JOC The Journal of Organic Chemistry

Article

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Visible Light Mediated Cyclization of Tertiary Anilines with Maleimides Using Nickel(II) Oxide Surface-Modified Titanium Dioxide Catalyst

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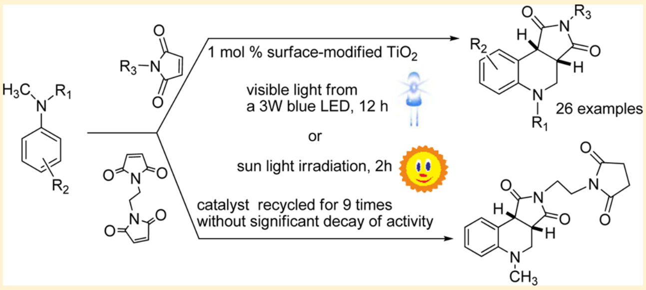
S *Supporting Information*



ABSTRACT: Surface-modified titanium dioxides by highly dispersed NiO particles have an extended absorption in the visible light region and a reduced hole−electron pair recombination than unmodified TiO_2. They have now been successfully applied as highly active heterogeneous photocatalysts in the visible light mediated direct cyclization of tertiary anilines with maleimides to give tetrahydroquinoline products in moderate to high yields at ambient temperature. In contrast with unmodified titanium dioxide catalysts that are conventionally used in a stoichiometric amount in combination with UVA light, only a catalytic amount (1 mol %) of the surface-modified TiO_2 catalyst is needed along with visible light to efficiently catalyze the reaction. Compared with transition-metal complexes such as $Ru(bpy)_3Cl_2$ or $Ir(ppy)_2(dtbbpy)PF_6$, advantages of these surface-modified titanium dioxides as photocatalyst include high catalytic activity, low cost, ease of recovering, and being able to be used for at least nine times without significant decay of catalytic activity.

■ INTRODUCTION

Visible light mediated photoredox catalysis is an effective and versatile method for inert C−H bond activation and functionalization.[1] Especially, the functionalization of the sp^3 C−H bond adjacent to a tertiary nitrogen atom has attracted increasing attention in recent years.[2] The normally used photocatalysts for the visible light mediated photoredox reactions are ruthenium or iridium complexes[1] and organic dyes.[1c,3] However, as homogeneous catalysts, these transition-metal complexes and organic dyes suffer from the drawbacks of high cost, difficult recovery, and an inability to be reused.[3]

Titanium dioxide (TiO_2) as a redox active heterogeneous photocatalyst has gathered much attention because of its easy availability, high photochemical and thermal stability, and nontoxicity. Furthermore, the solid catalyst can be easily recovered by either filtration or centrifugation and may be reused, providing remarkable advantages in view of economy, environmental benignancy, and operational simplicity.[4] Despite the significant advantages of heterogeneous semiconductor photocatalysts over homogeneous catalysts, their use in photocatalyzed organic synthesis in general,[5,6] and in C−H bond activation and C−C and C−heteroatom bond formation in particular,[5,7] is still quite limited.

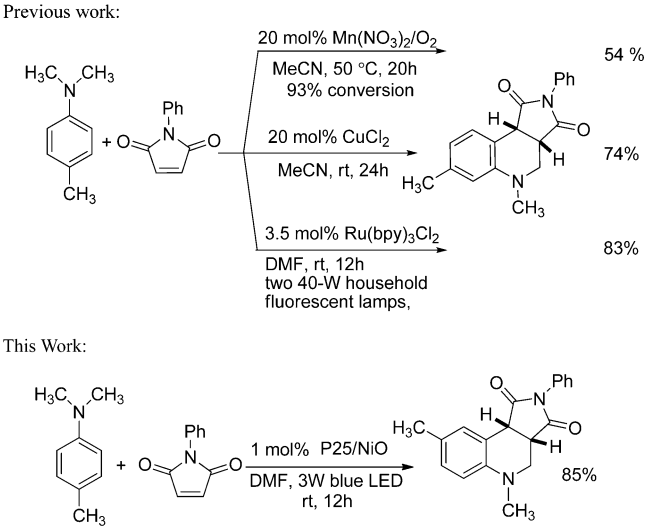
A limiting factor to the application of TiO_2 as a photocatalyst is that it has a band gap of ∼3.2 eV and absorbs chiefly in the UVA region, while UV light constitutes only 4% of total solar irradiation. This is also one of the main reasons why titanium dioxide has not gained wide application in organic synthesis as transition-metal complexes and organic dyes that have their absorption maxima in the visible region of the electromagnetic spectrum. There have been much effort in recent years to find ways to shift the band gap of TiO_2 to make it more efficient for visible light absorption.[8] In this respect, modification of TiO_2 with metal oxide nanoclusters as recently investigated by Libera et al.[9] and Tada et al.[10] has proven to be one of the most effective means. Tada and co-workers found that surface modification of TiO_2 with such metal oxides as NiO, FeO_X, or CuO could greatly

Received: December 22, 2014

enhance the visible light photocataltyic activity by narrowing the band gap and reducing the hole−electron pair recombination. Although these modified titanium dioxides with visible light response have shown to be highly effective in photocatalytic degradation of organic wastes, they have not found applications in photocatalyzed C−C and C−heteroatom bond formation reactions in organic synthesis. We envision that this narrowing of the band gap through raising the edge of the valence band, and the resulting decreased oxidizing ability, would have another advantage by making them as milder photocatalysts to be used to catalyze selective organic transformations of synthetic value, instead of leading to comprehensive bond breaking and profound degradation of the substrates as often happened when unmodified titanium dioxide is used as photocatalyst.

Therefore, we decided to investigate the use of this type of surface-modified TiO_2 catalysts in the visible light mediated functionalization of the sp^3 C−H bond adjacent to a tertiary nitrogen atom with the cyclization reaction of *N*,*N*-dimethylaniline with maleimides to form tetrahydroquinoline products as a model reaction. This type of transformation has recently been achieved in thermal reactions using $Mn(NO_3)_2$[11] or $CuCl_2$[12] as single electron oxidant and in visible light mediated reaction with $Ru(bpy)_3Cl_2$[13] as a photocatalyst.[14] In this paper, we report the result of using reusable and inexpensive surface-modified TiO_2 with NiO as visible light responsible photocatalyst to carry out this transformation (Scheme 1).

Scheme 1



RESULTS AND DISCUSSION

The surface modification of TiO_2 was achieved by the chemisorption−calcination cycle (CCC) technique[10] for forming extremely small metal oxide clusters on commercially available TiO_2 Degussa P25. These synthesized photocatalysts were characterized by means of X-ray powder diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and inductively coupled plasma spectroscopy (ICP). The Ni loading amount was determined by ICP, and four different P25/NiO(1), P25/NiO(2), P25/NiO(3), and P25/NiO(4) catalysts were prepared, with mass percentage of Ni ions loading amounts of 2.3, 6.5, 10.6, and 14.8%, respectively. Typical NiO crystal structure can be found in all P25/NiO samples with different Ni ions loading amounts, as in Figure 1, which can be indexed to the (200) plane, showing the formation of a P25/NiO composite, and with the mass percentage of Ni ions increasing from 2.0% to 14.8%, the peak at $2\theta = 43.265°$ for the P25/NiO successively enhances. The NiO clusters (<2 nm) are well dispersed on the surface of the P25 support in P25/NiO, as shown in Figure 2.[10]

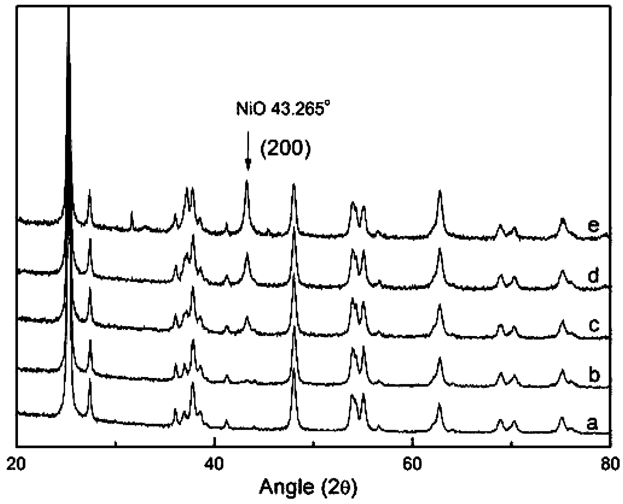


Figure 1. XRD patterns of (a) P25, (b) P25/NiO(1), (c) P25/NiO(2), (d) P25/NiO(3), and (e) P25/NiO(4).

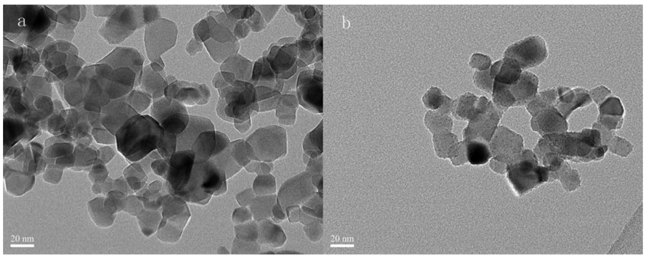


Figure 2. (a) TEM images of Degussa P25 and (b) P25/NiO with Ni ions loading amount of 10.6%.

UV−visible absorption spectral measurements (Figure 3) clearly show that, while TiO_2 itself has no significant absorption in the visible region, the surface-modified catalysts P25/NiO(1),

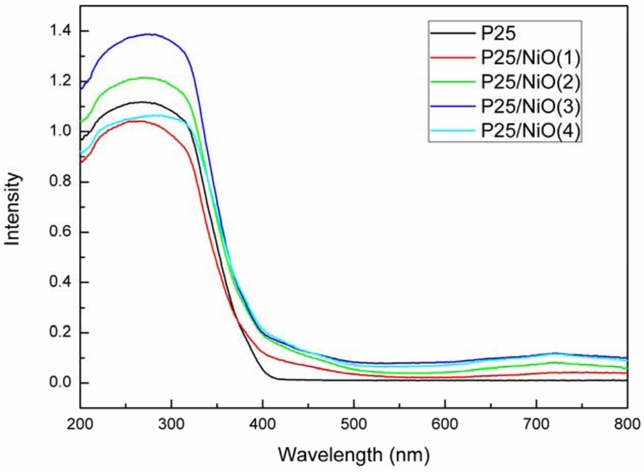


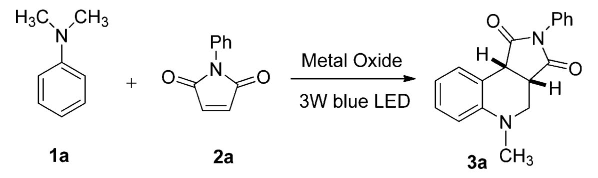
Figure 3. UV−visible absorption spectra of P25/NiO samples with varying Ni^{2+} loading amounts.

P25/NiO(2), P25/NiO(3), and P25/NiO(4) all have extended absorption in the visible region compared to bare P25, and the absorbability in the visible region increases with the increasing of Ni ions loading on the surface of the P25 until the Ni ions loading reaches 10.6%. The absorption spectra of P25/NiO show significant band gap narrowing, which is caused by the surface modification with NiO clusters. This red shift of the modified TiO_2 is induced by the rise in the VB top with nano NiO surface modification.[10f]

Initially, the reaction between *N*,*N*-dimethylaniline (**1a**) and *N*-phenylmaleimide (**2a**) was chosen for the optimization of reaction conditions (Table 1). First, we tested the performance of the four synthesized P25/NiO catalysts. We found that, under visible light irradiation of a 3W blue LED, these catalysts are highly active for the reaction between **1a** and **2a**, and only 1 mol % of the catalyst is needed for effectively bringing the cyclization process. Furthermore, when the mass percentage of nickel ions in the photocatalyst was increased from ~2% to ~11%, the product yield was increased from 48% to 83% (Table 1, entries 2−4). However, a further increase of the Ni^{2+} loading amount in the catalyst had a detrimental effect and led to a decreased yield of **3a** (entry 8). This kind of relationship between the photocatalytic activity and the NiO loading amount is also found in P25/NiO-catalyzed photodegradation of organic pollutants such as 2-naphthol and *p*-cresol,[10a,b] where there is always an optimum NiO loading, beyond which, a further increase of the NiO loading results in a reversal of the catalytic activity. This phenomenon shows that, while progressive increasing of NiO loading below the optimized amount results in band gap narrowing by raising the valence band edge to lead to increasing visible light absorption and higher catalytic activity, a further increase of the NiO loading exceeding the optimal amount would cause the valence band to be too high so that the oxidation ability of the catalyst may be too weak to induce the redox process with the substrate. Next, we turn our attention to the effect of the molar ratio of **2a** and **1a** and found that, when this ratio was adjusted to 1:1.5 and 1:1.2, the yield of **3a** decreased. The reactions in different solvents were then examined, and DMF turned out to be the best solvent. We have further found that, when the reaction was carried out in the absence of air in an argon atmosphere, no product formation can be detected (entry 15). Furthermore, the reaction could be accelerated in an oxygen atmosphere than in the air with a yield up to 78% (entry 16). For convenience, however, all the reactions were carried out under air atmosphere. Therefore, we choose the optimized reaction conditions as irradiating maleimide and *N*,*N*-dimethylaniline (2 equiv) in DMF in the presence of P25/NiO(3) (referred to as P25/NiO hereinafter) (1 mol %) under air.

The photoreactions of a series of *N*,*N*-dimethylanilines **1** and maleimides **2** with a range of substituents on the benzene ring of **1** and the N atom of **2**, respectively, were next examined under the

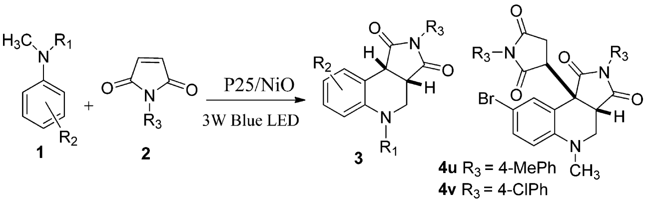
Table 1. Optimization Studies[a]



entry	catalyst/mol %	molar ratio (**2a**:**1a**)	solvent	yield (**3a**)/%[b]
1	P25/1.0	1:2	DMF	23
2	P25/NiO(1)/1.0	1:2	DMF	48
3	P25/NiO(2)/1.0	1:2	DMF	54
4	P25/NiO(3)/1.0	1:2	DMF	83
5	P25/NiO(3)/1.0	1:1.5	DMF	62
6	P25/NiO(3)/1.0	1:1.2	DMF	43
7	P25/NiO(3)/0.5	1:2	DMF	39
8	P25/NiO(4)/1.0	1:2	DMF	28
9	P25/NiO(3)/1.0	1:2	acetone	29
10	P25/NiO(3)/1.0	1:2	DCM	7
11	P25/NiO(3)/1.0	1:2	EtOH	41
12	P25/NiO(3)/1.0	1:2	NMP	18
13	P25/NiO(3)/1.0	1:2	CH_3CN	50
14	P25/NiO(3)/1.0	1:2	DMSO	37
15	P25/NiO(3)/1.0	1:2	DMF	ND[c]
16	P25/NiO(3)/1.0	1:2	DMF	78[d]

[a] Reaction conditions: A mixture of **1a** (0.25 mmol), **2a** (0.125 mmol), and metal oxide (1 mol % of **2a**) in the solvent (5 mL) was irradiated with a 3 W blue LED lamp in the air for 12 h. [b] Determined by HPLC (external standard method). [c] Reaction in an argon atmosphere. [d] Reaction in an oxygen atmosphere (1 atm, balloon) for 5 h.

Table 2. Visible Light Mediated Cyclization of Tertiary Anilines and Maleimides with P25/NiO as Photocatalyst[a]

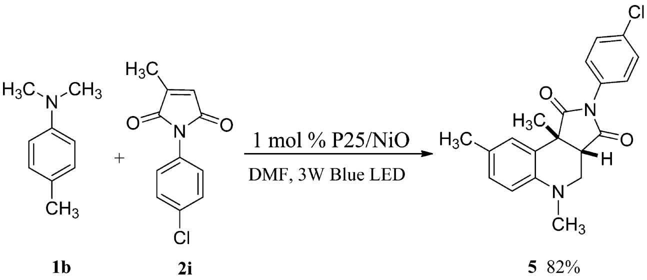


entry	R_1	R_2	**1**	R_3	**2**	**3**	yield/%[b]
1	Me	H	**1a**	Ph	**2a**	**3a**	75
2	Me	H	**1a**	4-MeOPh	**2b**	**3b**	64
3	Me	H	**1a**	4-MePh	**2c**	**3c**	89
4	Me	H	**1a**	4-FPh	**2d**	**3d**	81
5	Me	H	**1a**	4-ClPh	**2e**	**3e**	62
6	Me	H	**1a**	Me	**2f**	**3f**	67
7	Me	H	**1a**	*t*-Bu	**2g**	**3g**	69
8	Me	H	**1a**	Bn	**2h**	**3h**	68
9	Me	4-Me	**1b**	Ph	**2a**	**3i**	85
10	Me	4-Me	**1b**	4-MeOPh	**2b**	**3j**	68
11	Me	4-Me	**1b**	4-MePh	**2c**	**3k**	93
12	Me	4-Me	**1b**	4-FPh	**2d**	**3l**	86
13	Me	4-Me	**1b**	4-ClPh	**2e**	**3m**	73
14	Me	4-Me	**1b**	Me	**2f**	**3n**	73
15	Me	4-Me	**1b**	Bn	**2h**	**3o**	77
16	Me	4-MeO	**1c**	Ph	**2a**	**3p**	69
17	Me	2-Me	**1d**	Ph	**2a**	**3q**	64
18	Me	4-F	**1e**	Ph	**2a**	**3r**	86
19	Me	4-Cl	**1f**	Ph	**2a**	**3s**	75
20	Me	4-Br	**1g**	Ph	**2a**	**3t**	61
21	Me	4-Br	**1g**	4-MePh	**2c**	**3u**	68[c]
22	Me	4-Br	**1g**	4-ClPh	**2e**	**3v**	52[d]
23	Me	4-Br	**1g**	Me	**2f**	**3w**	65
24	Me	4-Br	**1g**	Bn	**2h**	**3x**	45
25	Et	H	**1h**	Ph	**2a**	**3y**	71
26	Ph	H	**1i**	4-MePh	**2c**	**3z**	48

[a] Reaction conditions: 1.25 mmol of **1a**, 0.625 mmol of **2a**, and 1 mol % P25/NiO, in 25 mL of DMF, irradiation with 3 W blue LED lamp for 12 h. [b] Yield after chromatographic purification. [c] A secondary product **4u** was also formed in 10% yield. [d] A secondary product **4v** was also formed in 8% yield.

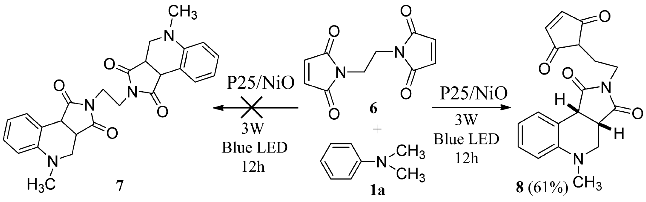
optimized conditions (Table 2). It is seen that the *N*-alkyl maleimide and *N*-aryl maleimide with either an electron-donating or an electron-withdrawing group on the aryl all reacted well with *N*,*N*-dimethylaniline to give the cyclization products in satisfactory yields (entries 1−8). Similarly, *N*,*N*-dimethylanilines with either an electron-donating or an electron-withdrawing substituent at the benzene ring took part in the reaction smoothly with various *N*-substituted maleimides **2a**−**2h**, respectively, to give the products in moderate to high yields (entries 9−26). Steric effect turned out to be important for the reaction, and the reaction of 2-methyl-*N*,*N*-dimethylaniline with **2a** led to a much lower product yield (64%) than the reaction of 4-methyl-*N*,*N*-dimethylaniline (85%) (entries 17 and 9), indicating an unfavorable effect of the 2-methyl in **1d** to the cyclization process. At the same time, a methyl group at the C═C bond of the maleimide seemed to have no significant impeding effect on the cyclization, as shown by the fact that photoinduced reaction of 4-methyl-*N*,*N*-dimethylaniline **1b** with *N*-(chlorophenyl)-2-methylmaleimide **2i** afforded the cyclization product **5** in 82% yield (Scheme 2). We also found that, in a few cases, the main products (**3u** and **3v**) could further react with maleimide under the reaction conditions to give the byproducts **4u** and **4v** (see the Supporting Information) respectively, leading to a reduction of the yield of the main products **3** (Table 2, entries 21 and 22). Control experiments showed that the byproduct **4u** can only be formed by irradiation of *N*-(4-methylphenyl)maleimide with the main product **3u** in the presence of both P25/NiO catalyst and oxygen, and no reaction took place between maleimide and **3u** when the irradiation was carried out in the absence of either P25/NiO or oxygen. The necessity of the photocatalyst clearly inducates that the byproduct was not formed by direct excitation of the maleimide, followed by hydrogen abstraction of the excited maleimide from **3u** at the benzylic position and the ensuing radical pair recombination. Meanwhile, the dependence on oxygen presence further suggests that the hydrogen abstraction event at the benzylic position of **3u** may be induced by the hydroperoxy radical (·OOH) formed by protonation of the superoxide anion radical, which, in turn, is generated by electron transfer between the excited photocatalyst and ground state oxygen.[15] Subsequent radical addition of the radical from **3u** to maleimide, followed by another H atom abstraction, affords the byproduct **4u** (Scheme 6).

Scheme 2

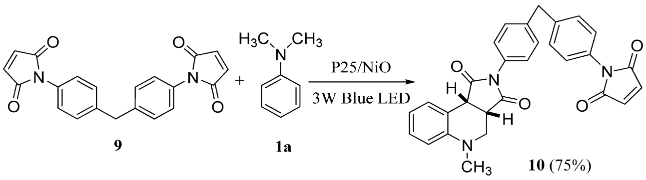


It was envisaged that a doubly annelated product **7** might be conveniently synthesized from commercially available 1,2-bismaleimidoethane **6** and *N*,*N*-dimethylaniline **1a** (Scheme 3). However, when **1a** (4 eqiv) and **6** (1 eqiv) were irradiated for 12 h under the optimized conditions, only a monocyclized compound **8** (see the Supporting Information) was formed. The same situation happened in the reaction of **1a** with 4,4′-methylenebis-(*N*-phenylmaleimide) **9** (Scheme 4).

Scheme 3

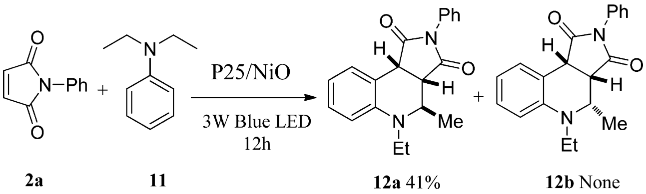


Scheme 4



It is noteworthy that, while the $CuCl_2/O_2$ system[12] failed to catalyze the reaction of *N*,*N*-diethylaniline **11** with **1a**, and $Ru(bpy)_3Cl_2$/visible light system[13] gave a pair of diastereoisomeric cyclization products (**12a**/22%, **12b**/24%), under our optimized reaction conditions, only one diastereomer **12a** was selectively formed with a 41% yield (Scheme 5).

Scheme 5



The remarkably high catalytic activity of the P25/NiO catalyst is also manifested by the result of a solar light induced reaction of **1a** with **2a** under otherwise the same conditions. This experiment was carried out on a clear day (Oct. 25, 2014) on a balcony at Shaoxing University (30°00′ north latitude and 120°34′ east longitude, 11 m above the sea level). It was found that the reaction proceeded swiftly under solar irradiation and it took only 2 h (from 12 at noon to 14 p.m., local time) to reach a completion to give the product **3a** in 70% yield.

After studying the scope of the reaction, we examined the recycling of the surface-modified TiO_2 photocatalyst. Experimentally, the catalyst is easily removed from the system after reaction by a simple centrifugal separation (see the Supporting Information, Figure 2s) and the catalyst was reused without further treatment (Table 3). Remarkably, we have found that the photocatalyst could be efficiently recycled in nine consecutive catalytic cycles without significant loss of reactivity and selectivity, indicating the efficiency of P25/NiO as a visible light photocatalyst for this reaction.

In order to get information about the catalyst structure before and after use in the photoredox oxidative cyclization reaction, we examined the P25/NiO catalyst by transmission electron microscopy (TEM). From these measurements, no significant morphological changes with regard to the shape and structure of the catalyst were found (Figure 4). This explained why the catalyst can be recycled for several times without loss of activity.

On the basis of these experimental results, a plausible reaction pathway for this visible light induced oxidative cyclization

Table 3. Catalyst Recycling in the Visible Light Mediated Direct Cyclization Reaction[a]

cycle	1	2	3	4	5	6	7	8	9
yield[b] of **3a** (%)	80	83	82	79	81	78	75	79	78

[a] Reaction conditions: 0.25 mmol of **1a**, 0.125 mmol of **2a**, and 1 mol % of P25/NiO, in 5 mL of DMF, irradiation with 3 W blue LED lamp in the air for 12 h. [b] Determined by HPLC (external standard method).

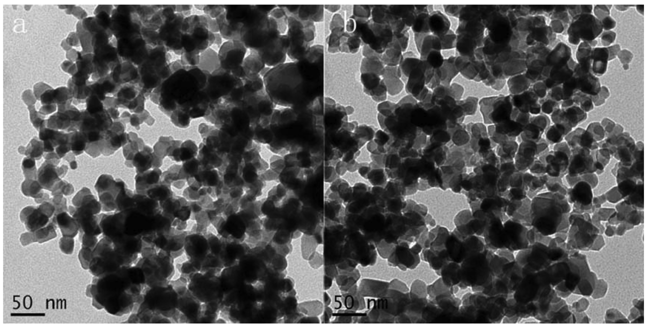
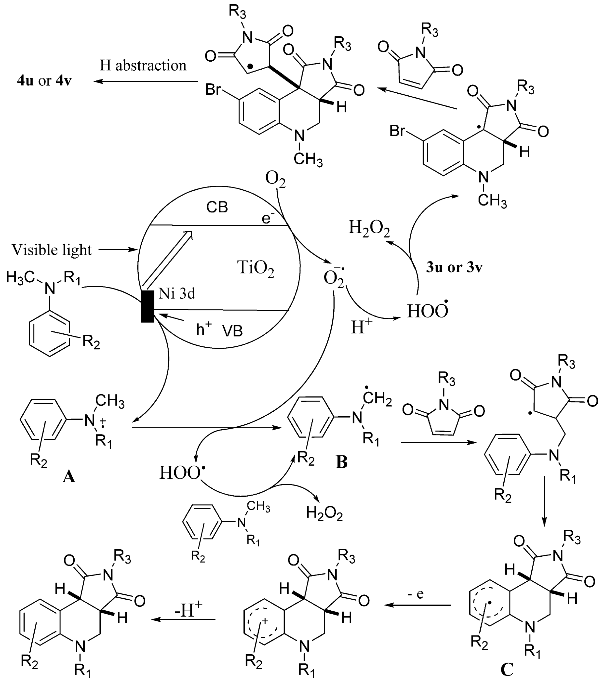


Figure 4. TEM analyses of P25/NiO before use (a) and after use for nine times (b).

Scheme 6. Proposed Reaction Mechanism for the Photoredox of Tertiary Anilines and Maleimides with Surface-Modified TiO_2



reaction catalyzed by surface-modified TiO_2 is proposed in Scheme 6. Single electron transfer (SET) from the tertiary amine **1** to the hole of the excited semiconductor catalyst leads to the amine cation radical **A**, while SET from the conducting band of the catalyst to ground state oxygen generates superoxide anion radical. Proton transfer from the amine cation radical **A** to the superoxide anion radical gives the α-aminoalkyl radical **B** and hydroperoxy radical. Radical addition of **B** to the maleimide, followed by intramolecular cyclization, leads to radical **C**. SET oxidation of **C** by oxygen or by the excited semiconductor catalyst to a carbocation, followed by deprotonation, furnishes the product. Meanwhile, the ·OOH radical may also abstract a hydrogen atom from *N*,*N*-dimethylaniline to contribute another pathway to the formation of the α-aminoalkyl radical **B**.[13]

CONCLUSION

In summary, we have used surface-modified titanium dioxide (TiO_2/NiO) as an efficient visible light responsive photocatalyst in sp^3 C−H bond activation in tertiary amines to perform the direct cyclization between a wide range of tertiary anilines with maleimides. To our knowledge, this is the first time that surface-modified TiO_2 is used beyond an environmental purpose to selectively catalyze synthetic organic reactions. In contrast to previously reported TiO_2 catalyzed organic reactions that typically use a stoichiometric amount of conventional unmodified TiO_2 (Degussa P25) in combination with UVA light, the extended absorption in the visible light region and the reduced hole−electron pair recombination of the NiO surface-modified catalysts allow them to be used in a catalytic amount as small as 1 mol % together with visible light irradiation to achieve high catalytic efficiency. Furthermore, the high thermal and photochemical stability of these modified photocatalysts enables them to be easily recovered by centrifugation and to be reused for at least nine times without significant decay of the catalytic activity.

EXPERIMENTAL SECTION

General Methods. All reagents were used without further purification. All solvents were dried according to standard procedures. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, using $CDCl_3$ as solvent. IR spectra were taken with an FT-IR spectrometer. Mass spectra were obtained using ESI techniques. For X-ray crystallographic analysis, the X-ray diffraction intensities and the unit cell parameters were determined on a CCD diffractometer employing graphite-monochromated (Mo−Kα) radiation (λ = 0.71073 Å).

Synthesis of P25/NiO Catalyst.[10e] 1 g of P25 particles had been added to of a $Ni(acac)_2(H_2O)_2$ solution (solvent: 100 mL of ethanol/*n*-hexane = 3:17 v/v); they were subjected to mechanical agitation for 24 h at 298 K. The concentration of the $Ni(acac)_2(H_2O)_2$ was maintained at 6.5×10^{-4} mol/L. The resulting samples were washed repeatedly with the same solvent to remove physisorbed complexes and then dried, followed by heating in air at 773 K for 1 h. The complex adsorption and the subsequent heating were repeated to increase the Ni loading amount.

General Procedure for the Visible Light Mediated Cyclization of Tertiary Anilines and Maleimides Reaction. In a vial (16 × 125 mm, 10 mL), P25/NiO (1 mol %), tertiary anilines **1** (1.25 mmol), and maleimides **2** (0.625 mmol) were dissolved in 25 mL DMF. The reaction mixture was stirred, and the vial was placed beside a 3 W blue LED lamp with an edge-to-edge distance of 2 cm for irradiation. After the reaction was completed, the catalyst was recovered by a simple centrifugal separation, and then the reaction mixture was poured into 50 mL of water. The aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude mixture was directly charged on silica gel and purified by column chromatography with petroleum ether/ethyl acetate as eluents (gradient elution).

(3aS,9bR*)-5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo-[3,4-c]quinoline-1,3(2H)-dione* ***(3a)***. Yield (137.0 mg, 75%). White solid: R_f = 0.41 (petroleum ether/ethyl acetate 6:1); mp 202−204 °C;[13] ^1H NMR (400 MHz, $CDCl_3$) δ 2.84 (s, 3H), 3.13 (dd, 1H, J = 11.6, 4.4 Hz), 3.53−3.57 (m, 1H), 3.62 (dd, 1H, J = 11.6, 2.6 Hz), 4.17 (d, 1H, J =

9.6 Hz), 6.75 (d, 1H, J = 8.4 Hz), 6.91 (t, 1H, J = 7.6 Hz), 7.22−7.28 (m, 3H), 7.36 (t, 1H, J = 7.2 Hz), 7.43 (t, 2H, J = 7.6 Hz), 7.53 (d, 1H, J = 7.6 Hz).

(3aS*,9bR*)-2-(4-Methoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3b)**. Yield (128.9 mg, 64%). White solid: R_f = 0.38 (petroleum ether/ethyl acetate 4:1); mp 222−224 °C; IR (KBr) ν 2960, 1783, 1712, 1577, 1511, 1439, 1251, 1201, 1163, 833, 620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (s, 3H), 3.09 (dd, 1H, J = 11.6, 4.4 Hz), 3.50 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.58 (dd, 1H, J = 11.6, 2.8 Hz), 3.78 (s, 3H), 4.12 (d, 1H, J = 9.6 Hz), 6.73 (dd, 1H, J = 8.4, 0.8 Hz), 6.88−6.94 (m, 3H), 7.16 (dt, 2H, J = 5.4, 3.4 Hz), 7.20−7.25 (m, 1H), 7.51 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5, 42.1, 43.5, 50.7, 55.5, 112.6, 114.3, 118.7, 119.7, 124.6, 127.6, 128.7, 130.3, 148.5, 159.4, 176.0, 178.0; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{19}H_{18}N_2O_3$ 323.14, found 323.17. EA found: C 70.71, H 5.68, N 8.62. Requires: C 70.79, H 5.63, N 8.69.

(3aS*,9bR*)-5-Methyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3c)**. Yield (155.1 mg, 89%). White solid: R_f = 0.43 (petroleum ether/ethyl acetate 7:1); mp 212−214 °C; IR (KBr) ν 3000, 1713, 1576, 1423, 1135, 951, 649, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.83 (s, 3H), 3.11 (dd, J = 11.2, 4.4 Hz, 1H), 3.50−3.54 (m, 1H), 3.60 (dd, 1H, J = 11.6, 2.8 Hz), 4.14 (d, 1H, J = 9.6 Hz), 6.74 (dd, 1H, J = 8.4, 0.4 Hz), 6.90 (td, 1H, J = 7.2, 1.0 Hz), 7.12−7.14 (m, 2H), 7.21−7.25 (m, 3H), 7.52 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 39.4, 42.1, 43.6, 50.7, 112.5, 118.6, 119.6, 126.2, 128.7, 129.3, 129.7, 130.3, 138.6, 148.5, 175.9, 177.8; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{19}H_{18}N_2O_2$ 307.14, found 307.17. EA found: C 74.47, H 5.95, N 9.12. Requires: C 74.49, H 5.92, N 9.14.

(3aS*,9bR*)-2-(4-Fluorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3d)**. Yield (157.1 mg, 81%). White solid: R_f = 0.39 (petroleum ether/ethyl acetate 6:1); mp 172−174 °C; IR (KBr) ν 2922, 1712, 1577, 1509, 1400, 1199, 1151, 1043, 813, 757, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3H), 3.10 (dd, 1H, J = 11.6, 4.4 Hz), 3.52 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.60 (dd, 1H, J = 11.4, 2.6 Hz), 4.15 (d, 1H, J = 9.6 Hz), 6.74 (d, 1H, J = 8.4 Hz), 6.91 (td, 1H, J = 7.4, 0.8 Hz), 7.07−7.13 (m, 2H), 7.21−7.28 (m, 3H), 7.51 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.4, 41.1, 42.6, 49.6, 111.6, 114.9, 115.1, 117.4, 118.7, 127.2, 127.7, 129.3, 147.5, 159.8, 162.3, 174.7, 176.7; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{18}H_{15}FN_2O_2$ 311.12, found 311.25. EA found: C 69.61, H 4.91, N 9.01. Requires: C 69.67, H 4.87, N 9.03.

(3aS*,9bR*)-2-(4-Chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3e)**. Yield (126.6 mg, 62%). White solid: R_f = 0.35 (petroleum ether/ethyl acetate 5:1); mp 188−190 °C; IR (KBr) ν 2861, 1783, 1713, 1575, 1493, 1398, 1201, 1018, 757, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3H), 3.10 (dd, 1H, J = 11.4, 4.2 Hz), 3.53 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.60 (dd, 1H, J = 11.4, 2.6 Hz), 4.15 (d, 1H, J = 9.6 Hz), 6.74 (dd, 1H, J = 8.2, 0.6 Hz), 6.91 (td, 1H, J = 7.4, 1.1 Hz), 7.22−7.26 (m, 3H), 7.37−7.40 (m, 2H), 7.51 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5, 42.1, 43.6, 50.6, 112.6, 118.4, 119.8, 127.6, 128.8, 129.2, 130.3, 130.4, 134.2, 148.5, 175.5, 177.5; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{18}H_{15}ClN_2O_2$ 327.09, found 327.08. EA found: C 66.18, H 4.66, N 8.53. Requires: C 66.16, H 4.63, N 8.57.

(3aS*,9bR*)-2,5-Dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3f)**. Yield (116.6 mg, 67%). White solid: R_f = 0.41 (petroleum ether/ethyl acetate 5:1); mp 170−172 °C; IR (KBr) ν 2869, 1778, 1698, 1577, 1498, 1437, 1126, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (s, 3H), 2.98 (s, 3H), 3.03 (dd, 1H, J = 11.6, 4.4 Hz), 3.36 (ddd, 1H, J = 6.8, 4.4, 2.4 Hz), 3.53 (dd, 1H, J = 11.6, 2.4 Hz), 4.00 (d, 1H, J = 9.6 Hz), 6.69 (d, 1H, J = 8.4 Hz), 6.89 (td, 1H, J = 7.6, 1.2 Hz), 7.21 (td, 1H, J = 7.6, 1.2 Hz), 7.47 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_{3,}$) δ 25.4, 39.4, 42.0, 43.6, 50.5, 112.5, 118.7, 119.6, 128.6, 130.2, 148.4, 176.8, 178.8; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{13}H_{14}N_2O_2$ 231.11, found 231.08. EA found: C 67.83, H 6.18, N 12.13. Requires: C 67.81, H 6.13, N 12.17.

X-ray Structure Analysis. $C_{13}H_{14}N_2O_2$ M = 230.26. Orthorhombic, space group $P2(1)2(1)2(1)$, a = 7.9707(19) Å, b = 8.873(2) Å, c = 16.273(4) Å, α = 90°, β = 90°, γ = 90°, V = 1150.9(5) Å, Z = 4, D_c = 1.329 g cm^{-3}, F(000) = 488.0, absorption coefficient 0.091 mm^{-1}, scan range for data collection 2.50 ≤ θ ≤ 26.65°, 5398 measured reflections, 2358 independent reflections, 1518 reflections with $I > 2\sigma(I)$, R_{int} = 0.0436, 157 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0433, wR_2 (F^2) = 0.0921.

(3aS*,9bR*)-2-(tert-Butyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3g)**. Yield (117.4 mg, 69%). White solid: R_f = 0.43 (petroleum ether/ethyl acetate 6:1); mp 76−78 °C; IR (KBr) ν 2918, 1702, 1577, 1444, 1340, 1162, 1134, 754, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 9H), 2.80 (s, 3H), 3.00 (dd, 1H, J = 11.2, 4.4 Hz), 3.21 (ddd, 1H, J = 7.6, 4.4, 3.0 Hz), 3.43 (dd, 1H, J = 11.4, 3.0 Hz), 3.83 (d, 1H, J = 9.6 Hz), 6.71 (d, 1H, J = 8.0 Hz), 6.88 (td, 1H, J = 7.6, 1.2 Hz), 7.21 (td, 1H, J = 8.2, 1.4 Hz), 7.44 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 39.4, 42.1, 43.1, 50.9, 58.7, 112.3, 119.2, 119.3, 128.4, 130.3, 148.3, 177.9, 179.6; ESI-MS M/Z [M + H]$^+$: Calcd for $C_{16}H_{20}N_2O_2$: 273.16, found 273.17. EA found: C 70.53, H 7.44, N 10.32. Requires: C 70.56, H 7.40, N 10.29.

(3aS*,9bR*)-2-Benzyl-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3h)**. Yield (130.2 mg, 68%). White solid: R_f = 0.42 (petroleum ether/ethyl acetate 5:1); mp 126−128 °C; IR (KBr) ν 2949, 2866, 1770, 1701, 1570, 1560, 1430, 1161, 998, 699, 628 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 3.00 (dd, 1H, J = 11.6, 4.4 Hz), 3.31 (ddd, 1H, J = 7.6, 4.8, 2.8 Hz), 3.46 (dd, 1H, J = 11.6, 2.8 Hz), 3.94 (d, 1H, J = 9.6 Hz), 4.62 (q, 2H, J = 14.3 Hz), 6.69 (d, 1H, J = 8.0 Hz), 6.87 (td, 1H, J = 7.6, 1.2 Hz), 7.17−7.29 (m, 6H), 7.44 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.3, 42.0, 42.7, 43.6, 50.7, 112.4, 118.8, 119.6, 127.7, 128.3, 128.5, 130.2, 135.5, 148.4, 176.4, 178.3; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{19}H_{18}N_2O_2$ 307.14, found 307.25. EA found: C 74.51, H 5.95, N 9.12. Requires: C 74.49, H 5.92, N 9.14.

(3aS*,9bR*)-5,8-Dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3i)**. Yield (162.8 mg, 85%). White solid: R_f = 0.48 (petroleum ether/ethyl acetate 7:1); mp 193−195 °C;[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.80 (s, 3H), 3.06 (dd, 1H, J = 11.2, 4.4 Hz), 3.52 (ddd, 1H, J = 6.8, 4.4, 2.6 Hz), 3.59 (dd, 1H, J = 11.2, 2.6 Hz), 4.12 (d, 1H, J = 9.6 Hz), 6.65 (d, 1H, J = 8.0 Hz), 7.04 (dd, 1H, J = 8.0, 2.0 Hz), 7.26−7.28 (m, 2H), 7.33−7.40 (m, 2H), 7.41−7.45 (m, 2H).

(3aS*,9bR*)-2-(4-Methoxyphenyl)-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3j)**. Yield (143.0 mg, 68%). White solid: R_f = 0.31 (petroleum ether/ethyl acetate 5:1); mp 180−182 °C;[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.80 (s, 3H), 3.05 (dd, 1H, J = 11.2, 4.4 Hz), 3.50 (ddd, 1H, J = 9.5, 4.3, 2.6 Hz), 3.58 (dd, 1H, J = 11.6, 2.8 Hz), 3.80 (s, 3H), 4.10 (d, 1H, J = 9.6 Hz), 6.65 (d, 1H, J = 8.4 Hz), 6.92−6.95 (m, 2H), 7.04 (dd, 1H, J = 8.4, 2.0 Hz), 7.16−7.20 (dt, 2H, J = 5.6, 3.6 Hz), 7.34 (d, 1H, J = 1.6 Hz).

(3aS*,9bR*)-5,8-Dimethyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3k)**. Yield (186.2 mg, 93%). White solid: R_f = 0.47 (petroleum ether/ethyl acetate 6:1); mp 207−209 °C; IR (KBr) ν 2955, 1713, 1577, 1511, 1444, 1195, 1164, 815, 650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.35 (s, 3H), 2.79 (s, 3H), 3.03 (dd, 1H, J = 11.6, 4.4 Hz), 3.49 (ddd, 1H, J = 6.8, 4.4, 2.8 Hz), 3.56 (dd, 1H, J = 11.4, 2.6 Hz), 4.09 (d, 1H, J = 9.6 Hz), 6.64 (d, 1H, J = 8.4 Hz), 7.03 (dd, 1H, J = 8.4, 1.6 Hz), 7.13 (d, 2H, J = 8.4 Hz), 7.22 (d, 2H, J = 8.0 Hz), 7.33 (d, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.2, 39.6, 42.2, 43.6, 51.0, 112.5, 118.6, 126.2, 129.0, 129.2, 129.4, 129.6, 130.8, 138.5, 146.4, 176.0, 178.0; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{20}H_{20}N_2O_2$ 321.16, found 321.25. EA found: C 74.93, H 6.31, N 8.75. Requires: C 74.98, H 6.29, N 8.74.

(3aS*,9bR*)-2-(4-Fluorophenyl)-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3l)**. Yield (174.3 mg, 86%). White solid: R_f = 0.41 (petroleum ether/ethyl acetate 7:1); mp 157−159 °C;[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.79 (s, 3H), 3.03 (dd, 1H, J = 11.4, 4.2 Hz), 3.50 (ddd, 1H, J = 9.6, 4.2, 2.6 Hz), 3.57 (dd, 1H, J = 11.4, 2.6 Hz), 4.10 (d, 1H, J = 9.2 Hz), 6.65 (d, 1H, J = 8.4 Hz), 7.04 (dd, 1H, J = 8.4, 1.6 Hz), 7.08−7.12 (m, 2H), 7.24−7.27 (m, 2H), 7.32 (d, 1H, J = 1.6 Hz).

(3aS*,9bR*)-2-(4-Chlorophenyl)-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione **(3m)**. Yield (155.5 mg, 73%). White solid: R_f = 0.36 (petroleum ether/ethyl acetate 5:1); mp 178−180 °C;[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.80 (s, 3H), 3.04 (dd, 1H, J = 11.4, 4.2 Hz), 3.51 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.58 (dd, 1H, J = 11.4, 2.6 Hz), 4.11 (d, 1H, J = 9.6 Hz), 6.65 (d, 1H, J =

8.4 Hz), 7.04 (dd, 1H, J = 8.0, 2.0 Hz), 7.23−7.26 (m, 2H), 7.33 (d, 1H, J = 2.0 Hz), 7.37−7.40 (m, 2H).

(3aS,9bR*)-2,5,8-Trimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo-[3,4-c]quinoline-1,3(2H)-dione (**3n**).* Yield (142.0 mg, 73%). White solid: R_f = 0.43 (petroleum ether/ethyl acetate 5:1); mp 173−176 °C;[12] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.30 (s, 3H), 2.76 (s, 3H), 2.95−2.99 (m, 4H), 3.34 (ddd, 1H, J = 6.6, 4.2, 2.2 Hz), 3.51 (dd, 1H, J = 11.4, 2.2 Hz), 3.96 (d, 1H, J = 9.6 Hz), 6.61 (d, 1H, J = 8.4 Hz), 7.01 (dd, 1H, J = 8.2, 1.8 Hz), 7.29 (d, 1H, J = 1.6 Hz).

(3aS,9bR*)-2-Benzyl-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3o**).* Yield (154.2 mg, 77%). White solid: R_f = 0.44 (petroleum ether/ethyl acetate 6:1); mp 120−122 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.29 (s, 3H), 2.76 (s, 3H), 2.98 (dd, 1H, J = 11.4, 4.6 Hz), 3.34 (ddd, 1H, J = 7.2, 4.8, 2.8 Hz), 3.47 (dd, 1H, J = 10.8, 2.6 Hz), 3.95 (d, 1H, J = 9.6 Hz), 4.65 (q, 2H, J = 14.7 Hz), 6.62 (d, 1H, J = 8.0 Hz), 7.02 (dd, 1H, J = 8.2, 2.2 Hz), 7.23−7.32 (m, 6H).

(3aS,9bR*)-8-Methoxy-5-methyl-2-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline-1,3(3aH,9bH)-dione (**3p**).* Yield (139.0 mg, 69%). White solid: R_f = 0.31 (petroleum ether/ethyl acetate 4:1); mp 164−166 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.79 (s, 3H), 3.03 (dd, 1H, J = 11.4, 4.2 Hz), 3.51 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.56 (dd, 1H, J = 11.2, 2.8 Hz), 3.79 (s, 3H), 4.12 (d, 1H, J = 9.6 Hz), 6.68 (d, 1H, J = 9.2 Hz), 6.81 (dd, 1H, J = 9.0, 3.0 Hz), 7.13 (d, 1H, J = 2.8 Hz), 7.26−7.28 (m, 2H), 7.35 (tt, 1H, J = 7.4, 1.2 Hz), 7.40−7.45 (m, 2H).

(3aS,9bR*)-5,6-Dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3q**).* Yield (122.5 mg, 64%). White solid: R_f = 0.45 (petroleum ether/ethyl acetate 5:1); mp 119−120 °C; IR (KBr) ν 2935, 1712, 1577, 1442, 1384, 1173, 766, 650 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.32 (s, 3H), 2.76 (s, 3H), 3.40 (dd, 1H, J = 13.4, 6.6 Hz), 3.50−3.59 (m, 2H), 4.18 (d, 1H, J = 8.8 Hz), 7.08 (t, 1H, J = 7.4 Hz), 7.16 (d, 1H, J = 7.2 Hz), 7.25−7.28 (m, 2H), 7.39 (tt, 1H, J = 7.4, 1.2 Hz), 7.44−7.49 (m, 2H), 7.58 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl$_{3,}$) δ 17.7, 38.9, 41.6, 42.0, 51.3, 122.9, 123.8, 126.3, 128.4, 128.7, 129.2, 130.5, 132.0, 132.8, 146.7, 175.8, 177.8; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{19}H_{18}N_2O_2$ 307.14, found 307.25. EA found: C 74.46, H 5.97, N 9.16. Requires: C 74.49, H 5.92, N 9.14.

(3aS,9bR*)-8-Fluoro-5-methyl-2-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline-1,3(3aH,9bH)-dione (**3r**).* Yield (166.8 mg, 86%). White solid: R_f = 0.34 (petroleum ether/ethyl acetate 4:1); mp 172−174 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.81 (s, 3H), 3.08 (dd, 1H, J = 11.2, 4.4 Hz), 3.53 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.59 (dd, 1H, J = 11.4, 2.6 Hz), 4.12 (d, 1H, J = 9.6 Hz), 6.67 (dd, 1H, J = 9.0, 4.6 Hz), 6.94 (td, 1H, J = 8.8, 3.2 Hz), 7.25−7.29 (m, 3H), 7.37 (tt, 1H, J = 7.4, 1.4 Hz), 7.41−7.46 (m, 2H).

(3aS,9bR*)-8-Chloro-5-methyl-2-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline-1,3(3aH,9bH)-dione (**3s**).* Yield (153.2 mg, 75%). White solid: R_f = 0.36 (petroleum ether/ethyl acetate 4:1); mp 157−159 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.82 (s, 3H), 3.10 (dd, 1H, J = 11.2, 4.4 Hz), 3.53 (ddd, 1H, J = 7.0, 4.2, 2.8 Hz), 3.61 (dd, 1H, J = 11.6, 2.8 Hz), 4.11 (d, 1H, J = 9.6 Hz), 6.66 (d, 1H, J = 8.8 Hz), 7.18 (dd, 1H, J = 8.8, 2.4 Hz), 7.25−7.28 (m, 2H), 7.35−7.39 (m, 1H), 7.42−7.46 (m, 2H), 7.51 (d, 1H, J = 2.0 Hz).

(3aS,9bR*)-8-Bromo-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3t**).* Yield (141.5 mg, 61%). White solid: R_f = 0.33 (petroleum ether/ethyl acetate 5:1); mp 159−161 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.81 (s, 3H), 3.10 (dd, 1H, J = 11.2, 4.2 Hz), 3.52 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.60 (dd, 1H, J = 11.2, 2.8 Hz), 4.09 (d, 1H, J = 9.6 Hz), 6.60 (d, 1H, J = 8.8 Hz), 7.24−7.27 (m, 2H), 7.31 (dd, 1H, J = 8.4, 2.4 Hz), 7.34−7.38 (m, 1H), 7.41−7.45 (m, 2H), 7.63 (dd, 1H, J = 2.2, 0.6 Hz).

(3aS,9bR*)-8-Bromo-5-methyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3u**).* Yield (163.7 mg, 68%). White solid: R_f = 0.45 (petroleum ether/ethyl acetate 6:1); mp 195−196 °C; IR (KBr) ν 2960, 1709, 1574, 1495, 1411, 1321, 1179, 813, 618 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.36 (s, 3H), 2.82 (s, 3H), 3.10 (dd, 1H, J = 11.6, 4.4 Hz), 3.52 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.60 (dd, 1H, J = 11.6, 2.8 Hz), 4.09 (d, 1H, J = 9.6 Hz), 6.60 (d, 1H, J = 8.8 Hz), 7.12−7.15 (m, 2H), 7.23 (d, 2H, J = 8.4 Hz), 7.31 (dd, 1H, J = 8.8, 2.4 Hz), 7.64 (dd, 1H, J = 2.4, 0.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.3, 39.5, 41.8, 43.3, 50.4, 111.7, 114.2, 120.5, 126.1, 129.2, 129.7, 131.5, 132.8, 138.8, 147.5, 175.3, 177.4; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{19}H_{17}BrN_2O_2$ 385.06, found 385.17. Found: C 59.20, H 4.43, N 7.24. Requires: C 59.23, H 4.45, N 7.27.

(3aS,9bR*)-8-Bromo-2-(4-chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3v**).* Yield (131.8 mg, 52%). White solid: R_f = 0.32 (petroleum ether/ethyl acetate 5:1); mp 178−180 °C; IR (KBr) ν 3435, 1716, 1639, 1575, 1494, 1414, 1176, 811, 646 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.81 (s, 3H), 3.10 (dd, 1H, J = 11.6, 4.4 Hz), 3.53 (ddd, 1H, J = 9.6, 4.2, 2.6 Hz), 3.60 (dd, 1H, J = 11.4, 2.6 Hz), 4.10 (d, 1H, J = 9.6 Hz), 6.61 (d, 1H, J = 8.8 Hz), 7.23−7.26 (m, 2H), 7.32 (dd, 1H, J = 8.8, 2.4 Hz), 7.39−7.42 (m, 2H), 7.63 (dd, 1H, J = 2.2, 0.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 39.5, 41.8, 43.3, 50.3, 111.8, 114.3, 120.2, 127.5, 129.2, 130.3, 131.6, 132.7, 134.4, 147.5, 174.9, 177.0; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{18}H_{14}BrClN_2O_2$ 405.00, found 405.00. EA found: C 53.25, H 3.43, N 6.88. Requires: C 53.29, H 3.48, N 6.91.

(3aS,9bR*)-8-Bromo-2,5-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3w**).* Yield (125.1 mg, 65%). White solid: R_f = 0.33 (petroleum ether/ethyl acetate 5:1); mp 188−190 °C; IR (KBr) ν 2872, 1770, 1692, 1572, 1494, 1432, 1320, 1121, 1024, 810, 625 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.78 (s, 3H), 2.99 (s, 3H), 3.02 (dd, 1H, J = 11.6, 4.4 Hz), 3.21 (ddd, 1H, J = 7.2, 4.4, 2.4 Hz), 3.53 (dd, 1H, J = 11.6, 2.4 Hz), 3.95 (d, 1H, J = 9.6 Hz), 6.56 (d, 1H, J = 8.8 Hz), 7.28 (dd, 1H, J = 8.8, 2.4 Hz), 7.59 (d, 1H, J = 2.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 25.5, 39.4, 41.7, 43.3, 50.2, 111.6, 114.2, 120.6, 131.3, 132.6, 147.4, 176.1, 178.3 ; ESI-MS M/Z [M-H]$^-$ Calcd for $C_{13}H_{13}BrN_2O_2$ 307.01, found 307.08. EA found: C 50.45, H 4.28, N 9.03. Requires: C 50.50, H 4.24, N 9.06.

(3aS,9bR*)-2-Benzyl-8-bromo-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3x**).* Yield (108.4 mg, 45%). White solid: R_f = 0.37 (petroleum ether/ethyl acetate 5:1); mp 148−150 °C; IR (KBr) ν 2925, 1699, 1578, 1495, 1438, 1340, 1145, 810, 716, 620 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.77 (s, 3H), 3.03 (dd, 1H, J = 11.6, 4.8 Hz), 3.35 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.47 (dd, 1H, J = 11.6, 2.8 Hz), 3.92 (d, 1H, J = 9.6 Hz), 4.64 (q, 2H, J = 14.1 Hz), 6.57 (d, 1H, J = 8.4 Hz), 7.26−7.30 (m, 6H), 7.57 (d, 1H, J = 2.4, 0.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 39.4, 41.7, 42.9, 43.4, 50.5, 111.7, 114.1, 120.7, 127.9, 128.4, 128.6, 131.3, 132.7, 135.4, 147.5, 175.2, 177.9; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{19}H_{17}BrN_2O_2$ 385.06, found 385.17. EA found: C 59.20, H 4.49, N 7.25. Requires: C 59.23, H 4.45, N 7.27.

(3aS,9bR*)-5-Ethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo-[3,4-c]quinoline-1,3(2H)-dione (**3y**).* Yield (135.9 mg, 71%). White solid: R_f = 0.43 (petroleum ether/ethyl acetate 6:1); mp 196−198 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.17 (t, 3H, J = 7.0 Hz), 3.16 (dd, 1H, J = 11.8, 4.2 Hz), 3.22−3.78 (m, 2H), 3.53 (ddd, 1H, J = 7.2, 4.4, 3.2 Hz), 3.64 (dd, 1H, J = 11.6, 2.8 Hz), 4.13 (d, 1H, J = 9.6 Hz), 6.77 (d, 1H, J = 8.4 Hz), 6.85 (td, 1H, J = 7.2, 0.8 Hz), 7.18−7.26 (m, 3H), 7.33−7.37 (m, 1H) 7.40−7.44 (m, 2H), 7.51 (d, 1H, J = 7.4 Hz).

(3aS,9bR*)-5-Phenyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3z**).* Yield (110.5 mg, 48%). White solid: R_f = 0.38 (petroleum ether/ethyl acetate 5:1); mp 196−198 °C; IR (KBr) ν 2922, 1712, 1576, 1397, 1334, 1276, 1200, 816, 754, 698, 623 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.35 (s, 3H), 3.64 (ddd, 1H, J = 7.2, 4.4, 2.8 Hz), 3.70 (dd, 1H, J = 11.8, 4.6 Hz), 4.19 (dd, 1H, J = 11.8, 3.0 Hz), 4.22 (d, 1H, J = 9.2 Hz), 6.77 (dd, 1H, J = 8.4, 1.2 Hz), 6.96 (td, 1H, J = 7.4, 1.2 Hz), 7.04 (dt, 2H, J = 4.0, 2.2 Hz), 7.07−7.11 (m, 4H), 7.21 (d, 2H, J = 8.0 Hz), 7.30−7.35 (m, 2H), 7.59 (d, 1H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.2, 42.4, 44.5, 48.4, 117.3, 120.6, 121.5, 122.9, 123.8, 126.1, 128.3, 129.2, 129.5, 129.7, 130.7, 138.7, 146.2, 146.4, 175.8, 177.2; ESI-MS M/Z [M + H]$^+$ Calcd for $C_{24}H_{20}N_2O_2$ 369.16, found 369.25. EA found: C 78.19, H 5.52, N 7.65. Requires: C 78.24, H 5.47, N 7.60.

(3aS,9bR*)-8-Bromo-9b-((S)-2,5-dioxo-1-(p-tolyl)pyrrolidin-3-yl)-5-methyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]-quinoline-1,3(2H)-dione (**4u**).* Yield (17.9 mg, 10%). White solid: R_f = 0.32 (petroleum ether/ethyl acetate 3:1); mp 276−278 °C; IR (KBr) ν 2926, 1712, 1573, 1416, 1137, 811, 645, 621 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.367 (s, 3H), 2.374 (s, 3H), 2.87 (s, 3H), 2.92 (d, 1H, J = 6.4 Hz), 2.98 (d, 1H, J = 9.2 Hz), 3.37 (dd, 1H, J = 12.0, 5.6 Hz), 3.58 (dd, 1H, J = 11.6, 4.0 Hz), 3.74 (t, 1H, J = 4.8 Hz), 4.06 (dd, 1H, J = 9.2, 6.4 Hz), 6.63 (d, 1H, J = 8.8 Hz), 7.09 (dd, 4H, J = 11.6, 8.4 Hz), 7.23−7.27

DOI: 10.1021/jo502901h
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(m, 4H), 7.35 (dd, 1H, J = 8.8, 2.4 Hz), 7.76 (d, 1H, J = 2.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.2, 32.2, 39.3, 44.9, 45.2, 47.3, 48.5, 111.0, 114.6, 120.7, 125.9, 126.1, 128.56, 128.60, 129.8, 129.9, 130.4, 132.5, 139.1, 146.3, 173.7, 174.8, 175.6, 176.1; ESI-MS M/Z [M + H]$^+$ Calcd for C$_{30}$H$_{26}$BrN$_3$O$_4$ 572.12; found 572.17. EA found: C 62.90, H 4.63, N 7.30. Requires: C 62.94, H 4.58, N 7.34.

(3aS,9bR*)-8-Bromo-2-(4-chlorophenyl)-9b-((S)-1-(4-chlorophenyl)-2,5-dioxopyrrolidin-3-yl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**4v**).* Yield (15.3 mg, 8%). White solid: R_f = 0.37 (petroleum ether/ethyl acetate 4:1); mp 258−260 °C; IR (KBr) ν 3001, 1713, 1578, 1426, 1166, 819, 649 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.88 (s, 3H), 2.95 (d, 2H, J = 8.0 Hz), 3.39 (dd, 1H, J = 11.8, 5.8 Hz), 3.55 (dd, 1H, J = 11.8, 4.6 Hz), 3.84 (t, 1H, J = 5.2 Hz), 4.02 (t, 1H, J = 8.0 Hz), 6.65 (d, 1H, J = 8.8 Hz), 7.19 (dd, 4H, J = 11.4, 8.6 Hz), 7.37 (dd, 1H, J = 8.8, 2.4 Hz), 7.43 (td, 4H, J = 6.4, 2.0 Hz), 7.71 (d, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 32.2, 39.3, 44.8, 45.4, 47.3, 48.4, 111.1, 114.8, 120.3, 127.4, 127.5, 129.4, 129.5, 129.6, 129.7, 130.3, 132.7, 134.8, 146.3, 173.1, 174.2, 175.4, 175.8; ESI-MS M/Z [M + H]$^+$ Calcd for C$_{28}$H$_{20}$BrCl$_2$N$_3$O$_4$ 612.01, found 612.00. EA found: C 54.88, H 3.35, N 6.82. Requires: C 54.84, H 3.29, N 6.85.

X-ray Structure Analysis. C$_{28}$H$_{20}$BrCl$_2$N$_3$O$_4$, 0.5(C$_4$H$_8$O$_2$) M = 657.32. Triclinic, space group $P\overline{1}$, a = 7.5950(4) Å, b = 13.7694(8) Å, c = 15.7113(12) Å, α = 64.051(2)°, β = 88.667(3)°, γ = 76.613(2) °, V = 1431.54(16) Å, Z = 2, D_c = 1.525 g cm^{-3}, F(000) = 668.0, absorption coefficient 1.668 mm^{-1}, scan range for data collection 3.01 ≤ θ ≤ 25.10°, 11 496 measured reflections, 4958 independent reflections, 3784 reflections with $I > 2\sigma(I)$, R_{int} = 0.0386, 461 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0421, wR$_2$ (F^2) = 0.1105.

(3aS,9bR*)-2-(4-Chlorophenyl)-5,8,9b-trimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**5**).* Yield (181.9 mg, 82%). White solid: R_f = 0.47 (petroleum ether/ethyl acetate 7:1); mp 204−206 °C; IR (KBr) ν 2975, 1781, 1718, 1577, 1493, 1444, 1205, 1129, 824, 649 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.81 (s, 3H), 2.28 (s, 3H), 2.85 (s, 3H), 3.09 (t, 1H, J = 3.2 Hz), 3.14 (dd, 1H, J = 11.4, 3.4 Hz), 3.67 (dd, 1H, J = 11.2, 2.8 Hz), 6.61 (d, 1H, J = 8.4 Hz), 7.01 (dd, 1H, J = 8.4, 2.0 Hz), 7.21 (dt, 2H, J = 9.6, 2.4 Hz), 7.37 (dt, 2H, J = 9.4, 2.3 Hz), 7.43 (d, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.5, 26.4, 39.7, 44.3, 47.7, 50.7, 112.4, 122.0, 127.5, 128.3, 129.1, 129.2, 129.5, 130.5, 134.1, 144.6, 175.9, 178.9; ESI-MS M/Z [M + H]$^+$ Calcd for C$_{20}$H$_{19}$ClN$_2$O$_2$ 355.12, found 355.08. EA found: C 67.68, H 5.45, N 7.91. Requires: C 67.70, H 5.40, N 7.89.

(3aS,9bR*)-2-(2-(2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**8**).* Yield (64.7 mg, 61%). White solid: R_f = 0.32 (petroleum ether/ethyl acetate 4:1); mp 176−178 °C; IR (KBr) ν 2935, 1705, 1577, 1499, 1435, 1152, 1133, 828, 650 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.79 (s, 3H), 3.02 (dd, 1H, J = 11.6, 4.4 Hz), 3.33 (ddd, 1H, J = 6.8, 4.4, 2.4 Hz), 3.49 (dd, 1H, J = 11.6, 2.4 Hz), 3.64−3.78 (m, 4H), 3.96 (d, 1H, J = 9.2 Hz), 6.61 (s, 2H), 6.69 (d, 1H, J = 7.8 Hz), 6.86 (td, 1H, J = 7.6, 1.2 Hz), 7.20 (td, 1H, J = 7.6, 1.2 Hz), 7.42 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 35.8, 37.9, 39.3, 41.9, 43.5, 50.1, 112.5, 118.3, 119.4, 128.6, 130.1, 134.1, 148.3, 170.5, 176.8, 178.7; ESI-MS M/Z [M + H]$^+$ Calcd for C$_{18}$H$_{17}$N$_3$O$_4$ 340.13, found 340.15. EA found: C 63.67, H 5.10, N 12.35. Requires: C 63.71, H 5.05, N 12.38.

X-ray Structure Analysis. C$_{18}$H$_{17}$N$_3$O$_4$ M = 339.35. Triclinic, space group $P\overline{1}$, a = 8.171(8) Å, b = 8.979(8) Å, c = 11.675(11) Å, α = 95.56(3)°, β = 95.62(3)°, γ = 101.11(3) °, V = 830.5(14) Å, Z = 2, D_c = 1.357 g cm^{-3}, F(000) = 356.0, absorption coefficient 0.098 mm^{-1}, scan range for data collection 1.77 ≤ θ ≤ 25.00°, 5502 measured reflections, 2827 independent reflections, 1126 reflections with $I > 2\sigma(I)$, R_{int} = 0.0803, 227 refinable parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.0880, wR$_2$ (F^2) = 0.2386.

(3aS,9bR*)-2-(4-(4-(2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzyl)phenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**10**).* Yield (111.9 mg, 75%). Yellow oil: R_f = 0.31 (petroleum ether/ethyl acetate 2:1); IR (KBr) ν 2931, 1714, 1576, 1427, 1134, 1067, 650, 619 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.83 (s, 3H), 3.12 (dd, 1H, J = 11.2, 4.4 Hz), 3.54 (ddd, 1H, J = 7.0, 4.2, 2.6 Hz), 3.61 (dd, 1H, J = 11.4, 2.6 Hz), 4.02 (s, 2H), 4.16 (d, 1H, J = 9.2 Hz), 6.74 (d, 1H, J = 8.4 Hz), 6.84 (s, 2H), 6.90 (td, 1H, J = 7.4, 1.0 Hz), 7.19−7.25 (m, 9H), 7.53 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 39.4, 41.1, 42.1, 43.6, 50.7, 112.5, 118.5, 119.6, 119.7, 126.1, 126.4, 128.7, 129.6, 129.7, 130.2, 130.3, 134.2, 140.3, 140.9, 148.5, 169.5, 169.6, 175.8, 177.7, 177.8; ESI-MS M/Z [M + H]$^+$ Calcd for C$_{29}$H$_{23}$N$_3$O$_4$ 478.18, found 478.18. EA found: C 72.90, H 4.81, N 8.85. Requires: C 72.94, H 4.85, N 8.80.

(3aR,4S,9bR*)-5-Ethyl-4-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-benzo[e]isoindole-1,3(2H)-dione (**12a**).* Yield (81.8 mg, 41%). White solid: R_f = 0.39 (petroleum ether/ethyl acetate 6:1); mp 199−201 °C;[13] ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.03 (d, 3H, J = 6.8 Hz), 1.28 (t, 3H, J = 7.2 Hz), 3.15 (qd, 1H, J = 14.2, 7.0 Hz), 3.48 (qd, 1H, J = 14.0, 7.0 Hz), 3.63 (dd, 1H, J = 9.0, 5.8 Hz), 4.00 (t, 1H, J = 6.4 Hz), 4.07 (d, 1H, J = 8.8 Hz), 6.79 (d, 1H, J = 7.2 Hz), 6.88 (t, 1H, J = 7.2 Hz), 7.21−7.30 (m, 3H), 7.38−7.43 (m, 1H), 7.46−7.50 (m, 2H), 7.78 (d, 1H, J = 7.6 Hz).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H of all compounds and ^{13}C NMR spectra of 18 new compounds. X-ray crystal structure data for **8**, **3f**, and **4v** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC 21202101 and 51372154), the Zhejiang Provincial Natural Science Foundation of China (Y15B020012), and the Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201306).

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DOI: 10.1021/jo502901h