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Efficient synthesis of furoquinolinones using Hendrickson reagent-initiated cascade annulation

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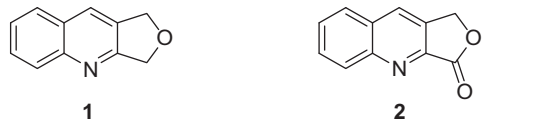
ABSTRACT

A new synthesis of furo[3,4-*b*]quinolin-3(1*H*)-one derivatives has been established in straightforward fashion in high overall yields. An efficient Hendrickson reagent-initiated cascade annulation, which is composed of mild conversion of the stable amide precursor to the reactive imido-carbonium intermediate and subsequent intramolecular aza Diels–Alder reaction, successfully serves as the key reaction in the synthesis. Final oxidative cleavage of the carbon–carbon double bond of representative tricyclic precursor **8g** led to completion of the synthesis of quinoline-lactone **2g** in a high yield.

1. Introduction

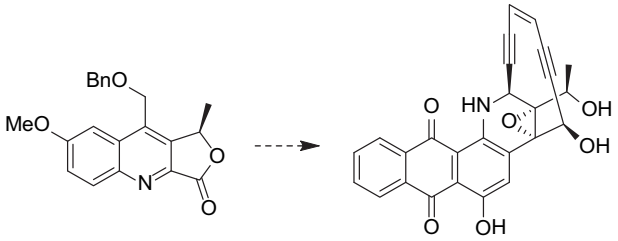
As a regioselective oxidation analogue of dihydrofuroquinoline **1** (Fig. 1), furoquinolinones **2** have attracted common interests for the potentials in their application as synthetic intermediates and their appearance as the structural cores in some biologically interesting natural products, such as uncialamycin **3** (Fig. 2).[1] In the past several decades, considerable attentions have been paid in organic synthesis to the construction of variously substituted quinoline-lactones.[1–5] Among these, two syntheses of quinoline-lactones have been reported utilizing an intramolecular aza Diels–Alder reaction.[1,2] However, involvement of unstable intermediates and low overall yields restrict their further applications in the syntheses of many useful products bearing multiple functionalities.



1 1,3-dihydrofuro[3,4-*b*]quinoline

2 furo[3,4-*b*]quinolin-3(1*H*)-one

Fig. 1. Dihydrofuroquinoline (**1**) and furoquinolinone (**2**).



uncialamycin **3**

Fig. 2. The transformation designed for the synthesis of uncialamycin via a furoquinolinone intermediate.[1]

In our recent work of total syntheses of camptothecin-family alkaloids,[6] Hendrickson reagent[7] was successfully employed as a powerful reagent to convert the stable aniline–amides to the corresponding highly reactive imidates at ambient temperature. Such mild procedure enables us to consider a similar strategy in the synthesis of furoquinolinone derivatives. Herein, an efficient approach to this class of heterocycles was reported with cascade aza Diels–Alder reaction and eliminative aromatization utilizing Hendrickson reagent under mild conditions.

According to our proposal (Fig. 3), the in situ generated imido-carboniums from amides **7** would be able to react with the alkyne functionality via an intramolecular aza Diels–Alder reaction.

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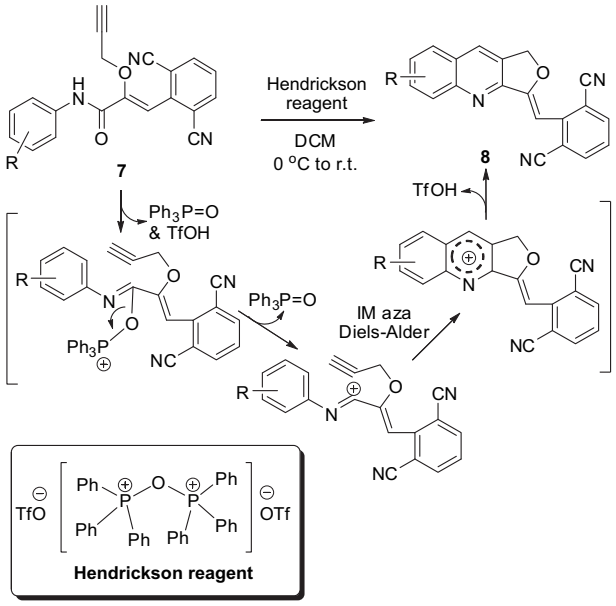
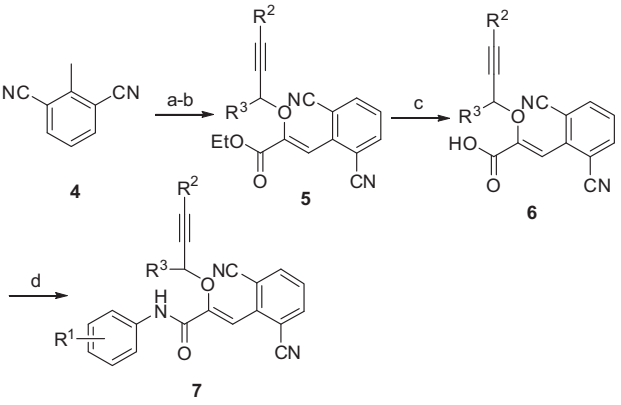


Fig. 3. The designed one-step cascade synthesis of dihydrofuroquinoline derivative **8** from amide **7**.

A subsequent eliminative aromatization would generate the dihydrofuroquinoline derivative **8** finally.

2. Results and discussion

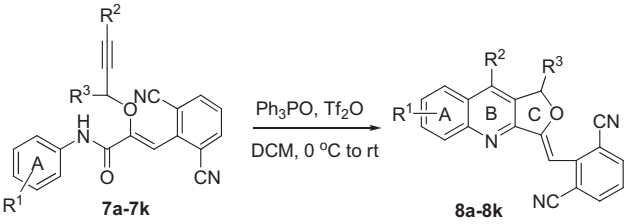
Starting from the commercially available 2,6-dicyanotoluene **4**, compounds **5a**–**d** were prepared in two steps by condensation of toluene **4** with diethyl oxalate and Mitsunobu enol ether synthesis with propargyl alcohol (Scheme 1). It is noteworthy here that suitable toluene substrate (2,6-dicyanotoluene, selected by the substrate screening) is not only required by the first step (condensation, sufficient acidity of the methyl group of toluene), but also needed by the second step to favor the formation of enol intermediate under Mitsunobu conditions through adequate electron-withdrawing effects caused by the two cyano groups. Basic hydrolysis of the methyl esters **5a**–**d** afforded corresponding acids **6a**–**d**, which were used directly for the next step without further purification except **6a** (isolated for the structure characterizations). Conversion of acids **6a**–**d** to the corresponding acid chlorides followed by acylation with various anilines afforded the amide precursors **7a**–**k** in good yields. In order to investigate the



Scheme 1. Synthesis of amide precursors **7a**–**k**. Reagents and conditions: (a) $(COOEt)_2$, *t*-BuOK; then saturated $NaHCO_3$; (b) prop-2-yn-1-ol, Bu_3P, DEAD. **5a** (R_2=H, R_3=H, 62% in two steps), **5b** (R_2=Et, R_3=H, 55%), **5c** (R_2=Ph, R_3=H, 72%), **5d** (R_2=H, R_3=Me, 47%); (c) LiOH, **6a** (94%); (d) $(COCl)_2$, DCM, then aniline, **7a** (76% from **5a**) (see Table 1 for the yields of **7a**–**k**).

effects of substituent group R^1 at the aniline phenyl ring A (entries 1–8, Table 1), amides **7a**–**h** were prepared by acylation of the corresponding anilines with the pre-prepared acid chlorides (Table 1). To examine the substrate scope, additional three representative amides **7i**–**k** bearing different substituent R^2 or R^3 (entries 9–11, Table 1) were also prepared.

Table 1
Synthesis of tricyclic precursors **8a**–**k** with a variable substituent R^1, R^2, and R^3



Entry	**7** (Yield)[a,b]	**8** (Yield)[a,d]
1	**7a** (R^1=R^2=R^3=H, 76%)	**8a** (90%)
2	**7b** (R^1=*p*-OMe; R^2=R^3=H, 90%)	**8b** (91%)
3	**7c** (R^1=*p*-Br; R^2=R^3=H, 86%)	**8c** (97%)
4	**7d** (R^1=*p*-F; R^2=R^3=H, 78%)	**8d** (93%)
5	**7e** (R^1=*p*-CO_2Me; R^2=R^3=H, 80%)	**8e** (92%)
6	**7f** (R^1=*o*-Me; R^2=R^3=H, 91%)	**8f** (96%)
7	**7g** (R^1=*p*-Me; R^2=R^3=H, 78%)	**8g** (95%)
8[c]	**7h** (R^1=*m*-Me; R^2=R^3=H, 84%)	**8h** (95%; regioselectivity 3:2)[c]
9	**7i** (R^2=Et; R^1=R^3=H, 81%)	**8i** (93%)
10	**7j** (R^2=Ph; R^1=R^3=H, 75%)	**8j** (97%)
11	**7k** (R^3=Me; R^1=R^2=H, 73%)	**8k** (94%)

[a] Isolated yields.
[b] Yields from **5** over two steps.
[c] The ratio of **8h** was determined by ^{1}H NMR.
[d] The reactions usually completed in 2 h.

With the aniline–amide substrates in hand, their reactions with bis(triphenyl)oxodiphosphonium trifluoromethanesulfonate (Hendrickson reagent) prepared in situ were examined under the standard conditions of our previous work (Table 1).[6,8] To our delight, the expected tricyclic quinoline-lactones **8a**–**k** were accordingly afforded in excellent isolated yields. For all the examined benzamides **7a**–**k**, either with or without electron-donating or electron-withdrawing group(s) in the phenyl ring of aniline moiety, the reactions completed smoothly and afforded the corresponding products in high yields (entries 1–11, Table 1).

To confirm the stereochemistry of the *exo* double bond in the products, an X-ray single crystal analysis of **8a** was carried out. It revealed that cis configuration was adopted by the double bond connecting to the 2,6-dicyanophenyl group in its solid state (Fig. 4). However, the cis isomers are not always stable enough in the solution. Transformation of *cis*-**8** to *trans*-**8** could be detected by ^{1}H NMR in the $CDCl_3$ solution, and it could be accelerated by the catalysis of trace acid (Scheme 2). Though pure *trans*-**8f** was not able to separate from *cis*-**8f** by silica gel chromatography, this

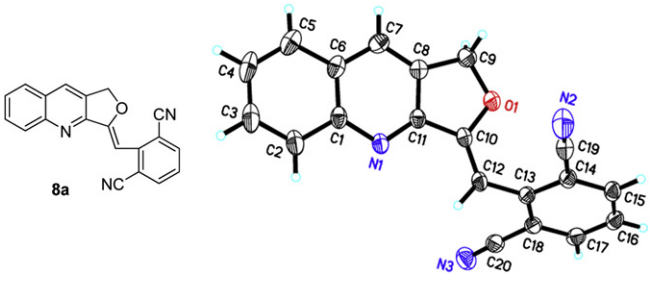
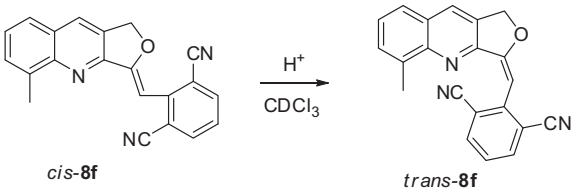


Fig. 4. Single crystal X-ray diffraction structure of **8a**.

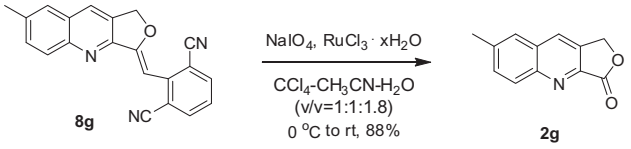


Scheme 2. Transformation of *cis*-**8f** to *trans*-**8f**.

transformation could be confirmed by the NMR studies of **8f** through mixing with the two isomers.[9] In order to avoid such isomerization, it is necessary to purify $CDCl_3$ with the basic materials for NMR measurements, such as K_2CO_3.

Poor regioselectivity was observed in the reaction of substrate **7h** bearing a methyl group at the *meta*-position of the phenyl ring (entry 8, Table 1). These two isomers could not be separated by silica gel flash column chromatography, but their ratio could be determined by the ^1H NMR.

Conversion of the representative tricyclic precursor **8g** to its corresponding furoquinolinone **2g** was finally attempted. Oxidative cleavage of the carbon–carbon double bond of **8g** was smoothly carried out by $NaIO_4$ oxidation in the presence of catalytic amount of $RuCl_3$ at room temperature, affording furoquinolinone **2g** (40% overall yield from 2,6-dicyanotoluene **4**) (Scheme 3).[10] No methyl-oxidation product was detected in our study. Thus, a short straightforward synthesis of furoquinolinones has been accomplished starting from the commercially available materials.



Scheme 3. Oxidative cleavage of the double bond of **8g**.

3. Conclusion

In summary, a new efficient approach has been developed for the synthesis of variously substituted furoquinolinones utilizing Hendrickson reagent-initiated cascade annulation and oxidative cleavage of *exo* carbon–carbon double bond. The short route and mild conditions used in this newly developed synthesis enable the tolerance of some common functional groups and thus facilitate future applications in preparation of medicinal and biologically interesting compounds.

4. Experimental section

4.1. General

Unless stated otherwise, all reactions were carried out in dried glassware under nitrogen atmosphere. All solvents were purified and dried prior to use. Flash chromatographies were performed on silica gel H (400 mesh). Elemental analyses were carried out at the Analytical Center of Nanjing University.

4.2. Typical procedures for the preparation of substituted (*Z*)-ethyl 3-(2,6-dicyanophenyl)-2-(prop-2-ynyloxy)acrylates (5a–d)

To a solution of the 2-methylisophthalonitrile **4** (3.5 mmol) in diethyl oxalate (4 mL) was added potassium *tert*-butoxide (7.4 mmol) under N_2 atmosphere. The reaction mixture was stirred for 6 h at room temperature. After addition of saturated sodium bicarbonate (2 mL), the reaction mixture was stirred for an additional hour and yielded a suspension. The resultant precipitate was filtered and dried, affording a yellowish solid.

To the stirred solution of the above solid in THF (25 mL) was successively added propargyl alcohol (4.2 mmol), n-Bu3P (5.3 mmol), DEAD (5.3 mmol) at 0 °C under N_2 atmosphere. The reaction was allowed to warm to room temperature and stirred for additional 3 h. Then, the reaction mixture was quenched by the addition of H_2O, and extracted with CH_2Cl_2. The combined organic phases were dried over with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (ethyl acetate/petroleum ether=1:3) to afford **5a** (0.61 g, 62% in two steps).

*4.2.1. (Z)-Ethyl 3-(2,6-dicyanophenyl)-2-(prop-2-ynyloxy)acrylate (**5a**).* Yellow solid, 62% yield (two steps), mp 85–86 °C. IR (KBr): ν_{max} 3276, 3084, 3001, 2904, 2241, 2129, 1721, 1631, 1469, 1446, 1397, 1380, 1335, 1288, 1253, 1234, 1216, 1141, 1108, 1027, 1007, 869, 808, 775, 762, 714, 663, 451 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.41 (3H, t, J=7.2 Hz), 2.45 (1H, t, J=2.4 Hz), 4.38 (2H, q, J=7.2 Hz), 4.85 (2H, d, J=2.1 Hz), 7.20 (1H, s), 7.55 (1H, t, J=7.8 Hz), 7.91 (2H, d, J=7.5 Hz). Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 9.99; found: C, 68.56; H, 4.58; N, 10.06. ESIMS (m/z): 281$(M+Na)^+$.

*4.2.2. (Z)-Ethyl 3-(2,6-dicyanophenyl)-2-(pent-2-ynyloxy)acrylate (**5b**).* White solid, 55% yield (two steps), mp 74–76 °C. IR (KBr): ν_{max} 3077, 2984, 2942, 2876, 2233, 1721, 1644, 1452, 1389, 1328, 1288, 1254, 1231, 1169, 1141, 1106, 1023, 1007, 982, 785 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.02 (3H, t, J=7.2 Hz), 1.38 (3H, t, J=6.9 Hz), 2.11 (2H, m), 4.34 (2H, q, J=7.2 Hz), 4.77 (2H, s), 7.13 (1H, s), 7.52 (1H, t, J=7.5 Hz), 7.88 (2H, d, J=7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.5, 13.5, 14.2, 60.0, 62.2, 73.6, 91.1, 114.7, 115.6, 116.2, 128.6, 136.5, 141.1, 148.3, 162.1. Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09; found: C, 69.97; H, 5.11; N, 9.07. ESIMS (m/z): 331.08 $(M+Na)^+$.

*4.2.3. (Z)-Ethyl 3-(2,6-dicyanophenyl)-2-(3-phenylprop-2-ynyloxy) acrylate (**5c**).* White solid, 72% yield (two steps), mp 107–109 °C. IR (KBr): ν_{max} 3076, 2971, 2926, 2871, 2232, 1727, 1638, 1445, 1379, 1261, 1092, 1050, 882, 802 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (3H, t, J=7.2 Hz), 4.36 (2H, q, J=7.2 Hz), 5.03 (2H, s), 7.20 (1H, s), 7.27–7.32 (5H, m), 7.43 (1H, t, J=7.8 Hz), 7. 78 (2H, d, J=8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2, 60.2, 62.3, 83.3, 88.3, 114.6, 116.1, 116.3, 121.9, 128.2, 128.6, 128.9, 131.9, 136.5, 140.8, 148.3, 162.1. Anal. Calcd for $C_{22}H_{16}N_2O_3$: C, 74.15; H, 4.53; N, 7.86; found: C, 74.21; H, 4.47; N, 7.81. ESIMS (m/z): 357.25 $(M+H)^+$, 379.25 $(M+Na)^+$

*4.2.4. (Z)-Ethyl 2-(but-3-yn-2-yloxy)-3-(2,6-dicyanophenyl)acrylate (**5d**).* White solid, 47% yield (two steps), mp 95–96 °C. IR (KBr): ν_{max} 3079, 2961, 2924, 2854, 2230, 1727, 1639, 1532, 1459, 1375, 1261, 1098, 1020, 864, 801, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.38(3H, t, J=7.2 Hz), 1.44 (3H, d, J=6.6 Hz), 2.31 (1H, d, J=2.1 Hz), 4.28–4.39 (2H, m), 5.15 (1H, qd, J=6.6 , 2.1 Hz), 7.28 (1H, s), 7.54 (1H, t, J=7.8 Hz), 7.91 (2H, d, J=7.8 Hz). (75 MHz, $CDCl_3$): δ 14.2, 21.9, 62.2, 67.7, 75.1, 81.6, 115.0, 116.2, 117.4, 128.7, 136.4, 141.1, 147.8, 162.2. Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52; found: C, 69.17; H, 4.75; N, 9.52. ESIMS (m/z): 317.17 $(M+Na)^+$.

4.3. Typical procedures for the preparation of substituted (*Z*)-3-(2,6-dicyanophenyl)-2-(prop-2-ynyloxy)acrylic acids (6a–d)

To a solution of ester **5a** (1.2 mmol) in THF (3 mL) and water (1 mL) was added lithium hydroxide monohydrate (1.8 mmol) at 0 °C. The reaction was allowed to warm to room temperature and stirred for additional 2 h. When the substrate was consumed, THF was removed in vacuo and the pH of the residue was adjusted to 4–5 by addition of 1 N HCl. The resultant precipitation was filtrated

and dried, giving acid **6a** (0.28 g). White solid, 94% yield. Mp 160–162 °C (dec). IR (KBr): ν_{max} 3262, 3082, 2120, 1739, 1715, 1654, 1642, 1574, 1450, 1434, 1388, 1322, 1307, 1288, 1269, 1174, 1108, 1019, 1002, 933, 918, 860, 804, 798, 754, 737, 691, 678, 652, 466 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 3.44 (1H, t, J=2.4 Hz), 4.71 (2H, d, J=2.4 Hz), 7.23 (1H, s), 7.72 (1H, t, J=7.8 Hz), 8.22 (2H, d, J=8.1 Hz). Anal. Calcd for $C_{14}H_8N_2O_3$: C, 66.67; H, 3.20; N, 11.11; found: C, 66.87; H, 3.47; N, 11.37. ESIMS (m/z): 251 ($M-H^+$).

Compound **6b–d** was prepared by a similar procedure as that for compound **6a**, and they were used directly for the next steps.

4.4. Typical procedures for the preparation of substituted (*Z*)-3-(2,6-dicyanophenyl)-*N*-phenyl-2-(prop-2-ynyloxy) acrylamides (7a–k)

To a solution of acid **6a** (4.0 mmol) in CH_2Cl_2 (35 mL) was added $(COCl)_2$ (12.0 mmol) and a catalytic amount of DMF at 0 °C. After gas evolution ceased, the reaction mixture was concentrated in vacuo. The residue was re-dissolved in dry CH_2Cl_2 (45 mL) and then was introduced into a suspension of corresponding aniline (4.0 mmol) in the presence of $NaHCO_3$ (12.0 mmol) in CH_2Cl_2 (10 mL). After 1 h, H_2O was added to quench the reaction and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether=1:3 to 2:3).

*4.4.1. (Z)-3-(2,6-Dicyanophenyl)-N-phenyl-2-(prop-2-ynyloxy)acrylamide (**7a**).* Yield: 76%, mp 144–146 °C. IR (KBr): ν_{max} 3318, 3273, 3074, 3052, 3016, 2927, 2235, 2120, 1675, 1649, 1598, 1575, 1526, 1494, 1456, 1442, 1374, 1323, 1296, 1241, 1178, 1102, 1077, 1008, 935, 913, 808, 780, 759, 725, 694, 654, 574 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 3.49 (1H, t, J=2.4 Hz), 4.59 (2H, d, J=2.1 Hz), 7.15 (2H, m), 7.38 (2H, t, J=8.0 Hz), 7.75 (1H, t, J=8.0 Hz), 7.80 (2H, d, J=8.1 Hz), 8.25 (2H, d, J=8.1 Hz), 10.41 (1H, s). Anal. Calcd for $C_{20}H_{13}N_3O_2$: C, 73.38; H, 4.00; N, 12.84; found: C, 73.33; H, 4.08; N, 12.76. ESIMS (m/z): 328 $(M+H)^+$.

*4.4.2. (Z)-3-(2,6-Dicyanophenyl)-N-(4-methoxyphenyl)-2-(prop-2-ynyloxy)acrylamide (**7b**).* White solid, 90% yield, mp 133–136 °C. IR (KBr): ν_{max} 3313, 3252, 3049, 3014, 2961, 2931, 2839, 2242, 2230, 2122, 1669, 1642, 1595, 1520, 1444, 1415, 1373, 1314, 1297, 1267, 1234, 1184, 1110, 1098, 1031, 996, 942, 829, 806, 740, 705, 438 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): δ 3.02 (1H, t, J=2.4 Hz), 3.80 (3H, s), 4.59 (2H, d, J=2.4 Hz), 6.93 (2H, m), 7.34 (1H, s), 7.77 (3H, m), 8.15 (2H, d, J=7.5 Hz), 9.61 (1H, s). ^{13}C NMR (75 MHz, acetone-d_6): δ 55.7, 60.6, 78.2, 78.5, 112.4, 114.6, 115.4, 117.0, 122.8, 130.2, 132.1, 137.8, 141.9, 152.7, 157.5, 160.3. Anal. Calcd for $C_{21}H_{15}N_3O_3$: C, 70.58; H, 4.23; N, 11.76; found: C, 70.47; H, 4.34; N, 11.63. ESIMS (m/z): 358.17$(M+H)^+$, 380.17$(M+Na)^+$.

*4.4.3. (Z)-N-(4-Bromophenyl)-3-(2,6-dicyanophenyl)-2-(prop-2-ynyloxy)acrylamide (**7c**).* Yellowish solid, 86% yield, mp 158–160 °C. IR (KBr): ν_{max} 3309, 3263, 3082, 3037, 2901, 2855, 2239, 2111, 1679, 1645, 1591, 1525, 1488, 1450, 1395, 1315, 1233, 1093, 1070, 1003, 833, 665, 446 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.57 (1H, t, J=2.4 Hz), 4.40 (2H, d, J=2.4 Hz), 7.42 (1H, s), 7.49 (2H, m), 7.55–7.62 (3H, m), 7.94 (2H, d, J=7.8 Hz), 8.51 (1H, s). ^{13}C NMR (75 MHz, acetone-d_6): δ 60.8, 78.0, 78.6, 113.2, 115.4, 116.9, 117.4, 123.1, 130.3, 132.5, 137.8, 138.4, 141.6, 152.1, 160.8. Anal. Calcd for $C_{20}H_{12}BrN_3O_2$: C, 59.13; H, 2.98; N, 10.34; found: C, 59.11; H, 2.97; N, 10.29. ESIMS (m/z): 428.08 ($C_{20}H_{12}{}^{79}BrN_3O_2+Na)^+$; 430.00 ($C_{20}H_{12}{}^{81}BrN_3O_2+Na)^+$.

*4.4.4. (Z)-3-(2,6-Dicyanophenyl)-N-(4-fluorophenyl)-2-(prop-2-ynyloxy)acrylamide (**7d**).* White solid, 78% yield, mp 145–148 °C. IR (KBr): ν_{max} 3337, 3289, 3074, 3011, 2935, 2880, 2243, 2235, 2121, 1689, 1669, 1646, 1608, 1532, 1509, 1450, 1408, 1381, 1318, 1301, 1227, 1213, 1159, 1098, 1002, 836, 809, 714, 681, 648, 520, 446 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.57 (1H, t, J=2.4 Hz), 4.41 (2H, d, J=2.4 Hz), 7.07 (2H, m), 7.42 (1H, s), 7.57–7.65 (3H, m), 7.95 (2H, d, J=7.8 Hz), 8.47 (1H, s). ^{13}C NMR (75 MHz, acetone-d_6): δ 60.7, 78.1, 78.6, 112.9, 115.4, 116.1 (d, $^2J_{CF}$=22.7 Hz), 117.0, 123.2 (d, $^3J_{CF}$=8.9 Hz), 130.3, 135.4 (d, $^4J_{CF}$=2.9 Hz), 137.8, 141.7, 152.3, 160.2 (d, $^1J_{CF}$=240 Hz), 160.7. Anal. Calcd for $C_{20}H_{12}FN_3O_2$: C, 69.56; H, 3.50; N, 12.17; found: C, 69.49; H, 3.57; N, 12.11. ESIMS (m/z): 346.17 $(M+H)^+$, 368.17 $(M+Na)^+$.

*4.4.5. (Z)-Methyl 4-(3-(2,6-dicyanophenyl)-2-(prop-2-ynyloxy)acrylamido)benzoate (**7e**).* White solid, 80% yield, mp 157–158 °C. IR (KBr): ν_{max} 3310, 3267, 3085, 3049, 2994, 2952, 2242, 2231, 2125, 1708, 1681, 1641, 1603, 1529, 1513, 1435, 1394, 1370, 1285, 1249, 1194, 1177, 1130, 1116, 1013, 997, 860, 837, 804, 770, 759, 715, 699, 674, 518, 483 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6): δ 3.05 (1H, t, J=2.4 Hz), 3.87 (3H, s), 4.61 (2H, d, J=2.4 Hz), 7.38 (1H, s), 7.80 (1H, t, J=7.8 Hz), 8.00 (4H, m), 8.17 (2H, d, J=7.8 Hz). ^{13}C NMR (75 MHz, acetone-d_6): δ 52.2, 60.7, 78.0, 78.7, 113.4, 115.4, 117.0, 120.6, 126.7, 130.4, 131.1, 137.9, 141.6, 143.2, 152.0, 161.2, 166.8. Anal. Calcd for $C_{22}H_{15}N_3O_4$: C, 68.57; H, 3.92; N, 10.90; found: C, 68.47; H, 3.97; N, 10.87. ESIMS (m/z): 386.33 $(M+H)^+$, 408.50 $(M+Na)^+$.

*4.4.6. (Z)-3-(2,6-Dicyanophenyl)-2-(prop-2-ynyloxy)-N-o-tolylacrylamide (**7f**).* Yellowish solid, 91% yield, mp 167–170 °C. IR (KBr): ν_{max} 3420, 3265, 3074, 3014, 2986, 2235, 2123, 1687, 1652, 1589, 1532, 1457, 1383, 1328, 1305, 1265, 1251, 1216, 1127, 1105, 1003, 829, 810, 762, 699, 655, 633, 447 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (3H, s), 2.57 (1H, t, J=2.4 Hz), 4.41 (2H, d, J=2.7 Hz), 7.14 (1H, m), 7.24 (2H, m), 7.41 (1H, s), 7.60 (1H, t, J=7.8 Hz), 7.95 (2H, d, J=7.8 Hz), 8.10 (1H, d, J=8.1 Hz), 8.42 (1H, br s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8, 60.8, 76.6, 78.1, 111.3, 114.9, 115.9, 122.3, 125.6, 127.1, 128.7, 129.2, 130.6, 135.0, 136.9, 141.1, 151.9, 159.2. Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31; found: C, 73.78; H, 4.41; N, 12.34. ESIMS (m/z): 342.08 $(M+H)^+$, 364.08 $(M+Na)^+$.

*4.4.7. (Z)-3-(2,6-Dicyanophenyl)-2-(prop-2-ynyloxy)-N-p-tolylacrylamide (**7g**).* White solid, 78% yield, mp 136–137 °C. IR (KBr): ν_{max} 3314, 3246, 3077, 3053, 3031, 2939, 2921, 2870, 2242, 2230, 2121, 1669, 1645, 1594, 1521, 1448, 1404, 1375, 1317, 1242, 1099, 1004, 805, 746, 706, 455 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (3H, s), 2.56 (1H, s), 4.42 (2H, d, J=1.8 Hz), 7.18 (2H, d, J=8.1 Hz), 7.40 (1H, s), 7.52–7.61 (3H, m), 7.94 (2H, d, J=8.1 Hz), 8.43 (1H, s). ^{13}C NMR (75 MHz, acetone-d_6): δ 20.9, 60.7, 78.1, 78.5, 112.5, 115.4, 117.0, 121.2, 130.0, 130.2, 134.7, 136.5, 137.8, 141.8, 152.6, 160.5. Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31; found: C, 73.84; H, 4.41; N, 12.22. ESIMS (m/z): 342.17 $(M+H)^+$, 364.17 $(M+Na)^+$.

*4.4.8. (Z)-3-(2,6-Dicyanophenyl)-2-(prop-2-ynyloxy)-N-m-tolylacrylamide (**7h**).* White solid, 84% yield, mp 145–147 °C. IR (KBr): ν_{max} 3324, 3256, 3080, 3020, 2924, 2876, 2237, 2119, 1680, 1649, 1595, 1577, 1536, 1489, 1455, 1430, 1368, 1313, 1293, 1234, 1104, 1002, 936, 793, 772, 705, 576, 437 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (3H, s), 2.56 (1H, t, J=2.4 Hz), 4.42 (2H, d, J=2.7 Hz), 6.98 (1H, d, J=7.5 Hz), 7.22–7.27 (1H, m), 7.42 (2H, m), 7.50 (1H, s), 7.58 (1H, t, J=7.8 Hz), 7.93 (2H, d, J=7.8 Hz), 8.46 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 60.7, 76.5, 78.1, 111.7, 114.8, 116.0, 117.3, 120.9, 126.0, 129.0, 129.2, 136.8, 136.9, 139.2, 141.0, 151.7, 159.2. Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31; found: C, 73.92; H, 4.37; N, 12.29. ESIMS (m/z): 342.08 $(M+H)^+$, 364.08 $(M+Na)^+$.

*4.4.9. (Z)-3-(2,6-Dicyanophenyl)-2-(pent-2-ynyloxy)-N-phenylacrylamide (**7i**).* White solid, 81% yield, mp 143–145 °C. IR (KBr): ν_{max} 3229, 3076, 3041, 2974, 2935, 2233, 1667, 1641, 1596, 1523,

1442, 1373, 1323, 1299, 1141, 1098, 974, 804, 771, 754, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (3H, t, J=7.5 Hz), 2.09–2.16 (2H, m), 4.36 (2H, s), 7.14 (1H, t, J=7.5 Hz), 7.33–7.40 (3H, m), 7.56 (1H, t, J=7.8 Hz), 7.65 (2H, d, J=7.5 Hz), 7.91 (2H, d, J=7.5 Hz), 8.61 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.4, 13.3, 61.6, 72.4, 92.5, 111.2, 114.6, 115.9, 120.0, 125.0, 129.0, 129.1, 136.7, 137.1, 141.2, 151.6, 159.5. Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82; found: C, 74.25; H, 4.82; N, 11.79. ESIMS (m/z): 356.00 $(M+H)^+$, 378.08 $(M+Na)^+$.

*4.4.10. (Z)-3-(2,6-Dicyanophenyl)-N-phenyl-2-(3-phenylprop-2-ynyloxy)acrylamide (**7j**).* Yellow solid, 75% yield, mp 109–111 °C. IR (KBr): ν_{max} 3383, 3328, 3051, 2924, 2857, 2233, 1670, 1643, 1597, 1527, 1490, 1442, 1320, 1234, 1099, 1073, 985, 959, 756, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.65 (2H, s), 7.14 (1H, t, J=7.2 Hz), 7.22–7.36 (7H, m), 7.47 (2H, m), 7.64 (2H, d, J=7.8 Hz), 7.83 (2H, d, J=8.1 Hz), 8.65 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.9, 82.0, 89.4, 112.1, 114.6, 116.0, 120.2, 121.2, 125.0, 128.3, 129.0, 129.1, 129.2, 132.0, 136.7, 137.0, 141.0, 152.0, 159.5. Anal. Calcd for $C_{26}H_{17}N_3O_2$: C, 77. 41; H, 4.25; N, 10.42; found: C, 77.23; H, 4.21; N, 10.34. ESIMS (m/z): 404.17 $(M+H)^+$, 426.33 $(M+Na)^+$.

*4.4.11. (Z)-2-(But-3-yn-2-yloxy)-3-(2,6-dicyanophenyl)-N-phenylacrylamide (**7k**).* White solid, 73% yield, mp 126–127 °C. IR (KBr): ν_{max} 3324, 3259, 3077, 2989, 2936, 2898, 2237, 1678, 1645, 1599, 1533, 1441, 1317, 1242, 1102, 1018, 957, 802, 754, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.50 (3H, d, J=6.6 Hz), 2.52 (1H, d, J=2.1 Hz), 4.38 (1H, qd, J=6.6 Hz, J=2.1 Hz), 7.17 (1H, t, J=7.2 Hz), 7.38 (2H, t, J=7.5 Hz), 7.50 (1H, s), 7.59 (1H, t, J=8.4 Hz), 7.65 (2H, m), 7.93 (2H, d, J=7.8 Hz), 8.49 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.5, 69.7, 76.6, 80.5, 113.1, 114.9, 116.0, 120.2, 125.2, 129.2, 129.3, 136.8, 137.1, 141.3, 151.4, 159.6. Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31; found: C, 73.74; H, 4.41; N, 12.34. ESIMS (m/z): 342.08 $(M+H)^+$, 364.17 $(M+Na)^+$.

4.5. General procedure for the cascade reactions and characterizations for the tricyclic products 8a–k

To a solution of triphenylphosphine oxide (1.87 g, 6.72 mmol) in dry CH_2Cl_2 (30 mL) was added trifluoromethanesulfonic anhydride (0.57 mL, 3.36 mmol) slowly at 0 °C under N_2 atmosphere. After the mixture was stirred at 0 °C for 30 min, the solution of substrate **7a** (0.73 g, 2.23 mmol) in dry CH_2Cl_2 (10 mL) was then added at the same temperature. The reaction was allowed to warm to room temperature and monitored by TLC (the reaction usually completed after 2 h). The reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4 or K_2CO_3, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel (dichloromethane/methanol=200:1–100:1) to afford pure **8a** (0.62 g, 90% yield).

*4.5.1. (Z)-2-(Furo[3,4-b]quinolin-3(1H)-ylidenemethyl)isophthalonitrile (**8a**).* Mp 252–254 °C. IR (KBr): ν_{max} 3070, 2239, 2228, 1688, 1662, 1621, 1615, 1572, 1502, 1458, 1446, 1359, 1349, 1245, 1162, 1038, 1002, 905, 899, 808, 773, 757, 706, 608 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.73 (2H, s), 6.95 (1H, s), 7.44 (1H, t, J=7.7 Hz), 7.62 (1H, t, J=7.5 Hz), 7.83–7.78 (1H, m), 7.92–7.87 (3H, m), 8.16 (1H, s), 8.22 (1H, d, J=8.4 Hz), 7.96 (2H, d, J=7.8 Hz), 8.50 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 68.7, 75.6, 79.5, 112.1, 113.9, 115.0, 119.2, 124.2, 128.2, 128.3, 135.8, 136.1, 140.3, 150.4, 158.6. Anal. Calcd for $C_{20}H_{11}N_3O$: C, 77.66; H, 3.58; N, 13.58; found: C, 77.75; H, 3.34; N, 13.54. HRMS (MALDI, m/z) calcd for $C_{20}H_{11}N_3O$ $(M+H)^+$: 310.0975; found: 310.0969.

*4.5.2. (Z)-2-((7-Methoxyfuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (**8b**).* Yellowish solid, 91% yield, mp 247–250 °C. IR (KBr): ν_{max} 3075, 2927, 2831, 2230, 1659, 1624, 1502, 1454, 1386, 1369, 1251, 1225, 1142, 1124, 1073, 1026 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.94 (3H, s), 5.66 (2H, s), 6.86 (1H, s), 7.07 (1H, d, J=2.7 Hz), 7.36–7.43 (2H, m), 7.86 (2H, d, J=7.8 Hz), 8.98 (1H, s), 8.06 (1H, d, J=9.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 72.7, 90.7, 105.4, 114.1, 117.2, 123.5, 126.7, 127.5, 129.6, 131.3, 131.5, 137.0, 143.4, 145.3, 149.9, 158.8. Anal. Calcd for $C_{21}H_{13}N_3O_2$: C, 74.33; H, 3.86; N, 12.38; found: C, 74.37; H, 3.97; N, 12.34. ESIMS (m/z): 340.33 $(M+H)^+$, 362.42 $(M+Na)^+$.

*4.5.3. (Z)-2-((7-Bromofuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (**8c**).* Yellow solid, 97% yield, mp 276 °C (dec). IR (KBr): ν_{max} 3077, 2926, 2869, 2851, 2229, 1663, 1603, 1487, 1457, 1387, 1359, 1239, 1141, 1060, 1040, 1004, 913, 823, 796, 780 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.71 (2H, s), 6.97 (1H, s), 7.44 (1H, t, ^3J=8.1 Hz), 7.85 (1H, dd, ^3J=9.0 Hz, ^4J=2.1 Hz), 7.90 (2H, d, ^3J=7.8 Hz), 8.03 (1H, d, ^4J=2.1 Hz), 8.06 (1H, s), 8.09 (1H, d, ^3J=9.0 Hz). ^{13}C NMR (75 MHz, pyridine-d_5): δ 73.6, 92.4, 114.6, 118.1, 122.0, 128.1, 129.3, 130.2, 131.1, 132.2, 132.9, 134.2, 137.8, 143.3, 148.3, 153.5, 159.1. Anal. Calcd for $C_{20}H_{10}BrN_3O$: C, 61.88; H, 2.60; N, 10.82; found: C, 61.73; H, 2.81; N, 10.64. ESIMS (m/z): 388.08 $(C_{20}H_{10}{}^{79}BrN_3O+H)^+$; 390.17 $(C_{20}H_{10}{}^{81}BrN_3O+H)^+$.

*4.5.4. (Z)-2-((7-Fluorofuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (**8d**).* Yellow solid, 93% yield, mp 254–257 °C. IR (KBr): ν_{max} 3079, 2951, 2933, 2922, 2882, 2230, 1665, 1631, 1505, 1458, 1359, 1207, 1142, 1043, 1006, 904, 830, 796 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.69 (2H, s), 6.91 (1H, s), 7.40–7.49 (2H, m), 7.52–7.59 (1H, m), 7.89 (2H, d, J=7.8 Hz), 8.08 (1H, s), 8.19 (1H, dd, J=9.3 , 5.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 72.6, 91.7, 111.2 (d, $^2J_{CF}$=22.7 Hz), 114.2, 117.2, 120.9 (d, $^2J_{CF}$=24.9 Hz), 127.0, 128.4 (d, $^4J_{CF}$=5.9 Hz), 129.0 (d, $^3J_{CF}$=10.1 Hz), 131.9, 132.5 (d, $^3J_{CF}$=9.2 Hz), 137.0, 143.1, 146.3, 152.0 (d, $^4J_{CF}$=2.9 Hz), 158.3, 161.3 (d, $^1J_{CF}$=248.6 Hz). Anal. Calcd for $C_{21}H_{10}FN_3O$: C, 73.39; H, 3.08; N, 12.84; found: C, 73.41; H, 3.18; N, 12.83. ESIMS (m/z): 328.17 $(M+H)^+$.

*4.5.5. (Z)-Methyl 3-(2,6-dicyanobenzylidene)-1,3-dihydrofuro[3,4-b]quinoline-7-carboxylate (**8e**).* Yellow solid, 92% yield, mp 234–237 °C. IR (KBr): ν_{max} 3072, 3004, 2954, 2877, 2232, 1725, 1665, 1621, 1458, 1267, 1171, 1102, 1041, 1000, 919, 805, 783 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.02 (3H, s), 5.74 (2H, s), 7.02 (1H, s), 7.46 (1H, t, J=7.8 Hz), 7.91 (2H, d, J=7.8 Hz), 8.26 (2H, m), 8.36 (1H, dd, J=9.0 , 1.8 Hz), 8.65 (1H, d, J=1.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.7, 72.6, 92.7, 114.4, 117.1, 127.2, 127.5, 129.2, 129.9, 130.4, 131.1, 131.8, 136.0, 137.1, 143.0, 151.2, 154.6, 158.2, 166.5. Anal. Calcd for $C_{22}H_{13}N_3O_3$: C, 71.93; H, 3.57; N, 11.44; found: C, 71.67; H, 3.74; N, 11.61. ESIMS (m/z): 368.25 $(M+H)^+$.

*4.5.6. (Z)-2-((5-Methylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (cis-**8f**).* Compound *cis*-**8f** was prepared according to the general procedure, except K_2CO_3 was used as the dehydrating agent in workup. Yellow solid, 96% yield, mp 249–250 °C. IR (KBr): ν_{max} 3082, 2919, 2878, 2852, 2231, 1661, 1578, 1501, 1455, 1441, 1378, 1161, 1150, 998 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.89 (3H, s), 5.72 (2H, s), 6.96 (1H, s), 7.42 (1H, t, J=7.8 Hz), 7.47–7.52 (1H, m), 7.62 (1H, d, J=6.9 Hz), 7.70 (1H, d, J=8.1 Hz), 7.89 (2H, d, J=7.5 Hz), 8.11 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.2, 72.8, 91.1, 114.1, 117.3, 126.0, 126.8, 127.6, 128.3, 129.2, 130.4, 136.1, 137.0, 138.3, 143.4, 148.4, 151.1, 159.0. Anal. Calcd for $C_{21}H_{13}N_3O$: C, 78.00; H, 4.05; N, 13.00; found: C, 77.97; H, 4.11; N, 13.00. ESIMS (m/z): 324.25 $(M+H)^+$; 362.33 $(M+K)^+$.

*4.5.7. (Z)-2-((7-Methylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (**8g**).* Yellow solid, 95% yield, mp 203–206 °C. IR (KBr): ν_{max} 3081, 2919, 2872, 2854, 2228, 1657, 1570, 1502, 1447, 1356, 1245, 1136, 1040, 999, 916, 824, 800 cm^{-1}. ^1H NMR (300 MHz,

$CDCl_3$): δ 2.55 (3H, s), 5.66 (2H, s), 6.89 (1H, s), 7.39 (1H, t, *J*=8.1 Hz), 7.60 (2H, m), 7.86 (2H, d, *J*=7.8 Hz), 8.01 (1H, s), 8.07 (1H, d, *J*=9.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 72.7, 91.2, 114.1, 117.2, 126.8, 126.9, 128.27, 128.32, 129.6, 131.0, 132.8, 137.0, 138.0, 143.3, 147.8, 151.4, 158.7. Anal. Calcd for $C_{21}H_{13}N_3O$: C, 78.00; H, 4.05; N, 13.00; found: C, 77.94; H, 4.21; N, 12.82. ESIMS (*m*/*z*): 324.33 $(M+H)^+$; 346.25 $(M+Na)^+$.

*4.5.8. (Z)-2-((6-Methylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl) isophthalonitrile and (Z)-2-((8-methylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (**8h**).* Yellow solid, 95% combined yield, mp 231–234 °C. IR (KBr): ν_{max} 3068, 2926, 2871, 2852, 2230, 1727, 1660, 1625, 1576, 1502, 1458, 1445, 1381, 1348, 1286, 1243, 1161, 1126, 1074, 1037, 1001 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (1.8H, s), 2.69 (1.2H, s), 5.66 (1.2H, s), 5.70 (0.8H, s), 6.91 (1H, s), 7.38–7.43 (2H, m), 7.65 (0.4H, t, *J*=7.7 Hz), 7.73 (0.6H, d, *J*=8.1 Hz), 7.87 (2H, d, *J*=7.8 Hz), 7.96 (0.6H, s), 8.04 (1H, m), 8.27 (0.4H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.1, 22.0, 72.7, 72.9, 91.3, 91.4, 114.2, 117.2, 125.5, 126.4, 126.79, 126.83, 127.6, 127.7, 128.3, 128.4, 128.7, 129.0, 130.0, 130.1, 130.2, 130.7, 134.7, 136.0, 137.0, 140.9, 143.28, 143.32, 149.6, 152.2, 158.9. Anal. Calcd for $C_{21}H_{13}N_3O$: C, 78.00; H, 4.05; N, 13.00; found: C, 77.93; H, 4.13; N, 13.12. ESIMS (*m*/*z*): 324.17 $(M+H)^+$.

*4.5.9. (Z)-2-((9-Ethylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl)isophthalonitrile (**8i**).* Yellow solid, 93% yield, mp 230–233 °C. IR (KBr): ν_{max} 3071, 2969, 2932, 2874, 2232, 1660, 1614, 1577, 1510, 1444, 1388, 1360, 1343, 1228, 1130, 1057, 1025, 991, 798, 760, 711 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, *J*=7.8 Hz), 3.04 (2H, q, *J*=7.8 Hz), 5.68 (2H, s), 6.92 (1H, s), 7.41 (1H, t, *J*=7.8 Hz), 7.62 (1H, t, *J*=8.4 Hz), 7.76 (1H, t, *J*=8.4 Hz), 7.88 (2H, d, *J*=8.1 Hz), 8.06 (1H, d, *J*=8.4 Hz), 8.21 (1H, d, *J*=8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 23.2, 72.3, 91.4, 114.1, 117.2, 123.3, 126.8, 127.1, 127.5, 129.2, 129.9, 130.9, 137.1, 143.3, 143.9, 149.7, 151.7, 159.3 ppm. Anal. Calcd for $C_{22}H_{15}N_3O$: C, 78.32; H, 4.48; N, 12.46; found: C, 78.17; H, 4.41; N, 12.27. ESIMS (*m*/*z*): 338.08 $(M+H)^+$; 360.08 $(M+Na)^+$.

*4.5.10. (Z)-2-((9-Phenylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl) isophthalonitrile (**8j**).* Yellow solid, 97% yield, mp 248–251 °C. IR (KBr): ν_{max} 3056, 2929, 2869, 2230, 1659, 1609, 1573, 1493, 1443, 1384, 1344, 1228, 1144, 1026, 798, 765, 703 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.55 (2H, s), 6.97 (1H, s), 7.39–7.44 (3H, m), 7.51–7.59 (4H, m), 7.76–7.82 (2H, m), 7.88 (2H, d, *J*=8.1 Hz), 8.26 (1H, d, *J*=8.1 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 72.8, 91.6, 114.1, 117.2, 120.2, 125.7, 126.8, 127.1, 127.7, 128.9, 129.2, 129.6, 130.1, 130.3, 134.9, 137.0, 142.4, 143.2, 150.0, 151.8, 159.2 ppm. Anal. Calcd for $C_{26}H_{15}N_3O$: C, 81.02; H, 3.92; N, 10.90; found: C, 81.01; H, 3.90; N, 10.94. ESIMS (*m*/*z*): 386.17 $(M+H)^+$.

*4.5.11. (Z)-2-((1-Methylfuro[3,4-b]quinolin-3(1H)-ylidene)methyl) isophthalonitrile (**8k**).* Yellowish solid, 94% yield, mp 229–231 °C. IR (KBr): ν_{max} 3065, 2974, 2921, 2849, 2229, 1661, 1616, 1569, 1501, 1448, 1407, 1385, 1244, 1162, 1073, 1050, 945, 908, 809, 770, 758 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78 (3H, d, *J*=6.6 Hz), 5.96 (1H, q, *J*=6.6 Hz), 6.92 (1H, s), 7.41 (1H, t, *J*=8.1 Hz), 7.60 (1H, t, *J*=8.1 Hz), 7.78 (1H, t, *J*=8.4 Hz), 7.85–7.89 (3H, m), 8.06 (1H, s), 8.21 (1H, d, *J*=8.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.9, 81.2, 91.1, 114.3, 117.2, 126.8, 127.7, 128.1, 128.4, 128.8, 130.0, 130.4, 135.7, 137.0, 143.3, 149.3, 152.4, 158.0. Anal. Calcd for $C_{21}H_{13}N_3O$: C, 78.00; H, 4.05; N, 13.00; found: C, 78.01; H, 4.23; N, 12.95. ESIMS (*m*/*z*): 324.25 $(M+H)^+$; 346.25 $(M+Na)^+$.

4.6. Preparation of furo[3,4-*b*]quinolin-3(1*H*)-one 2g

To a stirred solution of **8g** (70 mg, 0.22 mmol) in CCl_4 (1 mL), CH_3CN (1 mL) and water (1.8 mL) was successively added $NaIO_4$ (232 mg, 1.1 mmol), $RuCl_3 \cdot xH_2O$ (1.2 mg) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. Saturated aqueous $Na_2S_2O_3$ solution was added to quench the reaction and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (dichloromethane/methanol=70:1), affording 7-methylfuro[3,4-*b*]quinolin-3(1*H*)-one (**2g**) as a white solid (38 mg, 88% yield). Mp 252–253 °C. IR (KBr): ν_{max} 3045, 2981, 2955, 2923, 2852, 1773, 1616, 1568, 1499, 1465, 1376, 1341, 1303, 1234, 1143, 1054, 995, 913, 836 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (3H, s), 5.53 (2H, s), 7.69 (2H, m), 8.24 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 68.1, 126.8, 129.4, 129.7, 130.8, 133.6, 134.1, 140.1, 143.8, 148.8, 168.7. Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03; found: C, 72.31; H, 4.57; N, 7.17. ESIMS (*m*/*z*): 200.17 $(M+H)^+$; 222.17 $(M+Na)^+$.

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Supplementary data

Supplementary data of NMR spectra of new compounds are available. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.05.067.

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