DOI: 10.1002/ejoc.201201020

A Comparison of the Photosensitized Rearrangement and the Lewis-Acid-Catalyzed Rearrangement of Spirooxindole Epoxides

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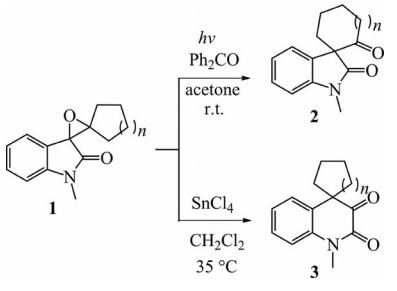
Keywords: Rearrangement / Photochemistry / Regioselectivity / Epoxides / Lewis acids / Nitrogen heterocycles

Spirooxindole epoxides undergo smooth rearrangement either under photosensitization conditions or under Lewis acid catalysis to give different products. The photosensitized rearrangement of spirooxindole epoxides leads to 3-acyl-2-indolones, such as spiro[cycloalkane-1,3′-indolin]-2,2′-diones, by cleavage of the C_α–O bond followed by alkyl migration. The $SnCl_4$-catalyzed rearrangement of spirooxindole epoxides gives 4,4-dialkylquinolin-2,3-diones, such as spiro[cycloalkane-1,4′-quinolin]-2′,3′-diones, by cleavage of the C_β–O bond followed by aryl migration.

Introduction

Epoxides are one of the most important and versatile precursors in organic synthesis, due to their ready availability and the ease of their transformation into a wide variety of functional groups.[1] The rearrangement of epoxides to carbonyl compounds is a useful synthetic transformation, and several procedures have been developed for this purpose, for example, the Lewis-acid-catalyzed rearrangement,[2] the Brønsted-acid-catalyzed rearrangement,[3] the photochemical rearrangement,[4] the electrochemical rearrangement,[5] and so on. Of these methods, the Lewis-acid-catalyzed rearrangement is the most popular, and it has been studied extensively. Many Lewis acid catalysts have been identified that catalyze the rearrangement of epoxides with varying degrees of success in terms of regioselectivity and stereoselectivity, and these include $BF_3{\cdot}Et_2O$,[2a] $InCl_3$,[2b] $Bi(OTf)_3$,[2c] $Cu(BF_4)_2$,[2d] $Er(OTf)_3$,[2e] $CrTPP(OTf)_2$ (TPP = tetraphenylporphyrin),[2f] $SnCl_4$,[2g] Et_2AlCl,[2h] $LiClO_4$,[2i] and $Au(PMe_3)Cl$.[2j] Epoxides bearing various substituents have been subjected to the rearrangement, including, for example, aryl-substituted epoxides,[6] 2,3-epoxy alcohols,[7] epoxy alkenes,[8] epoxy alkynes,[9] α,β-epoxy ketones,[10] steroidal epoxides,[11] and terpene epoxides.[12] Despite the fact that so many epoxides have been examined in the epoxide–ketone rearrangement, we found that reports about the rearrangement of α,β-epoxy amides were rare,[13] and we found no report in the literature about the rearrangement of spirooxindole epoxides in which both the aryl and acyl groups were attached to the α-carbon of an epoxide. Recently, we reported the synthesis of spiro[oxindole–furan] by the [3+2] reaction of spiro epoxides derived from oxindoles under irradiation.[14] Continuing from the synthesis of the spirooxindole, in this paper, we report the rearrangement of spirooxindole epoxides under both photosensitization and Lewis acid catalysis. It was found the regioselectivity of the two rearrangements was different. Under photosensitization conditions, 3-acyl-2-indolones, such as spiro[cycloalkane-1,3′-indolin]-2,2′-diones (**2**), were obtained as the sole products, arising from the cleavage of C_α–O bond and subsequent migration of an alkyl group; otherwise, 4,4-dialkylquinolin-2,3-diones, such as spiro[cycloalkane-1,4′-quinolin]-2′,3′-diones (**3**), were obtained as the sole products, arising from the cleavage of C_β–O bond and subsequent migration of an aryl group under $SnCl_4$ catalysis (Scheme 1).



Scheme 1. Photosensitized and $SnCl_4$-catalyzed rearrangement of spirooxindole epoxides.

Spirooxindoles are important structural motifs in biologically relevant compounds, including natural products and pharmaceuticals, and have shown an extensive range of bio-

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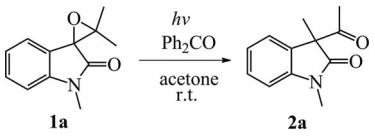
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201020.

logical effects, including antibacterial, antifungal, anticonvulsant, antiviral, and antiproliferative activities.[15] The spiroquinolinone scaffold is also found in alkaloids, and is important as a characteristic building block for a series of significant biologically active compounds.[16] Despite the large number of published synthetic routes to spirooxindole and spiroquinolinone derivatives, there are only a few papers that describe the synthesis of spiro[cycloalkane-1,3′-indoline] (**2**) or spiro[cycloalkane-1,4′-quinoline] (**3**). Generally, two routes have been established to construct the rings spiro-annulated with cycloalkanes at C-3 of 2-indolones or at C-4 of 2-quinolinones. One is based on the cyclization of spirocycloalkanes from functionalized 2-indolones or 2-quinolinones,[17a,17b] for example, the intramolecular Ullmann coupling and Claisen rearrangement 5-(2-iodioindol-3-yl)penten-3-ols to give spiro[cyclohexene-1,3′-indol]-2′-ones.[17a] The other route is to construct oxindoles or quinolinones from functionalized cycloalkanes,[17c,17g] for example, the aza-oxa [3,3]-sigmatropic rearrangement of *N*-[(cyclohexylcarbonyl)oxy]-*N*-phenylcarbamic acid methyl ester and subsequent cyclocondensation to give spiro[cyclohexane-1,3′-indol]-2′-one.[17c]

In this paper, we supply a new synthetic route to spiro[cycloalkane-1,3′-indol]-2,2′-diones by constructing spirocycloalkyl units from spirooxindole epoxides, and to spiro[cycloalkane-1,4′-quinolin]-2′,3′-diones by constructing spiroquinolinyl units from spirocycloalkane epoxides.

Results and Discussion

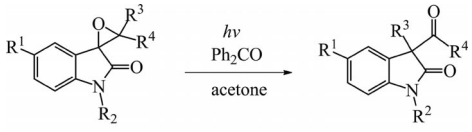
First, spirooxindole epoxide **1a** was used as a model substrate to explore the photosensitized rearrangement. After the simple optimization of the reaction conditions in terms of the sensitizers (acetone, benzophenone, chloranil, 9,10-dicyanoanthracene, 2,4,6-triphenylpyrylium tetrafluoroborate), and solvents (acetonitrile, dichloromethane, acetone), the optimum yield of product **2a** was obtained using benzophenone as the photosensitizer in acetone. By irradiation of a deaerated acetone solution of epoxide **1a** and a catalytic amount of benzophenone (5 mol-%) at $\lambda \geq 350$ nm at room temperature for 5 h, 3-acetyl-3-methyl-2-indolone (**2a**) was obtained in 93% yield (98% conversion). It could be speculated that both benzophenone and acetone are effective for the sensitization of the rearrangement of **1a**, because **2a** was also formed in 87% yield (82% conversion) in acetone alone after irradiation for 48 h, but the addition of benzophenone greatly promoted the photoreaction of **1a**. (Scheme 2).



Scheme 2. Benzophenone-sensitized rearrangement of **1a**.

The reaction of other differently substituted spirooxindole epoxides **1b**–**h** was examined under these conditions, and the results are listed in Table 1. All of the spirooxindole epoxides gave analogous 3-acyl-2-indolones products (i.e., **2a**–**e**), except for **1f**–**h**. The structures of the products were fully identified by ^{1}H and ^{13}C NMR spectroscopy, MS, and HRMS.

Table 1. Benzophenone-sensitized rearrangement reactions of spiro[indoline-3,2′-oxiran]-2-ones **1a**–**h**.



1a–h **2a–h**

Entry	Epoxide	R^1	R^2	R^3	R^4	*t* [h]	Conv.[a] [%]	Product	Yield[b] [%]
1	**1a**	H	CH_3	CH_3	CH_3	5	ca. 100	**2a**	93
2	**1b**	H	H	CH_3	CH_3	5	ca. 100	**2b**	90
3	**1c**	H	Ph	CH_3	CH_3	5	ca. 100	**2c**	96
5	**1d**	Br	CH_3	CH_3	CH_3	5	95	**2d**	94
6	**1e**	NO_2	CH_3	CH_3	CH_3	20	98	**2e**	91
7	**1f**	CH_3	CH_3	CH_3	CH_3	5	ca. 100	–	–
8	**1g**	H	CH_3	H	Ph	20	0	–	–

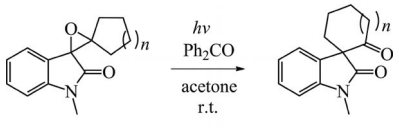
[a] Conversion was calculated on the basis of substrate **1a**–**h**. [b] Yield of isolated products was based on consumed substrates **1a**–**e**.

From a comparison of the structures of the epoxide starting materials (i.e., **1a**–**e**) and the products (i.e., **2a**–**e**), it could be seen that the benzophenone-sensitized ring-opening of **1a**–**e** occurs by a selective C_α–O bond cleavage followed by an alkyl group migration from C-β to C-α. This kind of rearrangement is similar to that of α-aryl epoxides, which is known to proceed under either photosensitization[4d] or Lewis acid catalysis.[2b,2c,6] The photoreaction of **1a**–**e** gave the rearrangement products (i.e., **2a**–**e**) in excellent yields, but for **1f**, none of the expected product was isolated because of the photoreaction of the 5-methyloxindole unit in **1f** with the solvent acetone. No reaction was detected with **1g**–**h**, even after prolonged irradiation. It seems that the migration was very difficult for a hydrogen atom or a phenyl group (probably due to steric hindrance) after the C_α–O bond cleavage of the epoxide ring.

Next, we turned our attention to the synthesis of two spiro[cycloalkane-1,3′-indol]-2,2′-diones by this benzopnenone-sensitized rearrangement of bispiro epoxides **1i**–**j**. Under the same conditions, the photoreactions of **1i**–**j** gave spiro[cycloalkane-1,3′-indol]-2,2′-diones **2f**–**g** in excellent yields (Table 2).

In order to compare the regioselectivities of the spirooxindole epoxide rearrangements under different reaction conditions, the reaction of **1a** was also carried out using Lewis acids as catalysts. After testing different catalysts, such as $BF_3{\cdot}Et_2O$, $SnCl_4$, $TiCl_4$, $ZnCl_2$, and TMSOTf, the best result was obtained in a reaction catalyzed by $SnCl_4$. In this case, only one product, quinoline-2,3-dione **3a**, which was different from **2a** produced under photosensitization conditions, was formed in excellent yield (96%) in chloroform at 35 °C (Scheme 3).

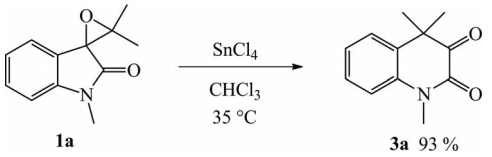
Table 2. Synthesis of spiro[cycloalkane-1,3′-indol]-2,2′-diones by benzophenone-sensitized rearrangement of **1i**–**j**.



1i, n = 1 **1j**, n = 2 **2f**, n = 1 **2g**, n = 2

Entry	Epoxide	n	Time [h]	Conv.[a] [%]	Product	Yield[b] [%]
1	**1i**	1	5	ca. 100	**2f**	90
2	**1j**	2	5	ca. 100	**2g**	93

[a] Conversion was calculated on the basis of substrates **1i**–**j**. [b] Yield of isolated products was based on consumed substrates **1i**–**j**.



1a **3a** 93 %

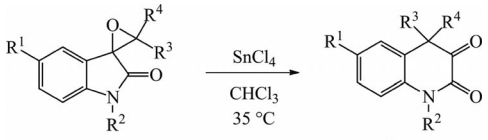
Scheme 3. $SnCl_4$-catalyzed rearrangement of **1a**.

Other spirooxindole epoxides **1b**–**h** were also examined under the optimized conditions (Table 3). It can be seen from the results in Table 3 that all the spirooxindole epoxides gave the rearrangement products (i.e., **3a**–**e**) in excellent yields, except for **1e** and **1g**–**h**. For epoxides **1a**–**d**,**f**, doubly methyl-substituted at C-β, the rearrangement products were derived from selective C_β–O bond cleavage and subsequent aryl group migration from C-α to C-β. This kind of rearrangement has not been reported before for α,β-epoxy ketones or α,β-epoxy lactams, because the Lewis-acid-catalyzed rearrangement of α,β-epoxy ketones[6] and α,β-epoxy lactams[13a] generally gave the 1,3-dicarbonyl compounds by C_β–O bond cleavage and subsequent acyl group shift. Substituent effects are also apparent from the results in Table 3. Electron-withdrawing groups, such as bromide or nitro groups retarded the rearrangement. Indeed, with a nitro group, no reaction could be detected, even after prolonged stirring. On the other hand, different products were obtained from the reactions of **1g** and **1h**, as shown in Schemes 4 and 5.

Obviously, both products **4** and **5** are derived from the $SnCl_4$-catalyzed C_α–O bond cleavage of **1g** and **1h**, which is different from the C_β–O bond cleavage that occurred with **1a**–**d** and **1f** under the same condition. A subsequent shift of the phenyl group from C-β to C-α and decarbonylation gave product **4**. For **1h**, trapping of the carbocation with a chloride ion before the migration of a hydrogen atom could take place led to product **5**. This kind of ring-opening was also observed in the reaction of ethyl 2,3-epoxy-2,3-diphenylpropionate catalyzed by $SnCl_4$.[18]

Next, another two spiro[cycloalkane-1,4′-quinolin]-2′,3′-diones **3f** and **3g** were synthesized by the $SnCl_4$-catalyzed rearrangement of spirooxindole epoxides **1i** and **1j** (Table 4). The two spiro[cycloalkane-1,4′-quinolin]-2′,3′-diones **3f** and **3g** were obtained in excellent yields after stirring the solutions of **1i** or **1j** and $SnCl_4$ in chloroform for 5 h. The structures of all products were identified by ^1H and ^{13}C NMR spectroscopy, MS, and HRMS, and the structure of **3g** was further confirmed by X-ray crystallography (Figure 1).

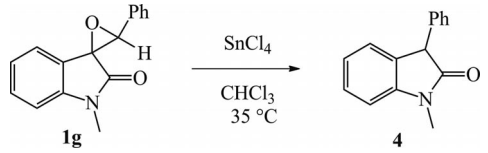
Table 3. $SnCl_4$-catalyzed rearrangement of spiro[indoline-3,2′-oxiran]-2-one **1a**–**h**.



1a–**g** **3a**–**g**

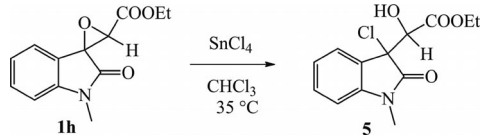
Entry	Epoxide	R^1	R^2	R^3	R^4	t [h]	Conv.[a] [%]	Product	Yield[b] [%]
1	**1a**	H	CH_3	CH_3	CH_3	3	100	**3a**	93
2	**1b**	H	H	CH_3	CH_3	3	100	**3b**	91
3	**1c**	H	Ph	CH_3	CH_3	3	100	**3c**	95
5	**1d**	Br	CH_3	CH_3	CH_3	5	100	**3d**	88
6	**1e**	NO_2	CH_3	CH_3	CH_3	20	ca. 0	–	–
4	**1f**	CH_3	CH_3	CH_3	CH_3	3	100	**3e**	95
8	**1g**	H	CH_3	H	CO_2Et	3	100	**4**	86
9	**1h**	H	CH_3	H	Ph	3	100	**5**	75

[a] Conversion was calculated on the basis of substrate **1a**–**h**. [b] Yield of isolated products was based on consumed substrates **1a**–**d** and **1f**–**h**.



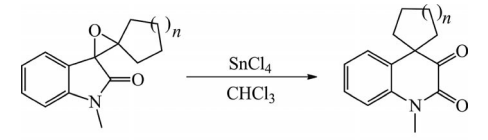
1g **4**

Scheme 4. $SnCl_4$-catalyzed fragmentation of **1g**.



1h **5**

Scheme 5. $SnCl_4$-catalyzed ring-opening of **1h**.



1h n = 1 **1i** n = 2 **3h** **3i**

Table 4. Synthesis of spiro[cycloalkane-1,4′-quinoline]-2′,3′-diones by the $SnCl_4$-catalyzed rearrangement of epoxides **1i** and**1j**.

Entry	Epoxide	n	t [h]	Conversion [%]	Product	Yield [%]
1	**1i**	1	5	100	**3f**	93
2	**1j**	2	5	100	**3g**	91

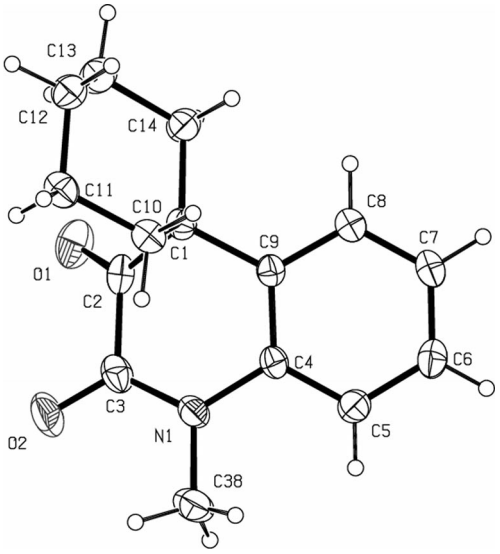


Figure 1. X-ray structure of **3g**.

Conclusions

The rearrangement of spirooxindole epoxides was found to proceed either under photosensitization conditions or under Lewis acid catalysis. However, two kinds of products were produced. 3-Acyloxindoles, such as spiro[cycloalkane-1,3′-indol]-2,2′-diones, were obtained as the sole products in a benzophenone-sensitized rearrangement by a selective C_α–O bond cleavage and subsequent migration of an alkyl group. 2,3-Quinolindiones, such as spiro[cycloalkane-1,4′-quinolin]-2′,3′-diones, were produced in excellent yields in a $SnCl_4$-catalyzed rearrangement by selective C_β–O bond cleavage and subsequent migration of an aryl group.

Experimental Section

General Methods: All reagents were purchased from commercial suppliers and were used without further purification. Flash chromatography was carried out with silica gel (200–300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^1H 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 ppm using TMS as internal standard, and spin–spin coupling constants (J) are given in Hz. High-resolution mass spectra (HRMS) were measured with a Bruker Daltonics APEX-47e spectrometer using the ESI technique. Compounds **1a**–**j** were prepared according to the reported methods.[19]

General Procedure for the Photochemical Reactions: Spiro[indoline-3,2′-oxiran]-2-one (**1a**, 1.0 mmol) and benzophenone (10 mg) were dissolved in anhydrous acetone (50 mL). The solution was deaerated by bubbling Ar through it for 30 min, and then irradiated at $\lambda \geq 350$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature until complete conversion of the starting material was observed. Progress of the reaction was monitored by TLC at regular intervals. The solvent was removed under reduced pressure, and then the residue was separated by flash chromatography on silica gel, eluting with hexane and acetone 16:1 (v/v), to give product **2a** (93%). Further purification was performed by recrystallization from ethanol.

General Procedure for $SnCl_4$-Catalyzed Reactions: $SnCl_4$ (52 mg, 0.2 mmol) was added slowly to a solution of spiro[indoline-3,2′-oxiran]-2-one (**1a**, 1.0 mmol) in anhydrous chloroform (25 mL), whilst stirring. The solution was heated to 35 °C and stirred for 3 h until the reaction was complete. The reaction was then quenched by the addition of saturated aqueous $NaHCO_3$ and crushed ice. The aqueous phase was extracted with chloroform (30 × 2 mL). The combined organic extracts were washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel, eluting with hexane and acetone 14:1 (v/v), to give product **3a** (93%), which was further purified by recrystallization from ethanol.

3-Acetyl-3-methylindolin-2-one (2a): Yellow solid; m.p. 95–97 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.77 (m, 1 H), 7.30 (t, J = 8.0 Hz, 1 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.07 (dd, J = 14.4, 7.6 Hz, 2 H), 2.05 (s, 3 H), 1.62 (s, 3 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.8, 178.8, 141.1, 130.1, 129.2, 123.6, 123.2, 110.6, 62.7, 25.9, 18.7 ppm. EI-MS: m/z (%) = 189 (4), 148 (12), 147 (100), 146 (64), 128 (31), 117 (8), 91 (7), 43 (12). HRMS (ESI): calcd. for $C_{11}H_{12}NO_2$ $[M + H]^+$ 190.0797; found 190.0795.

3-Acetyl-1,3-dimethylindolin-2-one (2b): Colorless grease. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (td, J = 8.0, 0.8 Hz, 1 H), 7.15 (d, J = 6.8 Hz, 1 H), 7.09 (t, J = 7.6 Hz, 1 H), 6.94 (d, J = 7.6 Hz, 1 H), 3.31 (s, 3 H), 1.96 (s, 3 H), 1.57 (s, 3 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.8, 175.7, 143.6, 129.3, 129.0, 123.4, 123.1, 108.5, 61.9, 26.5, 25.7, 18.8 ppm. EI-MS: m/z (%) = 203 (3), 161 (61), 160 (100), 132 (11), 117 (12), 43 (14). HRMS (ESI): calcd. for $C_{12}H_{14}NO_2$ $[M + H]^+$ 204.0953; found 204.0950.

3-Acetyl-1-phenylindolin-2-one (2c): Yellow solid; m.p. 101–103 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (t, J = 7.6 Hz, 2 H), 7.46–7.43 (m, 3 H), 7.28 (td, J = 7.6, 0.8 Hz, 1 H), 7.22 (d, J = 6.8 Hz, 1 H), 7.12 (t, J = 7.6 Hz, 1 H), 6.90 (d, J = 7.6 Hz, 1 H), 2.10 (s, 3 H), 1.70 (s, 3 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.5, 175.2, 143.6, 134.0, 129.7 (2 C), 129.6, 129.0, 128.4, 126.3 (2 C), 126.2, 123.8, 123.6, 109.9, 62.0, 25.9, 19.1 ppm. EI-MS: m/z (%) = 265 (7), 224 (17), 223 (100), 222 (53), 194 (12), 117 (5), 77 (6), 43 (7). HRMS (ESI): calcd. for $C_{17}H_{16}NO_2$ $[M + H]^+$ 266.1110; found 266.1107.

3-Acetyl-5-bromo-1,3-dimethylindolin-2-one (2d): Pale yellow solid; m.p. 109–111 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, J = 8.0, 2.0 Hz, 1 H), 7.29 (d, J = 1.6 Hz, 1 H), 6.81 (d, J = 8.4 Hz, 1 H), 3.29 (s, 3 H), 2.02 (s, 3 H), 1.58 (s, 3 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.2, 175.2, 142.6, 131.9, 131.2, 126.8, 115.7, 109.9, 61.8, 26.7, 26.0, 19.2 ppm. EI-MS: m/z (%) = 281 (11), 242 (10), 241 (95), 240 (56), 239 (100), 238 (48), 160 (15), 159 (22), 131 (19), 130 (23), 117 (13), 116 (9), 43 (30). HRMS (ESI): calcd. for $C_{12}H_{12}BrNO_2 + H^+$: 282.0058; found 282.0061.

3-Acetyl-1,3-dimethyl-5-nitroindolin-2-one (2e): Yellow grease. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.33 (dd, J = 8.4, 2.0 Hz, 1 H), 8.10 (d, J = 2.0 Hz, 1 H), 7.01 (d, J = 8.8 Hz, 1 H), 3.36 (s, 3 H), 2.12 (s, 3 H), 1.67 (s, 3 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 199.5, 175.7, 148.9, 143.8, 130.0, 126.2, 119.9, 108.1, 61.6, 27.2, 26.6, 19.8 ppm. EI-MS m/z (%): = 248 (10), 207 (11), 206 (100), 189 (10), 160 (23), 159 (17), 130 (13), 117 (20), 77 (6), 43 (18). HRMS (ESI): calcd. for $C_{12}H_{13}N_2O_4$ $[M + H]^+$ 249.0804; found 249.0806.

1′-Methylspiro[cyclohexane-1,3′-indolin]-2,2′-dione (2f): Yellow solid; m.p. 92–94 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, J =

7.2 Hz, 2 H), 7.09 (t, J = 7.6 Hz, 1 H), 6.84 (d, J = 8.0 Hz, 1 H), 3.19 (s, 3 H), 3.09–3.01 (m, 1 H), 2.62–2.56 (m, 1 H), 2.46–2.36 (m, 1 H), 2.27–1.83 (m, 5 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 204.9, 174.1, 143.1, 129.3, 128.5, 124.4, 122.5, 108.2, 63.5, 39.6, 37.1, 26.7, 26.3, 20.2 ppm. EI-MS: *m*/*z* (%) = 229 (37), 201 (18), 200 (18), 174 (12), 173 (100), 160 (25), 158 (11), 130 (17), 117 (11), 77(8). HRMS (ESI): calcd. for $C_{14}H_{16}NO_2$ $[M + H]^+$ 230.1110; found 230.1107.

1′-Methylspiro[cycloheptane-1,3′-indolin]-2,2′-dione (2g): Yellow solid; m.p. 104–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.25 (m, 2 H), 7.07 (t, J = 7.6 Hz, 1 H), 6.84 (d, J = 7.6 Hz, 1 H), 3.19 (s, 3 H), 3.08–3.01 (m, 1 H), 2.75–2.71 (m, 1 H), 2.35–1.78 (m, 8 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 207.4, 175.1, 143.3, 130.6, 128.5, 123.4, 122.6, 108.4, 7.37, 42.2, 34.7, 30.7, 26.6, 26.3, 25.2 ppm. EI-MS: *m*/*z* (%) = 243 (49), 215 (28), 187 (15), 186 (100), 160 (92), 159 (33), 147 (26), 130 (25), 117 (10), 77 (8). HRMS (ESI): calcd. for $C_{15}H_{18}NO_2$ $[M + H]^+$ 244.1266; found 244.1264.

4,4-Dimethylquinoline-2,3-dione (3a): Yellow grease. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.46 (s, 1 H), 7.33 (dd, J = 8, 1.2 Hz, 1 H), 7.30–7.26 (m, 1 H), 7.15 (td, J = 7.6, 1.2 Hz, 1 H), 7.09 (dd, J = 8, 1.2 Hz, 1 H), 1.57 (s, 6 H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ = 196.3, 156.7, 132.8, 130.7, 128.5, 125.9, 124.8, 117.2, 49.1, 24.8 (2C) ppm. EI-MS: *m*/*z* (%) = 190 (8), 189 (64), 161 (29), 146 (100), 133 (12), 132 (25), 128 (36), 118 (17), 117 (14), 91 (15), 77 (8), 65 (8). HRMS (ESI): calcd. for $C_{11}H_{12}NO_2$ $[M + H]^+$ 190.0797; found 190.0795.

1,4,4-Trimethylquinoline-2,3-dione (3b): Pale yellow solid; m.p. 96–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.35 (m, 2 H), 7.18 (t, J = 7.6 Hz, 1 H), 7.10 (d, J = 8 Hz, 1 H), 3.53 (s, 3 H), 1.54 (s, 6 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 195.4, 156.9, 136.5, 130.6, 128.5, 125.5, 124.6, 115.6, 48.2, 30.1, 23.8 (2 C) ppm. EI-MS: *m*/*z* (%) = 203 (44), 175 (27), 161 (10), 160 (100), 132 (28), 130 (9), 117 (18), 115 (6), 77 (8), 44(7). HRMS (ESI): calcd. for $C_{12}H_{14}NO_2$ $[M + H]^+$ 204.0907; found 204.0909.

4,4-Dimethyl-1-phenylquinoline-2,3-dione (3c): Pale yellow solid; m.p. 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (t, J = 7.2 Hz, 2 H), 7.50 (t, J = 7.2 Hz, 1 H), 7.41–7.38 (m, 1 H), 7.31 (d, J = 8.4 Hz, 2 H), 7.16–7.12 (m, 2 H), 6.48–6.46 (m, 1 H), 1.66 (s, 6 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 195.9, 156.6, 137.9, 136.7, 130.4, 130.2 (2 C), 129.0, 128.3 (2 C), 128.2, 125.5, 124.8, 118.2, 48.6, 23.7 (2 C) ppm. EI-MS: *m*/*z* (%) = 265 (50), 238 (28), 237 (100), 223 (33), 222 (87), 209 (22), 194 (76), 181 (31), 180 (27), 149 (39), 132 (30), 118 (28), 117 (20), 77 (22), 57 (22), 43 (30). HRMS (ESI): calcd. for $C_{17}H_{16}NO_2$ $[M + H]^+$ 266.1110; found 266.1111.

6-Bromo-1,4,4-trimethylquinoline-2,3-dione (3d): Pale yellow solid; m.p. 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 2.4 Hz, 1 H), 7.46 (s, 1 H), 6.97 (d, J = 8.4 Hz, 1 H), 3.50 (s, 3 H), 1.53 (s, 6 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 194.3, 156.5, 135.8, 132.8, 131.5, 128.7, 117.6, 117.2, 48.4, 30.3, 23.8 (2 C) ppm. EI-MS: *m*/*z* (%) = 283(47), 281 (46), 255 (55), 253 (58), 240 (100), 159 (57), 131 (87), 130 (57), 115 (14), 57 (13), 44 (15). HRMS (ESI): calcd. for $C_{12}H_{13}BrNO_2$ $[M + H]^+$ 282.0058; found 282.0061.

1,4,4,6-Tetramethylquinoline-2,3-dione (3e): Yellow solid; m.p. 95–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, J = 4.8 Hz, 2 H), 7.00–6.97 (m, 1 H), 3.50 (s, 3 H), 2.36 (s, 3 H), 1.52 (s, 6 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 159.7, 156.8, 134.3, 134.1, 130.4, 128.9, 126.2, 115.5, 48.2, 30.1, 23.9 (2 C), 20.8 ppm. EI-MS: *m*/*z* (%) = 217 (42), 189 (31), 175 (12), 174 (100), 159 (11), 146 (21), 131 (16), 130 (11), 77 (6), 72 (8). HRMS (ESI): calcd. for $C_{13}H_{16}NO_2$ $[M + H]^+$ 218.1110; found 218.1007.

1′-Methylspiro[cyclopentane-1,4′-quinolin]-2′,3′-dione (3f): Gray solid; m.p. 95–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, J = 7.6 Hz, 2 H), 7.10 (t, J = 7.6 Hz, 1 H), 6.84 (d, J = 7.2 Hz, 1 H), 3.20 (s, 3 H), 3.09–1.84 (m, 8 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 205.0, 174.1, 143.1, 129.3, 128.5, 124.4, 122.5, 108.3, 63.5, 39.6, 37.1, 26.8, 26.3, 20.2 ppm. EI-MS: *m*/*z* (%) = 229 (37), 201 (19), 200 (18), 173 (100), 160 (25), 130 (16), 117 (8), 77 (7). HRMS (ESI): calcd. for $C_{14}H_{16}NO_2$ $[M + H]^+$ 230.1110; found 230.1111.

1′-Methylspiro[cyclohexane-1,4′(1′*H*)-quinolin]-2′,3′-dione (3g): Yellow solid; m.p. 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, J = 8.4 Hz, 2 H), 7.16 (t, J = 7.6 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1 H), 3.47 (s, 3 H), 3.30 (d, J = 13.2 Hz, 2 H), 1.82–1.63 (m, 7 H), 1.32–1.23 (m, 1 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 197.7, 158.8, 137.3, 130.8, 128.4, 125.0, 124.6, 115.8, 52.1, 32.0 (2 C), 29.6, 25.5, 22.8 (2 C) ppm. EI-MS: *m*/*z* (%) = 243 (30), 215 (14), 189 (8), 161 (12), 160 (100), 159 (17), 147 (16), 130 (12), 77 (7). HRMS (ESI): calcd. for $C_{15}H_{18}NO_2$ $[M + H]^+$ 244.1266; found 244.1269.

Crystal Data for 3g: Recrystallization from ethanol, $C_{15}H_{17}NO_2$, M_r = 243.30, triclinic, a = 9.071(13) Å, b = 11.312(16) Å, c = 12.524(18) Å, β = 91.457(14)°, V = 1268(3) Å^3, yellow block, D_c = 1.275 g cm^{-3}, T = 296(2) K, space group: $P2_1/c$, Z = 4, μ (Mo-K_α) = 0.71073 mm^{-1}, $2\theta_{max}$ = 51.00, 4630 reflection collected, 2778 unique (R_{init} = 0.0657) which was used in all calculations. Final $wR(F^2)$ = 0.1636 (all data). CCDC file No. 894241.

1-Methyl-3-phenylindolin-2-one (4): Pale yellow solid; m.p. 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.25 (m, 4 H), 7.21–7.15 (m, 3 H), 7.06 (t, J = 7.6 Hz, 1 H), 6.90 (d, J = 7.6 Hz, 1 H), 4.60 (s, 1 H), 3.25 (s, 3 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 175.9, 144.4, 136.6, 128.8 (2 C), 128.7, 128.4 (2 C), 127.6, 125.0, 122.7, 108.1, 52.0, 26.4 ppm. EI-MS: *m*/*z* (%) = 224 (16), 223 (100), 195 (14), 194 (89), 165 (12), 146 (12), 118 (10), 97 (7). HRMS (ESI): calcd. for $C_{15}H_{14}NO$ $[M + H]^+$ 224.1004; found 224.1002.

Ethyl 2-Hydroxy-2-(3-chloro-1-methyl-2-oxoindolin-3-yl)acetate (5): Pale yellow solid; m.p. 101–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (td, J = 7.5, 1.2 Hz, 1 H), 7.31 (d, J = 7.5 Hz, 1 H), 7.11 (t, J = 7.8 Hz, 1 H), 6.87 (d, J = 7.8 Hz, 1 H), 4.74 (d, J = 9.9 Hz, 1 H), 4.24–4.15 (m, 2 H), 3.72 (d, J = 9.3 Hz, 1 H), 3.25 (s, 3 H), 1.19 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 172.4, 170.2, 143.7, 131.0, 125.2, 125.1, 123.3, 108.8, 74.7, 62.5, 62.2, 26.7, 13.9 ppm. EI-MS: *m*/*z* (%) = 283 (10), 183 (33), 181 (100), 180 (50), 146 (43), 118 (15), 117 (10), 91 (12), 44 (7). HRMS (ESI): calcd. for $C_{13}H_{15}ClNO_4$ $[M + H]^+$ 284.0618; found 284.0620.

Supporting Information (see footnote on the first page of this article): Analytical data of all substrates and copies of the ^{1}H and ^{13}C NMR spectra for all products.

Acknowledgments

We are grateful to the National Nature Science Foundation of China (NSFC) (grant numbers 20872056 and J1103307) for financial support.

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Received: July 30, 2012
Published Online: October 5, 2012

