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Metal-Free Radical Oxidative Cyclization of *o*-Azidoaryl Acetylenic Ketones with Sulfinic Acids To Access Sulfone-Containing 4-Quinolones

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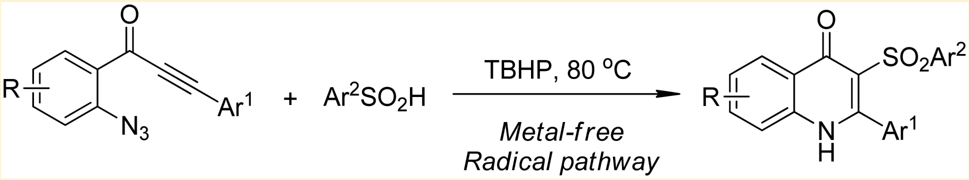
Supporting Information



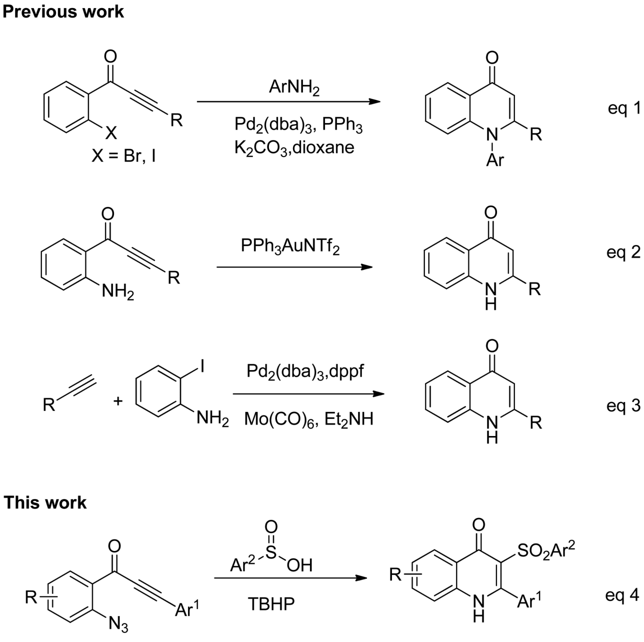
ABSTRACT: A novel one-pot synthesis of sulfone-containing 4-quinolones with easily available sulfinic acids as sulfonylating precursors is described. This reaction is characterized by mild reaction conditions, high functional-group tolerance and amenability to gram-scale synthesis.

INTRODUCTION

4-Quinolone skeleton has been widely found in natural products and pharmaceuticals[1] and biologically active molecules for antimitotic,[2] antimalarial,[3] anticancer,[4] xanthine oxidase, and cathepsins inhibitory activities.[5] Therefore, the efficient synthesis of 4-quinolones has attracted interest of chemists and pharmacologists.[6] In recent decades, many methods have been established in the construction of 4-quinolone framework. As is well-known, classical methods, such as Niementowski,[7] Conrad−Limpet,[8] and Camps cyclizations,[9] are based on cyclocondensation, which suffered from harsh reaction conditions and unavailability of starting materials. Recently, transition-metal-catalyzed synthesis of 4-quinolone derivatives has become a useful strategy.[10] Among selected elegant examples, Xu group employed a Pd-catalyzed addition reaction of *o*-azidoaryl acetylenic ketones and primary amines to provide 4-quinolones in 2010[10f] (Scheme 1, eq 1). Then, Helaja reported a gold-catalyzed intermolecular addition of amine to alkynes to form various 4-quinolones[10h] (Scheme 1, eq 2). Recently, Larhed described a Pd-catalyzed synthesis of 4-quinolones from 2-iodoanilines, alkynes and molybdenum hexacarbonyl[10g] (Scheme 1, eq 3). Although significant achievements have been made, a milder and more efficient method for the synthesis of functionalized 4-quinolones is still in demand.

Because of the unique chemical properties and biological activities of sulfones, construction of sulfone-containing molecules has an important effect on the design of lead compounds in agrochemicals and materials chemistry.[11] Consequently, a large number of methods for the incorporation of sulfonyl group have been extensively researched in the past decades.[12] Arylsulfinic acids are versatile, easy to handle, and have been widely used as sulfonylation reagents for the preparation of organosulfones.[13] However, to our best knowledge, a method for construction of molecules bearing both a 4-quinolone motif and a sulfonyl group was rarely reported.[14] Based on the importance of the sulfonyl group and

Scheme 1. Construction of 4-Quinolones Derivatives



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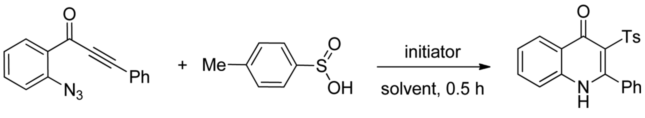
our continuing interest in the synthesis of heterocyclic scaffolds frameworks,[15] herein, we report a novel *tert*-butyl hydroperoxide (TBHP) initiated difunctionalization of alkynes with sulfinic acids via C−N and C−S bond formation for the synthesis of 3-sulfonated 4-quinolones under metal-free conditions (Scheme 1, eq 4).

RESULTS AND DISCUSSION

Initially, the reaction of 1-(2-azidophenyl)-3-phenylprop-2-yn-1-one (**1a**) with *p*-tolylsulfinic acid (**2a**) in the presence of the radical initiator azodiisibutyronitrile (AIBN) was examined. To our delight, the desired 2-phenyl-3-tosylquinolin-4(1H)-one (**3aa**) was obtained in 72% yield (Table 1, entry 1). After screening a series of radical initiators, such as di-*tert*-butyl peroxide (DTBP), *tert*-butyl hydroperoxide (TBHP), and *tert*-butyl peroxybenzoate (TBPB), *tert*-butyl hydroperoxide (TBHP) was found to be the most efficient (Table 1, entry 3). By increasing the amount of TBHP to 0.4 equiv, the yield of **3aa** was increased to 90% (Table 1, entry 6). Among the solvents screened such as EtOH, toluene, DMF, DMSO, and DMA, CH_3CN was proven to be the best choice for this reaction (Table 1, entries 7−11). There is no influence on reaction yield when the amount of TBHP was further increased (Table 1, entries 12−13). In the following study, 2 equiv was found to be the ideal amount of *p*-tolylsulfinic acid **2a** (Table 1, entries 14−15). Consequently, the optimum reaction conditions were determined to be TBHP (0.4 equiv) in CH_3CN at 80 °C under Ar for 0.5 h (Table 1, entry 6).

Table 1. Optimization of Reaction Condition[a]



1a **2a** **3aa**

entry	initiator	t (°C)	solvent	yield(%)[b]
1	AIBN(0.2 equiv)	80	MeCN	72
2[c]	TBHP(0.2 equiv)	80	MeCN	67
3	TBHP(0.2 equiv)	80	MeCN	76
4	DTBP(0.2 equiv)	100	MeCN	62
5	TBPB(0.2 equiv)	80	MeCN	65
6	TBHP(0.4 equiv)	80	MeCN	90
7	TBHP(0.4 equiv)	80	EtOH	83
8	TBHP(0.4 equiv)	80	toluene	76
9	TBHP(0.4 equiv)	80	DMF	81
10	TBHP(0.4 equiv)	80	DMSO	83
11	TBHP(0.4 equiv)	80	DMA	80
12	TBHP(0.5 equiv)	80	MeCN	91
13	TBHP(0.6 equiv)	80	MeCN	87
14[d]	TBHP(0.4 equiv)	80	MeCN	0
15[e]	TBHP(0.4 equiv)	80	MeCN	35

[a] All reactions were carried out by using **1a** (0.2 mmol), **2a** (2.0 equiv), TBHP (5−6 M in decane), and solvent (1 mL) under argon (1 atm) and stirred for 0.5 h, except as noted. [b] Isolated yield. [c] TBHP (70% aqueous). [d] **2a** (1.2 equiv) was used. [e] **2a** (1.5 equiv) was used.

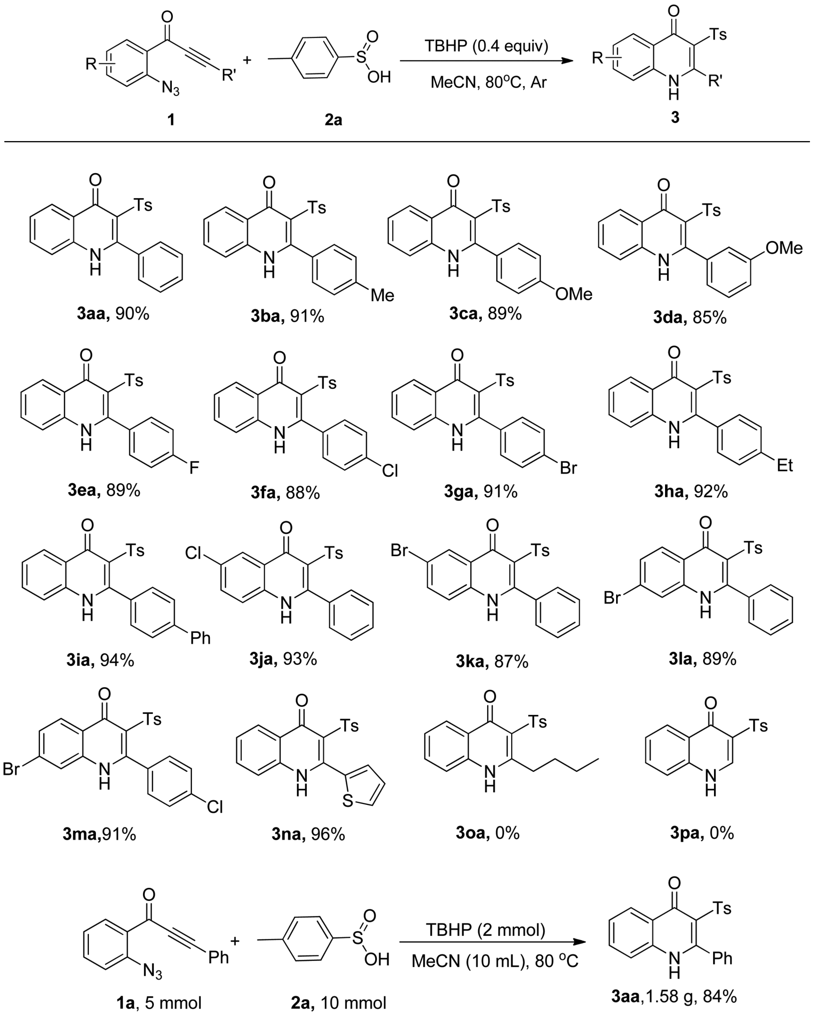
With the optimized conditions in hand (Table 1, entry 6), we then studied the scope of the cyclization of *p*-tolylsulfinic acid with a series of *o*-azidoaryl acetylenic ketones, as shown in Table 2. First, we examined the effect of the substitution pattern on the aryl ring attached to the triple bond. Both electron-donating (**1b**−**1d**) and electron-withdrawing (**1e**−**1g**) groups on the aromatic ring produced the corresponding 3-tosylquinolin-4(1H)-ones in good yields. The structure of **3fa** was confirmed by single-crystal X-ray analysis (see the Supporting Information). Other substitution pattern of the aryl ring directly bound to the triple bond such as 4-phenyl and 4-ethyl were also tolerated well in this process and smoothly converted into products **3ha** and **3ia** in 92 and 94% yields, respectively. Then, functional groups on the aromatic ring of the arylazide moiety, such as chloro and bromo groups, were examined and gave the corresponding products **3ja**−**3la** in 87−93% yields. When benzene rings were both substituted, the desired product **3ma** was formed in 91% yield. In addition, a substrate with thiophene attached to the triple bond (**1n**) could also provide the expected product in 96% yield. Unfortunately, there was no desired product detected when R′ in **1** was an atom H or an alkyl group *n*-C_4H_9. To further show the practical application of this method, 1-(2-azidophenyl)-3-phenylprop-2-yn-1-one (**1a**, 5 mmol) was employed in a gram-scale reaction and delivered **3aa** in 84% yield.

Next, the reactions of various sulfinic acids with 1-(2-azidophenyl)-3-phenylprop-2-yn-1-one **1a** were examined (Table 3). We were pleased to find that benzenesulfinic acid was able to furnish the desired product, 2-phenyl-3-(phenylsulfonyl) quinolin-4(1H)-one (**3ab**), in 88% yield. Gratifyingly, arylsulfinic acids **2**, bearing either electron-donating (MeO and *t*Bu) or electron-withdrawing (Br) groups at the 2 or 4 positions of the aromatic ring were compatible with the optimized conditions (**3ac**−**3af**). However, 2-bromobenzenesulfinic acid reacted with **1a** to afford **3ad** in 67% yield, suggesting that the reaction was influenced by the steric effect. Moreover, 2-naphthylsulfinic acid was also suitable for this conversion to give the corresponding desired product **3ag** in good yield (80%). Unfortunately, the aliphatic sulfinic acid, such as methanesulfinic acid, failed to react under the optimized reaction conditions.

4-Quinolone skeleton is a common-structure unit in organic synthesis. Further transformations of 4-quinolone can be used to prepare many important potentially bioactive molecules or important organic synthetic intermediates. As exemplified in Scheme 2, **3aa** can be easily converted to 1-methyl-2-phenyl-3-tosylquinolin-4(1H)-one (**4**) in 86% yield when reacted with iodomethane and NaH.

In order to understand the reaction mechanism, radical-trapping experiments were carried out. When the reaction was conducted with a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT), the reaction was substantially inhibited, suggesting that the reaction involves a radical process. On the base of the above-mentioned experiments and literature reports,[13d] two possible pathways may be involved in this reaction: (a) radical chain propagation mechanism; (b) radical−radical coupling mechanism. In path **a**, the initiate step begin with the reaction of sulfinic acid **2** with TBHP to generate the corresponding I, which could be resonating with sulfonyl radical **II**. Subsequently, the sulfonyl radical **II** adds to the alkynyl moiety of substrate **1a** to afford the vinyl radical **III**, which undergoes rapid intramolecular cyclization to give the N-radical intermediate **IV**. The N-radical **IV** could undergo hydrogen abstraction (HAT) from sulfinic acid to give the desired product **3** and regenerate radical **II** (propagation step). The radical−radical coupling pathway (path **b**) may be also possible in this reaction. First, nitrene intermediate **V** formed from substrate **1a** by releasing N_2 under heating condition. Then, the

Table 2. Synthesis of 2-Aryl-3-tosylquinolin-4(1H)-one Derivatives[a]



3aa, 90%; **3ba**, 91%; **3ca**, 89%; **3da**, 85%

3ea, 89%; **3fa**, 88%; **3ga**, 91%; **3ha**, 92%

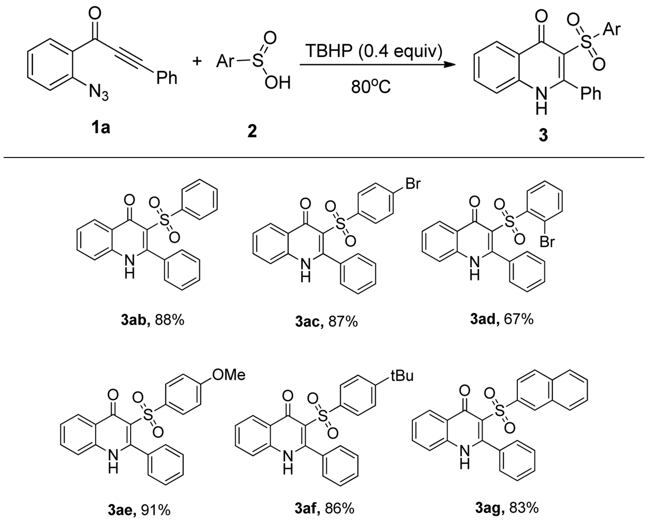
3ia, 94%; **3ja**, 93%; **3ka**, 87%; **3la**, 89%

3ma,91%; **3na**, 96%; **3oa**, 0%; **3pa**, 0%

1a, 5 mmol; **2a**, 10 mmol; **3aa**,1.58 g, 84%

[a]Reaction conditions: **1** (0.2 mmol), *p*-tolylsulfinic acid (2 equiv), and TBHP (0.4 equiv) in CH_3CN (1 mL) at 80 °C under an argon atmosphere for 0.5 h. Yields are given for isolated products.

Table 3. Scope of Sulfinic Acids[a]

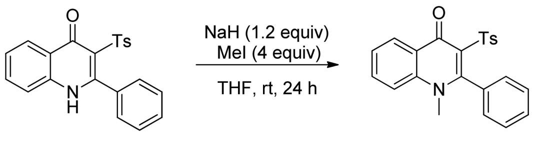


3ab, 88%; **3ac**, 87%; **3ad**, 67%

3ae, 91%; **3af**, 86%; **3ag**, 83%

[a]Reaction conditions: **1a** (0.2 mmol), **2** (2 equiv), and TBHP (0.4 equiv) in CH_3CN (1 mL) at 80 °C under an argon atmosphere for 0.5 h. Yields are given for isolated products.

Scheme 2. Follow-up Transformation of 3aa



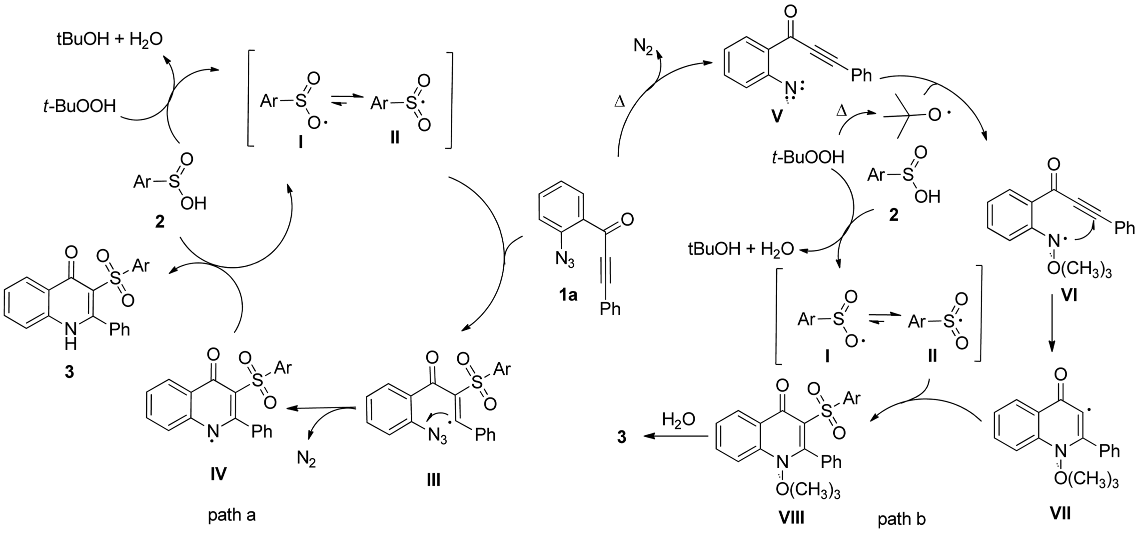
3aa **4**

nitrene intermediate **V** reacts with *tert*-butoxy radical to generate the intermediate **VI**,[16] which immediately undergoes intramolecular cyclization to yield the intermediate **VII**. The intermediate **VII** goes through cross-coupling with sulfonyl radical **II** to yield the intermediate **VIII**, which then hydrolyzed into product **3** (Scheme 3).

■ CONCLUSION

In summary, we have disclosed a method for TBHP-initiated cascade of S-central radical addition and cyclization of *o*-azidoaryl acetylenic ketones with sulfinic acids, providing direct access to various 3-sulfonated 4-quinolones. This new method is a mild, environmentally benign system and applicable to gram scale synthesis.

Scheme 3. Plausible Mechanism



EXPERIMENTAL SECTION

General Information. All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Sulfinic acids **2a**−**2g** were synthesized according to the literature.[17] ^{1}H NMR, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. High-resolution mass spectra were obtained on a high-resolution mass spectrometer in the ESI mode.

General Procedure for the Synthesis of *o*-Azidoaryl Acetylenic Ketones 1a−1i, 1n−1p.[18]

(1) Sodium azide (0.72 g, 11 mmol) was added to a stirring solution of 2-nitrobenzaldehydes (0.8 g, 5 mmol) in HMPA (15 mL) at 0 °C. The water bath was allowed to warm to ambient temperature and monitored by TLC. After the reaction was finished, the mixture extracted with methyl *tert*-butyl ether. The organic phase was washed with water, concentrated in vacuo, dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel using petroleum ether−ethyl acetate mixture as eluent (96:4 v/v).

(2) To a solution of phenylacetylene (1.1 equiv) in dry THF (15 mL) at 0 °C was added *n*-BuLi (2.5 M solution in hexane, 1.1 equiv) dropwise. The reaction mixture was stirred at −78 °C for 30 min. A solution of ortho-azidobenzaldehydes (1 equiv) in THF (10 mL) was then added slowly and stirred for 3 h. Saturated ammonium chloride was added in the mixture at room temperature. The THF layer was separated and the aqueous one was further extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was directly used in the next step without further purification.

(3) To a solution of the crude *o*-azidoaryl acetylenic alcohols in Et_2O (20 mL), the Jones' reagent (4 mL) was added dropwise slowly at 0 °C for 0.5 h. The mixture was allowed to warm to room temperature and stirred 1 h. After completion, the reaction was quenched with H_2O and extracted with Et_2O. The organic extracts were washed with brine, dried, and concentrated in vacuo. Purification of the residue was performed by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (40:1 v/v) to give the pure product.

1-(2-Azidophenyl)-3-phenylprop-2-yn-1-one (***1a***). Yellow solid; (0.753g, 61%); mp: 62−65 °C; R_f = 0.51 (hexanes/ethyl acetate 40:1);^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.67−7.65 (m, 2H), 7.62−7.58 (m, 1H), 7.51−7.46 (m, 1H), 7.44−7.40 (m, 2H), 7.30−7.25 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.1, 140.2, 134.2, 133.1, 130.8, 128.9, 128.7, 124.6, 120.1, 93.3, 88.3 ppm. MS m/z (relative intensity, %): 247 (0.9), 219 (20.6), 218 (6.4), 217 (100), 216 (16.2), 198 (21.5), 196 (24.8), 182 (14.5), 154 (10.2), 126 (32.1).

1-(2-Azidophenyl)-3-(p-tolyl)prop-2-yn-1-one (***1b***). Yellow solid; (0.717g, 55%); mp: 76−78 °C; R_f = 0.52 (hexanes/ethyl acetate 40:1);^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.61−7.54 (m, 3H), 7.29−7.21 (m, 4H), 2.40 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.1, 141.6, 140.1, 134.1, 133.1, 133.0, 129.5, 129.0, 124.5, 120.1,117.0, 94.1, 88.2, 21.8 ppm. MS m/z (relative intensity, %): 261 (5.8), 246 (20.6), 245 (17.4), 244 (100.0), 230 (16.2), 216 (26.5), 202 (14.8), 184 (7.5), 168 (30.2), 78 (22.1).

1-(2-Azidophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (***1c***). Yellow solid; (0.803g, 58%); mp: 78−81 °C; R_f = 0.51 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.63−7.56 (m, 3H), 7.30−7.25 (m, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.1, 161.8, 140.0, 135.2, 134.0, 132.9, 129.2, 124.5, 120.1, 114.4, 111.9, 94.6, 88.4, 55.4 ppm. MS m/z (relative intensity, %): 277 (14.5), 262 (20.6), 249 (14.6), 248 (100), 247 (16.2), 232 (26.5), 218 (14.8), 202 (14.5), 184 (20.2), 92 (22.1).

1-(2-Azidophenyl)-3-(3-methoxyphenyl)prop-2-yn-1-one (***1d***). Yellow solid; (0.623g, 45%); mp: 80−84 °C; R_f = 0.60 (hexanes/ethyl acetate 40:1);^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.62−7.58 (m, 1H), 7.34−7.24 (m, 4H), 7.16 (d, J = 0.8 Hz, 1H),7.04−7.02 (m, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.0, 159.4, 140.2, 134.2, 133.1, 129.7, 128.8, 125.5, 124.5,121.0, 120.1, 117.6, 117.5, 93.2, 87.9, 55.4 ppm. MS m/z (relative intensity, %): 277 (6.5), 262 (30.6), 246 (100.0), 235 (60.6), 244 (16.2), 230 (6.5), 216 (14.8), 186 (34.5), 172 (7.2), 86 (32.1).

1-(2-Azidophenyl)-3-(4-fluorophenyl)prop-2-yn-1-one (***1e***). Yellow solid; (0.742g, 56%); mp: 82−84 °C; R_f = 0.53 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.68−7.64 (m, 2H), 7.63−7.58 (m, 1H), 7.30−7.25 (m, 2H),7.15−7.09 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 175.9, 164.1 (d, J = 252.1 Hz), 140.2, 135.4, 135.3, 134.3, 133.0, 128.8, 124.6, 116.2 (d, J = 28.2 Hz), 92.3, 88.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): −105.95; MS m/z (relative intensity, %): 265 (4.5), 246 (20.6), 245 (100.0), 231 (60.6), 217 (26.2), 203 (26.5), 185 (24.8), 161 (4.5), 60 (22.1).

1-(2-Azidophenyl)-3-(4-chlorophenyl)prop-2-yn-1-one (***1f***). Yellow solid; (0.871, 62%); mp: 86−88 °C; R_f = 0.52 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.14 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.62−7.56 (m, 3H), 7.41−7.39 (m, 2H), 7.30−7.25 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 175.8, 140.3, 137.2, 134.4, 134.2, 133.0, 129.1, 128.7, 124.6, 120.1, 118.6, 91.8, 89.0 ppm. MS m/z (relative intensity, %): 281 (18.5), 245 (20.6), 244 (100.0), 243 (60.6), 229 (16.2), 215 (26.5), 201 (14.8), 185 (14.5), 169(20.2), 154 (22.1).

*1-(2-Azidophenyl)-3-(4-bromophenyl)prop-2-yn-1-one (**1g**).* Yellow solid; (1.05g, 65%); mp: 85−88 °C; R_f = 0.51 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.14 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.61−7.50 (m, 5H), 7.30−7.25 (m, 2H), ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 175.8, 140.3, 134.4, 134.3, 133.0, 132.1, 128.7, 125.6, 124.6, 120.1, 119.1, 91.9, 89.1 ppm. MS m/z (relative intensity, %): 326 (2.9), 324 (3.2), 298 (4.7), 296 (4.6), 228 (14.7), 227 (100.0), 225 (5.4), 201 (14.5), 200 (20.2), 101 (22.1).

*1-(2-Azidophenyl)-3-(4-ethylphenyl)prop-2-yn-1-one (**1h**).* Yellow solid; (0.866g, 63%); mp: 81−84 °C; R_f = 0.57 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.17 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.59−7.57 (m, 3H), 7.30−7.24 (m, 4H), 2.70 (q, J = 14.8 Hz, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 176.2, 147.8, 140.1, 134.1, 133.2, 133.1, 129.0, 128.3, 124.5, 120.1, 117.2, 94.1, 88.2, 29.0, 15.1 ppm. MS m/z (relative intensity, %): 275 (24.5), 248 (20.6), 247 (100.0), 246 (60.6), 245 (16.2), 244 (26.5), 234 (14.8), 220 (14.5), 219 (20.2), 170 (22.1).

*3-([1,1′-Biphenyl]-4-yl)-1-(2-azidophenyl)prop-2-yn-1-one (**1i**).* Yellow solid; (1.06g, 66%); mp: 87−91 °C; R_f = 0.54 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.17 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.70−7.68 (m, 2H), 7.62−7.57 (m, 5H), 7.46−7.42 (m, 2H), 7.38−7.35 (m, 1H), 7.27−7.24 (m, 1H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 175.9, 143.5, 140.0, 139.5, 134.1, 133.5, 133.0, 128.9, 128.7, 128.1, 127.2, 127.0, 124.5, 120.1, 118.7, 93.3, 88.9 ppm. MS m/z (relative intensity, %): 323 (18.5), 296 (20.6), 295 (100.0), 294 (60.6), 293 (16.2), 292 (26.5), 282 (14.8), 268 (14.5), 267 (20.2), 218(22.1).

*1-(2-Azidophenyl)-3-(thiophen-2-yl)prop-2-yn-1-one (**1n**).* Yellow solid; (0.518g, 41%); mp: 37−39 °C; R_f = 0.62 (hexanes/ethyl acetate 40:1)^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.10 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.62−7.53 (m, 3H), 7.30−7.25 (m, 2H), 7.10 (dd, J = 5.2 Hz, J = 4.0 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 175.4, 140.2, 136.8, 134.2, 132.7, 131.9, 128.7, 127.8, 124.6, 120.1, 120.0, 93.3, 87.5 ppm. MS m/z (relative intensity, %): 253 (18.6), 226 (12.9), 225 (64.2), 224 (100.0), 198 (9.2), 197 (8.0), 181 (10.4), 180 (10.1), 154 (6.4), 113 (9.8).

*1-(2-Azidophenyl)hept-2-yn-1-one (**1o**).* Yellow oil; (0.579g, 51%); R_f = 0.46 (hexanes/ethyl acetate 40:1);^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.08 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.56−7.54 (m, 1H), 7.27−7.21 (m, 2H), 2.48 (t, J = 7.6 Hz, 2H), 1.68−1.61 (m, 2H), 1.54−1.45 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 176.4, 140.0, 133.9, 133.2, 129.0, 124.4, 120.1, 97.2, 81.1, 29.7, 22.0, 19.0, 13.5 ppm. MS m/z (relative intensity, %): 227 (9.5), 200 (20.6), 199 (100.0), 198 (60.6), 197 (40.4), 196 (20.3), 180 (16.2), 165(50.7), 154(22.1), 128(27.1), 113 (12.8).

*1-(2-Azidophenyl)prop-2-yn-1-one (**1p**).* Yellow solid; (0.41g, 48%);mp: 41−42 °C; R_f = 0.51 (hexanes/ethyl acetate 40:1)^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.15 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.62−7.58 (m, 1H), 7.27−7.21 (dd, J = 16.0 Hz, J = 1.2 Hz, 2H), 3.48 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 175.3, 140.0, 134.7, 133.7, 127.8, 124.5, 120.1, 81.2, 80.9 ppm. MS m/z (relative intensity, %): 171 (6.5), 157 (21.6), 144 (20.2), 143 (46.7), 142 (100), 114(35.1), 95(32.1), 77 (29.1).

General Procedure for the Synthesis of *o*-Azidoaryl Acetylenic Ketones 1j−1m.[18] (1) Sodium azide (2.0 equiv) was added to a stirring solution of ortho-fluorobenzaldehydes (1.0 equiv) in DMSO under argon. The reaction mixture was stirred at 50 °C for 5−6 h. After the reaction was finished, the mixture was poured into ice-cold water and acidified with drops of concentrated HCl. It was then extracted with EtOAc and washed with water. The organic layer was dried over MgSO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel using petroleum ether-ethyl acetate mixture as eluent (96:4 v/v). Steps (2) and (3) are same as above-mentioned.

*1-(2-Azido-5-chlorophenyl)-3-phenylprop-2-yn-1-one (**1j**).* Yellow solid; (0.745g, 53%); mp: 76−79 °C; R_f = 0.51 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.81 (d, J = 2.8 Hz, 1H), 7.67−7.65 (m, 2H), 7.53−7.48 (m, 1H), 7.45−7.26 (m, 2H), 7.25−7.22 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 174.9, 136.8, 136.7, 133.2, 131.1, 129.9, 128.8, 124.7, 122.7, 121.8, 119.9, 93.4, 88.1 ppm. MS m/z (relative intensity, %): 281 (9.2), 236 (20.6), 235 (100.0), 234 (60.6), 233 (16.2), 232 (26.5), 208 (14.8), 206 (14.5), 204 (20.2), 180 (22.1).

*1-(2-Azido-5-bromophenyl)-3-phenylprop-2-yn-1-one (**1k**).* Yellow solid; (0.761g, 47%); mp: 88−91 °C; R_f = 0.49 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.24 (d, J = 2.0 Hz, 1H), 7.70−7.65 (m, 3H), 7.53−7.48 (m, 1H), 7.45−7.41 (m, 2H), 7.17 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 174.5, 139.3, 136.9, 135.4, 133.2, 131.1, 130.3, 128.7, 121.8, 119.9, 117.4, 94.4, 88.0 ppm. MS m/z (relative intensity, %): 326 (6.5), 324 (20.6), 298 (60.6), 296 (100), 260 (16.2), 258 (26.5), 246 (14.8), 244 (14.5), 230 (20.2), 180 (22.1).

*1-(2-Azido-4-bromophenyl)-3-phenylprop-2-yn-1-one (**1l**).* Yellow solid; (0.842g, 52%); mp: 91−95 °C; R_f = 0.46 (hexanes/ethyl acetate 40:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.02 (d, J = 8.4 Hz, 1H), 7.66−7.63 (m, 2H), 7.51−7.47 (m, 1H), 7.44−7.39 (m, 4H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 175.0, 141.4, 134.1, 133.1, 131.0, 128.8, 128.7, 127.9, 127.6, 123.2, 119.9, 93.9, 88.1 ppm. MS m/z (relative intensity, %): 326 (18.5), 324 (3.2), 306 (4.7), 304(4.6), 224 (14.7), 223 (100.0), 221 (5.4), 207 (6.4), 206 (16.0), 103 (16.1).

*1-(2-Azido-4-bromophenyl)-3-(4-chlorophenyl)prop-2-yn-1-one (**1m**).* Yellow solid; (0.972g, 54%); mp: 102−106 °C; R_f = 0.45 (hexanes/ethyl acetate 40:1);^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.00 (d, J = 8.4 Hz, 1H), 7.59−7.56 (m, 2H), 7.43−7.39 (m, 4H) ppm; ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 174.8, 141.5, 137.5, 134.3, 134.1, 129.2, 129.0, 128.0, 127.5, 123.3, 118.4, 93.4, 88.8 ppm. MS m/z (relative intensity, %): 360 (20.7), 358 (20.6), 357 (100.0), 356 (20.6), 355 (16.2), 354 (36.5), 326 (14.8), 310 (24.5), 309 (20.2), 291 (12.1).

General Procedure for Sulfone-Containing 4-Quinolones 3. Schlenk tube (10 mL) was equipped with a magnetic stir bar, *o*-azidoaryl acetylenic ketones **1** (0.2 mmol), sulfinic acids **2** (0.4 mmol, 2.0 equiv), and CH$_3$CN (1 mL). The flask was evacuated and backfilled with Ar for 3 times. TBHP (0.08 mmol, 0.4 equiv, 5−6 M in decane) was added with syringe under Ar. The tube was then sealed and the mixture was stirred for 0.5 h at 80 °C under Ar (1 atm). After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products **3**.

*2-Phenyl-3-tosylquinolin-4(1H)-one (**3aa**).* White solid; (67.5 mg, 90%); mp: 272−276 °C; R_f = 0.34 (CH$_2$Cl$_2$/methanol 20:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.38 (s, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.81−7.79 (m, 2H), 7.75−7.68 (m, 2H), 7.65−7.62 (m, 2H),7.58−7.55 (m, 3H), 7.43−7.39 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 154.7, 142.6, 140.1, 138.8, 134.2, 133.2, 129.5, 128.7, 128.4, 127.7, 127.6, 125.6, 125.2, 124.9, 119.0, 118.4, 21.0 ppm. ESI-HRMS: m/z Calcd for C$_{22}$H$_{17}$NO$_3$S+H$^+$: 376.1002, found 376.1004.

*2-(p-Tolyl)-3-tosylquinolin-4(1H)-one (**3ba**).* White solid; (70.8 mg, 91%); mp: 274−278 °C; R_f = 0.36 (CH$_2$Cl$_2$/methanol 20:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.30 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.79−7.77 (d, J = 8.0 Hz, 2H), 7.75−7.66 (m, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.43−7.35 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 154.9, 142.6, 140.2, 139.1, 138.8, 133.2, 131.4, 128.7, 128.4, 128.2, 127.7, 125.6, 125.1, 124.9, 119.0, 118.4, 21.0 ppm. ESI-HRMS: m/z Calcd for C$_{23}$H$_{19}$NO$_3$S+H$^+$: 390.1158, found 390.1160.

*2-(4-Methoxyphenyl)-3-tosylquinolin-4(1H)-one (**3ca**).* White solid; (72.1 mg, 89%); mp: 280−283 °C; R_f = 0.40 (CH$_2$Cl$_2$/methanol 20:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.27 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.78−7.67 (m, 4H), 7.58−7.55 (m, 2H),7.42−7.38 (m, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.12−7.10 (m, 2H), 3.86 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ

172.6, 160.4, 154.7, 142.6, 140.3, 138.8, 133.1, 130.2, 128.7, 127.7, 126.3, 125.6, 125.1, 124.9, 119.0, 118.4, 113.1, 55.3, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{23}H_{19}NO_4S+H^+$: 406.1108, found 406.1106.

*2-(3-Methoxyphenyl)-3-tosylquinolin-4(1H)-one (**3da**)*. White solid; (68.9 mg, 85%); mp: 275−278 °C; R_f = 0.36 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.38 (s, 1H), 8.00(d, *J* = 8.0 Hz, 1H), 7.81−7.76 (m, 2H), 7.74−7.68 (m, 2H),7.50−7.40 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22−7.10 (m, 3H), 3.85 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.6, 158.5, 154.4, 142.7, 140.1, 138.8, 135.5, 133.2, 128.9, 128.7, 127.7, 125.6, 125.2, 124.9, 121.1, 119.1, 118.3, 114.9, 114.2, 55.3 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{23}H_{19}NO_4S+H^+$: 406.1108, found 406.1104.

*2-(4-Fluorophenyl)-3-tosylquinolin-4(1H)-one (**3ea**)*. White solid; (70 mg, 89%); mp: 282−286 °C; R_f = 0.35 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.41 (s, 1H), 8.01(d, *J* = 8.0 Hz, 1H), 7.79−7.66 (m, 6H), 7.44−7.38 (m, 3H),7.31 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.6, 162.9 (d, *J* = 246.2 Hz), 153.8, 142.7, 140.0, 138.7, 133.2, 130.9 (d, *J* = 10.2 Hz), 130.5 (d, *J* = 5.2 Hz), 128.7, 127.7, 125.7, 125.1(d, *J* = 23.2 Hz), 119.0, 118.5, 114.8, 114.6 ppm, ^{19}F NMR (376 MHz, DMSO-d_6): −111.92 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{16}FNO_3S+H^+$: 394.0908, found 394.0910.

*2-(4-Chlorophenyl)-3-tosylquinolin-4(1H)-one (**3fa**)*. White solid; (72 mg, 88%); mp: 272−276 °C; R_f = 0.34 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.41 (s, 1H), 8.01(dd, *J* = 8.8 Hz, *J* = 0.8 Hz, 1H), 7.80−7.67 (m, 3H),7.65−7.61 (m, 5H), 7.44−7.40 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 153.6, 142.8, 139.9, 138.9, 134.3, 133.2, 130.4, 128.7, 127.8, 127.7, 125.7, 125.2, 124.9, 119.1, 118.4, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{16}ClNO_3S+H^+$:410.0612, found 410.0616.

*2-(4-Bromophenyl)-3-tosylquinolin-4(1H)-one (**3ga**)*. White solid; (82.4 mg, 91%); mp: 281−285 °C; R_f = 0.35 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.41 (s, 1H), 8.01(dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.80−7.72 (m, 5H), 7.66−7.59 (m, 3H),7.44−7.40 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 153.6, 142.8, 139.9, 138.8, 133.5, 133.3, 130.6, 128.7, 127.8, 125.7, 125.3, 124.9, 123.1, 119.0, 118.4, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{16}BrNO_3S+H^+$:454.0107, found 454.0110.

*2-(4-Ethylphenyl)-3-tosylquinolin-4(1H)-one (**3ha**)*. White solid; (71.6 mg, 92%); mp: 266−269 °C; R_f = 0.37 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.32 (s, 1H), 7.99 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.78−7.67 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.43−7.39 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 154.9, 145.3, 142.6, 140.2, 138.8, 133.2, 131.7, 128.7, 128.5, 127.7, 127.1, 125.1, 124.9, 119.0, 118.4, 28.1, 21.0, 15.6 ppm. ESI-HRMS: *m/z* Calcd for $C_{24}H_{21}NO_3S+H^+$:404.1315, found 404.1318

*2-([1,1′-Biphenyl]-4-yl)-3-tosylquinolin-4(1H)-one (**3ia**)*. White solid; (84.8 mg, 94%); mp: 282−286 °C; R_f = 0.36 (CH_2Cl_2/methanol 20:1); 1H NMR (400 MHz, DMSO-d_6): δ = 12.43 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.88−7.86 (m, 2H), 7.83−7.77(m, 4H), 7.75−7.69 (m, 4H),7.56−7.52 (m, 2H), 7.45−7.41 (m, 2H),7.33 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 154.5, 142.7, 141.2, 140.1, 139.4, 138.8, 133.4, 133.2, 129.1, 128.7, 127.9, 127.7, 127.1, 126.8, 125.9, 125.6, 125.2, 124.9, 119.0, 118.4, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{28}H_{21}NO_3S+H^+$:452.1315, found 452.1318.

*6-Chloro-2-phenyl-3-tosylquinolin-4(1H)-one (**3ja**)*. White solid; (80.6 mg, 89%); mp: 269−274 °C; R_f = 0.35 (CH_2Cl_2/methanol 20:1);^1H NMR (400 MHz, DMSO-d_6): δ = 12.52(s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.65−7.63 (m, 3H), 7.57−7.54(m, 3H), 7.49−7.46 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.1, 155.2, 142.8, 139.9, 139.7, 134.0, 129.7, 128.7, 128.4, 128.2, 128.0, 127.7, 127.2, 126.5, 125.5, 121.3, 119.0, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{16}ClNO_3S+H^+$:410.0612, found 410.0615.

*6-Bromo-2-phenyl-3-tosylquinolin-4(1H)-one (**3ka**)*. White solid; (88.5 mg, 91%); mp: 288−292 °C; R_f = 0.37 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.54 (s, 1H), 8.09 (d, *J* = 1.8 Hz, 1H), 7.90 (dd, *J* = 8.8 Hz, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66−7.63 (m, 3H), 7.59−7.56 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 153.8, 142.7, 140.0, 138.7, 133.2, 130.9, 130.8, 128.7, 127.7, 125.7, 125.2, 124.9, 119.0, 118.5, 114.8, 114.6, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{16}BrNO_3S+H^+$:454.0107, found 454.0104.

*7-Bromo-2-phenyl-3-tosylquinolin-4(1H)-one (**3la**)*. White solid; (76.1 mg, 93%); mp: 272−274 °C; R_f = 0.35 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.38 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.64−7.62 (m, 2H), 7.59−7.55 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 171.6, 154.3, 142.7, 140.0, 136.8, 136.0, 134.1, 129.6, 129.3, 128.7, 128.5, 127.8, 127.7, 126.9, 125.2, 121.3, 113.4, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{16}BrNO_3S+H^+$:454.0107, found 454.0110.

*7-Bromo-2-(4-chlorophenyl)-3-tosylquinolin-4(1H)-one (**3ma**)*. White solid; (78.8 mg, 87%); mp: 265−269 °C; R_f = 0.37 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.42 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 11.6 Hz, 2H), 7.77−7.63 (m, 4H), 7.59−7.56 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 171.3, 155.0, 142.8, 139.8, 137.8, 136.0, 134.0, 129.6, 128.7, 128.4, 127.8, 127.7, 127.0, 121.6, 118.9, 117.9, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{22}H_{15}BrClNO_3S+H^+$:487.9717, found 487.9714.

*2-(Thiophen-2-yl)-3-tosylquinolin-4(1H)-one (**3na**)*. White solid; (73.2 mg, 96%); mp: 252−256 °C; R_f = 0.44 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.53 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.77−7.67 (m, 2H), 7.51 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H),7.44−7.40 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 5.2 Hz, *J* = 3.6 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.4, 147.8, 142.8, 140.0, 138.7, 133.4, 132.8, 130.3, 129.0, 128.7, 126.8, 125.8, 125.4, 124.9, 119.8, 119.1, 21.0 ppm. ESI-HRMS: *m/z* Calcd for $C_{20}H_{15}NO_3S_2+H^+$:382.0566, found 382.0568.

*2-Phenyl-3-(phenylsulfonyl)quinolin-4(1H)-one (**3ab**)*. White solid; (63.5 mg, 88%); mp: 262−266 °C; R_f = 0.42 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.41 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.76−7.70 (m, 2H), 7.68−7.64(m, 2H),7.61−7.42 (m, 6H), 7.40 (t, *J* = 7.6 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.6, 154.9, 142.9, 138.8, 134.2, 133.3, 132.4, 129.5, 128.4, 128.3, 127.7, 127.5, 125.6, 125.2, 124.9, 119.1, 118.1 ppm. ESI-HRMS: *m/z* Calcd for $C_{21}H_{15}NO_3S+H^+$:362.0845, found 362.0848.

*3-((4-Bromophenyl)sulfonyl)-2-phenylquinolin-4(1H)-one (**3ac**)*. White solid; (76.2 mg, 87%); mp: 276−278 °C; R_f = 0.43 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.49 (s, 1H), 8.01 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.78−7.70 (m, 4H), 7.66−7.64 (m, 2H), 7.59−7.54 (m, 3H), 7.46−7.42 (m, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.6, 155.1, 142.2, 138.8, 134.0, 133.4, 131.4, 129.7, 128.5, 127.7, 126.3, 125.6, 125.4, 124.9, 119.1, 117.7 ppm. ESI-HRMS: *m/z* Calcd for $C_{21}H_{14}BrNO_3S+H^+$:439.9951, found 439.9948.

*3-((2-Bromophenyl)sulfonyl)-2-phenylquinolin-4(1H)-one (**3ad**)*. White solid; (58.7 mg, 67%); mp: 272−276 °C; R_f = 0.42 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.54 (s, 1H), 8.21 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.79−7.73 (m, 2H), 7.69 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2H), 7.62−7.42 (m, 5H), 7.41 (dd, *J* = 6.0 Hz, *J* = 2.0 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.1, 155.8, 141.7, 138.9, 134.4, 133.7, 133.3, 131.7, 130.0, 129.0, 127.8, 127.4, 125.3, 125.2, 124.9, 119.2, 118.5, 117.2 ppm. ESI-HRMS: *m/z* Calcd for $C_{21}H_{14}BrNO_3S+H^+$:439.9951, found 439.9948.

*3-((4-Methoxyphenyl)sulfonyl)-2-phenylquinolin-4(1H)-one (**3ae**)*. White solid; (71.2 mg, 91%); mp: 278−281 °C; R_f = 0.45 (CH_2Cl_2/methanol 20:1); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.35 (s, 1H), 8.03 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.85−7.83 (m, 2H), 7.76−7.67 (m, 2H), 7.63−7.61 (m, 2H), 7.58−7.55 (m, 3H), 7.44−

7.40 (m, 1H), 7.05−7.02 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.5, 162.3, 154.4, 138.8, 134.5, 134.2, 133.2, 130.1, 129.4, 128.4, 125.1, 124.9, 119.0, 118.9, 113.4, 55.6 ppm. ESI-HRMS: m/z Calcd for $C_{22}H_{17}NO_4S+H^+$:392.0951, found 392.0954.

*3-((4-(tert-Butyl)phenyl)sulfonyl)-2-phenylquinolin-4(1H)-one **(3af)**.* White solid; (70.9 mg, 86%); mp: 267−270 °C; R_f = 0.47 (CH_2Cl_2/methanol 20:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.38 (s, 1H), 8.03 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.76−7.67 (m, 2H), 7.64−7.62 (m, 2H),7.58−7.53 (m, 5H), 7.44−7.40 (m, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.6, 155.3, 154.8, 140.1, 138.8, 134.3, 133.2, 129.4, 128.4, 127.64, 127.60, 125.6, 125.2, 125.1, 124.9, 119.0, 118.3, 34.8, 30.8 ppm. ESI-HRMS: m/z Calcd for $C_{25}H_{23}NO_3S+H^+$:418.1471, found 418.1476.

*3-(Naphthalen-2-ylsulfonyl)-2-phenylquinolin-4(1H)-one **(3ag)**.* White solid; (68.2 mg, 83%); mp: 265−269 °C; R_f = 0.51(CH_2Cl_2/methanol 20:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.46 (s, 1H), 8.56 (s, 1H), 8.17−8.15 (d, J = 7.6 Hz, 1H), 8.03−7.96 (m, 3H), 7.86 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.75−7.59 (m, 9H), 7.41−7.37 (m, 1H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 172.6, 155.1, 154.8, 140.1, 138.8, 134.3, 134.2, 133.3, 131.4, 129.6, 129.3, 128.60, 128.56, 128.1, 127.7, 127.2, 125.6, 125.2, 124.8, 123.1, 119.1, 118.0 ppm. ESI-HRMS: m/z Calcd for $C_{25}H_{17}NO_3S+H^+$:412.1002, found 412.1006.

*1-Methyl-2-phenyl-3-tosylquinolin-4(1H)-one **(4)**.* White solid; (66.9 mg, 86%); mp: 255−257 °C; R_f = 0.36 (CH_2Cl_2/methanol 20:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 1.2 Hz, 1H), 8.39 (d, J = 1.6 Hz, 2H), 7.91−7.69 (m, 1H), 7.59−7.58 (m, 3H), 7.54 (d, J = 8.8 Hz, 1H), 7.45−7.39 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 3.43 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.1, 156.6, 143.1, 140.8, 139.9, 133.4, 133.3, 129.9, 128.8, 128.6, 128.3, 128.1, 127.7, 127.1, 125.4, 121.9, 116.5, 37.4, 21.5 ppm. ESI-HRMS: m/z Calcd for $C_{23}H_{19}NO_3S+H^+$: 390.1158, found 390.1156.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01847.

X-ray crystallographic data of compound **3fa** (CIF)

^{1}H, ^{19}F, and ^{13}C NMR spectra of compounds **1a−1p**, **3ba−3na**, and **3aa−3ag** (PDF)

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Notes

The authors declare no competing financial interest.

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