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Cyclization of *N*-Arylacrylamides via Radical Arylsulfenylation of Carbon–Carbon Double Bonds with Sulfonyl Hydrazides

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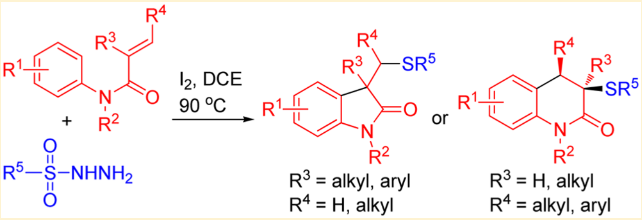
Ⓢ *Supporting Information*

ABSTRACT: An unprecedented tandem radical sulfenylation/cyclization reaction of *N*-arylacrylamides with sulfonyl hydrazides has been developed in the presence of iodine for the selective synthesis of 3-(sulfenylmethyl)oxindoles and 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-ones. Preliminary mechanistic studies showed that sulfonyl hydrazides decomposed completely at an early stage to thiosulfonates and disulfides, both of which underwent tandem radical sulfenylation/cyclization with *N*-arylacrylamides at a late stage.

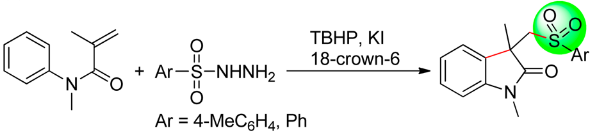


Sulfonyl hydrazides have recently emerged as useful sulfenylating agents for the functionalization of carbon–hydrogen bonds,[1] carbon–carbon multiple bonds,[2] carbon–heteroatom bonds,[3] and phosphorus–hydrogen bonds.[4] When compared to commonly employed sulfenylating agents such as thiols, disulfides, sulfenyl halides, sulfenate esters, and sulfenamides, sulfonyl hydrazides are much more amenable to handling because, in general, they are readily accessible solids, free of unpleasant odor, and compatible with moisture. Technically, the sulfenylation with sulfonyl hydrazides does not require external reductants to decrease the valence of sulfur from +6 to +2 in that the $NHNH_2$ moiety is utilized to remove the two oxygen atoms from the SO_2 group to generate sulfur electrophiles as well as water and molecular nitrogen as byproducts.

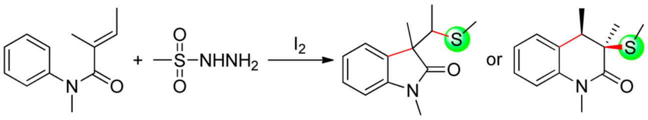
As part of our efforts in exploring the synthetic utilities of monosubstituted hydrazines,[1a,2b,3b,5] we have recently developed an iodine-catalyzed oxysulfenylation reaction of alkenes with sulfonyl hydrazides and alcohols, which, however, is not applicable to electron-deficient alkenes such as α,β-unsaturated amides.[2b] On the other hand, arenesulfonyl hydrazides were reported recently by Li, Xu, and co-workers to undergo tandem radical sulfonylation/cyclization with *N*-arylacrylamides in the presence of TBHP, KI, and 18-crown-6 to afford 3-(sulfonylmethyl)oxindoles (Scheme 1a).[6] It is noteworthy that *N*-arylacrylamides serve as versatile building blocks for the construction of functionalized oxindoles, which has been found in many biologically relevant compounds.[7] In this context, we wondered if iodine could render such a tandem process. However, to our surprise, sulfenylation rather than sulfonylation took place between sulfonyl hydrazides and *N*-arylacrylamides in the presence of iodine. Importantly, this tandem sulfenylation/cyclization reaction proceeded in a radical pathway to afford either 3-(sulfenylmethyl)oxindoles or 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-ones with high regioselectivity (Scheme 1b).[8,9]

Scheme 1. Cyclization of *N*-Arylacrylamides with Sulfonyl Hydrazides

(a) Li and Xu:[6]



(b) This work:



Initially, we employed 20 mol % iodine to catalyze the model reaction of *N*-arylacrylamide **1a** with sulfonyl hydrazide **2a** in 1,2-dichloroethane. The reaction mixture was heated under air in a sealed tube at 90 °C for 24 h and 3-(sulfenylmethyl)oxindole **3a** was isolated in 49% yield (Table 1, entry 1). Prolonging the reaction time to 48 h improved the yield to 73%, and on the other hand, elevating the temperature to 120 °C improved the yield to 86% (Table 1, entries 2 and 3). Since iodine is inexpensive, we increased its amount to 1 equiv and found that the yield was improved to 97% (Table 1, entry 4). The oxygen in air proved unnecessary according to the control experiment performed under nitrogen, which gave 3-(sulfenylmethyl)oxindole **3a** in 94% yield (Table 1, entry 5). Moreover, performing the reaction under oxygen led to a lower yield because a higher concentration of molecular oxygen could accelerate the decomposition of the sulfonyl hydrazide into a sulfonic acid via the intermediacy of a sulfinic acid (Table 1, entry 6).[10] Replacing iodine with NIS (*N*-iodosuccinimide) dramatically decreased the yield, and even no desired product

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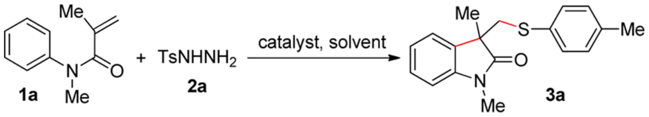
Table 1. Optimization of Reaction Conditions[a]



1a + **2a** → **3a**

entry	catalyst (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1	I_2 (0.2)	DCE	90	24	49
2	I_2 (0.2)	DCE	90	48	73
3	I_2 (0.2)	DCE	120	24	86
4	I_2 (1)	DCE	90	24	97
5[c]	I_2 (1)	DCE	90	24	94
6[d]	I_2 (1)	DCE	90	24	84
7	NIS (1)	DCE	90	24	37
8	^{n}Bu$_4$NI (1)	DCE	90	24	0
9	HI (1)	DCE	90	24	0
10	I_2 (1)	$CHCl_3$	90	24	95
11	I_2 (1)	PhMe	90	24	63
12	I_2 (1)	dioxane	90	24	54
13	I_2 (1)	CH_3CN	90	24	87
14	I_2 (1)	DMF	90	24	0
15	I_2 (1)	DMSO	90	24	0
16	I_2 (1)	EtOH	90	24	0

[a] Reaction conditions: *N*-arylacrylamide **1a** (0.20 mmol), sulfonyl hydrazide **2a** (0.24 mmol), catalyst (0.2−1 equiv), solvent (0.50 mL), under air at 90 °C (oil bath) for 24 h. [b] Isolated yield. [c] The reaction was run under nitrogen. [d] The reaction was run under oxygen.

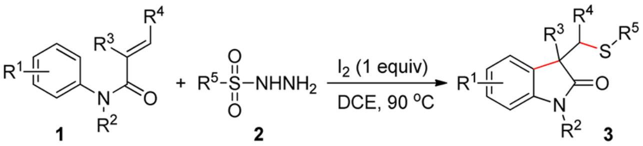
was isolated when using either ^{n}Bu$_4$NI or HI as the catalyst (Table 1, entries 7−9). Finally, a number of common organic solvents were examined, and no better yield was obtained (Table 1, entries 10−16).

Under the optimized conditions, a range of *β*-unsubstituted *N*-arylacrylamides smoothly underwent 5-exo-trig cyclization via iodine-catalyzed sulfenylation with sulfonyl hydrazides, and structurally diverse 3-(sulfenylmethyl)oxindoles were isolated in moderate to excellent yields (Table 2, **3a**−**w**). In general, the reaction with aromatic sulfonyl hydrazides gave much higher yields than that with aliphatic ones (**3a**−**i** versus **3j**), and notably, the cyclization proceeded with high regioselectivity regarding the carbon−carbon bond formation of the aromatic ring (**3r** and **3s**). Moreover, the reaction is highly sensitive to the nature of *N*-substituents in substrates **1** and no desired cyclization was observed when R^2 was hydrogen or an electron-withdrawing group such as a *p*-toluenesulfonyl group or an acetyl group.

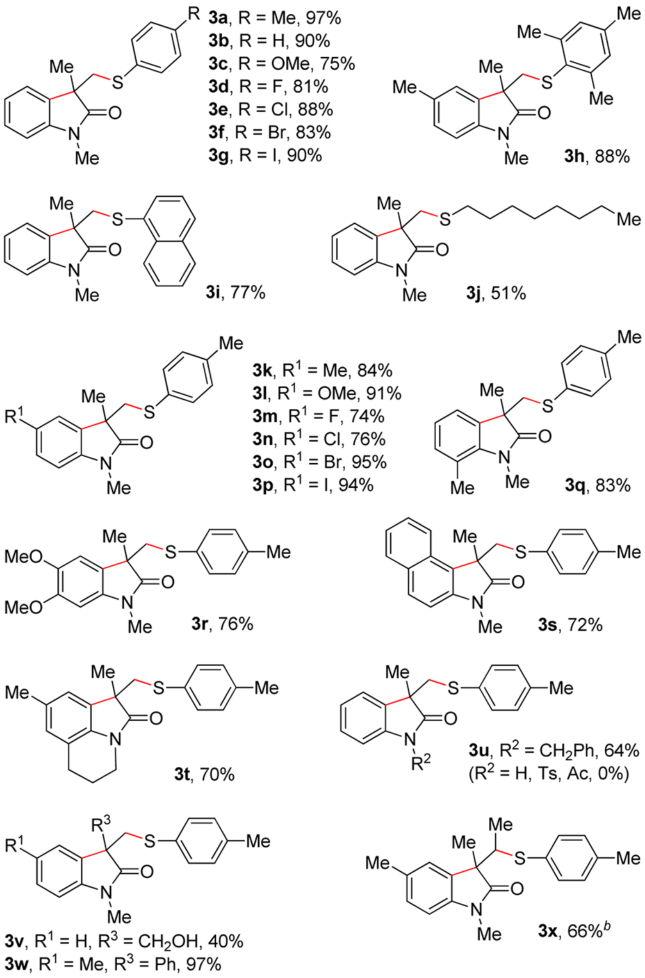
There are two cyclization modes, 5-exo-trig versus 6-endo-trig, identified for *β*-substituted *N*-arylacrylamides in their sulfenylation reaction with sulfonyl hydrazides, which required 2 equiv of iodine to achieve better yields. When R^3 and R^4 were both alkyl groups, a 3-(sulfenylmethyl)oxindole was isolated as the only cyclization product (Table 2, **3x**). In contrast, the reaction with a *β*-aryl-*N*-arylacrylamide or an *α*-unsubstituted *β*-alkyl-*N*-arylacrylamide only afforded a 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-one, whose structure was further confirmed by Raney Ni-mediated desulfuration (Scheme 2).[11] It is noteworthy that 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-ones **4a**−**c** were produced with very high diastereoselectivity according to NMR spectroscopic analysis.[12]

The cyclization reaction failed to proceed with *α*,*β*-unsubstituted *N*-arylacrylamides. For example, no cyclization product was detected at all in the reaction of *N*-arylacrylamide **1s** with sulfonyl hydrazide **2a** (eq 1). Instead, the reaction gave

Table 2. Sulfenylation of *N*-Arylacrylamides with Sulfonyl Hydrazides Leading to Functionalized Oxindoles[a]



1 + **2** → **3**



3a, R = Me, 97%
3b, R = H, 90%
3c, R = OMe, 75%
3d, R = F, 81%
3e, R = Cl, 88%
3f, R = Br, 83%
3g, R = I, 90%

3h, 88%

3i, 77%

3j, 51%

3k, R^1 = Me, 84%
3l, R^1 = OMe, 91%
3m, R^1 = F, 74%
3n, R^1 = Cl, 76%
3o, R^1 = Br, 95%
3p, R^1 = I, 94%

3q, 83%

3r, 76%

3s, 72%

3t, 70%

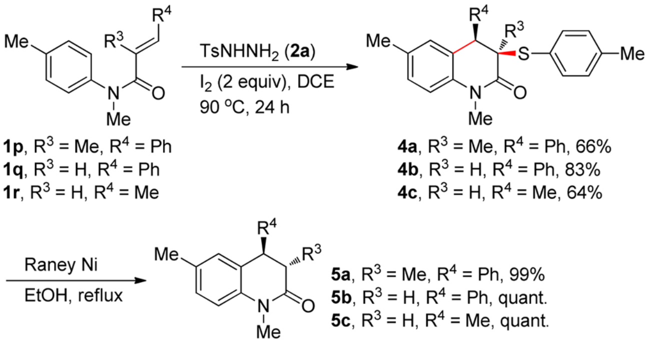
3u, R^2 = CH_2Ph, 64%
(R^2 = H, Ts, Ac, 0%)

3v, R^1 = H, R^3 = CH_2OH, 40%
3w, R^1 = Me, R^3 = Ph, 97%

3x, 66%[b]

[a] Reaction conditions: *N*-arylacrylamide **1** (0.20 mmol), sulfonyl hydrazide **2** (0.24 mmol), iodine (0.20 mmol), in DCE (0.50 mL) under air at 90 °C (oil bath) for 24 h. [b] Iodine (0.40 mmol) was used.

Scheme 2. Sulfenylation of *N*-Arylacrylamides with Sulfonyl Hydrazides Leading to Functionalized 3,4-Dihydroquinolin-2(1*H*)-ones

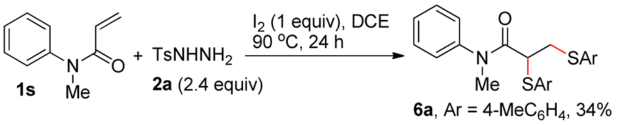


1p, R^3 = Me, R^4 = Ph
1q, R^3 = H, R^4 = Ph
1r, R^3 = H, R^4 = Me

4a, R^3 = Me, R^4 = Ph, 66%
4b, R^3 = H, R^4 = Ph, 83%
4c, R^3 = H, R^4 = Me, 64%

5a, R^3 = Me, R^4 = Ph, 99%
5b, R^3 = H, R^4 = Ph, quant.
5c, R^3 = H, R^4 = Me, quant.

bisthioether **6a** in 34% yield. On the other hand, TsNHNHCOPh (**2aa**) did not undergo cyclization with *N*-arylacrylamide **1a**, and this result suggests that the NHNH$_2$ group is essential for the sulfonyl hydrazide to serve as an effective sulfenylating agent (eq 2).

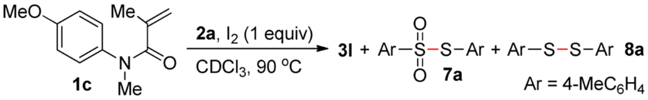


(1)

$$\mathbf{1a} + \underset{\mathbf{2aa}}{\text{TsNHNHCOPh}} \xrightarrow{\text{I}_2\text{ (1 equiv), DCE, 90 °C, 24 h}} \underset{0\%}{\mathbf{3a}} \quad (2)$$

To gain insights into the reaction mechanism, we carried out ^{1}H NMR spectroscopic analysis of the reaction mixture of *N*-arylacrylamide **1c** with sulfonyl hydrazide **2a** in deuterated chloroform and found that the sulfonyl hydrazide decomposed completely at an early stage to a 60:40 mixture of thiosulfonate **7a** and disulfide **8a**,[10] both of which were gradually converted to the desired oxindole **3l** at a late stage (Table 3).

Table 3. ^{1}H NMR Spectroscopic Analysis of the Reaction Mixture



entry	time (h)	**2a** (%)	**7a** (%)	**8a** (%)	**3l** (%)
1	0.5	10	55	35	0
2	1	0	56	38	6
3	2	0	49	36	15
4	5	0	31	24	45
5	24	0	0	5	95

Both intermediates **7a** and **8a** were isolated and underwent tandem sulfenylation/cyclization with *N*-arylacrylamide **1a** to give the desired oxindole product in good yields (Scheme 3).

Scheme 3. Transformations of Intermediates

$$\mathbf{1a} + \mathbf{7a\text{-}9a} \xrightarrow[\text{90 °C, 24 h}]{\text{I}_2\text{ (1 equiv), DCE}} \mathbf{3a}$$

ArSO$_2$SAr (**7a**, 0.6 equiv)	72%
ArSSAr (**8a**, 0.6 equiv)	60%
ArSO$_2$H (**9a**, 1.2 equiv)	33%

Ar = 4-MeC$_6$H$_4$

$$\mathbf{7a} \xrightarrow[\text{90 °C, 24 h}]{\text{I}_2\text{ (1 equiv), DCE}} \underset{35\%}{\mathbf{8a}}$$

$$\mathbf{9a} \xrightarrow[\text{90 °C, 24 h}]{\text{I}_2\text{ (1 equiv), DCE}} \underset{60\%}{\mathbf{7a}} + \underset{15\%}{\mathbf{8a}}$$

Moreover, treatment of thiosulfonate **7a** with 1 equiv of iodine gave disulfide **8a** in 35% yield under the standard conditions. Although sulfinic acid **9a** was not detected by the aforementioned ^{1}H NMR spectroscopic analysis (Table 3), it was reported previously to be generated through the decomposition of the corresponding sulfonyl hydrazide upon heating.[10] Therefore, we carried out the reaction of sulfinic acid **9a** with *N*-arylacrylamide **1a** and found that 3-(sulfenylmethyl)-oxindole **3a** was produced, albeit in a lower yield. Moreover, in the presence of iodine, sulfinic acid **9a** was converted to thiosulfonate **7a** in 60% yield together with disulfide **8a** in 15% yield.

Addition of 1 equiv of 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the reaction mixture of *N*-arylacrylamide **1a**, sulfonyl hydrazide **2a**, and iodine significantly decreased the yield (from 97% to 34%) for the formation of the desired cyclization product. Moreover, replacement of BHT with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) almost completely inhibited the desired reaction. These results suggest that the reaction may proceed via a radical pathway, which is substantially supported by the following experiment. The electron paramagnetic resonance (EPR) spectrum of the same reaction mixture displayed the resonance characteristic of a tertiary carbon radical having β-hydrogens with an absorption maximum at $g = 2.0050$ (Figure 1).[12]

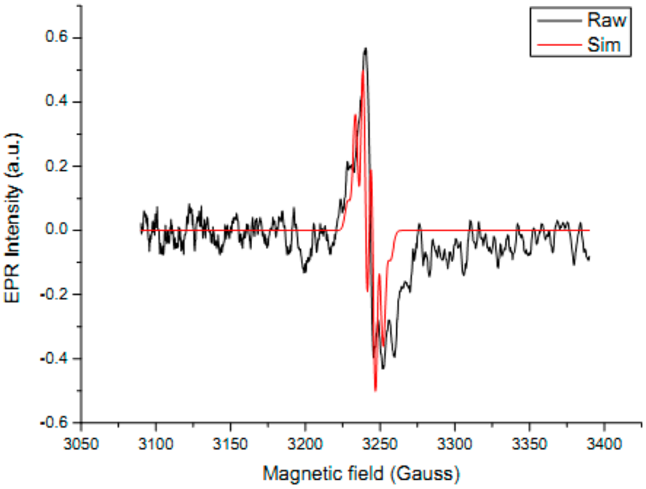
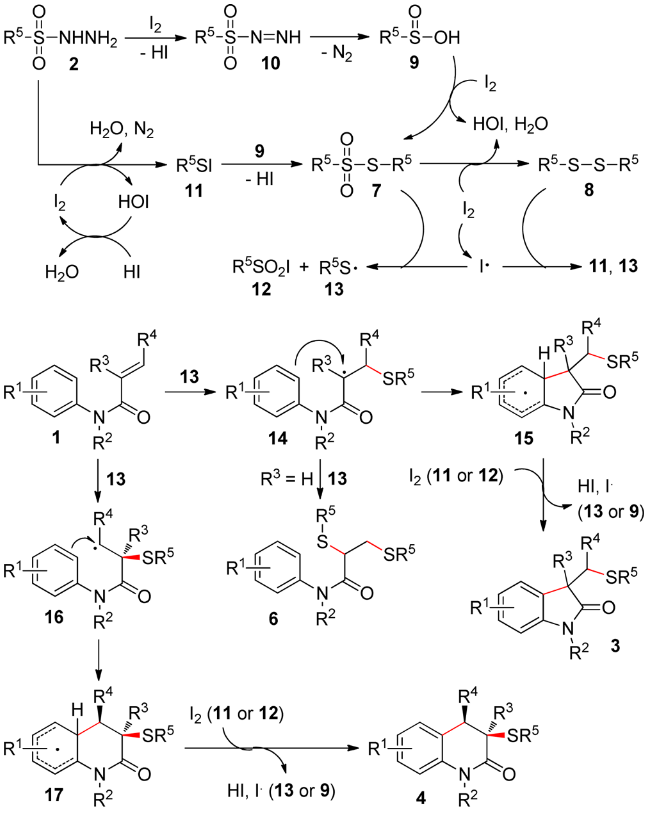


Figure 1. EPR spectrum of the reaction mixture.

According to the above experimental results and previous studies,[1a,7] we propose the following reaction pathways for the tandem sulfenylation/cyclization of *N*-arylacrylamides with sulfonyl hydrazides, wherein iodine plays multiple roles as an oxidant, a reductant, and a radical initiator (Scheme 4). Initially, sulfonyl hydrazide **2** reacts with iodine to give sulfinic acid **9** and sulfenyl iodide **11**.[1a] The two intermediates undergo nucleophilic substitution to give thiosulfonate **7**, which is reduced by iodine to give disulfide **8**. Alternatively, thiosulfonate **7** is also generated through reduction of sulfinic acid **9** with iodine. In these steps, iodine is converted to HI and HOI, the two of which react to give water and regenerate iodine. Both thiosulfonate **7** and disulfide **8** are attacked by iodine radical, generated from iodine upon heating,[13] to give sulfenyl radical **13**. Regioselective addition of radical **13** to *N*-arylacrylamide **1** leads to the formation of alkyl radical **14** or **16**, depending on which one is more stable. Cyclization of radical **14**, followed by aromatization, gives 3-(sulfenylmethyl)-oxindole **3**.[7] On the other hand, tandem cyclization/aromatization of radical **16** gives 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-one **4**.[9] However, when R^3 is hydrogen, the conformation required for the cyclization is unfavorable, and consequently, radical **14** prefers to couple with radical **13** to give bisthioether **6**.

In summary, we have developed an unprecedented tandem sulfenylation/cyclization reaction of *N*-arylacrylamides with sulfonyl hydrazides, selectively leading to 3-(sulfenylmethyl)-oxindoles and 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-ones. In the presence of iodine, β-unsubstituted *N*-arylacrylamides underwent sulfenylation with sulfonyl hydrazides, followed by 5-exo-trig cyclization to afford structurally diverse 3-(sulfenyl-methyl)oxindoles in moderate to excellent yields. In contrast, the reaction with β-substituted *N*-arylacrylamides afforded

Scheme 4. Proposed Reaction Pathways



either 3-(sulfenylmethyl)oxindoles or 3-sulfenyl-3,4-dihydroquinolin-2(1*H*)-ones with high regioselectivity depending on the nature of *α*- and *β*-substituents. Preliminary mechanistic studies showed that sulfonyl hydrazides decomposed completely at an early stage to thiosulfonates and disulfides, both of which underwent tandem radical sulfenylation/cyclization with *N*-arylacrylamides at a late stage.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded using tetramethylsilane as an internal reference. Chemical shifts (*δ*) and coupling constants (*J*) were expressed in ppm and Hz, respectively. High-resolution mass spectra (HRMS) were recorded on an LC-TOF spectrometer using electron spray ionization (ESI) techniques. *N*-Arylacrylamides **1**,[14] sulfonyl hydrazides **2** (except **2a**),[15] thiosulfonate **7a**, disulfide **8a**, sulfinic acid **9a**, and compound **2aa**[1a,2b] were prepared according to literature procedures.

General Procedure for the Sulfenylation of *N*-Arylacrylamides with Sulfonyl Hydrazides (Table 2, Scheme 2, and eq 1). A mixture of *N*-arylacrylamide **1** (0.20 mmol), sulfonyl hydrazide **2** (0.24 mmol; for the synthesis of bisthioether **6a**: 0.48 mmol), and iodine (50.8 mg, 0.20 mmol; for the synthesis of oxindole **3x** and dihydroquinolin-2(1*H*)-one **4**: 101.6 mg, 0.40 mmol) in 1,2-dichloroethane (0.50 mL) was heated at 90 °C (oil bath) under air for 24 h. The mixture was cooled to room temperature and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:1 to 1:10), to give oxindole **3**, 3,4-dihydroquinolin-2(1*H*)-one **4**, or bisthioether **6a**. The structure of compounds **3a**, **3x**, and **4a**−**c** was further confirmed by desulfuration (see below). The relative stereochemistry of compounds **4a** and **5a** was assigned by 2D NOESY spectroscopic ananlysis and that of compounds **4b**−**c** was assigned according to the vicinal proton−proton NMR coupling constants.

*1,3-Dimethyl-3-((p-tolylthio)methyl)indolin-2-one (**3a**).* Colorless oil (57.6 mg, 97%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.30−7.27 (m, 1H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02−6.96 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.38 (d, *J* = 12.7 Hz, 1H), 3.33 (d, *J* = 12.7 Hz, 1H), 3.21 (s, 3H), 2.28 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 179.1, 143.4, 136.6, 132.4, 131.2, 129.5, 128.2, 123.3, 122.5, 108.0, 49.1, 43.4, 26.3, 23.0, 21.0; HRMS (ESI) calcd for $C_{18}H_{20}NOS^+$ $(M + H)^+$ 298.1260, found 298.1257.

*1,3-Dimethyl-3-((phenylthio)methyl)indolin-2-one (**3b**).* Colorless oil (50.9 mg, 90%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.30−7.27 (m, 1H), 7.22−7.12 (m, 6H), 7.01−6.95 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.42 (d, *J* = 12.7 Hz, 1H), 3.37 (d, *J* = 12.7 Hz, 1H), 3.21 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 179.0, 143.4, 136.1, 132.3, 130.5, 128.7, 128.3, 126.4, 123.3, 122.5, 108.0, 49.0, 42.8, 26.3, 23.0; HRMS (ESI) calcd for $C_{17}H_{18}NOS^+$ $(M + H)^+$ 284.1104, found 284.1102.

*3-(((4-Methoxyphenyl)thio)methyl)-1,3-dimethylindolin-2-one (**3c**).* Colorless oil (46.9 mg, 75%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.31−7.27 (m, 1H), 7.17−7.10 (m, 3H), 7.02−6.96 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.31 (s, 2H), 3.21 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 179.1, 159.0, 143.5, 133.9, 132.4, 128.2, 126.4, 123.3, 122.5, 114.3, 108.0, 55.3, 49.3, 44.5, 26.3, 23.1; HRMS (ESI) calcd for $C_{18}H_{20}NO_2S^+$ $(M + H)^+$ 314.1209, found 314.1207.

*3-(((4-Fluorophenyl)thio)methyl)-1,3-dimethylindolin-2-one (**3d**).* Colorless oil (48.8 mg, 81%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.31−7.25 (m, 1H), 7.17−7.09 (m, 3H), 7.00−6.94 (m, 1H), 6.90−6.82 (m, 3H), 3.35 (s, 2H), 3.22 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 179.0, 162.0 (d, *J* = 245.3 Hz), 143.5, 133.5 (d, *J* = 8.1 Hz), 132.1, 131.0, 128.3, 122.9 (d, *J* = 69.7 Hz), 115.7 (d, *J* = 21.7 Hz), 108.0, 49.3, 43.9, 26.3, 23.2; HRMS (ESI) calcd for $C_{17}H_{17}FNOS^+$ $(M + H)^+$ 302.1009, found 302.1009.

*3-(((4-Chlorophenyl)thio)methyl)-1,3-dimethylindolin-2-one (**3e**).* Colorless oil (55.8 mg, 88%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.32−7.28 (m, 1H), 7.15−7.07 (m, 5H), 7.01−6.95 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.39 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 3.21 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 178.9, 143.4, 134.6, 132.5, 132.1, 132.0, 128.8, 128.4, 123.2, 122.5, 108.1, 49.1, 43.0, 26.3, 23.1; HRMS (ESI) calcd for $C_{17}H_{17}ClNOS^+$ $(M + H)^+$ 318.0714, found 318.0717.

*3-(((4-Bromophenyl)thio)methyl)-1,3-dimethylindolin-2-one (**3f**).* Colorless oil (60.0 mg, 83%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.47 (d, *J* = 8.4 Hz, 2H), 7.32−7.27 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.02−6.96 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.39 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 3.21 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 178.9, 143.4, 135.3, 132.1, 132.0, 131.7, 128.4, 123.2, 122.5, 120.5, 108.1, 49.1, 42.8, 26.3, 23.1; HRMS (ESI) calcd for $C_{17}H_{17}BrNOS^+$ $(M + H)^+$ 362.0209, found 362.0206.

*3-(((4-Iodophenyl)thio)methyl)-1,3-dimethylindolin-2-one (**3g**).* Colorless oil (73.6 mg, 90%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.47 (d, *J* = 8.4 Hz, 2H), 7.31−7.25 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.01−6.96 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.39 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 3.21 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 178.9, 143.4, 137.6, 136.2, 132.1, 132.0, 128.4, 123.2, 122.6, 108.1, 91.5, 49.0, 42.6, 26.3, 23.1; HRMS (ESI) calcd for $C_{17}H_{17}INOS^+$ $(M + H)^+$ 410.0070, found 410.0064.

*3-((Mesitylthio)methyl)-1,3,5-trimethylindolin-2-one (**3h**).* Colorless oil (59.7 mg, 88%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.06 (d, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 6.80 (s, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 3.19 (s, 3H), 3.11 (d, *J* = 12.2 Hz, 1H), 3.05 (d, *J* = 12.2 Hz, 1H), 2.29 (s, 9H), 2.20 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 179.0, 142.3, 141.1, 137.7, 132.5, 131.9, 130.4, 128.7, 128.4, 123.9, 107.7, 49.0, 42.8, 26.2, 23.5, 21.6, 21.1, 20.9; HRMS (ESI) calcd for $C_{21}H_{26}NOS^+$ $(M + H)^+$ 340.1730, found 340.1727.

*1,3-Dimethyl-3-((naphthalen-1-ylthio)methyl)indolin-2-one (**3i**).* Colorless oil (51.3 mg, 77%); ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 8.23−8.19 (m, 1H), 7.81−7.76 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.49−7.41 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.22−7.18 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.94−6.89 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 12.8 Hz, 1H), 3.41 (d, *J* = 12.8 Hz, 1H), 3.15 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.9, 143.4, 133.9, 133.4, 133.0, 132.3, 130.8, 128.4, 128.1, 126.3, 126.0, 125.4, 123.2, 122.3, 108.1, 49.3, 43.2, 26.2, 23.3; HRMS (ESI) calcd for C$_{21}$H$_{20}$NOS$^+$ (M + H)$^+$ 334.1260, found 334.1257.

1,3-Dimethyl-3-((octylthio)methyl)indolin-2-one ***(3j)***. Colorless oil (32.5 mg, 51%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25−7.18 (m, 2H), 7.03−6.97 (m, 1H), 6.79 (d, J = 7.6 Hz, 1H), 3.17 (s, 3H), 2.95 (d, J = 12.8 Hz, 1H), 2.84 (d, J = 12.8 Hz, 1H), 2.25 (t, J = 7.2 Hz, 2H), 1.37−1.33 (m, 4H), 1.23−1.13 (m, 11H), 0.80 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.6, 143.5, 133.0, 128.2, 123.0, 122.4, 108.0, 31.8, 29.2, 29.1, 28.7, 26.3, 22.9, 22.6, 14.1; HRMS (ESI) calcd for C$_{19}$H$_{30}$NOS$^+$ (M + H)$^+$ 320.2043, found 320.2039.

1,3,5-Trimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3k)***. Colorless oil (52.2 mg, 84%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08−7.01 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H), 6.88 (s, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.35 (d, J = 13.0 Hz, 1H), 3.30 (d, J = 13.0 Hz, 1H), 3.19 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.0, 141.0, 136.4, 132.4, 132.2, 131.9, 131.3, 129.4, 128.3, 124.2, 107.7, 49.3, 43.4, 26.3, 23.1, 21.0; HRMS (ESI) calcd for C$_{19}$H$_{22}$NOS$^+$ (M + H)$^+$ 312.1417, found 312.1415.

5-Methoxy-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3l)***. Colorless oil (59.5 mg, 91%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.07 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.80−6.70 (m, 3H), 3.71 (s, 3H), 3.35 (d, J = 12.8 Hz, 1H), 3.32 (d, J = 12.8 Hz, 1H), 3.19 (s, 3H), 2.27 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.8, 155.9, 136.9, 136.6, 133.6, 132.4, 131.3, 129.4, 112.5, 110.7, 108.2, 55.6, 49.7, 43.5, 26.3, 23.1, 21.0; HRMS (ESI) calcd for C$_{19}$H$_{22}$NO$_2$S$^+$ (M + H)$^+$ 328.1366, found 328.1362.

5-Fluoro-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3m)***. Colorless oil (46.6 mg, 74%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.07 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.93 (dd, J = 8.8, 2.4 Hz, 1H), 6.85 (dd, J = 8.0, 2.4 Hz, 1H), 6.74 (dd, J = 8.4, 4.0 Hz, 1H), 3.34 (d, J = 13.2 Hz, 1H), 3.30 (d, J = 13.2 Hz, 1H), 3.19 (s, 3H), 2.27 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.7, 159.2 (d, J = 239.1 Hz), 139.4, 136.9, 134.0 (d, J = 8.0 Hz), 132.0, 131.4, 129.5, 114.3 (d, J = 23.4 Hz), 111.6 (d, J = 24.7 Hz), 108.3 (d, J = 8.1 Hz), 49.8, 43.3, 26.4, 23.0, 21.0; HRMS (ESI) calcd for C$_{18}$H$_{19}$FNOS$^+$ (M + H)$^+$ 316.1166, found 316.1164.

5-Chloro-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3n)***. Colorless oil (50.3 mg, 76%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (dd, J = 8.4, 2.0 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.98−6.94 (m, 3H), 6.74 (d, J = 8.4 Hz, 1H), 3.32 (s, 2H), 3.19 (s, 3H), 2.28 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.6, 142.0, 137.0, 133.9, 131.9, 131.5, 129.5, 128.0, 127.9, 124.0, 108.8, 49.8, 43.3, 26.3, 23.0, 21.0; HRMS (ESI) calcd for C$_{18}$H$_{19}$ClNOS$^+$ (M + H)$^+$ 332.0870, found 332.0866.

5-Bromo-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3o)***. Colorless oil (71.3 mg, 95%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (dd, J = 8.4, 2.0 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 8.4 Hz, 1H), 3.31 (s, 2H), 3.19 (s, 3H), 2.28 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.5, 142.5, 137.0, 134.2, 131.8, 131.5, 130.8, 129.5, 126.7, 115.2, 109.3, 49.7, 43.3, 26.3 23.0, 21.1; HRMS (ESI) calcd for C$_{18}$H$_{19}$BrNOS$^+$ (M + H)$^+$ 376.0365, found 376.0361.

5-Iodo-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3p)***. Colorless oil (79.5 mg, 94%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (dd, J = 8.4, 2.0 Hz, 1H), 7.22 (d, J = 1.6 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 1H), 3.33 (d, J = 13.2 Hz, 1H), 3.29 (d, J = 13.2 Hz, 1H), 3.19 (s, 3H), 2.30 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.3, 143.2, 137.0, 136.8, 134.5, 132.3, 131.8, 131.5, 129.5, 109.9, 85.1, 49.6, 43.4, 26.3, 23.0, 21.2; HRMS (ESI) calcd for C$_{18}$H$_{19}$INOS$^+$ (M + H)$^+$ 424.0227, found 424.0222.

1,3,7-Trimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3q)***. Colorless oil (51.6 mg, 83%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 (d, J = 8.4 Hz, 2H), 7.05−6.97 (m, 4H), 6.91−6.85 (m, 1H), 3.48 (s, 3H), 3.33 (s, 2H), 2.59 (s, 3H), 2.27 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.8, 141.2, 136.5, 133.0, 132.5, 131.9, 131.2, 129.5, 122.4, 121.1, 119.6, 48.3, 43.7, 29.6, 23.5, 21.0, 19.1; HRMS (ESI) calcd for C$_{19}$H$_{22}$NOS$^+$ (M + H)$^+$ 312.1417, found 312.1412.

5,6-Dimethoxy-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one ***(3r)***. Colorless oil (54.3 mg, 76%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.06 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.66 (s, 1H), 6.49 (s, 1H), 3.94 (s, 3H), 3.72 (s, 3H), 3.32 (s, 2H), 3.22 (s, 3H), 2.27 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.4, 149.5, 145.0, 137.0, 136.6, 132.6, 131.3, 129.4, 123.0, 108.4, 94.1, 56.4, 49.6, 43.7, 29.7, 26.4, 23.2, 21.0; HRMS (ESI) calcd for C$_{20}$H$_{24}$NO$_3$S$^+$ (M + H)$^+$ 358.1471, found 358.1469.

1,3-Dimethyl-1-((p-tolylthio)methyl)-1H-benzo[e]indol-2(3H)-one ***(3s)***. Colorless oil (49.9 mg, 72%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.40−7.35 (m, 1H), 7.31−7.25 (m, 1H), 7.19 (d, J = 8.8 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 3.79 (d, J = 13.0 Hz, 1H), 3.61 (d, J = 13.0 Hz, 1H), 3.31 (s, 3H), 2.14 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 180.3, 136.4, 131.6, 131.2, 130.4, 129.7, 129.6, 129.0, 127.0, 123.5, 123.2, 121.7, 109.4, 51.2, 43.2, 26.5, 23.4, 20.9; HRMS (ESI) calcd for C$_{22}$H$_{22}$NOS$^+$ (M + H)$^+$ 348.1417, found 348.1415.

1,8-Dimethyl-1-((p-tolylthio)methyl)-5,6-dihydro-1H-pyrrolo-[3,2,1-ij]quinolin-2(4H)-one ***(3t)***. Colorless oil (47.2 mg, 70%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 6.77 (s, 1H), 3.76−3.63 (m, 2H), 3.36 (d, J = 12.8 Hz, 1H), 3.30 (d, J = 12.8 Hz, 1H), 2.82−2.67 (m, 2H), 2.27 (s, 3H), 2.22 (s, 3H), 2.07−1.94 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 177.8, 136.7, 136.4, 132.6, 131.4, 131.1, 130.9, 129.4, 127.3, 122.0, 119.7, 50.6, 43.3, 38.9, 24.5, 22.8, 21.4, 21.3, 21.0; HRMS (ESI) calcd for C$_{21}$H$_{24}$NOS$^+$ (M + H)$^+$ 338.1573, found 338.1569.

1-Benzyl-3-methyl-3-((p-tolylthio)methyl)indolin-2-one ***(3u)***. Colorless oil (47.7 mg, 64%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39−7.35 (m, 2H), 7.32−7.22 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.94−6.88 (m, 1H), 6.69 (d, J = 7.6 Hz, 1H), 5.05 (d, J = 15.7 Hz, 1H), 4.83 (d, J = 15.7 Hz, 1H), 3.47 (d, J = 12.7 Hz, 1H), 3.41 (d, J = 12.7 Hz, 1H), 2.27 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.3, 142.5, 136.6, 135.8, 132.6, 132.3, 131.1, 129.5, 128.7, 128.1, 127.5, 127.3, 123.3, 122.5, 109.1, 49.3, 43.9, 43.5, 23.5, 21.0; HRMS (ESI) calcd for C$_{24}$H$_{24}$NOS$^+$ (M + H)$^+$ 374.1573, found 374.1570.

3-(Hydroxymethyl)-1-methyl-3-((p-tolylthio)methyl)indolin-2-one ***(3v)***. Colorless oil (25.0 mg, 40%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35−7.29 (m, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.05−6.97 (m, 3H), 6.88 (d, J = 8.0 Hz, 1H), 3.91 (d, J = 11.2 Hz, 1H), 3.78 (d, J = 11.2 Hz, 1H), 3.53 (d, J = 13.1 Hz, 1H), 3.50 (d, J = 13.1 Hz, 1H), 3.21 (s, 3H), 2.28 (s, 3H), 2.01 (s, br, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 177.9, 144.2, 136.8, 132.1, 131.3, 129.5, 128.9, 128.4, 123.9, 122.7, 108.3, 66.3, 54.5, 38.9, 26.3, 21.0; HRMS (ESI) calcd for C$_{18}$H$_{20}$NO$_2$S$^+$ (M + H)$^+$ 314.1209, found 314.1210.

1,5-Dimethyl-3-phenyl-3-((p-tolylthio)methyl)indolin-2-one ***(3w)***. Colorless oil (72.4 mg, 97%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, J = 7.6 Hz, 1H), 7.22−7.12 (m, 4H), 7.04−6.96 (m, 3H), 6.89−6.85 (m, 3H), 6.70 (d, J = 7.6 Hz, 1H), 3.74 (d, J = 13.2 Hz, 1H), 3.71 (d, J = 13.2 Hz, 1H), 3.12 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 177.0, 141.9, 139.0, 136.6, 132.4, 131.9, 131.5, 130.1, 129.3, 128.8, 128.5, 127.6, 126.9, 126.4, 107.9, 57.2, 43.7, 26.5, 21.1, 20.9; HRMS (ESI) calcd for C$_{24}$H$_{24}$NOS$^+$ (M + H)$^+$ 374.1573, found 374.1569.

1,3,5-Trimethyl-3-(1-(p-tolylthio)ethyl)indolin-2-one ***(3x)***. Obtained as an inseparable mixture of two diastereomers (We failed to determine the diastereomeric ratio by either NMR or HPLC analysis.); Colorless oil (42.9 mg, 66%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37−7.33 (m, 3H), 7.12−7.08 (m, 3H), 6.74 (d, J = 8.0 Hz, 1H), 3.59 (q, J = 6.8 Hz, 1H), 3.20 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H), 1.55 (s, 3H), 0.99 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.3, 141.0, 137.2, 132.4, 132.2, 132.1, 131.6, 129.8, 128.4, 125.3, 107.6, 52.9, 52.4, 26.2, 23.2, 21.3, 21.1, 18.2; HRMS (ESI) calcd for C$_{20}$H$_{24}$NOS$^+$ (M + H)$^+$ 326.1573, found 326.1573.

cis-1,3,6-Trimethyl-4-phenyl-3-(p-tolylthio)-3,4-dihydroquinolin-2(1H)-one ***(4a)***. Colorless oil (51.1 mg, 66%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25−7.13 (m, 5H), 7.12−7.06 (m, 3H), 7.00−6.93 (m, 4H), 4.05 (s, 1H), 3.46 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.5, 140.0, 139.7, 137.1, 137.0, 132.8, 129.7, 129.4, 128.9, 128.6, 128.0, 127.4, 127.3, 127.0, 114.6, 54.7, 54.6, 30.1, 22.4, 21.3, 20.6; HRMS (ESI) calcd for $C_{25}H_{26}NOS^+$ $(M + H)^+$ 388.1730, found 388.1732.

*cis-1,6-Dimethyl-4-phenyl-3-(p-tolylthio)-3,4-dihydroquinolin-2(1H)-one (**4b**).* Colorless oil (61.9 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.35 (m, 2H), 7.27−7.08 (m, 6H), 7.01 (s, 1H), 6.97−6.91 (m, 3H), 4.31−4.29 (m, 1H), 4.14 (d, *J* = 2.0 Hz, 1H), 3.34 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 140.4, 138.3, 137.3, 133.5, 133.2, 130.4, 129.8, 129.4, 129.0, 128.9, 127.3, 127.1, 124.8, 114.9, 54.2, 48.5, 29.8, 21.2, 20.7; HRMS (ESI) calcd for $C_{24}H_{24}NOS^+$ $(M + H)^+$ 374.1573, found 374.1576.

*cis-1,4,6-Trimethyl-3-(p-tolylthio)-3,4-dihydroquinolin-2(1H)-one (**4c**).* Colorless oil (39.8 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.09−7.05 (m, 3H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.80 (d, *J* = 2.0 Hz, 1H), 3.35 (s, 3H), 3.13−3.07 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.22 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 138.1, 136.0, 133.4, 132.9, 129.7, 129.5, 129.0, 128.3, 128.1, 114.8, 53.9, 38.3, 29.7, 21.2, 20.9, 20.7; HRMS (ESI) calcd for $C_{19}H_{22}NOS^+$ $(M + H)^+$ 312.1417, found 312.1419.

*N-Methyl-N-phenyl-2,3-bis(p-tolylthio)propanamide (**6a**).* Colorless oil (27.7 mg, 34%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.21 (m, 1H), 7.20−7.14 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 2H),3.67 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.50 (dd, *J* = 13.6, 11.2 Hz, 1H), 3.30 (s, 3H), 3.07 (dd, *J* = 13.6, 3.2 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 142.9, 138.4, 135.7, 133.7, 131.7, 129.7, 129.5, 129.3, 128.9, 128.8, 127.7, 47.5, 37.7, 35.4, 21.1, 21.0; HRMS (ESI) calcd for $C_{24}H_{26}NOS_2^+$ $(M + H)^+$ 408.1450, found 408.1445.

Desulfuration of Compounds 3a, 3x, and 4a−c. A mixture of compound **3a** (**3x** or **4a**−**c**) (0.20 mmol) and Raney nickel (2.0 g) in ethanol (25 mL) was refluxed for 3 h.[11] After the nickel was filtered and washed with ethanol, the combined filtrate and washing solutions were evaporated under reduced pressure. The residue was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:3 to 1:10), to give oxindole **3aa** (or **3xa**) (known compounds) or 3,4-dihydroquinolin-2(1*H*)-one **5a**−**c**.

*trans-1,3,6-Trimethyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**5a**).* Colorless oil (52.5 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.16 (m, 3H), 7.08 (d, *J* = 9.6 Hz, 1H), 7.03−6.95 (m, 4H), 4.00 (d, *J* = 6.0 Hz, 1H), 3.43 (s, 3H), 3.06−2.97 (m, 1H), 2.25 (s, 3H), 1.14 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 139.3, 137.8, 132.6, 129.5, 129.1, 128.6, 128.3, 128.2, 127.1, 115.2, 48.4, 40.0, 29.8, 20.6, 13.1; HRMS (ESI) calcd for $C_{18}H_{20}NO^+$ $(M + H)^+$ 266.1539, found 266.1539.

*1,6-Dimethyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**5b**).* Colorless oil (50.2 mg, quant.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.30 (m, 2H), 7.28−7.23 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.74 (s, 1H), 4.19 (t, *J* = 7.2 Hz, 1H), 3.37 (s, 3H), 2.94 (d, *J* = 7.2 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 141.3, 138.0, 132.6, 128.9, 128.8, 128.7, 128.3, 127.8, 127.1, 114.8, 41.5, 39.0, 29.6, 20.6; HRMS (ESI) calcd for $C_{17}H_{18}NO^+$ $(M + H)^+$ 252.1383, found 252.1378.

*1,4,6-Trimethyl-3,4-dihydroquinolin-2(1H)-one (**5c**).* Colorless oil (37.8 mg, quant.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 1H), 6.94 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.99−2.89 (m, 1H), 2.64 (dd, *J* = 15.6, 5.2 Hz, 1H), 2.37 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.25 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 137.4, 132.6, 130.9, 127.7, 127.0, 114.7, 39.2, 30.3, 29.4, 20.7, 19.3; HRMS (ESI) calcd for $C_{12}H_{16}NO^+$ $(M + H)^+$ 190.1226, found 190.1228.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02322.

Copies of ^{1}H NMR, ^{13}C NMR, and 2D NOESY spectra for products and EPR analysis (PDF)

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Notes

The authors declare no competing financial interest.

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