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A Cascade Reaction of Michael Addition and Truce-Smiles Rearrangement to Synthesize Trisubstituted 4-Quinolone Derivatives

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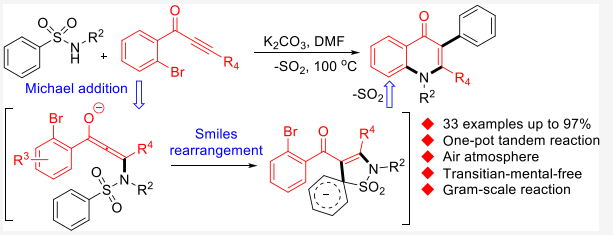
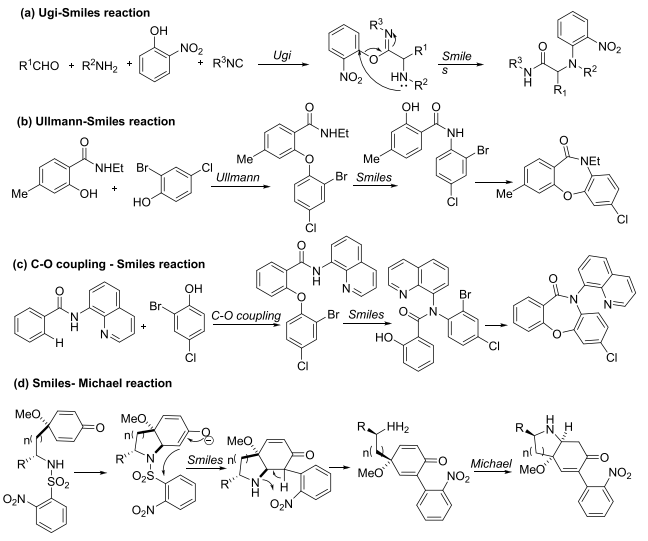
ABSTRACT: A novel transition-metal-free cascade reaction to synthesize 4-quinolone derivatives has been demonstrated. Michael addition and Truce-Smiles rearrangement are included in this protocol, providing a broad scope of 4-quinolones in moderate-to-excellent yields. This work serves as an example of the use of sulfonamides through Truce−Smiles rearrangement to build heterocyclic compounds under mild conditions.



INTRODUCTION

The Smiles rearrangement reaction, as an intramolecular nucleophilic aromatic substitution reaction, has been used to construct a lot of heterocyclic compounds.[1] However, a vigorous revival of this reaction appeared in recent years, and it is usually applied to cascade reactions.[2] For example, Grimaud reported a phenol Ugi−Smiles system for four-component reaction (Scheme 1a).[3] In 2012, a domino reaction to construct dibenzoxazepinones *via* copper-catalyzed Ullmann reaction, Smiles rearrangement, and ring-closing process was reported (Scheme 1b).[4] Recently, a cascade reaction of copper-catalyzed C−H etherification and C−N Smiles rearrangement to construct this skeleton was reported (Scheme 1c).[5] In addition, Canesi demonstrated a tandem Smiles−Michael process using a nosyl group as a functional protecting group to develop indole derivatives (Scheme 1d).[6] In addition, they have reported a Michael−Smiles ring-closure cascade process to construct arylated cyclopropane.[7]

Scheme 1. Examples of Applications of Smiles Rearrangement in Recent Years



The 4-quinolone scaffold is a promising bioactive structure and exhibits superior qualities in the treatment of human disease.[8] For example, dorfloxacin, ciprofloxacin, and ofloxacin are widely used in varieties of acute and chronic bacterial infections.[9] In addition, 4-quinolone derivatives are very important units of alkaloids, which exist in natural molecules and have wide utility values.[10−13] Furthermore, by means of the modifications of the 4-quinolone skeleton, the specific medicinal values were achieved, such as antibacterial,[14] antitumor,[15] antimalarial,[16] and other activities.[17]

On account of these, many methods (Scheme 2) have been reported to construct this skeleton catalyzed by transition-metal catalysts such as Cu (a),[18] Ni (b),[19] Au (c),[20] Rh (d),[21] and Pd (e).[22] A strategy without transition-metal catalysts was reported; however, peroxide TBHP was involved in this report (f).[23] Hence, a simple and effective method for synthesizing 4-quinolones is worthy of study. Based on our previous works[1e1f] with the Smiles rearrangement applied on building heterocyclic compounds, we envisaged that a cascade reaction of Michael-addition and Smiles rearrangement between benzene sulfonamides and 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ones

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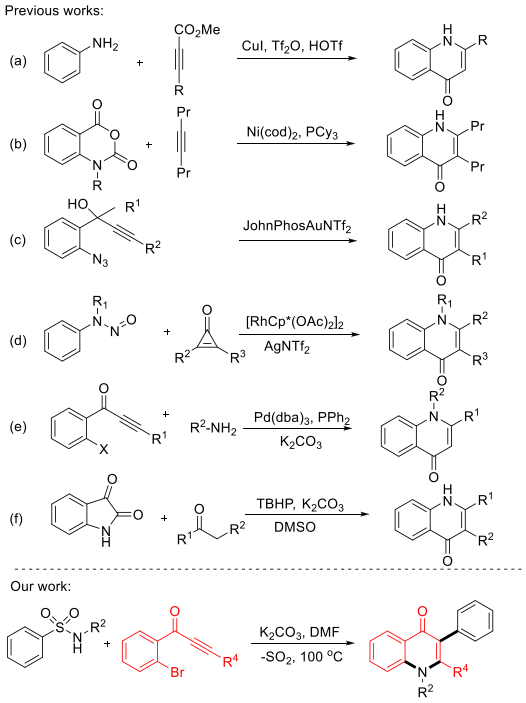
Scheme 2. Synthetic Methods of 4-Quinolone Derivatives

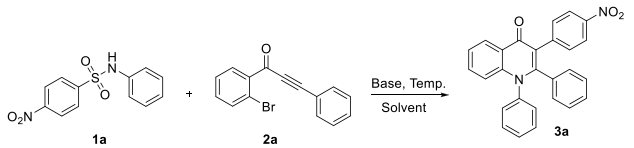


would allow access to trisubstituted 4-quinolones with a loss of sulfur dioxide.[24]

RESULTS AND DISCUSSION

To confirm the feasibility of this approach, we used 4-nitrobenzenesulfonamide and 1-(2-bromophenyl)-3-phenylprop-2-yn-1-one as the model substrates to test our assumption (Table 1). Our initial experiment was promoted by Cs_2CO_3 in DMSO at 100 °C with a reactant ratio of 1:1. Also, the desired product **3a** was obtained in a yield of 39% (entry 1). Then, the feed ratio was adjusted to 1:2, and the yield of the product was improved to 78% (entry 2). Then, several bases were investigated under the same conditions and K_2CO_3 was proved to be the most effective base (entries 2−6). On this basis, a screening of solvents was carried out, and the results indicated that the most appropriate solvent was DMF (entries 7−9). No satisfactory yield of the desired product was obtained whether increasing or decreasing the reaction temperature (entries 10−11). However, when 2 equiv of K_2CO_3 were used, the desired product with a yield of 95% was obtained (entries 12−14). Therefore, the optimized reaction conditions are summarized in entry 12.

Table 1. Optimization of Reaction Conditions[a]



entry	base	solvent	temperature	yield (%)[b]
1	Cs_2CO_3	DMSO	100	39[c]
2	Cs_2CO_3	DMSO	100	78
3	K_2CO_3	DMSO	100	90
4	K_3PO_4	DMSO	100	63
5	NaOH	DMSO	100	33
6	*t*-BuOK	DMSO	100	29
7	K_2CO_3	DMF	100	92
8	K_2CO_3	toluene	100	trace
9	K_2CO_3	CH_3CN	100	43
10	K_2CO_3	DMF	80	68
11	K_2CO_3	DMF	120	45
12	K_2CO_3 (2 equiv)	DMF	100	95
13	K_2CO_3 (1 equiv)	DMF	100	65
14	K_2CO_3 (4 equiv)	DMF	100	88

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), solvent (2 mL), base (3 equiv), temperature, air, TLC monitored the end of the reaction. [b]Isolated yield. [c]**1a** (0.3 mmol), **2a** (0.3 mmol)

With the optimized conditions in hand, the generality of the methodology was further extended and the results are shown in Table 2. First, the reaction underwent smoothly to give the desired products in moderate-to-excellent yields when R^2 was phenyl with different substituents (**3a**−**3g**). A benzyl group was also compatible, affording the corresponding products **3h**, with a lower yield of 48%. Surprisingly, naphthyl-substituted benzene sulfonamide succeeded in giving the desired product **3i** in a satisfactory yield. In addition, alkyl-substituted benzene sulfonamides could also be subjected to this reaction to form the products in moderate yields (**3j**−**3l**); it was a breakthrough compared with the previous report.[25] We then proceeded to examine the scope of R^1, and compounds **1** with strong electron-withdrawing groups like $-CF_3$ and $-CN$ could also be applied to this reaction (**3m**−**3o**). In addition, when $-NO_2$ was positioned ortho to the sulfamide, the reaction took place smoothly (**3o**).

After getting these promising results, we turned to investigate the substituent effects of 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ones. As for the R^3 group, both electron-donating groups and electron-withdrawing groups were tolerated, and compounds bearing electron-withdrawing groups (**3r**, **3s**, **3nb**) gave better yields than those bearing electron-donating groups (**3p**, **3q**, **3na**). Also, electron effects of R^4 groups have no significant influence on the reaction and the desired products were obtained in moderate-to-excellent yields (**3t**−**3x**, **3oc**, **3od**). Surprisingly, a free alkyne or TMS-protected alkyne (**2ba** and **2bc**) both could work in this procedure and gave the same product **3ba** in acceptable yields. Furthermore, compound **3bb** could be obtained in a yield of 74% in this reaction with an aliphatic alkyne used as a reactant.

To confirm the structure of the product, an X-ray structure of product **3a** was obtained by X-ray crystallographic analysis and is shown in Figure 1 (CCDC number: 2008744). In addition, to examine the scalability of the present strategy, a gram-scale reaction of compounds **1a** and **2a** was carried out (Scheme 3). The corresponding product **3a** was obtained in 77% isolated yield, which indicated a good practical utility of the method.

From the overall results and previously published works,[25,26] a possible mechanism is proposed (Scheme 4). First, the intermediate **6** was obtained via Michael addition. Then, Truce−Smiles rearrangement occurred driven by a loss of sulfur dioxide, giving the intermediate **8**. Also, its geometric isomer **9** could be interconverted. Subsequently, an intramolecular nucleophilic substitution happened and the desired products 4-quinolone derivatives **4** were obtained.

CONCLUSIONS

To conclude, we have described a transition metal-free cascade reaction from benzene sulfonamides and 1-(2-bromophenyl)-

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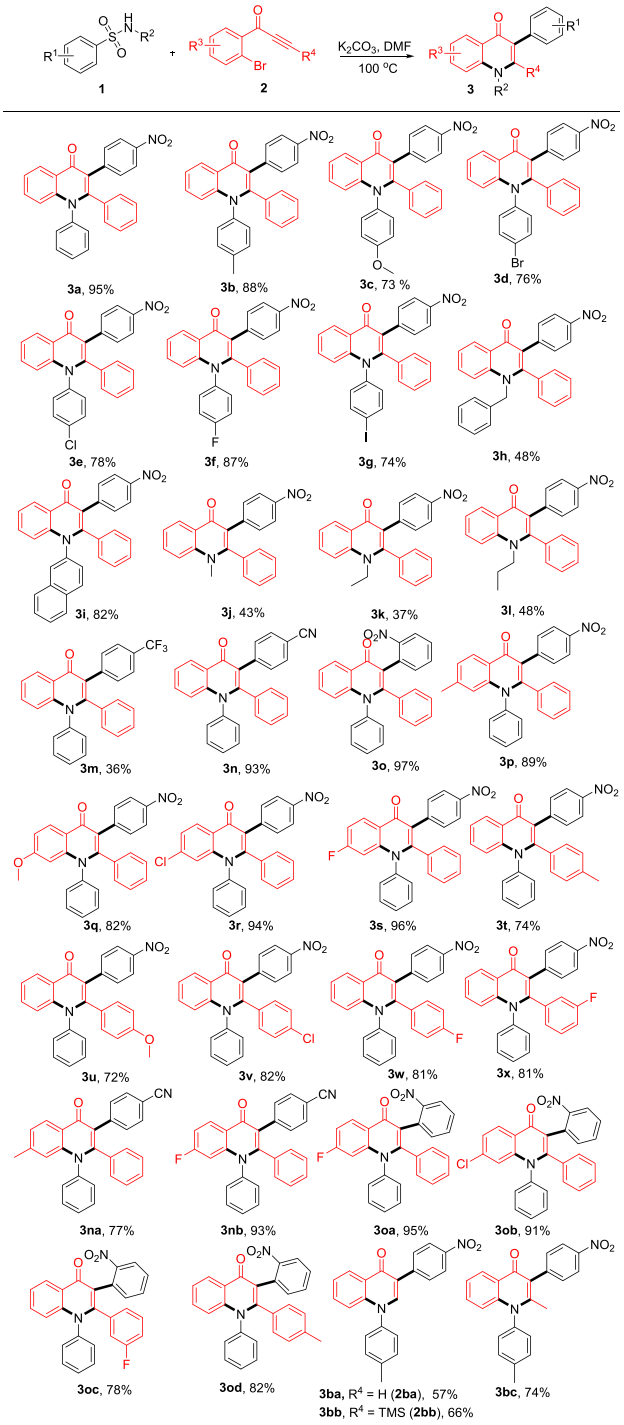
J. Org. Chem. XXXX, XXX, XXX−XXX

Table 2. Substrate Scope[a,b]



[a]Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), DMF (2 mL), K_2CO_3 (2 equiv), 100 °C, air, TLC monitored the end of the reaction. [b]Isolated yield.

3-phenylprop-2-yn-1-ones to construct 4-quinolone derivatives. The cascade reaction includes Michael addition, Truce-Smiles rearrangement, and intramolecular nucleophilic substitution under mild conditions. A wide range of densely functionalized 4-quinolone derivatives could be obtained through this process, which has potential applications in biomedical research. The use of sulfonamides though Michael−Smiles rearrangement sets up a novel method for constructing heterocyclic compounds. Applications of this cascade strategy to construct heterocyclic compounds with bioactivities are under study in our laboratory.

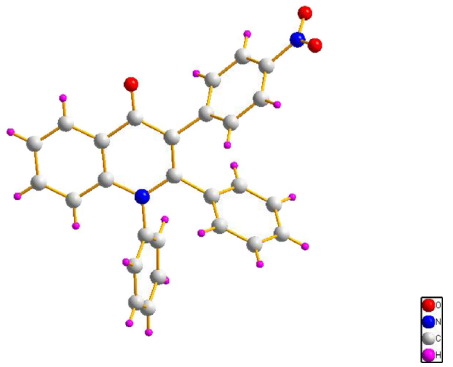
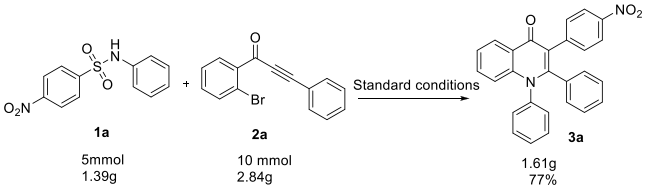
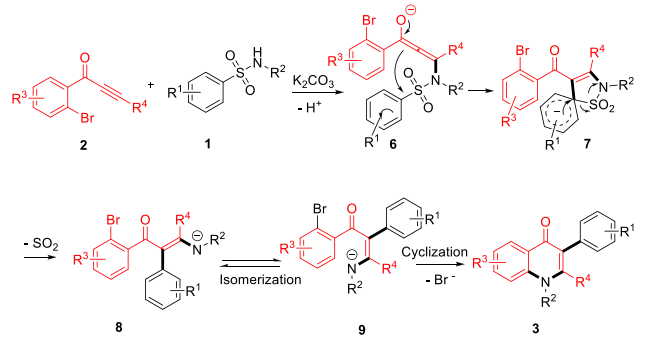


Figure 1. X-ray structure of compound **3a**.

Scheme 3. Gram-Scale Reactions of 1a and 2a



Scheme 4. Proposed Reaction Mechanism



EXPERIMENTAL SECTION

General Information. Benzenesulfonamides and 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ones were prepared according to literature procedures.[27−30] Other reagents were commercially available and were used without further purification. All reactions were monitored by thin-layer chromatography (TLC). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using $CDCl_3$ or DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. HRMS spectra were determined on a Q-TOF 6510 spectrograph (Agilent). Melting points were determined on an XD-4 digital micro melting-point apparatus.

General Experimental Procedures for the Synthesis of Benzenesulfonamides 1.[27] A solution of substituted aniline (5 mmol) and NaOAc (6 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature. Substituted benzenesulfonyl chloride (5 mmol) was diluted in CH_2Cl_2 and then added into the mixture dropwise. Then, the mixture was stirred overnight and the white solid was separated out. The solid was purified through filtration, washing, and recrystallization to give the desired product **1**.

General Experimental Procedures for the Synthesis of 1-(2-Bromophenyl)-3-phenylprop-2-yn-1-ones.[28] A solution of alkyne (12 mmol) in anhydrous THF (30 mL) and *n*-BuLi (2.5 M, 10 mmol) was stirred at −78 °C under and an N_2 atmosphere for 1 h.

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J. Org. Chem. XXXX, XXX, XXX−XXX

Then, the aldehyde (10 mmol) was added slowly and the mixture was warmed to room temperature for 3 h, until the TLC monitored the end of the reaction. The mixture was quenched with saturated solution of NH_4Cl and extracted with dichloromethane (30 mL × 3). The combined organic layers were washed, dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The organic layer was mixed with IBX (12 mmol) and DMSO (20 mL), and then the mixture was stirred at room temperature for about 12 h until the TLC monitored the end of the reaction. The mixture was quenched with water (30 mL) and extracted with ethyl acetate (30 mL × 3). The organic layers were combined, dried, filtered, and concentrated. The product **2a**−**2od** was purified by column chromatography with petroleum ether/ethyl acetate = 10:1−20:1.

General Experimental Procedures for the Syntheses of 2ba and 2bc.[29] A solution of aldehyde (10 mmol) in anhydrous THF (30 mL) was stirred at 0 °C under an N_2 atmosphere. A solution of ethynylmagnesium bromide or 1-propynylmagnesium bromide in THF (0.5 M solution, 13 mmol) was added dropwise at 0 °C for about 30 min, warmed to room temperature, and then stirred for about 4 h. Saturated aqueous NH_4Cl solution (30 mL) was added, and the mixture was evaporated in vacuo, separated by EtOAc and saturated aqueous NaCl solution. The organic layer was dried by Na_2SO_4 and evaporated in vacuo to obtain the intermediate. Then, the intermediate, NaBr (10 mmol), $NaHCO_3$ (20 mmol), and TEMPO (0.5 mmol) were stirred in CH_2Cl_2 (50 mL) at 0 °C. A solution of NaOCl (12%, 30 mmol) was added slowly, and the mixture were stirred at this temperature until TLC monitored the end of the reaction. The mixture was separated by CH_2Cl_2 and saturated aqueous NaCl solution. The organic layers were combined, dried, filtered, and concentrated. The product **2ba** or **2bc** was purified by column chromatography with petroleum ether/ethyl acetate = 100:1.

General Experimental Procedures for the Synthesis of 2bb.[30] A solution of trimethylsilylacetylene (10.4 mmol) in anhydrous THF (30 mL) was stirred at 0 °C under an N_2 atmosphere. A solution of *i*-PrMgBr in THF (1.0 mol/L, 10.2 mL) was added dropwise at 0 °C for about 40 min, and the mixtures were stirred for another 15 min at this temperature. Then, the aldehyde (12 mL) was added slowly and the mixtures were stirred for 30 min, then warmed to room temperature, and again stirred for about 4 h. Saturated aqueous NH_4Cl solution (30 mL) was added, and the mixture was evaporated in vacuo, separated by EtOAc and saturated aqueous NaCl solution. Next, the same procedure as compound **2ba** or **2bc** was carried out to get the desired product **2bb**.

General Experimental Procedures for the Synthesis of 4-Quinolones. A mixture of compound **1** (0.3 mmol), compound **2** (0.6 mmol), K_2CO_3 (0.6 mmol), and DMF was stirred in a sealed tube, and the mixture was heated to 100 °C with an oil bath. TLC monitored the end of the reaction. Then, the mixture was cooled to room temperature and brine (50 mL) was poured into the solution. The mixture was extracted with EtOAc (5 × 50 mL). The organic layers were combined and dried using anhydrous Na_2SO_4. After that, the product was purified by column chromatography with petroleum ether/ethyl acetate = 3:1−1:1, and the desired product was obtained after vacuum-rotary evaporation.

*3-(4-Nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3a**, 119 mg, 95%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 279−281 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.98 (d, J = 8.8 Hz, 2H), 7.54−7.49 (m, 1H), 7.44−7.40 (m, 1H), 7.37−7.28 (m, 5H), 7.18−7.16 (m, 2H), 7.00−6.92 (m, 5H), 6.9 (d, J = 8.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 151.9, 146.0, 143.3, 142.1, 139.1, 133.9, 132.4, 132.3, 130.3, 130.0, 129.6, 129.0, 128.4, 127.7, 126.7, 125.8, 124.2, 122.6, 121.8, 118.3. HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{27}H_{18}N_2O_3$ 419.1390; found 419.1390.

*3-(4-Nitrophenyl)-2-phenyl-1-(p-tolyl)quinolin-4(1H)-one (**3b**, 114 mg, 88%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Off-white solid, mp 291−293 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 7.98 (d, J = 8.8 Hz, 2H), 7.53−7.48 (m, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.04−6.97 (m, 5H), 6.94 (dd, J = 1.6 Hz, 7.2 Hz, 2H), 6.89 (d, J = 8.4 Hz, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 152.0, 146.0, 143.4, 142.3, 139.1, 136.6, 134.0, 132.4, 132.2, 130.3, 130.2, 129.7, 128.3, 127.7, 125.9, 124.2, 122.6, 121.8, 118.4, 21.2. HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_3$ 433.1547; found 433.1540.

*1-(4-Methoxyphenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3c**, 98 mg, 73%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 261−263 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.97 (dd, J = 6.8 Hz, 1.6 Hz, 2H), 7.54−7.49 (m, 1H), 7.43−7.38 (m, 1H), 7.30−7.27 (m, 2H), 7.08 (dd, J = 6.8 Hz, 2.4 Hz, 2H), 7.02−6.99 (m, 3H), 6.95−6.89 (m, 3H), 6.83 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175. 9, 159.4, 152.3, 146.0, 143.4, 142.5, 134.0, 132.4, 132.3, 131.7, 130.9, 130.3, 128.3, 127.7, 126.7, 125.9, 124.2, 122.6, 121.8, 118.4, 114.6, 55.5. HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_4$ 449.1496; found 449.1498.

*1-(4-Bromophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3d**, 113 mg, 76%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Off-white solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.6 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 8.0 (d, J = 8.4 Hz, 2H), 7.6−7.4 (m, 4H), 7.3 (s, 2H), 7.1−7.0 (m, 5H), 6.9−6.9 (m, 2H), 6.9 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 75.9, 151.5, 146.2, 142.9, 142.0, 138.3, 133.6, 132.9, 132.5, 132.4, 131.7, 130.3, 128.7, 128.0, 127.0, 125.9, 124.5, 123.1, 122.7, 122.2, 118.0. HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3Br$ 497.0496; found 497.0492.

*1-(4-Chlorophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3e**, 106 mg, 78%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 311−313 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.55−7.51 (m, 1H), 7.44−7.40 (m, 1H), 7.34−7.27 (m, 4H), 7.14−7.11 (m, 2H), 7.08−7.00 (m, 3H), 6.94 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 6.85 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 151.6, 146.1, 143.0, 142.0, 137.7, 135.0, 133.6, 132.5, 132.4, 131.4, 130.2, 129.9, 128.7, 128.0, 126.9, 125.8, 124.4, 122.7, 122.1, 118.0. HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3Cl$ 453.1000; found 453.1004.

*1-(4-Fluorophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3f**, 114 mg, 87%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.97−7.94 (m, 2H), 7.56−7.51 (m, 1H), 7.44−7.40 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.19−7.14 (m, 2H), 7.06−7.00 (m, 5H), 6.96−6.92 (m, 2H), 6.86 (d, J = 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.91, 163.3 (d, $^1J_{C,F}$ = 248.0 Hz, 1C), 151.9, 1456.1, 143.1, 142.2, 135.2 (d, $^4J_{C,F}$ = 3.4 Hz, 1C), 133.8, 132.5, 132.4, 131.9 (d, $^3J_{C,F}$ = 8.7 Hz, 1C), 130.3, 128.6, 127.9, 126.9, 125.8, 124.4, 122.7, 122.0, 118.1, 116.8 (d, $^2J_{C,F}$ = 23.0 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ = −110.5 (s, 1F). HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3F$ 437.1296; found 437.1297.

*1-(4-Iodophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3g**, 121 mg, 74%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.55−7.51 (m, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.09−7.01 (m, 3H), 6.93 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 151.5, 146.2, 143.0, 141.9, 139.0, 138.9, 133.6, 132.5, 132.4, 131.9, 130.3, 128.8, 128.0, 127.0, 125.9, 124.5, 122.7, 118.0, 94.7. HRMS (ESI-TOF) m/z: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3I$ 545.0357; found 545.0355.

*1-Benzyl-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3h**, 62 mg, 48%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 196−198 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.61 (td, J = 7.2 Hz, 1.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.34−7.27 (m, 4H), 7.25−7.22 (m, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.09−7.07 (m, 2H), 7.01−7.99 (m, 2H), 5.27 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.7, 152.8, 146.1, 143.5, 140.7, 136.1, 132.8, 132.4,

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J. Org. Chem. XXXX, XXX, XXX−XXX

129.5, 129.1, 129.1, 128.5, 127.7, 127.3, 126.8, 125.5, 124.3, 122.7, 122.5, 117.4, 52.7. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_3$ 433.1547; found 433.1549.

*1-(Naphthalen-2-yl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3i**, 115 mg, 82%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Off-white solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62−8.60 (m, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.85−7.79 (m, 2H), 7.52−7.48 (m, 3H), 7.40−7.34 (m, 6H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.69−6.59 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.1, 152.7, 146.1, 143.3, 142.2, 132.5, 132.5, 131.1, 130.3, 129.9, 128.8, 128.6, 128.6, 128.5, 127.9, 127.4, 127.2, 127.0, 126.8, 125.9, 125.2, 124.4, 122.6, 122.6, 122.13, 118.5. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{31}H_{20}N_2O_3$ 469.1547; found 469.1544.

*1-Methyl-3-(4-nirophenyl)-2-phenylquinolin-4(1H)-one (**3j**, 46 mg, 43%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz. $CDCl_3$): δ = 8.58 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.98−7.95 (m, 2H), 7.79−7.75 (m, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.50−7.46 (m, 1H), 7.35−7.30 (m, 3H), 7.24−7.20 (m, 2H), 7.19−7.15 (m, 2H), 3.59 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.5, 152.4, 146.0, 143.5, 141.4, 134.2, 132.8, 132.4, 129.5, 128.8, 127.3, 126.6, 124.2, 122.6, 122.1, 116.1, 37.8. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{22}H_{16}N_2O_3$ 357.1234; found 357.1232.

*1-Ethyl-3-(4-nitrophenyl)-2-phenylquinolin-4(1H)-one (**3k**, 41 mg, 37%).* Eluent in chromatography:petroleum ether/EtOAc 3:1. Light yellow solid, mp 151−153 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.77−7.73 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.48−7.44 (m, 1H), 7.33−7.30 (m, 3H), 7.23−7.19 (m, 4H), 4.13 (q, *J* = 3.2 Hz, 2H), 1.33 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.4, 152.1, 146.0, 143.7, 139.9, 134.1, 132.7, 132.4, 129.4, 139.1, 128.7, 127.6, 127.1, 124.1, 122.3, 122.4, 116.3, 43.8, 14.4. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{23}H_{18}N_2O_3$ 371.1390; found 371.1390.

*3-(4-Nitrophenyl)-2-phenyl-1-propylquinolin-4(1H)-one (**3l**, 55 mg, 48%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 169−171 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.77−7.73 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.33−7.30 (m, 3H), 7.22−7.17 (m, 4H), 3.97 (t, *J* = 8.0 Hz, 2H), 1.81−1.72 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.4, 152.3, 146.0, 143.6, 140.2, 134.1, 132.7, 132.4, 129.4, 129.3, 128.7, 127.5, 127.0, 124.1, 122.6, 122.3, 116.4, 50.4, 22.3, 10.9. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{24}H_{20}N_2O_3$ 385.1547; found 385.1544.

*1,2-Diphenyl-3-(4-(trifluoromethyl)phenyl)quinolin-4(1H)-one (**3m**, 48 mg, 36%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. White solid, mp 289−290 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.51−7.46 (m, 1H), 7.41−7.27 (m, 6H), 7.26−7.23 (m, 2H), 7.17−7.14 (m, 2H), 6.98−6.91 (m, 5H), 6.87 (d, *J* = 8.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.3, 151.7, 142.2, 139.6, 139.4, 134.2, 132.1, 131.8, 130.4, 130.1, 129.6, 128.9, 128.6 (q, $^2J_{C,F}$ = 32.0 Hz, 1C), 128.37 (q, $^1J_{C,F}$ = 270 Hz, 1C), 128.1, 128.0, 127.6, 126.8, 125.9, 124.5 (q, $^3J_{C,F}$ = 3.6 Hz), 124.0, 122.7, 118.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.5 (s, 3F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{18}NOF_3$ 442.1413; found 442.1418.

*4-(4-Oxo-1,2-diphenyl-1,4-dihydroquinolin-3-yl)benzonitrile (**3n**, 111 mg, 93%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 249−250 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.53−7.48 (m, 1H), 7.43−7.38 (m, 3H), 7.36−7.37 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.00−6.96 (m, 3H), 6.92−6.90 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.0, 151.8, 142.2, 141.1, 139.2, 134.0, 132.3, 132.3, 131.3, 130.4, 130.1, 129.6, 129.0, 128.3, 127.7, 126.8, 125.9, 124.2, 119.2, 118.3, 109.8. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{18}N_2O$ 399.1492; found 399.1496.

*3-(2-Nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3o**, 122 mg, 97%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 254−256 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.90 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.49−7.45 (m, 1H), 7.41−7.33 (m, 3H), 7.30−7.27 (m, 3H), 7.24−7.19 (m, 1H), 7.11−7.08 (m, 1H), 7.06−7.04 (m, 2H), 7.01−6.91 (m, 4H), 6.88 (d, *J* = 8.4 Hz 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.4, 150.4, 149.9, 142.3, 139.3, 134.2, 132.3, 132., 131.3, 130.2, 130.1, 129.9, 129.5, 129.2, 128.9, 128.3, 128.1, 127.7, 127.1, 126.8, 125.3, 124.0, 123.9, 121.5, 118.1. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{18}N_2O_3$ 419.1390; found 419.1395.

*7-Methyl-3-(4-nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3p**, 115 mg, 89%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 256−258 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.36−7.24 (m, 6H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.99−6.92 (m, 5H), 6.62 (s, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.7, 151.7, 146.1, 143.3, 142.3, 139.2, 134.0, 132.5, 130.4, 130.1, 129.6, 129.0, 128.4, 127.7, 126.8, 126.1, 123.8, 122.7, 121.7, 117.9, 22.2. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_3$ 433.1547; found 433.1544.

*7-Methoxy-3-(4-nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3q**, 110 mg, 82%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 289−291 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.34−7.27 (m, 5H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.03−6.91 (m, 6H), 6.21−6.20 (d, *J* = 2.0 Hz, 1H), 3.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.4, 162.8, 146.0, 143.9, 143.4, 139.3, 134.0, 132.5, 130.4, 130.0, 129.6, 129.0, 128.8, 128.3, 127.7, 122.6, 112.9, 101.1, 55.4. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_4$ 449.1496; found 449.1498.

*7-Chloro-3-(4-nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3r**, 128 mg, 94%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Off-white solid, mp 275−277 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.38−7.32 (m, 4H), 7.29−7.27 (m, 2H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.01−6.96 (m, 3H), 6.92−6.90 (m, 2H), 6.85 (d, *J* = 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.4, 152.3, 146.2, 142.8, 142.8, 138.8, 138.7, 133.6, 132.4, 130.3, 129.9, 129.4, 128.6, 128.6, 127.8, 125.0, 124.2, 122.8, 122.4, 117.9, HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3Cl$ 453.1000; found 453.0999.

*7-Fluoro-3-(4-nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3s**, 126 mg, 96%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Off-white solid, mp 311−313 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (t, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.38−7.26 (m, 5H), 7.18−7.12 (m, 3H), 7.00−6.92 (m, 5H), 6.53 (d, *J* = 10.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.3, 166.3 (d, $^1J_{C,F}$ = 250 Hz, 1H), 152.3, 146.2, 143.7, (d, $^3J_{C,F}$ = 11.3 Hz, 1C), 142.8, 138.9, 133.7, 132.4, 130.3, 130.0 (d, $^3J_{C,F}$ = 10.6 Hz, 1C), 129.8 (d, $^4J_{C,F}$ = 1.6 Hz, 1C), 129.4, 128.6, 127.8, 122.7, 122.6, 122.2, 113.3 (d, $^2J_{C,F}$ = 23.1 Hz, 1C), 104.5 (d, $^2J_{C,F}$ = 27.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −104.2 (m, 1F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd $C_{27}H_{17}N_2O_3F$ 437.1296; found 437.1295.

*3-(4-Nitrophenyl)-1-phenyl-2-(p-tolyl)quinolin-4(1H)-one (**3t**, 96 mg, 74%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36−7.28 (m, 5H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.80 (t, *J* = 8.8 Hz, 4H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.0, 152.1, 146.0, 143.4, 142.2, 139.3, 138.3, 132.4, 132.2, 130.9, 130.2, 130.0, 129.6, 128.9, 128.4, 126.8, 125.8, 124.2, 122.7, 122.0, 118.3, 21.2; HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_3$ 433.1547; found 433.1541.

*2-(4-Methoxyphenyl)-3-(4-nitrophenyl)-1-phenylquinolin-4(1H)-one (**3u**, 97 mg, 72%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 274−276 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.52−7.49 (m, 1H), 7.43−7.29 (m, 6H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.87−6.81 (m, 3H), 6.51 (d, *J* = 8.0 Hz, 2H), 3.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 159.1, 151.9, 146.0, 143.5, 142.2, 139.4, 132.4, 132.3, 131.7, 130.0, 129.7, 129.0, 126.8, 126.1, 125.8,

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J. Org. Chem. XXXX, XXX, XXX−XXX

124.2, 122.7, 122.1, 118.3, 113.1, 55.0. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_4$ 449.1496; found 449.1499.

*2-(4-Chlorophenyl)-3-(4-nitrophenyl)-1-phenylquinolin-4(1H)-one (**3v**, 111 mg, 82%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 6.8 Hz, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.54−7.50 (m, 1H), 7.45−7.33 (m, 4H), 7.21 (d, J = 8.8 Hz, 2H), 7.17 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.89−6.85 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 150.5, 146.3, 142.8, 142.2, 139.0, 134.6, 132.5, 132.4, 131.6, 1230.0, 129.9, 129.3, 128.1, 126.8, 125.8, 124.4, 122.9, 122.1, 118.3; HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3Cl$ 453.1000; found 453.1008.

*2-(4-Fluorophenyl)-3-(4-nitrophenyl)-1-phenylquinolin-4(1H)-one (**3w**, 106 mg, 81%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (dd, J = 8.0 Hz, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.54−7.52 (m, 1H), 7.45−7.41 (m, 1H), 7.39−7.34 (m, 3H), 7.30 (d, J = 8.8 Hz, 2H); 7.17−7.15 (m, 2H), 6.94−6.90 (m, 2H), 6.87 (d, J = 8.8 Hz, 1H), 6.72 (t, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175. 9, 163.2 (d, $^1J_{C,F}$ = 249 Hz, 1C), 150.8, 146.2, 143.0, 142.2, 139.1, 132.4, 132.4, 132.3 (d, $^3J_{C,F}$ = 8.5 Hz, 1C), 130.1 (d, $^4J_{C,F}$ = 3.8 Hz, 1C), 130.0, 129.8, 129.2, 126.8, 125.8, 124.4, 122.8, 122.2, 118.3, 115.2 (d, $^2J_{C,F}$ = 21.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −110.8 (m, 1F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3F$ 437.1296; found 437.1298.

*2-(3-Fluorophenyl)-3-(4-nitrophenyl)-1-phenylquinolin-4(1H)-one (**3x**, 106 mg, 81%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Off-white solid, mp 273−274 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.55−7.51 (m, 1H), 7.45−7.29 (m, 6H), 7.22−7.16 (m, 2H), 7.01 (dd, J = 13.6 Hz, 7.6 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 6.76−6.67 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.9, 162.9 (d, $^1J_{C,F}$ = 247 Hz, 1C), 150.2, 146.3, 142.8, 142.2, 138.9, 135.8 (d, $^3J_{C,F}$ = 7.7 Hz, 1C), 132.5, 132. 4, 1230.0, 129.8 (d, $^4J_{C,F}$ = 4.1 Hz, 1C), 129.6 (d, $^3J_{C,F}$ = 8.2 Hz, 1C), 129.3, 126. 8, 126.4, 126.4, 125.8, 124.5, 122.8, 121.9, 118.4, 117.7 (d, $^2J_{C,F}$ = 22.6 Hz, 1C), 115.7 (d, $^2J_{C,F}$ = 20.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −112.0 (m, 1F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3F$ 437.1296; found 437.1295.

*4-(7-Methyl-4-oxo-1,2-diphenyl-1,4-dihydroquinolin-3-yl)-benzonitrile (**3na**, 95 mg, 77%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. White solid, mp 268−270 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.36−7.27 (m, 3H), 7.23 (d, J = 8.4 Hz, 3H), 7.16−7.14 (m, 2H), 6.99−6.94 (m, 3H), 6.91−6.88 (m, 2H), 6.61 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 151.5, 143.1, 142.3, 141.2, 139.3, 134.1, 132.3, 131.2, 130.4, 130.1, 129.5, 128.9, 128.2, 127.6, 126.7, 125.9, 123.8, 122.1, 119.2, 117.8. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{29}H_{20}N_2O$ 413.1648; found 413.1642.

*4-(7-Fluoro-4-oxo-1,2-diphenyl-1,4-dihydroquinolin-3-yl)-benzonitrile (**3nb**, 116 mg, 93%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. White solid, mp 269−271 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (dd, J = 8.8 Hz, 6.4 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.37−7.29 (m, 3H), 7.23−7.21 (m, 2H), 7.17−7.15 (m, 2H), 7.14−7.09 (m, 1H), 7.03−6.96 (m, 3H), 6.94−6.90 (m, 2H), 6.52 (dd, J = 10.8 Hz, 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.3, 166.2 (d, $^1J_{C,F}$ = 250 Hz, 1C), 152.2, 143.7 (d, $^3J_{C,F}$ = 11.3 Hz, 1C), 140.7, 138.9, 133.7, 132.2, 131.3, 130.3, 129.9, 129.8, 129.3, 128.4, 127.7, 122.6 (d, $^4J_{C,F}$ = 1.2 Hz, 1C), 122.5, 119.1, 113.1 (d, $^2J_{C,F}$ = 23.0 Hz, 1C), 104.4 (d, $^2J_{C,F}$ = 27.0 Hz, 1C), 110.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −104.5 (m, 1F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{17}N_2OF$ 417.1398; found 417.1396.

*7-Fluoro-3-(2-nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3oa**, 124 mg, 95%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 254−256 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (dd, J = 8.8 Hz, 6.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.45−7.41 (m, 1H), 7.37−7.26 (m, 5H), 7.13−7.05 (m, 4H), 7.01−6.94 (m, 4H), 6.55 (dd, J = 11.2 Hz, 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 174.84, 166.21 (d, $^1J_{C,F}$ = 250 Hz, 1C), 150.77, 149.89, 143.86 (d, $^3J_{C,F}$ = 11.3 Hz, 1C), 134.06, 133.95, 132.41, 130.99, 130.14 (d, $^3J_{C,F}$ = 4.9 Hz, 1C), 130.06, 129.95, 129.49 (d, $^4J_{C,F}$ = 3.0 Hz, 1C), 129.21, 128.44, 128.20, 127.90, 127.20, 124.05, 122.05, 121.87, 112.88 (d, $^2J_{C,F}$ = 23.1 Hz, 1C), 104.23 (d, $^2J_{C,F}$ = 27.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −104.5 (s, 1F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3F$ 437.1296; found 437.1296.

*7-Chloro-3-(2-nitrophenyl)-1,2-diphenylquinolin-4(1H)-one (**3ob**, 123 mg, 91%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp >300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 8.8 Hz, 1H), 7.95 (dd, J = 8.0 Hz, 6.4 Hz, 1H), 7.46−7.42 (m, 1H), 7.31−7.37 (m, 5H), 7.30−7.25 (m, 1H), 7.11−7.06 (m, 3H), 7.02−6.96 (m, 4H), 6.88 (d, J = 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 174.9, 150.7, 149.8, 143.0, 138.9, 138.6, 134.0, 133.9, 132.4, 130.1, 130.1, 130.1, 130.0, 129.5, 129.5, 129.3, 128.7, 128.4, 128.2, 127.9, 127.2, 124.7, 124.1, 123.7, 122.1. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3Cl$ [(M + H)$^+$]: 453.1000; found 453.1004.

*2-(4-Fluorophenyl)-3-(2-nitrophenyl)-1-phenylquinolin-4(1H)-one (**3oc**, 102 mg, 78%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Light yellow solid, mp 210−212 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.94 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.53−7.48 (m, 1H), 7.44−7.28 (m, 7H), 7.15−7.11 (m, 1H), 7.08−7.04 (m, 2H), 7.03−6.99 (m, 1H), 6.89 (d, J = 8.8 Hz, 1H), 6.73−6.64 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.4, 163.3 (d, $^1J_{C,F}$ = 248 Hz, 1C), 150.0, 149.4, 142.3, 139.3. 134.1, 132.5, 132.2, 132.1 (d, $^3J_{C,F}$ = 8.3 Hz, 1C), 131.7 (d, $^3J_{C,F}$ = 8.5 Hz, 1C), 131. 1, 130.4 (d, $^4J_{C,F}$ = 3.6 Hz, 1C), 130.2, 130.1, 130.1, 129.4, 129.1, 127.9, 126.9, 125.3, 124.1, 124.0, 121.8, 118.1, 115.5 (d, $^2J_{C,F}$ = 21.6 Hz, 1C), 114.6 (d, $^2J_{C,F}$ = 21.8 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −111.4 (m, 1F). HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{27}H_{17}N_2O_3F$ 437.1296; found 437.1290.

*3-(2-Nitrophenyl)-1-phenyl-2-(p-tolyl)quinolin-4(1H)-one (**3od**, 106 mg, 82%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Yellow solid, mp 234−236 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.93 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.50−7.46 (m, 1H), 7.44−7.22 (m, 7H), 7.08−7.05 (m, 2H), 7.00−6.98 (m, 1H), 6.89−6.86 (m, 2H), 6.79−6.64 (m, 2H), 2.11 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.5, 150.7, 150.0, 142.4, 139.5, 138.1, 134.2, 132.3, 132.0, 130.2, 130.2, 130.1, 129.5, 128.8, 128.8, 127.8, 127.6, 126.9, 125.3, 124.0, 123.8, 121.6, 118.1, 21.2. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{28}H_{20}N_2O_3$ 433.1547; found 433.1543.

*3-(4-Nitrophenyl)-1-(p-tolyl)quinolin-4(1H)-one (**3ba**, 70 mg, 66%; **3bb**, 61 mg, 57%).* Eluent in chromatography: petroleum ether/EtOAc 3:1. Yellow solid, mp 201−202 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 3H), 7.56−7.52 (m, 1H), 7.45−7.41 (m, 3H), 7.37 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.5, 146.5, 142.5, 142.4, 140.9, 140.2, 138.5, 132.2, 131.1, 129.0, 127.3, 127.2, 124.6, 123.6, 119.4, 117.6, 21.3. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{22}H_{16}N_2O_3$ 357.1234; found 357.1234.

*2-Methyl-3-(4-nitrophenyl)-1-(p-tolyl)quinolin-4(1H)-one (**3bc**, 82 mg, 74%).* Eluent in chromatography: petroleum ether/EtOAc 3:1−1:1. Off-white solid, mp 272−273 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.48−7.44 (m, 3H), 7.38−7.34 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 175.5, 148.5, 146.9, 144.0, 142.5, 140.2, 136.6, 132.2, 132.0, 131.3, 128.6, 126.6, 125.3, 123.9, 123.5, 121.6, 117.9, 21.3, 20.7. HRMS (ESI-TOF) *m/z*: [(M + H)$^+$] Calcd for $C_{23}H_{18}N_2O_3$ 371.1390; found 371.1390.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR spectra for products and X-ray data for **3a** in CIF format (PDF)

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CCDC 2008744 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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J. Org. Chem. XXXX, XXX, XXX−XXX