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Base-Promoted Michael Addition/Smiles Rearrangement/*N*-Arylation Cascade: One-Step Synthesis of 1,2,3-Trisubstituted 4-Quinolones from Ynones and Sulfonamides

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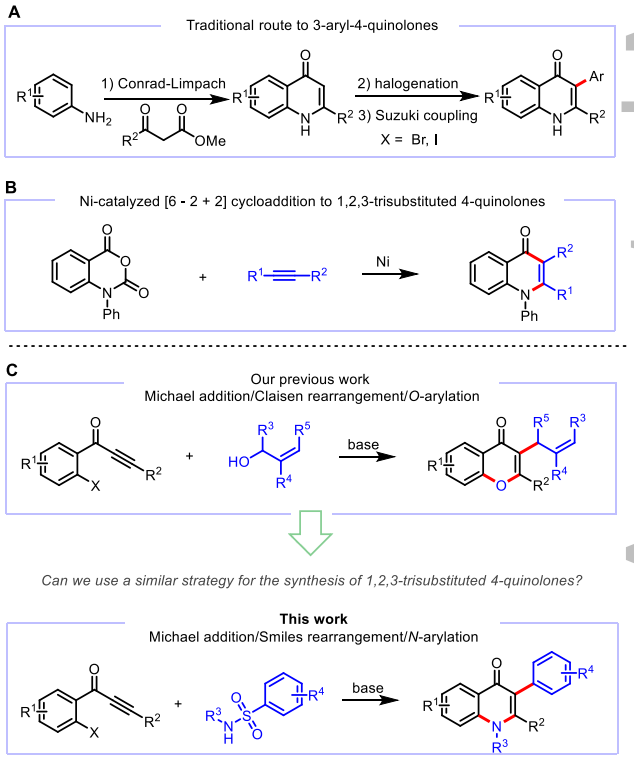
Abstract. A general, practical, and environmentally friendly protocol to synthesize 1,2,3-trisubstituted 4-quinolones from readily available ynones and sulfonamides was developed. The construction of one C–C bond and two C–N bonds *via* cleavage of one N–S, one C–S, and one C–X (X = F, Cl, Br, O) bond is achieved under transition-metal-free conditions in one step. This transformation generates 1 equiv of sulfur dioxide and 1 equiv of hydrogen halide as the byproducts. The broad substrate scope and functional group tolerance are demonstrated by 52 examples of 1,2,3-trisubstituted 4-quinolones. A preliminary mechanistic study supports a sequential Michael addition/Smiles rearrangement/*N*-arylation reaction pathway.

Keywords: transition metal-free; Smiles rearrangement; C–N bond formation; annulation; enaminone; quinolone

Introduction

4-Quinolone features a vital substructure that exists in numerous natural products and pharmaceuticals.[1] Among them, 3-aryl-4-quinolones have attracted much research interest because they have many potential biological activities, such as alkaline phosphatase inhibition,[2a] NO production inhibition,[2b] topoisomerase I inhibition,[2c] efflux pumps inhibition,[2d] antimalarial activity,[2e–g] and antiproliferative activity.[2h] Traditional methods, including the Conrad-Limpach and the Gould-Jacobs reactions, have been widely adopted for the preparation of 4-quinolones,[3] but these reactions are far from ideal in terms of their practicality and generality. Besides, harsh reaction conditions and tedious purification steps are usually required in these procedures, and the cyclization step using sterically hindered 2-aryl β-keto esters gives 3-aryl-4-quinolones in poor yields. Although the development of methods to generate 4-quinolones has been an active area of research for the past decades,[4,5] synthetic methods for the construction of 4-quinolone core bearing an aryl group at C3 position are extremely rare. In this regard, the direct C3 functionalization of the 4-quinolone core represents an attractive route to 3-substituted 4-quinolones.[6] For example, a three-step procedure *via* Conrad-Limpach/halogenation/Suzuki coupling has been well developed to access 3-aryl-4-quinolones (Scheme 1A).[7] However, transition metals and prefunctionalized 4-quinolone core are required.



Scheme 1. Methods for the synthesis of 1,2,3-trisubstituted 4-quinolones.

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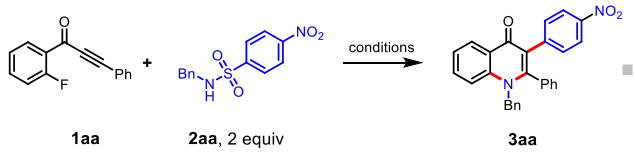
In 2009, Matsubara and co-workers reported an unprecedented synthetic entry to 1,2,3-trisubstituted 4-quinolones from alkynes and isatoic anhydrides through Ni-catalyzed [6-2+2] cycloaddition (Scheme 1B).[8] Various versatile products, including 1,2,3-triphenyl 4-quinolones, were obtained in moderate to good yields. Matsubara's work is the only example to date that constructs the 3-aryl-4-quinolones in one step. However, the application potential of this synthetic strategy is limited by using unsymmetrical alkynes as substrates, delivering regioisomers in a range of ratios from 2/1 to 6/1. Thus, the development of a general, practical, and environmentally friendly approach toward 3-aryl-4-quinolones from readily available starting materials under transition metal-free conditions is in high demand.

We previous reported a base-promoted tandem Michael addition/Claisen rearrangement/*O*-arylation of *ortho*-halogen aroyl ynones with allyl alcohols to form 3-allyl-chromones (Scheme 1C).[9] We questioned whether this open shell reaction mechanism might be translated to other cascade reaction, thereby delivering a general and efficient route to multisubstituted 4-quinolones. As part of our ongoing interest in ynone chemistry,[10] we report herein a base-mediated sequential Michael addition/Smiles rearrangement[11]/*N*-arylation to generate 1,2,3-trisubstituted 4-quinolones in one step.

Results and Discussion

At the outset, 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-one **1aa** and *N*-benzyl-4-nitrobenzenesulfonamide **2aa** was selected as the model substrates to examine the feasibility of our protocol. When the reaction of **1aa** (0.1 mmol) and **2aa** (0.2 mmol) was carried out in the presence of K_2CO_3 (2 equiv) in *N*,*N*-dimethylformamide (0.2 M) under air at 100 °C for 24 h, the desired product **3aa** was afforded in 73% yield (Table 1, entry 1). The effect of the bases was subsequently investigated (entries 2–7). Na_2CO_3 and Cs_2CO_3 could provide the desired product in good yields (entries 2,3), while lower yields of **3aa** were obtained in the present of $KHCO_3$, $NaHCO_3$, and K_3PO_4 (entries 4–6). However, the target product was not detected and only a complex mixture was obtained when a strong base KO^{t}Bu was involved in the reaction (entry 7). Moreover, the corresponding product was not formed in the absence of a base (entry 8). The solvents also played a vital role in this transformation (entries 9–14). Among them, DMSO, DMA, NMP, and DMPU were suitable solvents for this transformation, and DMSO proved the best choice (entry 9). Both increasing and decreasing the reaction temperatures would result in slight lower yields (entries 15, 16). Remarkably, 3 equiv of Cs_2CO_3 could promote this reaction to afford **3aa** in a higher yield (entry 17, 90%), whereas the yield of the product was reduced to 81% when the loadings of Cs_2CO_3 were decreased to 1.5 equiv (entry 18). Product **3aa** could be obtained in 79% yield when a K_2CO_3/DMSO system was used (entry 19). Finally, the optimal results were identified as follows: **1aa** (0.1 mmol), **2aa** (0.2 mmol), DMSO (0.2 M) as the solvent, and Cs_2CO_3 (3 equiv) as the base under air at 100 °C for 24 h.

Table 1. Screening of the reaction conditions[a]



1aa **2aa**, 2 equiv **3aa**

Entry	Solvent	Base	Temp °C	Yield[%][b]
1	DMF	K_2CO_3	100	73
2	DMF	Na_2CO_3	100	61
3	DMF	Cs_2CO_3	100	74
4	DMF	$KHCO_3$	100	40
5	DMF	$NaHCO_3$	100	35
6	DMF	K_3PO_4	100	45
7	DMF	KO^{t}Bu	100	0
8	DMF	-	100	0
9	DMSO	Cs_2CO_3	100	88
10	DMA	Cs_2CO_3	100	84
11	NMP	Cs_2CO_3	100	80
12	DMPU	Cs_2CO_3	100	76
13	THF	Cs_2CO_3	100	20
14	CH_3CN	Cs_2CO_3	100	23
15	DMSO	Cs_2CO_3	80	79
16	DMSO	Cs_2CO_3	120	80
17[c]	**DMSO**	**Cs_2CO_3**	**100**	**90**
18[d]	DMSO	Cs_2CO_3	100	81
19	DMSO	K_2CO_3	100	79

[a] *Reaction conditions*: **1aa** (0.1 mmol), **2aa** (0.2 mmol), base (2 equiv), solvent (0.2 M) at a corresponding temperature under air atmosphere for 24 h.
[b] Isolated yield.
[c] 3 equiv of base were used.
[d] 1.5 equiv of base was used. DMF = *N*,*N*-dimethylformamide. DMSO = dimethylsulfoxide. NMP = *N*-methyl-2-pyrrolidone. DMPU = *N*,*N*-dimethyl propionyl urea. DMA = *N*,*N*-dimethylethanamide.

With the optimal reaction conditions in hand, the effect of the X substituent on the formation of the 4-quinolone was first investigated (eq. 1). When fluoro was replaced by chloro or bromo, the yields of **3aa** were decreased to 42% and 57%, respectively. Interestingly, the desired product can be afforded in 14% yield by using methoxy-substituted substrate.

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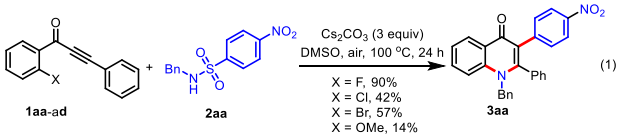
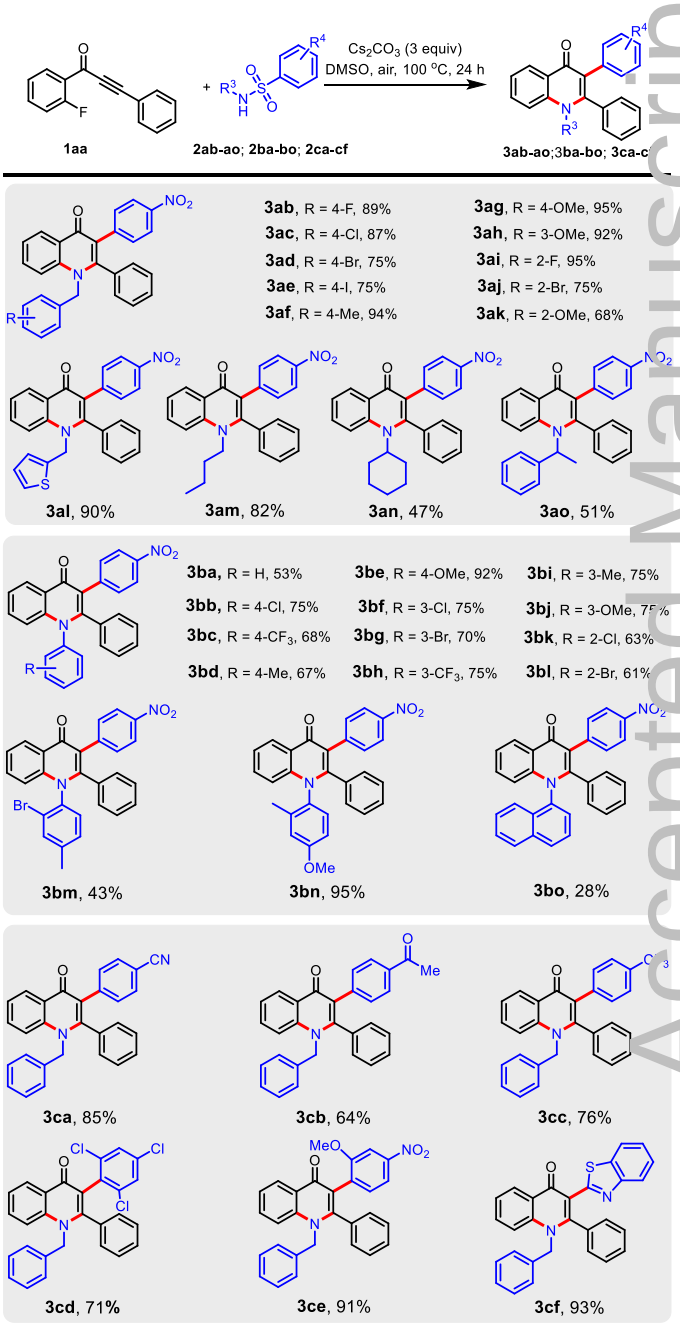


Subsequently, the scope of sulfonamides was investigated as shown in Scheme 2. A range of *N*-alkyl substituted 4-nitrobenzenesulfonamides (**2ab**-**ao**) were investigated. Having proved the good matching of this reaction system with a variety of *N*-(substituted benzyl) sulfonamides, the corresponding products (**3ab**–**ak**) were obtained in moderate to excellent yields (68%-95%). It is noteworthy that various sulfonamides with halogen substituent, including -F, -Cl, -Br, and -I, were well-tolerated (**3ab**–**ae, 3ai, 3aj**). Notably, these halogen-containing products are difficult to be synthesized by transition metal-catalyzed reactions, and could be further elaborated through well-established cross-coupling reactions. In addition, thiophen-2-ylmethyl substrate was also tolerated, giving the corresponding product (**3al**) in 90% yield. Importantly, *N*-cyclohexyl and *N*-(1-phenylethyl) quinolones (**3an** and **3ao**) could also be obtained, albeit in relatively low yields due to the increased bulkiness.

Inspired by these exciting results, we further explored *N*-aryl substituted substrates. A range of *N*-aryl substituted sulfonamides were applied in this transformation, giving the desired products in moderate to excellent yields (**3ba**–**bo**). Various valuable functional groups such as halogen, methyl, methoxyl, and trifluoromethyl at *para*-, *meta*-, and *ortho*-position of *N*-aryl rings were tolerated. The electronic properties of the *N*-phenyl rings were observed to affect the reactivity slightly and the substrates with electron-withdrawing groups (**3bb**, **3bc**) gave lower yields than that with electron-donating group (**3be**). The reaction efficiency was sensitive to the steric hindrance of the *N*-phenyl rings, and moderate yields were obtained when *ortho*-Cl and -Br substituted substrates were used (**3bk**–**bm**). The *N*-(2-methyl-4-methoxylphenyl) substrate could give the desired product (**3bn**) in 95% yield, probably because the methoxyl-containing substrate matched the reaction preferably. However, the naphthalenyl substrate afforded the corresponding product only in 28% yield (**3bo**). Finally, this reaction was not applicable to 4-nitrobenzenesulfonamide and 4-nitrobenzenesulfonic acid.[13]

It is an inherent fact that the Smiles rearrangement commonly requires strong electron-withdrawing groups to stabilize the Meisenheimer intermediate,[11a,b] and it was no exception in our reaction system. For instance, substrates with electron-donating groups on benzenesulfonyl moiety, such as methyl and methoxyl, all proved inefficient. To our delight, substrates with cyano, acetyl, and trifluoromethyl groups were suitable, affording the corresponding products in moderate to good yields (**3ca**–**cc**). The trichloro-substituted sulfonamide proceeded smoothly, generating the target product (**3cd**) in 71% yield. Interestingly, an electron-donating group (methoxyl) at the *ortho*-position of 4-nitrobenzenesulfonyl ring did not retard the reactivity, and the desired product was obtained in excellent yield (**3ce**). Finally, heteroaryl sulfonamide was also employed, giving the corresponding product in 93% yield (**3cf**). The structures of (**3bi**) and **(3cd)** were unambiguously verified by single-crystal X-ray diffraction.[12]



Scheme 2. Scope of sulfonamides.

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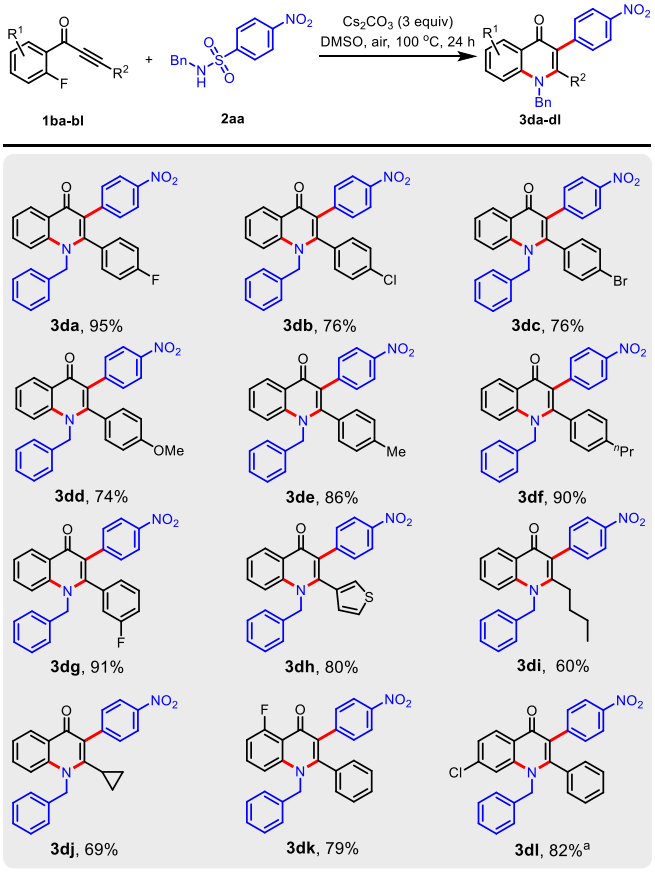
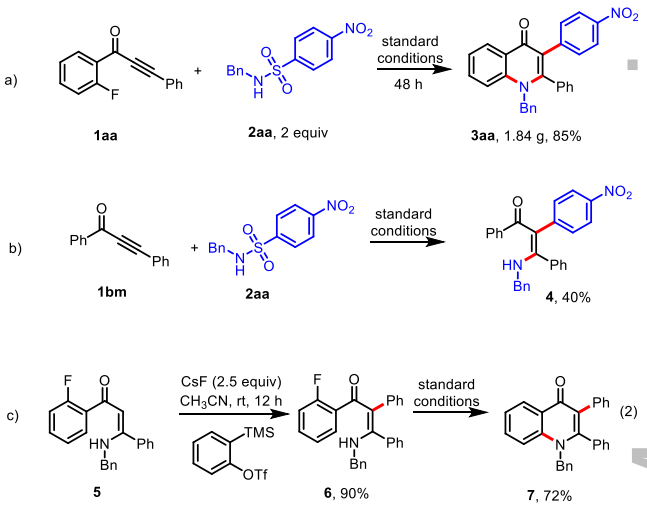
Besides, the scope of the reaction was then explored with various ynone derivatives (Scheme 3). To our delight, the reaction proceeded well with various aryl and alkyl substituted ynones. Ynones with either electron-withdrawing groups (F, Cl, and Br) or electron-donating groups (Me, OMe, and Et) on R^2 could generate the corresponding products in good yields (**3da**–**dg**, 76–95%). 2-Thienyl-4-quinolone was also formed in this transformation with high efficiency (**3dh**, 80%). 60% and 69% yields of the target products (**3di** and **3dj**) were respectively obtained when ^{n}butyl and cyclopropyl substrates were involved in the reaction. No corresponding product was found when R^2 was a ^{t}butyl group, presumably because the high bulkiness prevents the effective conjugate addition. Finally, the halogen groups, including -F and -Cl, on the aroyl moiety were also investigated, affording the desired product in good yields (**3dk**, **3dl**, 79% and 82%). 1-(2-Fluorophenyl)prop-2-yn-1-one and 1-fluoro-2-(phenylethynyl)benzene failed to provide the desired products, indicating that the R^2 substituents and the carbonyl group are indispensable moieties for this transformation.



Scheme 3. Scope of ynones. [a]1-(2,4-dichlorophenyl)-3-phenylprop-2-yn-1-one was used as substrate.

A gram-scale conversion was performed using **1aa** and **2aa** as starting substrates, and the target product **3aa** was obtained in 85% isolated yield, demonstrating the potential value of this reaction (Scheme 4a). Furthermore, control experiments were performed to explore the mechanistic hypothesis. Thus, the reaction of ynone **1bm** and sulfonamide **2aa** could give the Smiles rearrangement product **4** in 40% yield under the standard conditions (Scheme 4b). Subsequently, the independently synthesized enaminone intermediate **6** was subjected to the standard reaction conditions, and the target 2,3-diphenyl-4-quinolone **7** was obtained in 72% yield (Scheme 4c).



Scheme 4. Gram-scale reaction and controlled experiments.

On the basis of the experimental results and literature reports, the reaction mechanism is proposed as shown in Scheme 5. The initial Michael addition of ynone **1** and sulfonamide **2** under basic conditions affords the active enaminone anion **A**. Subsequently, this anion is poised for intramolecular cyclization to give the Meisenheimer intermediate **B**. Extrusion of SO_2 results in the Smiles rearrangement product **C**. Isomerization of the double bond of **C** leads to enaminone **D**, which undergoes base-promoted intramolecular S_NAr reaction to furnish the final 4-quinolone product **3**.

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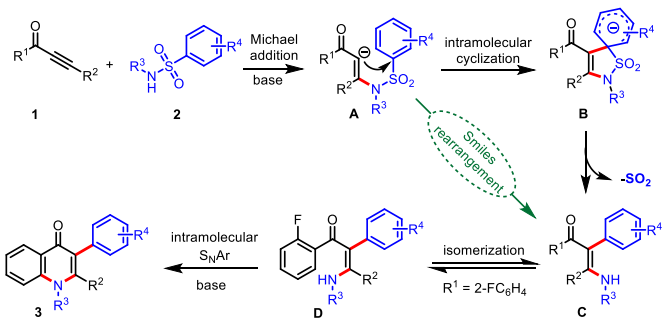

Scheme 5. Plausible reaction mechanism.

Conclusion

In summary, we have develop a general, practical, and efficient protocol to prepare 1,2,3-trisubstituted 4-quinolones from ynones and sulfonamides under transition-metal free conditions. This transformation is understood to proceed through a tandem Michael addition/Smiles rearrangement/*N*-arylation reaction. The compatibility of this protocol with various functional groups has been proven. This cost-effective and environmental-friendly method would be expected to find wide applications in pharmaceutical chemistry and chemical biology.

Experimental Section

General Information

All the solvents were used without further purification. The other commercial chemicals were used without further purification. All reactions were performed under an inert atmosphere of nitrogen in flame-dried glassware, unless otherwise stated. Analytical thin-layer chromatography was performed on 0.25 mm silica gel, 60-F254. Visualization was carried out with UV light and Vogel's permanganate. Preparative TLC was performed on 1.0 mm silica gel. ^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument (500 MHz). ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument (126 MHz) and were fully decoupled by broad band proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 mass spectrometer using ESI-TOF (electrospray ionization time-of-flight). NMR spectra were recorded in $CDCl_3$. ^{1}H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are reported in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

General Procedure for the preparation of 1,2,3-trisubstituted 4-quinolones

A dried 10 mL Schlenk tube was charged with ynone **1aa** (0.1 mmol), sulfonamide **2aa** (0.2 mmol), Cs_2CO_3 (0.3 mmol), and DMSO (0.5 mL). The reaction mixture was heated to 100 °C for 24 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, and the reaction mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The resulting residue was purified by preparative thin layer chromatograpy (PTLC) with ethyl acetate : hexane = 1 : 4 (v/v) to give the corresponding products.

1-benzyl-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3aa) (38.5 mg, 90%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.56 (m, 1H), 7.97 (d, *J* = 8.9 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.25 (m, 3H), 7.25 – 7.22 (m, 1H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 2H), 7.00 (d, *J* = 6.9 Hz, 2H), 5.28 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 152.8 , 146.0 , 143.4 , 140.7 , 136.0 , 133.6 , 132.8 , 132.3 , 129.5 , 129.0 , 128.5 , 127.7 , 127.3 , 126.8 , 125.4 , 124.3 , 122.6 , 122.5 , 117.3 , 52.7; HRMS (EI) for $C_{28}H_{21}N_2O_3^+$ $(M+H)^+$: calculated 433.1547, found 433.1543.

1-(4-fluorobenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ab) (40.0 mg, 89%). white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 3H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.03 – 6.95 (m, 4H), 5.25 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 162.0 (d, J = 246.9 Hz), 152.6 , 146.0 , 143.2 , 140.5 , 133.5 , 132.9 , 132.3 , 131.6 (d, J = 3.2 Hz), 129.6 , 129.0 , 128.5 , 127.3 , 127.1 (d, J = 8.1 Hz), 126.7 , 124.3 , 122.6 , 117.1 , 116.0 (d, J = 21.8 Hz), 52.0; HRMS (EI) for $C_{28}H_{20}FN_2O_3^+$ $(M+H)^+$: calculated 451.1452, found 451.1447.

1-(4-chlorobenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ac) (40.4 mg, 87%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.24 – 7.15 (m, 5H), 7.11 (t, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.16 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 152.6 , 146.0 , 143.2 , 140.5 , 134.5 , 133.6 , 133.5 , 132.9 , 132.3 , 129.6 , 129.2 , 128.9 , 128.6 , 127.4 , 126.8 , 124.4 , 122.6 , 117.1 , 52.1; HRMS (EI) for $C_{28}H_{20}ClN_2O_3^+$ $(M+H)^+$: calculated 467.1157, found 467.1157.

1-(4-bromobenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ad) (38.4 mg, 75%).

white solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.47 – 7.42 (m, 3H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.21 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.66 , 152.59 , 146.02 , 143.17 , 140.47 , 135.05 , 133.49 , 132.92 , 132.26 , 132.16 , 129.62 , 128.92 , 128.62 , 127.40 , 127.13 , 126.73 , 124.41 , 122.65 , 122.60 , 121.60 , 117.04 , 52.11; HRMS (EI) for $C_{28}H_{20}BrN_2O_3^+$ $(M+H)^+$: calculated 511.0652, found 511.0648.

1-(4-iodobenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ae) (41.9 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 – 8.57 (m, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.68 – 7.60 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 5.22 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6 , 152.6 , 146.01 , 143.2 , 140.5 , 138.1 , 135.8 , 133.5 , 132.9 , 132.3 , 129.6 , 128.9 , 128.6 , 127.4 , 127.3 , 126.7 , 124.4 , 122.7 , 122.6 , 117.0 , 93.06 , 52.19; HRMS (EI) for $C_{28}H_{20}IN_2O_3^+$ $(M+H)^+$: calculated 559.0513, found 559.0507.

1-(4-methylbenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3af) (41.3 mg, 94%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.45 – 7.40 (m, 2H), 7.28 – 7.22 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 2H), 7.13 – 7.07 (m, 4H), 6.89 (d, *J* = 7.9 Hz, 2H), 5.24 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 152.9 , 146.0 , 143.4 , 140.7 , 137.5 , 133.7 , 132.9 , 132.8 , 132.3 , 129.7 , 129.5 , 129.0 , 128.5 , 127.2 , 126.7 , 125.3 , 124.3 , 122.6 , 122.4 , 117.4 , 52.6 , 21.0; HRMS (EI) for $C_{29}H_{23}N_2O_3^+$ $(M+H)^+$: calculated 447.1703, found 447.1699.

1-(4-methoxybenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ag) (43.9 mg, 95%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.48 (m, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.36 (t, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 3H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 5.14 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 175.7 , 159.0 , 152.8 , 146.0 , 143.4 , 140.7 , 133.7 , 132.7 , 132.3 , 129.5 , 129.1 , 128.5 , 127.8 , 127.3 , 126.8 , 126.6 , 124.2 , 122.6 , 122.4 , 117.4 , 114.4 , 55.3 , 52.2; HRMS (EI) for $C_{29}H_{23}N_2O_4^+$ $(M+H)^+$: calculated 463.1652, found 463.1652.

1-(3-methoxybenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ah) (42.9 mg, 92%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.59 (t, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.82 – 6.78 (m, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.54 (s, 1H), 5.24 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 160.0 , 152.7 , 145.9 , 143.4 , 140.6 , 137.7 , 133.6 , 132.8 , 132.3 , 130.1 , 129.5 , 129.0 , 128.5 , 127.2 , 126.7 , 124.2 , 122.6 , 122.4 , 117.6 , 117.3 , 112.3 , 111.7 , 55.2 , 52.6; HRMS (EI) for $C_{29}H_{23}N_2O_4^+$ $(M+H)^+$: calculated 463.1652, found 463.1649.

1-(2-fluorobenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ai) (42.8 mg, 95%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 – 8.48 (m, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.24 – 7.16 (m, 4H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.01 (q, *J* = 10.4, 9.5 Hz, 4H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.22 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 175.7, 159.4 (d, *J* = 246.2 Hz), 152.8, 146.1, 143.2, 140.5, 133.5, 133.0, 132.3, 129.7, 129.5 (d, *J* = 8.2 Hz), 128.9, 128.6, 127.4, 127.1 (d, *J* = 3.4 Hz), 126.8, 124.6 (d, *J* = 3.4 Hz), 124.4, 123.2 (d, *J* = 14.2 Hz), 122.7, 122.7, 116.8, 115.6 (d, *J* = 20.4 Hz), 47.0 (d, *J* = 6.3 Hz); HRMS (EI) for $C_{28}H_{20}FN_2O_3^+$ $(M+H)^+$: calculated 451.1452, found 451.1451.

1-(2-bromobenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3aj) (38.3 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.16 (m, 5H), 7.11 (q, *J* = 7.2 Hz, 3H), 6.97 (d, *J* = 7.1 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 5.15 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.73 , 152.69 , 146.06 , 143.19 , 140.48 , 134.84 , 133.38 , 133.11 , 133.06 , 132.31 , 129.67 , 129.31 , 128.79 , 128.64 , 127.94 , 127.44 , 127.14 , 126.71 , 124.46 , 122.70 , 121.45 , 116.92 , 53.21; HRMS (EI) for $C_{28}H_{20}BrN_2O_3^+$ $(M+H)^+$: calculated 511.0652, found 511.0651.

1-(2-methoxybenzyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ak) (32.6 mg, 68%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.21 – 7.12 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.82 – 6.76 (m, 2H), 6.74 (d, *J* = 7.3 Hz, 1H), 5.14 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 155.7 , 153.0 , 145.9 , 143.5 , 140.6 , 133.7 , 132.8 , 132.3 , 129.3 , 128.9 128.7 , 128.4 , 127.1 , 126.7 , 126.2 , 124.2 , 124.0 , 122.6 , 122.4 , 120.7 , 117.3 , 110.2 , 55.2 , 48.3; HRMS (EI) for $C_{29}H_{23}N_2O_4^+$ $(M+H)^+$: calculated 463.1652, found 463.1653.

3-(4-nitrophenyl)-2-phenyl-1-(thiophen-2-ylmethyl)quinolin-4(1*H*)-one (3al) (39.5 mg, 90%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 – 8.47 (m, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.13 (m, 5H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.87 – 6.84 (m, 1H), 6.68 – 6.66 (m,

1H), 5.32 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 152.2 , 146.0 , 143.3 , 140.5 , 138.7 , 133.4 , 132.8 , 132.3 , 129.6 , 129.3 , 128.6 , 127.4 , 127.0 , 126.8 , 125.6 , 125.2 , 124.4 , 122.8 , 122.7 , 116.9 , 48.6; HRMS (EI) for $C_{26}H_{19}N_2O_3S^+$ $(M+H)^+$: calculated 439.1111, found 439.1114.

1-butyl-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3am) (34.2 mg, 82%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.77 – 7.71 (m, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.23 – 7.15 (m, 4H), 4.03 – 3.94 (m, 2H), 1.77 – 1.64 (m, 2H), 1.17 (q, *J* = 7.4 Hz, 2H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3 , 152.1 , 145.9 , 143.5 , 140.1 , 134.0 , 132.6 , 132.3 , 129.3 , 129.2 , 128.5 , 127.4 , 126.9 , 124.0 , 122.5 , 122.2 , 116.3 , 48.9 , 30.7 , 19.6 , 13.3; HRMS (EI) for $C_{25}H_{23}N_2O_3^+$ $(M+H)^+$: calculated 399.1703, found 399.1699.

1-cyclohexyl-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3an) (20.0 mg, 47%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 – 8.54 (m, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.70 – 7.65 (m, 1H), 7.44 – 7.39 (m, 1H), 7.33 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 7.17 – 7.13 (m, 2H), 4.17 – 4.07 (m, 1H), 2.48 (q, *J* = 12.1 Hz, 2H), 1.93 – 1.77 (m, 4H), 1.60 (d, *J* = 13.5 Hz, 1H), 1.23 – 1.14 (m, 1H), 0.98 – 0.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2 , 153.2 , 145.9 , 143.8 , 140.4 , 135.1 , 132.3 , 131.2 , 129.2 , 128.7 , 127.7 , 127.5 , 123.8 , 122.6 , 122.4 , 119.0 , 63.8 , 30.8 , 26.4 , 25.0; HRMS (EI) for $C_{27}H_{25}N_2O_3^+$ $(M+H)^+$: calculated 425.1860, found 425.1855.

3-(4-nitrophenyl)-2-phenyl-1-(1-phenylethyl)quinolin-4(1*H*)-one (3ao) (23.8 mg, 51%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.44 (m, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 3H), 7.25 – 7.12 (m, 12H), 5.69 (q, *J* = 7.0 Hz, 1H), 1.90 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.51 , 153.06 , 145.93 , 143.73 , 140.02 , 138.83 , 134.49 , 132.29 , 131.23 , 129.45 , 129.16 , 128.94 , 128.85 , 128.76 , 128.21 , 127.77 , 127.41 , 127.31 , 125.01 , 123.80 , 122.61 , 122.47 , 119.98 , 59.05 , 17.64; HRMS (EI) for $C_{29}H_{23}N_2O_3^+$ $(M+H)^+$: calculated 447.1703, found 447.1699.

3-(4-nitrophenyl)-1,2-diphenylquinolin-4(1*H*)-one (3ba) (22.2 mg, 53%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 – 8.58 (m, 1H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.48 – 7.43 (m, 1H), 7.39 – 7.30 (m, 5H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.04 – 6.98 (m, 3H), 6.97 – 6.92 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 , 151.8 , 146.0 , 143.2 , 142.1 , 139.1 , 133.8 , 132.4 , 132.3 , 130.3 , 130.0 , 129.6 , 129.0 , 128.4 , 127.7 , 126.8 , 125.8 , 124.3 , 122.7 , 121.9 , 118.3; HRMS (EI) for $C_{27}H_{19}N_2O_3^+$ $(M+H)^+$: calculated 419.1390, found 419.1385.

1-(4-chlorophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bb) (33.5 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.50 (m, 1H), 7.99 – 7.90 (m, 2H), 7.57 – 7.49 (m, 1H), 7.45 – 7.39 (m, 1H), 7.35 – 7.25 (m, 4H), 7.15 – 7.09 (m, 2H), 7.07 – 7.00 (m, 3H), 6.96 – 6.91 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8 , 151.5 , 145.9 , 142.9 , 141.9 , 137.6 , 134.9 , 133.5 , 132.4 , 132.3 , 131.2 , 130.1 , 129.8 , 128.6 , 127.8 , 126.7 , 125.7 , 124.3 , 122.6 , 121.9 , 117.9; HRMS (EI) for $C_{27}H_{18}ClN_2O_3^+$ $(M+H)^+$: calculated 453.1000, found 453.0995.

3-(4-nitrophenyl)-2-phenyl-1-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3bc) (33.0 mg, 68%). white solid. ^{1}H NMR (500 MHz, CDCl3) δ 8.51 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.29 – 7.20 (m, 4H), 6.95 (q, J = 7.5, 6.4 Hz, 3H), 6.85 (d, J = 6.8 Hz, 2H), 6.72 (d, J = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 151.2, 146.2, 142.7, 142.3, 141.7, 133.3, 132.6, 132.3, 132.2 (q, *J* = 33.3 Hz), 130.8, 130.2, 128.8, 128.0, 127.1, 126.8 (q, *J* = 3.6 Hz), 125.8, 124.6, 123.0 (q, *J* = 272.7 Hz),122.7, 122.3, 117.8; HRMS (ESI-TOF) m/z: calcd for $C_{28}H_{17}F_3N_2NaO_3$ $(M+Na)^+$: calculated 509.1083, found 509.1084.

3-(4-nitrophenyl)-2-phenyl-1-(*p*-tolyl)quinolin-4(1*H*)-one (3bd) (29.0 mg, 67%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.46 (m, 1H), 7.92 – 7.86 (m, 2H), 7.45 – 7.41 (m, 1H), 7.36 – 7.32 (m, 1H), 7.23 – 7.20 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.91 (m, 5H), 6.87 – 6.84 (m, 2H), 6.81 (d, *J* = 8.6 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 , 152.0 , 146.0 , 143.3 , 142.3 , 139.0 , 136.5 , 133.9 , 132.4 , 132.2 , 130.3 , 130.1 , 129.6 , 128.3 , 127.6 , 126.7 , 125.8 , 124.2 , 122.6 , 121.8 , 118.4 , 21.1; HRMS (EI) for $C_{28}H_{21}N_2O_3^+$ $(M+H)^+$: calculated 433.1547, found 433.1543.

1-(4-methoxyphenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3be) (41.4 mg, 92%). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.02 – 6.97 (m, 2H), 6.96 – 6.91 (m, 3H), 6.87 – 6.81 (m, 3H), 6.77 – 6.73 (m, 2H), 3.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 , 159.4 , 152.2 , 146.0 143.3 , 142.5 , 134.0 , 132.4 , 132.2 , 131.8 , 130.9 , 130.2 , 128.3 , 127.7 , 126.7 , 125.9 , 124.2 , 122.7 , 121.9 , 118.3 , 114.6 , 55.4; HRMS (EI) for $C_{28}H_{21}N_2O_4^+$ $(M+H)^+$: calculated 449.1496, found 449.1492.

1-(3-chlorophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bf) (34.0 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.14 (s, 1H), 7.04 – 7.00 (m,

1H), 7.00 – 6.92 (m, 3H), 6.90 – 6.83 (m, 2H), 6.79 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.91 , 151.42 , 146.10 , 142.83 , 141.79 , 140.16 , 135.22 , 133.44 , 132.51 , 132.32 , 130.49 , 130.37 , 130.22 , 130.14 , 129.37 , 128.68 , 128.36 , 127.93 , 127.86 , 126.91 , 125.71 , 124.46 , 122.69 , 122.08 , 117.94; HRMS (EI) for $C_{27}H_{18}ClN_2O_3^+$ $(M+H)^+$: calculated 453.1000, found 453.0997.

1-(3-bromophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bg) (34.8 mg, 70%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.47 – 7.42 (m, 2H), 7.37 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.09 – 6.99 (m, 3H), 6.97 – 6.90 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.91 , 151.42 , 146.11 , 142.83 , 141.80 , 140.26 , 133.45 , 133.25 , 132.52 , 132.32 , 132.26 , 130.71 , 130.24 , 130.13 , 128.80 , 128.70 , 127.93 , 127.87 , 126.93 , 125.71 , 124.46 , 122.87 , 122.70 , 122.08 , 117.96; HRMS (ESI-TOF) m/z: calcd for $C_{27}H_{17}BrN_2NaO_3^+$ $(M+Na)^+$: calculated 519.0315, found 519.0312.

3-(4-nitrophenyl)-2-phenyl-1-(3-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3bh) (36.5 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.90 (m, 3H), 6.89 – 6.86 (m, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 151.4, 146.1, 142.7, 141.7, 139.7, 133.5, 133.4, 132.6, 132.3, δ 132.2 (q, *J* = 33.3 Hz), 130.3, 130.2, 130.1, 128.7, 128.0, 127.9, 127.3 (q, *J* = 3.7 Hz), 127.0, 125.8 (q, *J* = 3.8 Hz), 124.5, 123.0 (q, *J* = 272.7 Hz), 122.7, 117.7; HRMS (ESI-TOF) m/z: calcd for $C_{28}H_{17}F_3N_2NaO_3^+$ $(M+Na)^+$: calculated 509.1083, found 509.1079.

3-(4-nitrophenyl)-2-phenyl-1-(*m*-tolyl)quinolin-4(1*H*)-one (3bi) (30.3 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.52 (m, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.49 (m, 1H), 7.43 – 7.40 (m, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.88 (m, 8H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 , 151.8 , 145.9 , 143.3 , 142.1 , 139.7 , 138.9 , 133.8 , 132.4 , 132.2 , 130.4 , 130.2 , 129.6 , 129.2 , 128.3 , 127.6 , 127.5 , 126.9 , 126.6 , 125.7 , 124.2 , 122.6 , 121.7 , 118.4 , 21.1; HRMS (ESI-TOF) m/z: calcd for $C_{28}H_{20}N_2NaO_3^+$ $(M+Na)^+$: 455.1366, found 455.1361.

1-(3-methoxyphenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bj) (33.5 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.55 (m, 1H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.04 – 6.93 (m, 6H), 6.85 – 6.82 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.68 (t, *J* = 1.9 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.90 , 160.35 , 151.66 , 146.02 , 143.17 , 141.95 , 140.04 , 133.80 , 132.39 , 132.30 , 130.31 , 130.18 , 130.17 , 128.45 , 127.67 , 126.74 , 125.75 , 124.28 , 122.67 , 122.24 , 121.86 , 118.32 , 115.77 , 114.66 , 55.50 ; HRMS (EI) for $C_{28}H_{21}N_2O_4^+$ $(M+H)^+$: calculated 449.1496, found 449.1493.

1-(2-bromophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bk) (28.5 mg, 61%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.17 (m, 5H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.01 – 6.86 (m, 4H), 6.65 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2 , 151.5 , 146.1 , 142.9 , 141.1 , 136.8 , 134.0 , 133.3 , 132.7 , 132.4 , 132.1 , 130.7 , 130.6 , 130.2 , 128.9 , 128.7 , 127.9 , 127.9 , 127.6 , 127.0 , 125.8 , 124.5 , 122.7 , 122.4 , 117.3; HRMS (EI) for $C_{27}H_{18}ClN_2O_3^+$ $(M+H)^+$: calculated 453.1000, found 453.0997.

1-(2-bromophenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bl) (31.4 mg, 63%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.57 (m, 1H), 7.56 – 7.52 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 7.05 – 6.96 (m, 4H), 6.72 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1 , 151.3 , 146.1 , 143.0 , 141.0 , 138.3 , 133.9 , 133.3 , 132.6 , 132.4 , 132.3 , 130.8 , 130.3 , 128.9 , 128.8 , 128.5 , 127.8 , 127.5 , 127.0 , 125.8 , 124.5 , 124.4 , 122.6 , 122.4 , 117.4; HRMS (EI) for $C_{27}H_{18}BrN_2O_3^+$ $(M+H)^+$: calculated 497.0495, found 497.0490.

1-(2-bromo-4-methylphenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bm) (23.6 mg, 43%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.53 (m, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.07 – 6.95 (m, 4H), 6.73 (d, *J* = 8.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1 , 151.5 , 146.1 , 143.1 , 141.4 , 141.2 , 135.6 , 134.2 , 133.4 , 132.6 , 132.4 , 131.7 , 130.3 129.3 , 129.0 , 128.8 , 127.8 , 127.5 , 126.9 , 125.8 , 124.4 , 124.0 , 122.7 , 122.4 , 117.5 , 20.9; HRMS (EI) for $C_{28}H_{20}BrN_2O_3^+$ $(M+H)^+$: calculated 511.0652, found 511.0655.

1-(4-methoxy-2-methylphenyl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bn) (44.0 mg, 95%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 1H), 7.97 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.44 – 7.39 (m, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.07 – 7.00 (m, 4H), 6.99 – 6.93 (m, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* =

8.5 Hz, 1H), 6.70 – 6.65 (m, 2H), 3.75 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 , 159.6 , 152.2 , 145.9 , 143.3 , 141.7 , 137.5 , 133.7 , 132.5 , 132.4 , 131.3 , 130.7 , 130.6 , 128.5 , 127.7 , 127.5 , 126.8 , 125.9 , 124.3 , 122.6 , 122.0 , 117.7 , 116.0 , 112.3 , 55.3 , 17.9; HRMS (EI) for $C_{29}H_{23}N_2O_4^+$ $(M+H)^+$: calculated 463.1652, found 463.1647.

1-(naphthalen-1-yl)-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3bo) (13.1 mg, 28%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 – 8.58 (m, 1H), 8.02 – 7.95 (m, 2H), 7.89 – 7.83 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.46 – 7.36 (m, 3H), 7.39 – 7.32 (m, 3H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.69 – 6.65 (m, 1H), 6.65 – 6.57 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1 , 152.6 , 146.0 , 143.1 , 142.1 , 135.5 , 134.1 , 133.6 , 132.5 , 132.4 , 131.0 , 130.2 , 129.8 , 128.7 , 128.6 , 128.5 , 128.4 , 127.9 , 127.4 , 127.1 , 126.9 , 126.8 , 125.8 , 125.1 , 124.4 , 122.7 , 122.5 , 122.2 , 118.4; HRMS (EI) for $C_{31}H_{21}N_2O_3^+$ $(M+H)^+$: calculated 469.1547, found 469.1550.

4-(1-benzyl-4-oxo-2-phenyl-1,4-dihydroquinolin-3-yl)benzonitrile (3ca) (35.1 mg, 85%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 1H), 7.61 – 7.55 (m, 1H), 7.44 – 7.36 (m, 4H), 7.34 – 7.27 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.1 Hz, 2H), 7.00 (d, *J* = 7.0 Hz, 2H), 5.26 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 152.7 , 141.2 , 140.7 , 136.1 , 133.7 , 132.7 , 132.2 , 131.2 , 129.4 , 129.1 , 129.0 , 128.4 , 127.7 , 127.3 , 126.8 , 125.4 , 124.2 , 122.9 , 119.1 , 117.3 , 109.8 , 52.7; HRMS (EI) for $C_{29}H_{21}N_2O^+$ $(M+H)^+$: calculated 413.1648, found 413.1645.

3-(4-acetylphenyl)-1-benzyl-2-phenylquinolin-4(1*H*)-one (3cb) (27.3 mg, 64%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.49 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.14 – 7.09 (m, 3H), 7.05 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.1 Hz, 2H), 6.92 (d, *J* = 6.9 Hz, 2H), 5.18 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1 , 176.0 , 152.5 , 141.3 , 140.7 , 136.2 , 134.8 , 134.0 , 132.5 , 131.6 , 129.1 , 129.1 , 128.9 , 128.3 , 127.6 , 127.5 , 127.3 , 126.8 , 125.4 , 123.9 , 123.5 , 117.2 , 52.6 , 26.5; HRMS (EI) for $C_{30}H_{24}NO_2^+$ $(M+H)^+$: calculated 430.1802, found 430.1801.

1-benzyl-2-phenyl-3-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3cc) (34.6 mg, 76%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 – 8.57 (m, 1H), 7.59 – 7.55 (m, 1H), 7.43 – 7.35 (m, 4H), 7.33 – 7.26 (m, 3H), 7.24 – 7.18 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 7.1 Hz, 2H), 7.00 (d, *J* = 7.0 Hz, 2H), 5.26 (s, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 152.7, 140.7, 139.7, 136.2, 133.9, 132.6, 131.7, 129.2, 129.0, 129.0, 128.3, 128.1 (q, *J* = 32.1 Hz), 127.6, 127.3, 126.8, 125.4, 124.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.0 Hz), 124.0, 123.3, 117.2; HRMS (EI) for $C_{29}H_{21}F_3NO^+$ $(M+H)^+$: calculated 456.1570, found 456.1570.

1-benzyl-2-phenyl-3-(2,4,6-trichlorophenyl)quinolin-4(1*H*)-one (3cd) (34.8 mg, 71%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.55 (m, 1H), 7.57 – 7.51 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.19 (d, *J* = 8.9 Hz, 4H), 7.02 (d, *J* = 7.2 Hz, 2H), 5.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.71 , 152.84 , 140.71 , 136.68 , 135.99 , 133.77 , 133.64 , 133.44 , 132.54 , 129.68 , 128.91 , 128.13 , 127.52 , 127.50 , 127.21 , 126.82 , 126.49 , 125.28 , 123.94 , 118.88 , 117.26 , 52.35; HRMS (ESI-TOF) m/z: calcd for $C_{28}H_{18}Cl_3NNaO^+$: 512.0346 $(M + Na)^+$, found: 512.0347.

1-benzyl-3-(2-methoxy-4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3ce) (42.1 mg, 91%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.53 (m, 1H), 7.65 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.33 – 7.24 (m, 3H), 7.22 – 7.08 (m, 5H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.1 Hz, 2H), 5.26 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6 , 157.5 , 152.8 , 147.8 , 140.7 , 136.1 , 133.8 , 133.2 , 133.0 , 132.4 , 129.3 , 128.9 , 128.5 , 128.0 , 127.6 , 127.5 , 127.1 , 126.5 , 125.4 , 123.9 , 119.3 , 117.2 , 115.3 , 105.3 , 55.7 , 52.5; HRMS (EI) for $C_{29}H_{23}N_2O_4^+$ $(M+H)^+$: calculated 463.1652, found 463.1647.

3-(benzo[*d*]thiazol-2-yl)-1-benzyl-2-phenylquinolin-4(1*H*)-one (3cf) (41.4 mg, 93%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 – 8.61 (m, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.32 – 7.18 (m, 10H), 7.01 (d, *J* = 6.9 Hz, 2H), 5.31 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4 , 162.4 , 155.1 , 152.0 , 140.2 , 136.1 , 135.8 , 134.1 , 132.8 , 129.2 , 128.9 , 128.6 , 128.3 , 127.6 , 127.3 , 126.8 , 125.4 , 125.1 , 124.6 , 124.3 , 122.7 , 121.0 , 117.5 , 116.5 , 52.7 .HRMS (EI) for $C_{29}H_{21}N_2OS^+$ $(M+H)^+$: calculated 445.1369, found 445.1370.

1-benzyl-2-(4-fluorophenyl)-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3da) (44.5 mg, 95%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.46 – 7.39 (m, 2H), 7.35 – 7.28 (m, 3H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.99 (d, *J* = 7.1 Hz, 2H), 6.86 (t, *J* = 8.0 Hz, 2H), 5.26 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6 , 162.8 (d, *J* = 251.7 Hz), 151.7 , 146.1 , 143.1 , 140.7 , 135.8 , 133.0 , 132.3 , 131.0 (d, *J* = 8.4 Hz), 129.7 (d, *J* = 3.8 Hz), 129.1 , 127.8 , 127.3 , 126.7 , 125.3 , 124.4 , 122.8 , 117.3 , 115.8 (d,

J = 21.9 Hz), 52.7 .HRMS (EI) for $C_{28}H_{20}FN_2O_3^+$ $(M+H)^+$: calculated 451.1452, found 451.1447.

1-benzyl-2-(4-chlorophenyl)-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3db) (35.5 mg, 76%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.35 – 7.27 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.04 – 6.97 (m, 4H), 5.25 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 151.5 , 146.2 , 142.9 , 140.7 , 135.8 , 135.7 , 133.0 , 132.3 , 132.0 , 130.3 , 129.1 , 128.9 , 127.9 , 127.3 , 126.6 , 125.3 , 124.5 , 122.9 , 122.6 , 117.3 , 52.7; HRMS (EI) for $C_{28}H_{20}ClN_2O_3^+$ $(M+H)^+$: calculated 467.1157, found 467.1155.

1-benzyl-2-(4-bromophenyl)-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3dc) (35.5 mg, 76%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 – 8.54 (m, 1H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 5H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.02 – 6.94 (m, 4H), 5.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6 , 151.4 , 146.2 , 143.0 , 140.7 , 135.7 , 132.9 , 132.5 , 132.3 , 131.8 , 130.6 , 129.1 , 127.8 , 127.2 , 126.7 , 125.3 , 124.4 , 124.0 , 122.8 , 122.5 , 117.3 , 52.7; HRMS (EI) for $C_{28}H_{20}BrN_2O_3^+$ $(M+H)^+$: calculated 511.0652, found 511.0646.

1-benzyl-2-(4-methoxyphenyl)-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3dd) (34.3 mg, 74%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 – 8.47 (m, 1H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.36 – 7.30 (m, 2H), 7.26 – 7.17 (m, 5H), 6.96 – 6.89 (m, 4H), 6.59 (d, *J* = 8.1 Hz, 2H), 5.22 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.67 , 160.03 , 152.84 , 145.88 , 143.68 , 140.69 , 136.14 , 132.70 , 132.31 , 130.42 , 128.98 , 127.63 , 127.20 , 126.73 , 125.80 , 125.39 , 124.17 , 122.70 , 122.66 , 117.38 , 113.85 , 55.15 , 52.62; HRMS (EI) for $C_{29}H_{23}N_2O_4^+$ $(M+H)^+$: calculated 463.1652, found 463.1646.

1-benzyl-3-(4-nitrophenyl)-2-(*p*-tolyl)quinolin-4(1*H*)-one (3de) (38.2 mg, 86%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.45 (m, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.36 – 7.30 (m, 2H), 7.26 – 7.16 (m, 5H), 6.93 (d, *J* = 7.1 Hz, 2H), 6.89 (s, 4H), 5.20 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 153.1 , 145.9 , 143.6 , 140.6 , 139.6 , 136.1 , 132.7 , 132.3 , 130.7 , 129.2 , 129.0 , 128.8 , 127.6 , 127.2 , 126.7 , 125.4 , 124.2 , 122.6 , 122.5 , 117.4 , 52.6 , 21.2; HRMS (EI) for $C_{29}H_{23}N_2O_3^+$ $(M+H)^+$: calculated 447.1703, found 447.1701.

1-benzyl-3-(4-nitrophenyl)-2-(4-propylphenyl)quinolin-4(1*H*)-one (3df) (42.7 mg, 90%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 1H), 7.90 – 7.86 (m, 2H), 7.53 – 7.48 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.15 (m, 5H), 6.93 (d, *J* = 6.9 Hz, 2H), 6.89 (s, 4H), 5.22 (s, 2H), 2.43 – 2.37 (m, 2H), 1.49 – 1.40 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.64 , 153.12 , 145.86 , 144.24 , 143.59 , 140.64 , 136.16 , 132.68 , 132.30 , 130.92 , 128.96 , 128.91 , 128.51 , 127.63 , 127.22 , 126.76 , 125.42 , 124.17 , 122.53 , 122.47 , 117.35 , 52.67 , 37.43 , 23.93 , 13.37; HRMS (EI) for $C_{31}H_{27}N_2O_3^+$ $(M+H)^+$: calculated 475.2016, found 475.2011.

1-benzyl-2-(3-fluorophenyl)-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3dg) (41.4 mg, 91%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.48 (m, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.40 – 7.33 (m, 2H), 7.29 – 7.17 (m, 5H), 7.09 (q, *J* = 7.8 Hz, 1H), 6.95 – 6.86 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 162.1 (d, *J* = 249.8 Hz), 151.1, 146.2, 142.9, 140.7, 135.7, 135.5 (d, *J* = 7.8 Hz), 133.0, 132.2, 130.4 (d, *J* = 8.3 Hz), 129.1, 127.9, 127.3, 126.7, 125.3, 125.0 (d, *J* = 3.3 Hz), 124.5, 122.8, 122.5, 117.3, 116.7 (d, *J* = 20.7 Hz), 116.4 (d, *J* = 22.7 Hz); HRMS (EI) for $C_{28}H_{20}FN_2O_3^+$ $(M+H)^+$: calculated 451.1452, found 451.1447.

1-benzyl-3-(4-nitrophenyl)-2-(thiophen-3-yl)quinolin-4(1*H*)-one (3dh) (35.1 mg, 80%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.43 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.46 (m, 1H), 7.38 – 7.29 (m, 2H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.13 – 7.07 (m, 1H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.95 – 6.89 (m, 1H), 6.71 (d, *J* = 4.8 Hz, 1H), 5.24 (d, *J* = 9.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4 , 148.3 , 146.0 , 143.5 , 140.7 , 136.2 , 133.5 , 132.8 , 131.9 , 129.1 , 128.0 , 127.8 , 127.2 , 127.0 , 126.8 , 126.7 , 125.3 , 124.3 , 123.0 , 122.7 , 117.3 , 52.8; HRMS (EI) for $C_{26}H_{19}N_2O_3S^+$ $(M+H)^+$: calculated 439.1111, found 439.1107.

1-benzyl-2-butyl-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3di) (24.9 mg, 60%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.45 (m, 1H), 8.31 (d, *J* = 8.8 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.51 (s, 2H), 2.61 – 2.45 (m, 2H), 1.59 – 1.43 (m, 2H), 1.15 (q, *J* = 7.3 Hz, 2H), 0.69 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9 , 152.5 , 147.0 144.4 , 141.1 , 135.5 , 132.5 , 132.1 , 129.3 , 128.0 , 127.1 , 126.3 , 125.2 , 123.9 , 123.6 , 122.3 , 116.4 , 50.5 , 31.2 (d, J = 19.9 Hz), 22.5 , 13.3; HRMS (EI) for $C_{26}H_{25}N_2O_3^+$ $(M+H)^+$: calculated 413.1860, found 413.1863.

1-benzyl-2-cyclopropyl-3-(4-nitrophenyl)quinolin-4(1*H*)-one (3dj) (27.4 mg, 69%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.46 (m, 1H), 8.23 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.34 (q, *J* = 6.8 Hz, 3H), 7.29 (t, *J* = 7.3

Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 5.95 (s, 2H), 1.95 – 1.86 (m, 1H), 0.82 (d, *J* = 7.6 Hz, 2H), 0.39 (d, *J* = 5.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 , 152.0 , 146.2 , 143.9 , 140.9 , 136.0 , 132.6 , 132.2 , 129.1 , 127.6 , 127.0 , 126.2 , 125.2 , 123.8 , 122.6 , 122.6 , 116.6 , 50.4 , 14.5 , 11.2; HRMS (ESI-TOF) m/z: calcd for $C_{25}H_{20}KN_2O_3^+$: 435.1106 $(M+K)^+$, found: 435.1102.

1-benzyl-5-fluoro-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3dk) (35.8 mg, 79%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.39 – 7.31 (m, 3H), 7.31 – 7.27 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 3H), 7.12 (d, *J* = 7.4 Hz, 2H), 7.09 – 7.02 (m, 3H), 5.26 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.67, 162.36 (d, *J* = 264.8 Hz), 152.21, 146.05, 142.81, 142.77, 135.65, 133.33, 132.83 (d, *J* = 11.0 Hz), 132.38, 129.59, 129.06, 128.94, 128.57, 127.79, 125.35, 123.98, 122.54, 116.98 (d, *J* = 7.6 Hz), 113.15 (d, *J* = 4.6 Hz), 110.77 (d, *J* = 21.5 Hz) , 53.38; HRMS (ESI-TOF) m/z: calcd for $C_{28}H_{19}FKN_2O_3^+$: 489.1011 $(M+K)^+$, found: 489.1006.

1-benzyl-7-chloro-3-(4-nitrophenyl)-2-phenylquinolin-4(1*H*)-one (3dl) (38.5 mg, 82%). White solid. ethyl acetate : hexane = 1 : 4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.29 (m, 5H), 7.24 (d, *J* = 8.8 Hz, 3H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 6.9 Hz, 2H), 5.22 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.16 , 153.15 , 146.14 , 142.84 , 141.44 , 139.29 , 135.36 , 133.29 , 132.22 , 129.69 , 129.19 , 129.03 , 128.96 , 128.60 , 127.98 , 125.36 , 125.13 , 125.06 , 123.08 , 122.73 , 117.04 , 52.77; HRMS (EI) for $C_{28}H_{20}ClN_2O_3^+$ $(M+H)^+$: calculated 467.1157, found 467.1155.

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[12] CCDC 1919690 (3bi) and CCDC 1918494 (3cd) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] See Supporting Information for more failed substrates.

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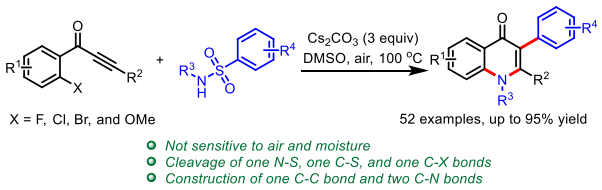
FULL PAPER

Base-Promoted Michael Addition/Smiles Rearrangement/*N*-Arylation Cascade: One-Step Synthesis of 1,2,3-Trisubstituted 4-Quinolones from Ynones and Sulfonamides



Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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