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# Synthesis of 3-substituted-4-hydroxyquinoline *N*-oxides from the Baylis–Hillman adducts of *o*-nitrobenzaldehydes

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**Abstract**—The reaction of the Baylis–Hillman adducts **1b–f** derived from *o*-nitrobenzaldehydes in trifluoroacetic acid in the presence of triflic acid (0.2 equiv.) afforded 3-substituted-4-hydroxyquinoline *N*-oxides **2b–e** and **2a** in good to moderate yields. The reaction mechanism was evidenced by the experiment with **1f**, the Baylis–Hillman adduct of 2-nitrobenzaldehyde *N*-tosylimine, as the one involving *N*-hydroxyisoxazoline as the key intermediate. 

The Baylis–Hillman reaction is well known as a coupling reaction of aldehydes and activated alkenes catalyzed by tertiary amines or tertiary phosphines.[1] The versatility of the functionality have made the Baylis–Hillman adducts valuable synthetic intermediates.[1] Besides the usefulness of these Baylis–Hillman adducts themselves, further derivatization with various nucleophilic reagents towards synthetically useful compounds has been studied in depth by us[2] and other groups.[3] Some papers have been reported on the formation of heterocyclic compounds including quinolines and dihydroquinolines from the Baylis–Hillman adducts.[2d,f,3a,b,4]

Recently, we have reported on the synthesis of 3-ethoxycarbonyl-4-hydroxyquinoline *N*-oxides such as **2a** from the easily available Baylis–Hillman adduct **1a** in trifluoroacetic acid (entry 1 in Table 1).[4a] In the reaction we have proposed a mechanism involving *N*-hydroxyisoxazoline intermediate.[4a,5] Another mechanism involving 6π-electrocyclization pathway was also possible and stated therein.[4a,6] However, any experimental evidence for the mechanism has not been suggested. Moreover, variation of the substituent at the 3-position other than ethoxycarbonyl group was impossible. As an example, the Baylis–Hillman adduct of 2-nitrobenzaldehyde and methyl vinyl ketone, **1b**, did not produce the expected 3-acetyl-4-hydroxyquinoline *N*-oxide (**2b**) at all in the same reaction conditions (60–70°C in trifluoroacetic acid) of our previous paper.[4a] Instead, rearranged allylic alcohol derivative **3** was isolated in 22% yield (Scheme 1), as in our previous report on the rearrangement of the Baylis–Hillman adducts.[2g]

In these respects, we examined the reaction conditions for the successful formation of quinoline *N*-oxides containing acetyl or benzenesulfonyl group at the 3-position, and wish to report herein the results. After much trials, we have found appropriate conditions for the formation of **2b** in reasonable yield by increasing the acidity of the reaction medium with catalytic amounts of triflic acid (Scheme 1).[7]

As shown in Table 1, the Baylis–Hillman adducts **1b–f**, which were derived from methyl vinyl ketone, phenyl vinyl sulfone, and ethyl acrylate, respectively, gave the expected quinoline *N*-oxide derivatives **2b–e** and **2a** in good to moderate yields in trifluoroacetic acid in the presence of triflic acid (0.2 equiv.). Without triflic acid the reaction did not afford the corresponding quinoline *N*-oxides at all or low yields of products were formed depending on the substrates.

The mechanism for the formation of quinoline *N*-oxides can be rationalized as we have already proposed (Scheme 2).[4a] The remaining possibility involving electrocyclization pathway can be excluded by the following observations. The Baylis–Hillman adduct **1f**, derived from *N*-tosylimine of 2-nitrobenzaldehyde and ethyl acrylate, afforded 4-hydroxyquinoline derivative **2a** in 81% yield. The results suggested that our proposed reaction mechanism (path a, Scheme 2)[4a] would be more plausible than the 6π-electrocyclization pathway (path b, Scheme 3).[6] As shown in Scheme 2, **2a** can be produced according to the reported mechanism involving the *N*-hydroxyisoxazoline intermediate **II**, whereas the corresponding 3-ethoxycarbonyl-4-tosylamidoquinoline *N*-oxide **2f** would be formed according to the electrocyclization pathway.

The possibility of formation of allylic alcohol derivative such as **1a** from **1f** by the exchange of tosylamido group with trace amounts of moisture present in the reaction

*Keywords*: quinoline *N*-oxides; Baylis–Hillman adducts; *o*-nitrobenzaldehydes; triflic acid.

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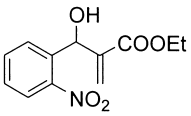
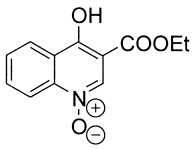
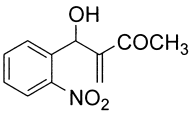
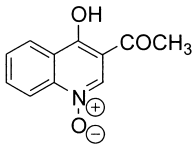
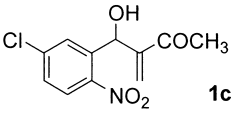
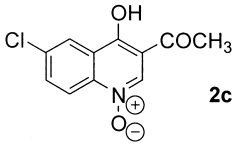
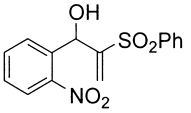
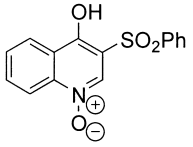
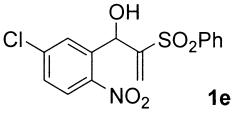
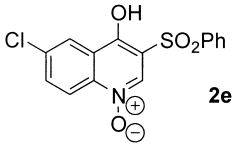
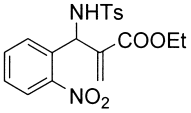
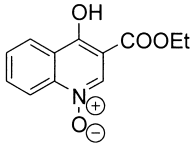
**Table 1**. Synthesis of 3-substituted-4-hydroxyquinoline *N*-oxides **2**

| Entry | B–H adducts (**1**) | Conditions | Products (**2**) | Yield (%) |
|---|---|---|---|---|
| 1 |  **1a** | TFA, 60–70°C, 20 h |  **2a**[4a] | 82 |
| 2 |  **1b** | TFA, TfOH (0.2 equiv.) 30–40°C, 10 h |  **2b** | 78 |
| 3 |  **1c** | TFA, TfOH (0.2 equiv.) 40–50°C, 20 h |  **2c** | 68 |
| 4 |  **1d** | TFA, TfOH (0.2 equiv.) 30–40°C, 10 h |  **2d** | 81 |
| 5 |  **1e** | TFA, TfOH (0.2 equiv.) 30–40°C, 10 h |  **2e** | 49 |
| 6 |  **1f** | TFA, TfOH (0.2 equiv.) 30–40°C, 10 h |  **2a** | 81 |

medium and subsequent transformation toward quinoline ring **2a** could be ruled out by the supplementary experiment shown in Scheme 4. The Baylis–Hillman adduct of benzaldehyde *N*-tosylimine **1g**,[2b] lack of the *ortho*-nitro group, was subjected to the same reaction conditions. As expected we cannot detect nor isolate the allylic alcohol derivatives **4** and **5**.[2g] From the results, we could conclude that the path a is a more reliable one for the formation of quinoline *N*-oxides.

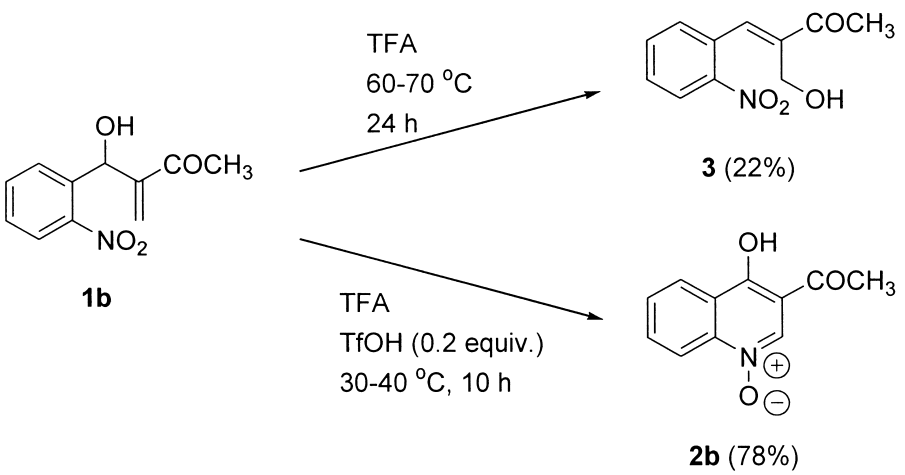
Unfortunately, we could not prepare the corresponding quinoline *N*-oxide from the Baylis–Hillman adduct, 2-[hydroxy-(2-nitrophenyl)methyl]acrylonitrile (**1h**), derived from acrylonitrile, in trifluoroacetic acid with or without triflic acid. Intractable mixtures of products were observed on TLC.

In conclusion, we have disclosed the synthesis of some 3-substituted-4-hydroxyquinoline *N*-oxides **2**. We also found a beneficial experimental evidence for the reaction mechanism.

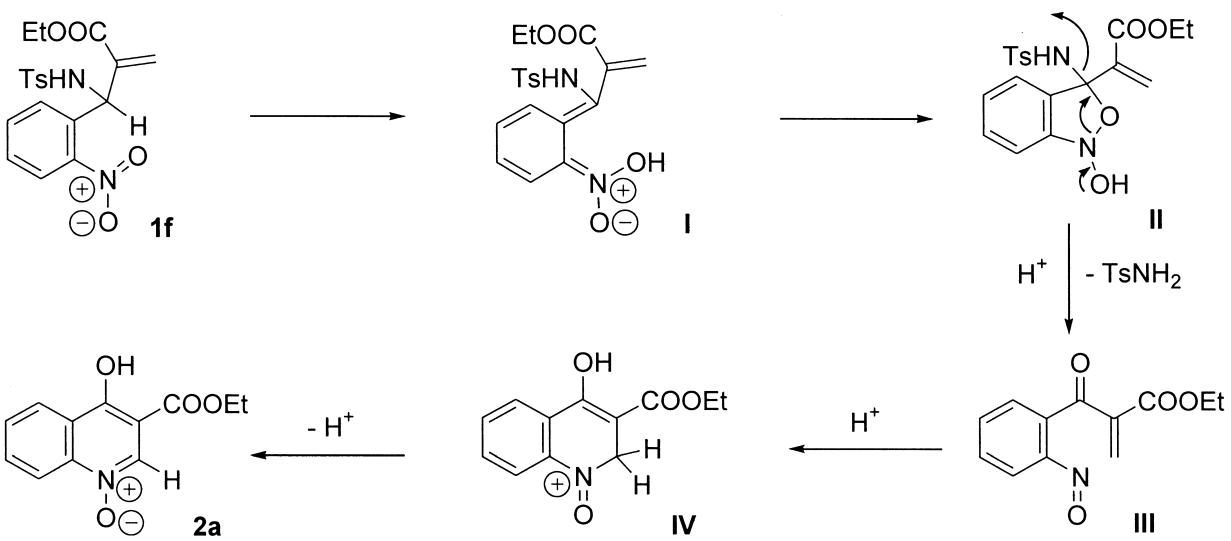
## 1. Experimental

### 1.1. General procedure

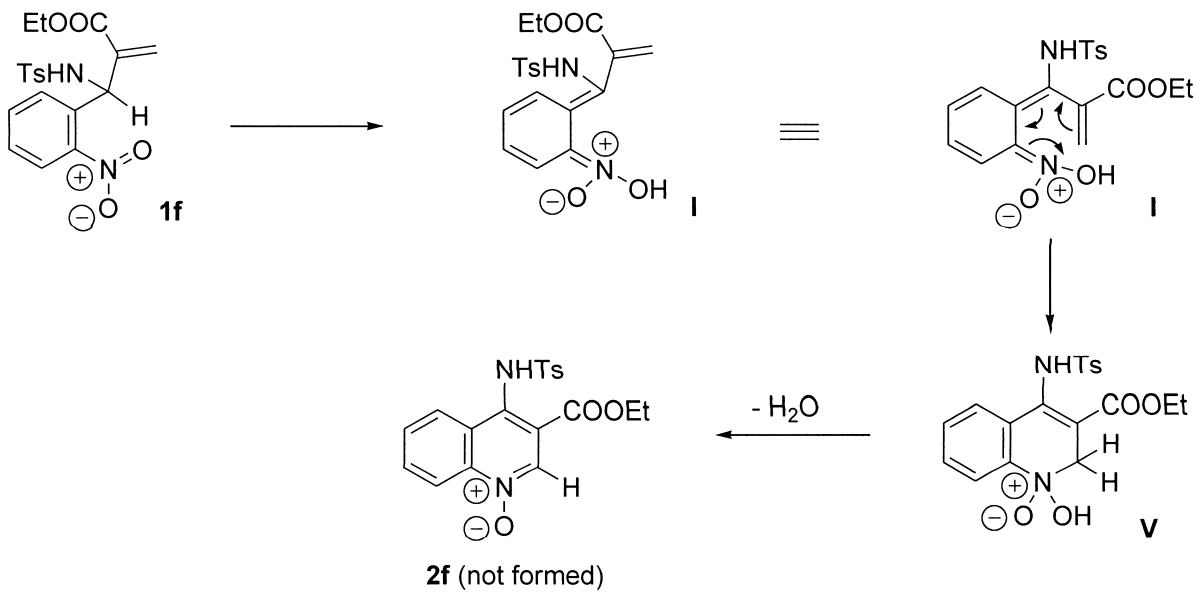
$^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded in $CDCl_3$ and in DMSO-$d_6$. The signal positions are reported in ppm relative to TMS ($\delta$ scale) used as an internal standard. The separations were carried out by flash column chromatography over silica gel (230–400 mesh ASTM). Organic extracts were dried over anhydrous



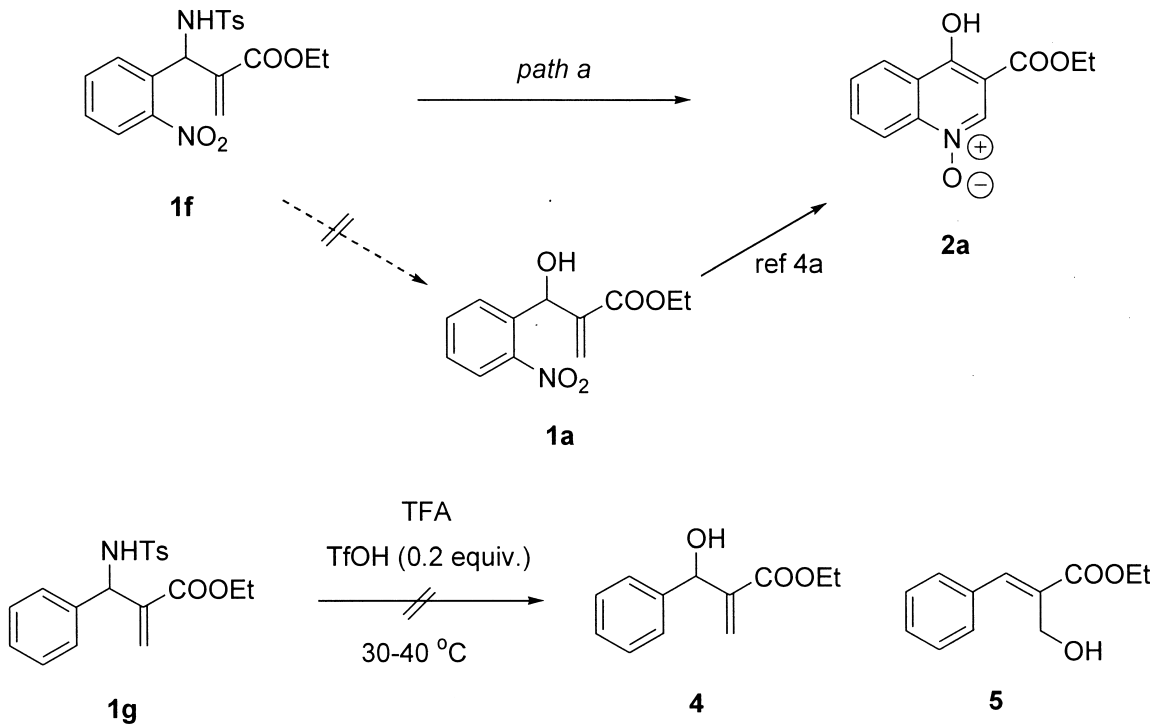

**Scheme 1.**




**Scheme 2.** Mechanism involving *N*-hydroxyisoxazoline (path a).




**Scheme 3.** Mechanism involving electrocyclization process (path b).




**Scheme 4.**

$MgSO_4$ and the solvents were evaporated on a rotary evaporator under water aspirator pressure. IR spectra are reported in $cm^{-1}$. Mass spectra were obtained from the Korea Basic Science Institute (Kwangju branch). Melting points are uncorrected. The combustion analyses were carried out at Korea Research Institute of Chemical Technology, Daejeon, Korea.

### 1.2. General procedure for the synthesis of Baylis–Hillman adducts

General synthetic method of the starting materials was reported previously[4a] and further references cited therein: to a stirred solution of the corresponding *o*-nitrobenzaldehyde (2 mmol) and activated vinyl compounds, ethyl acrylate (0.6 mL), acrylonitrile (0.6 mL), methyl vinyl ketone (0.6 mL), or phenyl vinyl sulfone (2 mmol in 3 mL of THF) was added DABCO (225 mg, 0.2 mmol), and the solution was stirred at rt–70°C for 3–7 days. After the usual workup, pure products **1a–e** and **1h** were obtained by column chromatography on silica gel (hexane/ether, 7:3). *N*-Tosylamido derivative **1f** was prepared from *N*-tosylimine of *o*-nitrobenzaldehyde and ethyl acrylate by the same procedure. Baylis–Hillman adduct **1g** was prepared according to our previous paper.[2b]

**1.2.1. 2-[Hydroxy-(2-nitrophenyl)methyl]acrylic acid ethyl ester (1a).**[4a] Oil; IR (KBr) 3465, 1713, 1528, 1351 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.22 (t, $J$=7.2 Hz, 3H), 3.55 (br s, 1H), 4.17 (qd, $J$=1.2, 7.2 Hz, 2H), 5.74 (s, 1H), 6.19 (s, 1H), 6.38 (s, 1H), 7.47 (t, $J$=7.8 Hz, 1H), 7.65 (t, $J$=7.8 Hz, 1H), 7.76 (d, $J$=7.8 Hz, 1H), 7.95 (d, $J$=7.8 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.99, 61.19, 67.74, 124.57, 126.29, 128.69, 128.92, 133.49, 136.21, 140.88, 148.39, 165.96.

**1.2.2. 3-[Hydroxy-(2-nitrophenyl)methyl]but-3-en-2-one (1b).**[4b] Oil; IR (KBr) 3432, 1723, 1674, 1525, 1350 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.37 (s, 3H), 5.80 (s, 1H), 6.18 (s, 1H), 6.23 (s, 1H), 7.48 (t, $J$=8.1 Hz, 1H), 7.65 (t, $J$=7.8 Hz, 1H), 7.77 (d, $J$=7.8 Hz, 1H), 7.96 (d, $J$=8.1 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.98, 66.03, 123.58, 125.60, 127.48, 127.80, 132.47, 135.60, 146.89, 147.97, 198.77.

**1.2.3. 3-[(5-Chloro-2-nitrophenyl)hydroxymethyl]but-3-en-2-one (1c).** Oil; IR (KBr) 3439, 1676, 1524, 1343 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.39 (s, 3H), 3.42 (br s, 1H), 5.78 (s, 1H), 6.17 (s, 1H), 6.24 (s, 1H), 7.42 (dd, $J$=2.1, 9.0 Hz, 1H), 7.79 (d, $J$=2.1 Hz, 1H), 7.96 (d, $J$=9.0 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 25.92, 67.18, 126.22, 126.53, 128.63, 129.11, 138.72, 140,29, 146,08, 148.60, 199.68.

**1.2.4. 2-Benzenesulfonyl-1-(2-nitrophenyl)prop-2-en-1-ol (1d).** Oil; IR (KBr) 3482, 1525, 1347, 1306, 1160, 1134 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) $\delta$ 6.03 (s, 1H), 6.14 (s, 1H), 6.32 (br s, 1H), 6.47 (s, 1H), 7.44–7.98 (m, 9H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 67.15, 124.78, 127.04, 128.24, 129.22, 129.30, 129.64, 133.81, 133.95, 134.01, 138.32, 147.38, 151.09.

**1.2.5. 2-Benzenesulfonyl-1-(5-chloro-2-nitrophenyl)-prop-2-en-1-ol (1e).** Oil; IR (KBr) 3479, 1603, 1571, 1525, 1342, 1306, 1163 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.08 (br s, 1H), 5.60 (s, 1H), 6.01 (s, 1H), 6.44 (s, 1H), 7.32–7.84 (m, 8H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 67.01, 126.38, 127.19, 128.27, 129.36, 129.38, 129.75, 134.15, 136.00, 137.99, 140.82, 145.35, 150.44.

**1.2.6. 2-[(2-Nitrophenyl)(toluene-4-sulfonylamino)-methyl]acrylic acid ethyl ester (1f).** White solid; mp 99–100°C; IR (KBr) 1720, 1528, 1349, 1161 $cm^{-1}$; $^1H$

NMR ($CDCl_3$) $\delta$ 1.07 (t, $J$=7.1 Hz, 3H), 2.31 (s, 3H), 3.90–4.01 (m, 2H), 5.61 (s, 1H), 5.97 (d, $J$=8.8 Hz, 1H), 6.03 (d, $J$=8.8 Hz, 1H), 6.14 (s, 1H), 7.14 (d, $J$=8.5 Hz, 2H), 7.30 (t, $J$=8.1 Hz, 1H), 7.43 (t, $J$=6.8 Hz, 1H), 7.57 (d, $J$=6.8 Hz, 1H), 7.61 (d, $J$=8.5 Hz, 2H), 7.74 (d, $J$=8.1 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.84, 21.45, 54.47, 61.28, 124.84, 127.16, 128.65, 128.73, 129.50, 130.13, 133.00, 133.38, 137.23, 137.50, 143.53, 148.09, 165.00.

**1.2.7. 2-[Hydroxy-(2-nitrophenyl)methyl]acrylonitrile (1h).**[4c] Oil; IR (KBr) 3439, 2228, 1526, 1348 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.70 (br s, 1H), 6.02 (s, 1H), 6.14 (s, 1H), 6.17 (s, 1H), 7.56 (t, $J$=7.7 Hz, 1H), 7.74 (t, $J$=7.7 Hz, 1H), 7.86 (d, $J$=8.1 Hz, 1H), 8.04 (d, $J$=8.1 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 68.48, 116.56, 124.06, 124.73, 128.70, 129.41, 132.34, 134.01, 134.27, 147.31.

### 1.3. General procedure for the synthesis of 4-hydroxyquinoline *N*-oxides

To a stirred solution of **1b** (221 mg, 1 mmol) in trifluoroacetic acid (2 mL) was added triflic acid (30 mg, 0.2 mmol) at rt, and warmed to 30–40°C during 10 h. After cooling to rt, the reaction mixture was poured into water and extracted with chloroform (2×30 mL). The organic layers were dried ($MgSO_4$) and evaporated to give crude **2b**. Column chromatography on silica gel ($CH_2Cl_2$/MeOH, 14:1) afforded analytically pure **2b** as a white solid, 158 mg (78%). Other compounds were synthesized analogously.

**1.3.1. 1-(4-Hydroxy-1-oxyquinolin-3-yl)ethanone (2b).** 78%; mp 209–210°C; IR (KBr) 3099, 2528, 1672, 1609, 1527, 1451 cm$^{-1}$; $^1$H NMR (DMSO-$d_6$) $\delta$ 2.61 (s, 3H), 7.50–7.56 (m, 1H), 7.83–7.86 (m, 2H), 8.27 (d, $J$=8.1 Hz, 1H), 8.60 (s, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 31.22, 115.61, 115.84, 125.85, 126.36, 128.32, 133.30, 139.16, 143.79, 173.77, 195.50; ESI MS *m/z* calcd for $C_{11}H_9NO_3$ 203.0, positive mode 226.0 $[M+Na]^+$. Anal. calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 65.12; H, 4.48; N, 6.78.

**1.3.2. 1-(6-Chloro-4-hydroxy-1-oxyquinolin-3-yl)ethanone (2c).** 68%; mp 228–230°C; IR (EtOH) 3427, 2975, 2928, 1674, 1599 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.60 (s, 3H), 7.88 (d, $J$=1.5 Hz, 2H), 8.18 (t, $J$=1.5 Hz, 1H), 8.60 (s, 1H), 12.94 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 31.05, 116.22, 118.14, 125.31, 129.40, 130.62, 133.19, 137.84, 143.97, 172.50, 195.15; FAB Mass 238 ($M^+$+1). Anal. calcd for $C_{11}H_8ClNO_3$: C, 55.60; H, 3.39; N, 5.89. Found: C, 55.57; H, 3.41; N, 5.80.

**1.3.3. 3-Benzenesulfonyl-1-oxyquinolin-4-ol (2d).** 81%; mp 289–290°C; IR (KBr) 3101, 2740, 1607, 1532, 1311, 1291, 1138 cm$^{-1}$; $^1$H NMR (DMSO-$d_6$) $\delta$ 7.50–7.66 (m, 4H), 7.85–7.90 (m, 2H), 8.02–8.12 (m, 3H), 8.84 (s, 1H), 12.90 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 116.16, 116.72, 125.88, 126.44, 127.15, 128.26, 129.12, 133.55, 134.13, 139.95, 141.38, 143.17, 170.20; ESI MS *m/z* calcd for $C_{15}H_{11}NO_4S$ 300.9, positive mode 323.9 $[M+Na]^+$. Anal. calcd for $C_{15}H_{11}NO_4S$: C, 59.79; H, 3.68; N, 4.65. Found: C, 59.59; H, 3.80; N, 4.64.

**1.3.4. 3-Benzenesulfonyl-6-chloro-1-oxyquinolin-4-ol (2e).** 49%; mp 294–296°C; IR (EtOH) 3446, 1725, 1525 cm$^{-1}$; $^1$H NMR (DMSO-$d_6$) $\delta$ 7.54–7.66 (m, 3H), 7.87–7.90 (m, 2H), 8.00–8.05 (m, 3H), 8.85 (s, 1H);$^{13}$C NMR (DMSO-$d_6$) $\delta$ 67.01, 126.38, 127.19, 128.27, 129.36, 129.38, 129.75, 134.15, 136.00, 137.99, 140.82, 145.35, 150.44; FAB Mass 336 ($M^+$+1). Anal. calcd for $C_{15}H_{10}ClNO_4S$: C, 53.66; H, 3.00; N, 4.17. Found: C, 53.41; H, 3.15; N, 4.20.

**1.3.5. 3-Hydroxymethyl-4-(2-nitrophenyl)but-3-en-2-one (3).** Oil; IR (KBr) 3486, 1661, 1517, 1340, 1233 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.54 (s, 3H), 2.74 (br s, 1H), 4.24 (s, 2H), 7.56–7.77 (m, 3H), 7.97 (s, 1H), 8.24 (d, $J$=8.7 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.90, 57.77, 125.17, 130,06, 130.64, 131.83, 134.03, 139.52, 140.15, 147.28, 201.31.

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6. The possibility of 6π-electrocyclization was suggested by one of the reviewers during the course of evaluation of Ref. 4a. The possibility of thermal electrocyclization pathway was examined with **1a** and **1b** at around 220°C in diphenyl ether. However, no reaction was observed.
7. Scrutinizing the reaction mechanism that have proposed in our previous paper,[4a] we think the acidity of the reaction medium might play an important role for the formation of quinoline *N*-oxides.