1486 (m), 1465, 1367 (m), 1348 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.71 (d, J=7.2 Hz, 1H), 7.51–7.47 (m, 4H), 7.40–7.31 (m, 5H), 7.25–7.21 (m, 2H), 7.13 (t, J=7.6 Hz, 1H), 6.82 (d, J=7.6 Hz, 1H), 3.45 (d, J=13.2 Hz, 1H), 2.74 (d, J=13.2 Hz, 1H), 1.76 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 175.85, 151.19, 143.18, 134.60, 131.91, 129.53, 129.53, 128.00, 127.89, 127.89, 127.82, 126.76, 126.76, 126.18, 125.96, 124.74, 124.74, 122.50, 109.25, 86.31, 83.21, 61.55, 50.21, 34.30, 26.50, 25.94; ESI-HRMS: m/z calcd for $C_{26}H_{25}NO_2+H^+$: 384.1958, found 384.1955.

*4.2.9. 2,2-Dimethyl-5,5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3g**).* Pale yellow solid; mp: 265–266 °C; IR (KBr): 3390 (b), 2917, 2847, 1778 (m), 1599 (s), 1501 (m), 1348 (m), 1159 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.91 (s, 1H), 7.61 (d, J=8.0 Hz, 4H), 7.30–7.07 (m, 7H), 6.79 (d, J=8.0 Hz, 1H), 6.72 (dt, J=7.6, 0.8 Hz, 1H), 6.66 (d, J=7.2 Hz, 1H), 3.60 (d, J=13.2 Hz, 1H), 3.28 (d, J=13.2 Hz, 1H), 1.29 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 178.48, 150.48, 148.81, 139.89, 132.06, 128.20, 128.20, 128.01, 128.01, 127.67, 126.34, 126.21, 126.14, 125.10, 125.10, 124.95, 124.95, 122.06, 109.17, 86.14, 86.05, 61.73, 49.39, 26.39, 25.51; ESI-HRMS: m/z calcd for $C_{25}H_{23}NO_2+H^+$: 370.1802, found 370.1800.

*4.2.10. 1′,2,2-Trimethyl-5,5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3h**).* Pale yellow solid; mp: 160–162 °C; IR (KBr): 3037, 3028, 2935 (m), 2872, 1768 (s), 1605, 1482 (m), 1453 (m), 1368 (m), 1347 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.60 (d, J=8.0 Hz, 4H), 7.29–7.24 (m, 4H), 7.18–7.10 (m, 3H), 6.78–6.70 (m, 3H), 3.68 (d, J=12.8 Hz, 1H), 3.25 (d, J=13.2 Hz, 1H), 1.28 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 176.46, 150.49, 148.87, 142.98, 131.51, 128.15, 128.15, 127.98, 127.98, 127.65, 126.27, 126.10, 125.75, 125.08, 125.08, 124.90, 124.90, 122.00, 107.55, 86.03, 85.91, 61.31, 49.41, 26.43, 26.33, 25.55; ESI-HRMS: m/z calcd for $C_{26}H_{25}NO_2+H^+$: 384.1958, found 384.1955.

*4.2.11. 2,2-Dimethyl-1′,5,5-triphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3i**).* Yellow grease; IR (KBr): 3045, 3031, 2925 (m), 2868, 1756 (s), 1609 (m), 1478, 1460 (m), 1372 (m), 1350 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.63 (t, J=9.2 Hz, 4H), 7.48 (dd, J=8.4, 6.8 Hz, 2H), 7.38–7.34 (m, 3H), 7.31–7.21 (m, 4H), 7.14 (t, J=7.6 Hz, 1H), 7.10–7.05 (m, 2H), 6.80–6.73 (m, 3H), 3.78 (d, J=13.2 Hz, 1H), 3.40 (d, J=13.2 Hz, 1H), 1.34 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 175.92, 150.34, 148.92, 142.95, 134.61, 131.21, 129.52, 129.52, 128.19, 128.19, 128.00, 128.00, 127.96, 127.57, 126.69, 126.69, 126.34, 126.13, 126.01, 125.15, 125.15, 124.95, 124.95, 122.43, 108.85, 86.32, 86.20, 61.49, 49.48, 26.36, 25.80; ESI-HRMS: m/z calcd for $C_{31}H_{27}NO_2+H^+$: 446.2115, found 446.2117.

*4.2.12. 2,2-Dimethyl-2,3a,4,8b-tetrahydrospiro[indeno[1,2-b]furan-3,3′-indolin]-2′-one (**3j**).* Pale yellow solid; mp: 223–225 °C; IR (KBr): 3052, 3023, 2925 (m), 2855, 1710 (s), 1609 (m), 1478 (m), 1454 (m), 1368 (m), 1352 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.76 (s, 1H), 7.54 (t, J=4.4 Hz, 1H), 7.39 (d, J=7.6 Hz, 1H), 7.31–7.17 (m, 4H), 7.08 (dt, J=7.6, 1.2 Hz, 1H), 5.85 (d, J=4.2 Hz, 1H), 3.64–3.58 (m, 1H), 3.39 (dd, J=17.6, 3.2 Hz, 1H), 3.0 (dd, J=17.2, 9.2 Hz, 1H), 1.31 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 177.17, 143.40, 141.98, 140.44, 131.23, 128.64, 128.13, 127.00, 125.43, 124.97, 124.44, 122.25, 109.30, 86.43, 86.01, 64.01, 51.24, 33.25, 25.01, 24.34; ESI-HRMS: m/z calcd for $C_{20}H_{19}NO_2+H^+$: 306.3777, found 306.3774.

*4.2.13. 1′,2,2-Trimethyl-2,3a,4,8b-tetrahydrospiro[indeno[1,2-b]furan-3,3′-indolin]-2′-one (**3k**).* Pale yellow solid; mp: 135–136 °C; IR (KBr): 3050, 3021, 2927 (m), 2857, 1708 (s), 1609 (s), 1490 (m), 1468 (m), 1374 (m), 1346 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.55–7.53 (m, 1H), 7.42 (d, J=7.6 Hz, 1H), 7.34–7.27 (m, 3H), 7.20 (d, J=8.4 Hz, 1H), 7.11 (dt, J=7.6, 0.8 Hz, 1H), 6.85 (d, J=7.6 Hz, 1H), 5.87 (d, J=8.0 Hz, 1H), 3.60–3.54 (m, 1H), 3.47 (dd, J=17.6, 3.6 Hz, 1H), 3.19 (s, 3H), 2.96 (dd, J=17.2, 10.0 Hz, 1H), 1.22 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 175.23, 143.44, 143.24, 142.08, 131.10, 128.64, 128.06, 126.84, 125.38, 124.50, 124.42, 122.24, 107.70, 86.42, 86.14, 63.40, 50.92, 33.09, 26.05, 25.12, 24.41; ESI-HRMS: m/z calcd for $C_{21}H_{21}NO_2+H^+$: 320.1645, found 320.1648.

*4.2.14. 2,2-Dimethyl-1′-phexyl-2,3a,4,8b-tetrahydrospiro [indeno[1,2-b]furan-3,3′-indolin]-2′-one (**3l**).* Pale yellow solid; mp: 161 °C; IR (KBr): 3048, 3025, 2932 (m), 2859, 1705 (s), 1608 (m), 1488 (m), 1364 (m), 1376 (m), 1347 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.54–7.47 (m, 4H), 7.39–7.35 (m, 3H), 7.27–7.11 (m, 5H), 6.84 (d, J=7.6 Hz, 1H), 5.91 (d, J=8.0 Hz, 1H), 3.71–3.65 (m, 1H), 3.58 (dd, J=17.6, 3.6 Hz, 1H), 3.04 (dd, J=17.6, 10.4 Hz, 1H), 1.29 (s, 3H), 1.21 (s, 3H);^{13}C NMR (400 MHz, CDCl$_3$) δ ppm 174.66, 143.42, 143.15, 142.07, 134.51, 131.06, 129.48, 129.48, 128.69, 127.98, 127.89, 126.89, 126.69, 126.69, 125.41, 124.79, 124.61, 122.72, 109.07, 86.92, 86.35, 63.37, 51.25, 33.22, 25.26, 24.56; ESI-HRMS: m/z calcd for $C_{26}H_{23}NO_2+H^+$: 382.1802, found 382.1805.

*4.2.15. 5′-Bromo-1′,2,2-trimethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3m**).* Yellow grease; IR (KBr): 3065, 3025, 2968, 2925, 1712 (s), 1610, 1473 (m), 1453 (m), 1378, 1335 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 7.45 (d, J=7.2 Hz, 2H), 7.38 (t, J=7.2 Hz, 3H), 7.33 (d, J=2.0 Hz, 1H), 7.28 (t, J=7.2 Hz, 1H), 6.70 (d, J=8.4 Hz, 1H), 5.70 (t, J=8.0 Hz, 1H), 3.21 (s, 3H), 2.89 (dd, J=12.8, 7.6 Hz, 1H), 2.38 (dd, J=13.2, 8.8 Hz, 1H), 1.37 (s, 3H), 1.28 (s, 3H); ^{13}C

NMR (400 MHz, $CDCl_3$) δ ppm 177.24, 142.75, 142.68, 132.16, 130.98, 128.45, 128.45, 128.26, 127.25, 125.38, 125.38, 114.84, 109.19, 84.86, 77.43, 60.91, 44.36, 27.14, 26.32, 23.83; ESI-HRMS: *m*/*z* calcd for $C_{20}H_{20}BrNO_2+H^+$: 386.0750, found 386.0753.

*4.2.16. 1′,2,2,5,5′-Pentamethyl-5-diphenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3n**).* Pale yellow solid; mp: 112 °C; IR (KBr): 3056, 2976, 2932, 1711 (s), 1606, 1497 (m), 1448, 1352 (m); ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.49–7.47 (m, 3H), 7.33 (t, *J*=7.6 Hz, 2H), 7.24–7.19 (m, 1H), 7.1 (dd, *J*=8.0, 0.8 Hz, 1H), 6.73 (d, *J*=8.0 Hz, 1H), 3.33 (d, *J*=13.2 Hz, 1H), 3.15 (s, 3H), 2.58 (d, *J*=13.2 Hz, 1H), 2.39 (s, 3H), 1.72 (s, 3H), 1.14 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.21, 151.28, 140.81, 132.17, 131.44, 128.07, 127.80, 127.80, 126.46, 126.08, 124.66, 124.66, 107.58, 85.86, 82.95, 61.41, 49.97, 34.18, 26.39, 25.65, 21.24; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{25}NO_2+H^+$: 336.1958, found 336.1960.

*4.2.17. 5′-Methoxy-1′,2,2,5-tetramethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3o**).* Yellow grease; IR (KBr): 3053, 3022, 2926 (m), 2855, 1696 (s), 1601 (s), 1495 (m), 1468 (m), 1371 (m), 1342 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, *J*=8.4 Hz, 2H), 7.33 (t, *J*=7.6 Hz, 2H), 7.29 (d, *J*=2.4 Hz, 1H), 7.22 (t, *J*=7.2 Hz, 1H), 6.84 (dd, *J*=8.4, 2.4 Hz, 1H), 6.75 (d, *J*=8.4 Hz, 1H), 3.83 (s, 3H), 3.34 (d, *J*=13.2 Hz, 1H), 3.16 (s, 3H), 2.58 (d, *J*=13.2 Hz, 1H), 1.72 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.95, 155.56, 151.27, 136.77, 133.53, 127.85, 127.85, 126.15, 124.69, 124.69, 113.26, 112.19, 108.07, 85.90, 82.97, 61.80, 55.84, 50.05, 34.20, 26.52, 26.50, 25.54; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{25}NO_3+H^+$: 352.1841, found 352.1844.

*4.2.18. 5′-Bromo-1′,2,2,5-tetramethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**3p**).* Yellow grease; IR (KBr): 3062, 2968, 2945, 1710 (s), 1610 (m), 1478 (m), 1449 (m), 1368 (m), 1337 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, *J*=1.6 Hz, 1H), 7.47–7.42 (m, 3H), 7.33 (t, *J*=7.2 Hz, 2H), 7.23 (d, *J*=7.2 Hz, 1H), 6.72 (d, *J*=8.4 Hz, 1H), 3.33 (d, *J*=13.2 Hz, 1H), 3.16 (s, 3H), 2.57 (d, *J*=13.2 Hz, 1H), 1.70 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.74, 151.02, 142.23, 134.25, 130.76, 128.75, 127.92, 127.92, 126.27, 124.66, 124.66, 114.88, 109.31, 85.94, 83.09, 61.63, 49.97, 34.24, 26.52, 26.35, 25.62; ESI-HRMS: *m*/*z* calcd for $C_{21}H_{22}BrNO_2+H^+$: 400.0907, found 400.0909.

*4.2.19. 5′-Bromo-1′,2,2,5-tetramethyl-5-phenyl-4,5-dihydro-2H-spiro[furan-3,3′-indolin]-2′-one (**4p**).* Pale yellow solid; mp: 164–166 °C; IR (KBr): 3060, 2970, 2948, 1712 (s), 1608 (m), 1476 (m), 1446 (m), 1370 (m), 1342 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (d, *J*=7.6 Hz, 2H), 7.38–7.32 (m. 3H), 7.28–7.24 (m, 1H), 6.97 (d, *J*=2.0 Hz, 1H), 6.65 (d, *J*=8.4 Hz, 1H), 3.19 (s, 3H), 2.90 (dd, *J*=25.6, 13.2 Hz, 1H), 1.80 (s, 3H), 1.35 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 177.50, 150.89, 142.80, 131.57, 130.86, 128.51, 128.09, 128.09, 126.41, 124.71, 124.71, 114.56, 109.01, 85.52, 83.68, 61.93, 48.76, 34.05, 27.24, 26.29, 25.16; ESI-HRMS: *m*/*z* calcd for $C_{21}H_{22}BrNO_2+H^+$: 400.0907, found 400.0904.

*4.2.20. 1′,2,2,5′-Tetramethyl-2,3a,4,8b-tetrahydrospiro [indeno[1,2-b] furan-3,3′-indolin]-2′-one (**3q**).* Yellow grease; IR (KBr): 3055, 3027, 2935 (m), 2853, 1708 (s), 1612 (m), 1465 (m), 1367 (m), 1336 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.54–7.52 (m, 1H), 7.29–7.18 (m, 4H), 7.10 (dd, *J*=8.0, 0.8 Hz, 1H), 6.73 (d, *J*=7.6 Hz, 1H), 5.87 (d, *J*=8.0 Hz, 1H), 3.57–3.50 (m, 2H), 3.17 (s, 3H), 3.00–2.91 (m, 1H), 1.19 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.20, 143.55, 142.30, 140.86, 131.78, 131.53, 128.68, 128.29, 126.87, 125.46, 125.29, 124.59, 107.42, 86.48, 86.29, 63.37, 51.13, 33.09, 26.14, 25.27, 24.63, 21.25; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_2+H^+$: 334.1802, found 334.1800.

*4.2.21. 5′-Bromo-1′,2,2-trimethyl-2,3a,4,8b-tetrahydrospiro [indeno [1,2-b]furan-3,3′-indolin]-2′-one (**3r**).* Pale yellow solid; mp: 223–224 °C; IR (KBr): 3068, 3025, 2927, 1712 (s), 1607 (m), 1468 (m), 1462 (m), 1363 (m), 1341 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.53 (d, *J*=1.6 Hz, 2H), 7.43 (dd, *J*=8.0, 1.6 Hz, 1H), 7.28 (t, *J*=3.6 Hz, 2H), 7.19 (d, *J*=7.6 Hz, 1H), 6.72 (d, *J*=8.4 Hz, 1H), 5.86 (d, *J*=8.0 Hz, 1H), 3.54 (t, *J*=3.6 Hz, 1H), 3.51–3.48 (m, 1H), 3.17 (s, 3H), 2.96 (dd, *J*=18.4, 10.8 Hz, 1H), 1.19 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 174.62, 143.24, 142.22, 142.05, 133.59, 130.90, 128.79, 127.57, 126.98, 125.49, 124.56, 115.02, 109.13, 86.49, 86.29, 63.49, 51.16, 32.96, 26.21, 25.24, 24.55; ESI-HRMS: *m*/*z* calcd for $C_{21}H_{20}BrNO_2+H^+$: 398.0750, found 398.0747.

*4.2.22. Ethyl 1′,5-dimethyl-2′-oxo-5-phenyl-4,5-dihydro-2H-spiro [furan-3,3′-indolin]-2-carboxylate (**3s**).* Pale yellow solid; mp:119–121 °C; IR (KBr): 3048, 3027, 2965, 2937, 1753 (m), 1710 (s), 1608 (s), 1457, 1436, 1368 (m), 1351 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.61 (d, *J*=6.8 Hz, 2H), 7.39 (t, *J*=7.2 Hz, 2H), 7.29 (d, *J*=7.2 Hz, 1H), 7.17 (dt, *J*=7.6, 2.0 Hz, 1H), 6.78 (t, *J*=8.0 Hz, 3H), 5.08 (s, 1H), 3.78–3.68 (m, 2H), 3.26 (s, 3H), 2.92 (d, *J*=13.2 Hz, 1H), 2.76 (d, *J*=12.8 Hz, 1H), 1.82 (s, 3H), 0.72 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.31, 167.89, 146.96, 143.25, 130.64, 128.30, 128.30, 128.26, 126.81, 124.59, 124.59, 124.40, 122.73, 107.54, 85.88, 82.92, 60.49, 58.02, 51.56, 30.47, 26.55, 13.49; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_4+H^+$: 366.1700, found 336.1702.

*4.2.23. Ethyl 1′,5-dimethyl-2′-oxo-5-phenyl-4,5-dihydro-2H-spiro [furan-3,3′-indolin]-2-carboxylate (**4s**).* Yellow grease; IR (KBr): 3046, 3028, 2968, 2942, 1754 (m), 1711 (s), 1610 (s), 1456, 1436, 1366 (m), 1355 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (dd, *J*=13.6, 7.2 Hz, 3H), 7.38 (t, *J*=7.6 Hz, 2H), 7.31–7.28 (m, 2H), 7.09 (t, *J*=6.8 Hz, 1H), 6.83 (d, *J*=7.6 Hz, 1H), 4.74 (s, 1H), 3.83–3.66 (m, 2H), 3.20 (s, 3H), 3.19 (d, *J*=13.2 Hz, 1H), 2.50 (d, *J*=13.2 Hz, 1H), 1.82 (s, 3H), 0.70 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.96, 167.51, 146.60, 143.42, 131.30, 128.62, 128.54, 128.54, 127.03, 124.66, 124.66, 123.93, 122.91, 107.74, 85.77, 82.83, 60.51, 58.15, 50.81, 31.96, 26.44, 13.54; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_4+H^+$: 366.1700, found 336.1703.

*4.2.24. Ethyl 1′-methyl-2′-oxo-5,5-diphenyl-4,5-dihydro-2H-spiro [furan-3,3′-indoline]-2-carboxylate (**3t**).* Pale yellow solid; mp:148–150 °C; IR (KBr): 3057, 3024, 2969, 2926, 1757 (m), 1716 (s), 1610 (s), 1468, 1446, 1376 (m), 1353 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (dd, *J*=10.8, 7.6 Hz, 4H), 7.33 (t, *J*=7.2 Hz, 4H), 7.25–7.17 (m, 3H), 6.83 (d, *J*=4.0 Hz, 2H), 6.77 (d, *J*=7.6 Hz, 1H), 4.94 (s, 1H), 3.75–3.68 (m, 2H), 3.62 (d, *J*=13.6 Hz, 1H), 3.22 (s, 3H), 2.96 (d, *J*=13.2 Hz, 1H), 0.70 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.89, 167.50, 146.01, 145.68, 143.32, 130.45, 128.41, 128.41, 128.39, 128.24, 128.24, 127.22, 126.92, 125.94, 125.94, 125.43, 125.43, 124.56, 122.71, 107.53, 88.99, 82.99, 60.42, 58.00, 50.20, 26.47, 13.48; ESI-HRMS: *m*/*z* calcd for $C_{27}H_{25}NO_4+H^+$: 428.1857, found 428.1859.

*4.2.25. Ethyl 1′-methyl-2′-oxo-2,3a,4,8b-tetrahydrospiro [indeno [1,2-b]furan-3,3′-indoline]-2-carboxylate (**3u**).* Pale yellow solid; mp:154–156 °C; IR (KBr): 3052, 3030, 2973, 2942, 1756 (m), 1711 (s), 1612 (s), 1465, 1462, 1374 (m), 1346 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J*=6.8 Hz, 1H), 7.47 (d, *J*=7.2 Hz, 1H), 7.34–7.28 (m, 4H), 7.09 (t, *J*=7.6 Hz, 1H), 6.85 (d, *J*=8.0 Hz, 1H), 6.08 (d, *J*=6.8 Hz, 1H), 4.68 (s, 1H), 4.06 (dd, *J*=17.6, 4.8 Hz, 1H), 3.87–3.70 (m, 2H), 3.29–3.25 (m, 4H), 2.90 (dd, *J*=17.2, 9.2 Hz, 1H), 0.73 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 174.22, 167.87, 143.80, 142.71, 139.51, 131.10, 129.58, 128.66, 127.09, 125.96, 124.68, 123.75, 123.02, 107.74, 88.68, 81.93, 60.65, 58.81, 52.26, 31.48, 26.52, 13.64; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{21}NO_4+H^+$: 364.1544, found 364.1546.

*4.2.26. l′,5-Dimethyl-2,5-diphenyl-4,5-dihydro-2H-spiro [furan-3,3′-indolin]-2′-one (**3v**).* Yellow grease; IR (KBr): 3051, 3021, 2971, 2910, 1711 (s), 1608 (m), 1487 (m), 1458 (m), 1371 (m), 1342 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.65 (d, *J*=8.0 Hz, 2H), 7.44 (t, *J*=7.6 Hz, 2H), 7.32 (t, *J*=8.0 Hz, 1H), 7.16 (d, *J*=7.2 Hz, 2H), 7.08–7.02 (m, 4H), 6.94 (dt, *J*=7.6, 1.2 Hz, 1H), 6.34 (t, *J*=7.6 Hz, 1H), 6.49 (d, *J*=8.0 Hz, 1H), 5.61 (s, 1H), 3.16 (s, 3H), 3.10 (d, *J*=13.2 Hz, 1H), 2.74 (d, *J*=12.8 Hz, 1H), 1.88 (s. 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.81, 148.12, 136.40, 130.95, 128.50, 128.32, 128.32, 127.70, 127.48, 127.48, 127.44, 126.96, 125.47, 125.47, 125.17, 124.69, 124.69, 122.07, 107.30, 85.95, 83.93, 61.14, 51.18, 31.49, 26.33; ESI-HRMS: *m*/*z* calcd for $C_{25}H_{23}NO_2+H^+$: 370.1802, found 370.1800.

*4.2.27. 1′-Methyl-2-phexyl-2,3a,4,8b-tetrahydrospiro [indeno[1,2-b] furan-3,3′-indolin]-2′-one (**3w**).* Pale yellow solid; mp: 195–196 °C; IR (KBr): 3042, 3028, 2966 (m), 2859, 1715 (s), 1611 (m), 1465 (m), 1377 (m), 1337 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J*=7.2 Hz, 1H), 7.50 (d, *J*=7.6 Hz, 1H), 7.40–7.27 (m, 3H), 7.14 (dt, *J*=8.0, 1.2 Hz, 1H), 7.12–6.98 (m, 6H), 6.59 (d, *J*=8.0 Hz, 1H), 6.13 (d, *J*=6.8 Hz, 1H), 5.09 (s, 1H), 4.37 (dd, *J*=17.6, 4.8 Hz, 1H), 3.45–3.40 (m, 1H), 2.97 (dd, *J*=17.6, 10.0 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.09, 144.37, 141.97, 140.33, 135.51, 131.32, 129.32, 127.81, 127.41, 127.34, 127.34, 127.01, 125.94, 125.94, 124.71, 124.58, 122.35, 118.00, 107.54, 87.67, 84.26, 61.89, 51.86, 31.33, 26.15; ESI-HRMS: *m*/*z* calcd for $C_{25}H_{21}NO_2+H^+$: 368.1645, found 368.1643.

*4.2.28. 1″-Methyl-5′-phenyl-4,5-dihydro-2H-dispiro [cyclopentane-1,2′-furan-3′,3″-indolin]-2″-one (**5a**).* Yellow grease; IR (KBr): 3045, 3031, 2972, 2886, 1710 (s), 1608 (s), 1476 (m), 1459 (m), 1375 (m), 1347 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 2H), 7.30–7.23 (m, 3H), 7.00 (t, *J*=7.2 Hz, 1H), 6.82 (d, *J*=7.6 Hz, 1H), 5.57 (t, *J*=8.0 Hz, 1H), 3.23 (s, 3H), 2.90 (dd, *J*=12.8, 7.2 Hz, 1H), 2.34 (dd, *J*=12.8, 8.4 Hz, 1H), 1.99 (m, 1H), 1.80 (d, *J*=5.2 Hz, 4H), 1.49 (d, *J*=7.2 Hz, 2H), 1.28 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 177.73, 143.44, 142.72, 131.36, 128.37, 128.37, 127.95, 127.13, 125.58, 125.58, 124.97, 122.21, 107.71, 95.38, 77.18, 59.04, 45.19, 36.59, 33.24, 26.25, 23.47, 23.31; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_2+H^+$: 334.1802, found 334.1800.

*4.2.29. 1″-Methyl-5′-phenyl-4,5-dihydro-2H-dispiro [cyclopentane-1,2′-furan-3′,3″-indolin]-2″-one (**6a**).* Yellow grease; IR (KBr): 3048, 3032, 2975, 2891, 1710 (s), 1607 (s), 1474 (m), 1461 (m), 1374 (m), 1348 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (d, *J*=7.6 Hz, 2H), 7.46 (d, *J*=7.6 Hz, 1H), 7.37 (t, *J*=7.2 Hz, 2H), 7.29 (dd, *J*=10.8, 7.6 Hz, 2H), 7.11 (t, *J*=7.6 Hz, 1H), 6.87 (d, *J*=7.6 Hz, 1H), 5.45 (t, *J*=8.4 Hz, 1H), 3.23 (s, 3H), 2.72 (dd, *J*=12.4, 9.6 Hz, 1H), 2.57 (dd, *J*=12.4, 7.2 Hz, 1H), 1.97–1.82 (m, 3H), 1.72 (q, *J*=9.2 Hz, 2H), 1.55 (dd, *J*=8.0, 4.0 Hz, 1H), 1.44–1.18 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.55, 143.11, 142.99, 131.62, 128.35, 128.35, 128.04, 127.26, 125.85, 125.85, 124.73, 122.38, 107.88, 95.83, 78.33, 59.16, 45.31, 34.89, 34.79, 26.38, 23.68, 23.17; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_2+H^+$: 334.1802, found 334.1805.

*4.2.30. 1″,5′-Dimethyl-5′-phenyl-4,5-dihydro-2H-dispiro [cyclopentane-1,2′-furan-3′,3″-indolin]-2″-one (**5b**).* Yellow grease; IR (KBr): 3052, 2965, 2938, 2928, 1712 (s), 1610 (m), 1492 (m), 1462 (m), 1369 (m), 1338 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71 (d, *J*=7.6 Hz, 1H), 7.49 (d, *J*=7.6 Hz, 2H), 7.36–7.29 (m, 3H), 7.23 (t, *J*=7.2 Hz, 1H), 7.10 (t, *J*=6.8 Hz, 1H), 6.86 (d, *J*=7.2 Hz, 1H), 3.32 (d, *J*=13.2 Hz, 1H), 3.21 (s, 3H), 2.57 (d, *J*=13.2 Hz, 1H), 1.74–1.53 (m, 8H), 1.44–0.98 (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.14, 151.34, 143.03, 133.22, 127.91, 127.91, 127.81, 126.27, 125.52, 124.64, 124.64, 122.17, 107.83, 96.90, 83.00, 60.11, 50.24, 35.69, 34.00, 33.28, 26.48, 23.76, 22.65; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{25}NO_2+H^+$: 348.1958, found 348.1961.

*4.2.31. 1″-Methyl-5′,5′-phenyl-4,5-dihydro-2H-dispiro [cyclopentane-1,2′-furan-3′,3″-indolin]-2″-one (**5c**).* Pale yellow solid; mp: 193–194 °C; IR (KBr): 3058, 3028, 2928 (m), 2856, 1712 (s), 1610 (m), 1488 (m), 1452 (m), 1371 (m), 1350 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J*=8.0 Hz, 4H), 7.26 (dd, *J*=15.2, 7.2 Hz, 4H), 7.17–7.11 (m, 3H), 6.75 (dd, *J*=10.8, 7.6 Hz, 3H), 3.63 (d, *J*=12.8 Hz, 1H), 3.19 (s, 3H), 1.87–1.58 (m, 5H), 1.51–1.47 (m, 1H), 1.41–1.36 (m, 1H), 1.04–0.98 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.32, 150.51, 148.71, 142.85, 132.28, 128.14, 128.14, 128.01, 128.01, 127.55, 126.29, 126.19, 125.60, 125.14, 125.14, 124.92, 124.92, 122.08, 107.44, 96.68, 86.04, 59.92, 49.71, 35.46, 33.86, 26.47, 23.74, 22.79; ESI-HRMS: *m*/*z* calcd for $C_{28}H_{27}NO_2+H^+$: 410.2115, found 410.2118.

*4.2.32. 1″-Methyl-4,5-dihydro-2H-dispiro[cyclopentane-1,2′-indeno [1,2-b]furan-3′,3″-indolin]-2″-one (**5d**).* Pale yellow solid; mp: 132–134 °C; IR (KBr): 3051, 3025, 2926 (m), 2859, 1705 (s), 1609 (m), 1468 (m), 1374 (m), 1347 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (d, *J*=7.2 Hz, 1H), 7.47 (d, *J*=7.6 Hz,), 7.32–7.22 (m, 4H), 7.11 (t, *J*=7.2 Hz, 1H), 6.86 (d, *J*=7.6 Hz, 1H), 5.86 (d, *J*=7.6 Hz, 1H), 4.06 (dd, *J*=17.6, 4.8 Hz, 1H), 3.38–3.32 (m, 1H), 3.26–3.23 (m, 3H), 2.90 (dd, *J*=17.6, 10.0 Hz, 1H), 2.01–1.94 (m, 1H), 1.54 (d, *J*=7.2 Hz, 3H), 1.33–1.25 (m, 3H), 1.10–1.07 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 174.89, 143.69, 142.30, 142.25, 133.57, 128.74, 127.79, 126.80, 125.61, 124.65, 124.20, 122.60, 107.58, 96.59, 86.65, 60.65, 51.49, 35.72, 33.25, 31.98, 26.28, 24.47, 22.64; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{23}NO_2+H^+$: 346.1802, found 346.1799.

*4.2.33. 1″-Methyl-5′-phenyl-4,5-dihydro-2H-dispiro [cyclohexane-1,2′-furan-3′,3″-indolin]-2″-one (**5e**).* Yellow grease; IR (KBr): 3055, 3025, 2965, 2934, 1710 (s), 1611 (s), 1491 (m), 1469 (m), 1365 (m), 1342 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, *J*=7.6 Hz, 2H), 7.42–7.32 (m, 3H), 7.28 (q, *J*=6.8 Hz, 2H), 7.09 (t, *J*=7.2 Hz, 1H), 6.85 (d, *J*=8.0 Hz, 1H), 5.41 (t, *J*=8.0 Hz, 1H), 3.20 (s, 3H), 2.70 (dd, *J*=12.8, 8.8 Hz, 1H), 2.58 (dd, *J*=12.8, 7.2 Hz, 1H), 2.05 (d, *J*=13.2 Hz, 1H), 1.86–1.42 (m, 6H), 1.36 (dt, *J*=13.2, 4.0 Hz, 1H), 1.06–0.98 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 177.37, 143.51, 143.02, 130.47, 128.30, 128.30, 128.02, 127.28, 126.21, 126.21, 125.20, 121.98, 107.89, 86.56, 78.20, 61.40, 44.36, 33.16, 32.89, 26.29, 25.33, 22.60, 22.55; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{25}NO_2+H^+$: 348.1958, found 348.1955.

*4.2.34. 1″-Methyl-5′-phenyl-4,5-dihydro-2H-dispiro [cyclohexane-1,2′-furan-3′,3″-indolin]-2″-one (**6e**).* Yellow grease; IR (KBr): 3056, 3025, 2966, 2932, 1711 (s), 1610 (s), 1493 (m), 1465 (m), 1368 (m), 1342 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (d, *J*=7.6 Hz, 2H), 7.37 (t, *J*=7.6 Hz, 2H), 7.29–7.24 (m, 2H), 7.19 (d, *J*=7.2 Hz, 1H), 6.99 (t, *J*=7.2 Hz, 1H), 6.81 (d, *J*=7.6 Hz, 1H), 5.72 (t, *J*=7.6 Hz, 1H), 3.21 (s, 3H), 2.86 (dd, *J*=12.8, 7.2 Hz, 1H), 2.40 (dd, *J*=12.8, 9.2 Hz, 1H), 2.12 (d, *J*=13.2 Hz, 1H), 1.85–1.01 (m, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 178.11, 143.82, 143.58, 129.67, 128.33, 128.33, 128.07, 127.00, 125.51, 125.51, 125.47, 121.88, 107.72, 85.83, 77.53, 61.63, 44.14, 35.37, 31.74, 26.13, 25.38, 22.67, 22.61; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{25}NO_2+H^+$: 348.1958, found 348.1956.

*4.2.35. 1″,5′-Dimethyl-5′-phenyl-4,5-dihydro-2H-dispiro [cyclohexane-1,2′-furan-3′,3″-indolin]-2″-one (**5f**).* Yellow grease; IR (KBr): 3049, 2974, 2935, 1709 (s), 1609 (m), 1498 (m), 1469 (m), 1371 (m), 1337 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (dd, *J*=7.2, 3.6 Hz, 3H), 7.36–7.20 (m, 4H), 7.08 (t, *J*=7.6 Hz, 1H), 6.81 (d, *J*=8.0 Hz, 1H), 3.28 (d, *J*=13.2 Hz, 1H), 3.14 (s, 3H), 2.59 (d, *J*=13.2 Hz, 1H), 1.76–1.62 (m, 7H), 1.46 (d, *J*=13.2 Hz, 1H), 1.34–1.30 (m, 2H), 1.78 (dt, *J*=13.2, 4.0 Hz, 1H), 1.03–0.94 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 177.09, 150.95, 143.58, 130.95, 127.91, 127.70, 127.70, 126.07, 125.99, 124.74, 124.74, 121.70, 107.81, 87.17, 83.07, 62.50, 48.91, 34.84, 34.79, 32.43, 26.31, 25.40, 23.02, 22.38; ESI-HRMS: *m*/*z* calcd for $C_{24}H_{27}NO_2+H^+$: 362.2115, found 362.2117.

4.2.36. 1″-Methyl-5′,5′-phenyl-4,5-dihydro-2H-dispiro [cyclohexane-1,2′-furan-3′,3″-indolin]-2″-one (**5g**). Pale yellow solid; mp: 188–190 °C; IR (KBr): 3057, 3024, 2930 (m), 2856, 1712 (s), 1609 (m), 1490 (m), 1448 (m), 1371 (m), 1350 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, J=8.4 Hz, 4H), 7.26 (q, J=8.0 Hz, 4H), 7.16–7.09 (m, 3H), 6.73 (t, J=8.4 Hz, 2H), 6.65 (d, J=7.2 Hz, 1H), 3.70 (d, J=13.2 Hz, 1H), 3.21 (d, J=13.2 Hz, 1H), 3.15 (s, 3H), 1.92 (dd, J=13.6, 2.0 Hz, 1H), 1.85–1.69 (m, 2H), 1.61 (d, J=0.4 Hz, 1H), 1.54 (dd, J=13.2, 2.4 Hz, 1H), 1.44–1.38 (m, 2H), 1.32–1.25 (m, 2H), 1.05 (td, J=12.8, 3.6 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 176.85, 150.17, 149.33, 143.10, 130.87, 128.08, 128.08, 127.85, 127.85, 127.59, 126.22, 126.13, 126.09, 125.10, 125.10, 125.00, 125.00, 121.72, 107.50, 87.34, 86.15, 62.33, 48.64, 34.02, 33.02, 26.41, 25.35, 23.22, 22.38; ESI-HRMS: m/z calcd for $C_{29}H_{29}NO_2+H^+$: 424.2271, found 424.2274.

4.2.37. 1″-Methyl-4,5-dihydro-2H-dispiro[cyclohexane-1,2′-indeno [1,2-b]furan-3′,3″-indolin]-2″-one (**5h**). Pale yellow solid; mp: 152–154 °C; IR (KBr): 3052, 3027, 2931 (m), 2901, 1708 (s), 1610 (m), 1465 (m), 1367 (m), 1342 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, J=8.4 Hz, 1H), 7.38 (d, J=7.2 Hz, 1H), 7.32–7.26 (m, 3H), 7.17 (t, J=4.0 Hz, 1H), 7.09 (t, J=7.6 Hz, 1H), 6.82 (d, J=7.6 Hz, 1H), 5.81 (d, J=8.0 Hz, 1H), 3.57–3.51 (m, 1H), 3.45 (dd, J=17.6, 3.6 Hz, 1H), 3.17 (s, 3H), 2.94 (dd, J=17.6, 10.4 Hz, 1H), 1.84 (dd, J=13.2, 2.4 Hz, 1H), 1.72–1.44 (m, 6H), 1.28 (dd, J=16.0 Hz, 1H), 1.15–1.07 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 175.40, 143.52, 143.43, 142.31, 131.00, 128.58, 127.94, 126.80, 125.49, 124.79, 124.49, 122.04, 107.62, 88.21, 85.80, 64.48, 50.67, 33.15, 32.42, 32.03, 26.07, 25.48, 22.47, 22.14; ESI-HRMS: m/z calcd for $C_{24}H_{25}NO_2+H^+$: 360.1958, found 360.1961.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.12.018. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. (a) Griesbeck, A. G.; Hoffmann, N.; Warzecha, K.-D. *Acc. Chem. Res.* **2007**, *40*, 128–140; (b) Fagnoni, M.; Dondi, D.; Ravelli, D.; Albini, A. *Chem. Rev.* **2007**, *107*, 2725–2756; (c) Santamaria, J. *Pure Appl. Chem.* **1995**, *67*, 141–149; (d) Miranda, M. A.; Garcia, H. *Chem. Rev.* **1994**, *94*, 1063–1089; (e) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825–845; (f) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449.
2. (a) Claweon, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 153–157; (b) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, P.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229–2235; (c) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 134–135; (d) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2986–2990.
3. (a) Mueller, F.; Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 206–221; (b) Maer, F.; Karwe, A.; Mattav, J. *J. Org. Chem.* **1992**, *57*, 6080–6082; (c) Miiller, F.; Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1336–1337.
4. (a) Cair, V.; Laurent, A.; Laurent, E.; Tardivel, R.; Cebulska, Z.; Bartnik, R. *Nouv. J. Chim.* **1987**, *11*, 351–357; (b) Schaap, A. P.; Siddiqui, S.; Praead, G.; Rahman, A. F. M.; Oliver, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6087–6088; (c) Schaap, A. P.; Prasad, G.; Siddiqui, S. *Tetrahedron Lett.* **1984**, *25*, 3035–3038.
5. (a) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H.; Otsuji, Y.; Yasuda, M.; Hashiguchi, M.; Shima, K. *Tetrahedron Lett.* **2001**, *42*, 3363–3366; (b) Dinnocenzo, J. P.; Todd, M. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462–2464.
6. Pan, J.; Zhang, W.; Zhang, J.; Lu, S. *Tetrahedron Lett.* **2007**, *48*, 2781–2785.
7. (a) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748–8758; (b) Alluri, S.; Feng, H.; Livings, M.; Samp, L.; Biswas, D.; Lam, T. W.; Lobkovsky, E.; Ganguly, A. K. *Tetrahedron Lett.* **2011**, *52*, 3945–3948; (c) Pedras, M.; Soledade, C.; Hossain, M. *Org. Biomol. Chem.* **2006**, *4*, 2581–2590; (d) Bignan, G. C.; Battista, K.; Connolly, P. J.; Orsini, M. J.; Liu, J.; Middleton, S. A.; Reitz, A. B. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5022–5026; (e) Kyei, A. S.; Tchabanenko, K.; Baldwin, J. E.; Adlington, R. M. *Tetrahedron Lett.* **2004**, *45*, 8931–8934; (f) Efange, S. M. N.; Kamath, A. P.; Khare, A. B.; Kung, M.-P.; Mach, R. H.; Parsons, S. M. *J. Med. Chem.* **1997**, *40*, 3905–3914; (g) Cui, C.-B.; Kakeya, H.; Okada, G.; Onose, R.; Osada, H. *J. Antibiot.* **1996**, *49*, 527–533; (h) Smallheer, J. M.; Otto, M. J.; Amaral-Ly, C. A.; Earl, R. A.; Myers, M. J.; Pennev, P.; Montefiori, D. C.; Wuonola, M. A. *Antiviral Chem. Chemother.* **1993**, *4*, 27–39.
8. (a) Marti, C.; Carreira, E. M. *Eur. J. Org. Chem.* **2003**, *12*, 2209–2219; (b) White, J. D.; Li, Y.; Ihle, D. C. *J. Org. Chem.* **2010**, *75*, 3569–3577; (c) Thomson, J. E.; Kyle, A. F.; Ling, K. B.; Smith, S. R.; Slawin, A. M. Z.; Smith, A. D. *Tetrahedron* **2010**, *66*, 3801–3813; (d) Allous, I.; Comesse, S.; Berkes, D.; Alkyat, A.; Daich, A. *Tetrahedron Lett.* **2009**, *50*, 4411–4415; (e) Iwasaki, H.; Eguchi, T.; Tsutsui, N.; Ohno, H.; Tanaka, T. *J. Org. Chem.* **2008**, *73*, 7145–7152.
9. (a) Grubb, G. S.; Zhi, L.; Jones, T. K.; Tegley, C. M.; Fensome, A.; Miller, L. L.; Ullrich, J. W.; Bender, R. H. W.; Zhang, P.; Wrobel, J. E.; Edwards, J. P. PCT Int. Appl. Patent 2,000,066,167, 2000. (b) Demerson, C. A.; Humber, L. G. U.S. Patent 4,226,860 A, 1980. (c) Chafeev, M.; Chowdhury, S.; Fraser, R.; Fu, J.; Kamboj, R.; Hou, D.; Liu, S.; Bagherzadeh, M. S.; Sviridov, S.; Sun, S. i; Sun, J. u; Chakka, N.; Hsieh, T.; Raina, V. PCT Int. Appl. Patent 2,006,110,917, 2006.
10. (a) Alcaide, B.; Almendros, P.; Rodríguez-Acebes, R. *J. Org. Chem.* **2006**, *71*, 2346–2351; (b) Alcaide, B.; Almendros, P.; Rodriguez-Acebes, R. *Chem.—Eur. J.* **2005**, *11*, 5708–5712; (c) Ganguly, A. K.; Wang, C. H.; Chan, T. M.; Ing, Y. H.; Buevich, A. V. *Tetrahedron Lett.* **2004**, *45*, 883–886; (d) López-Alvarado, P.; Steinhoff, J.; Miranda, S.; Avendaño, C.; Menéndez, J. C. *Tetrahedron* **2009**, *65*, 1660–1672; (e) Tratrat, C.; Giorgi-Renault, S.; Husson, H.-P. *J. Org. Chem.* **2000**, *65*, 6773–6776.
11. X-ray data for compound **3q**: $C_{21}H_{20}BrNO_2$, Mr=398.29, monoclinic, space group $P2(1)/c$, a=10.532(3) Å, b=8.343(3) Å, c=20.446(6) Å, β=100.037(3)°, V=1769.0(9) $Å^3$. Colorless block, D_c=1.495 g cm^{-3}, T=296(2) K, Z=4, μ(Mo Kα)=0.71073 mm^{-1}, $2\theta_{max}$=51.0°, 3271 reflections measured, 2213 unique, (R_{int}=0.0657), which were used in all calculations. The final $wR(F^2)$ was 0.0788 (for all data), R_1=0.0905. CCDC 842521.
12. (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271; (b) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93–98.
13. (a) Martiny, M.; Steckhan, E.; Esch, T. *Chem. Ber.* **1993**, *126*, 1671–1682; (b) Mattay, J.; Vondenhof, M.; Dening, R. *Chem. Ber.* **1989**, *122*, 951–958; (c) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677–678.
14. (a) Anthony, W. C. *J. Org. Chem.* **1966**, *31*, 77–81; (b) Baiocchi, L.; Giannangeli, M. *J. Heterocycl. Chem.* **1988**, *25*, 1905–1909.