Palladium-Catalyzed Intermolecular Domino Reaction of *gem*-Dibromoenynes with Anilines; A One-Pot Synthesis of Quinolines and Quinolinones

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Abstract: An efficient domino process involving palladium-catalyzed amination of an alkenyl bromide, 1,5-H transfer, annulation via 6-*exo*-*dig* electrophilic cyclization, and palladium-catalyzed etherification, is described. This reaction provides an efficient one-pot synthesis of multi-substituted quinolines and quinolinones from *gem*-dibromoenynes and anilines.

Key words: alkenes, enynes, etherification, quinoline, quinolinone

The *gem*-dihaloolefins have become important and versatile building blocks in palladium-catalyzed domino reactions leading to heterocyclic compounds.[1] Recently, several elegant methods have been discovered that can be used to convert *gem*-dihaloolefins into indoles,[2] benzothiophenes,[2a,3] benzofurans,[2a,4] isocoumarins,[5] and other heterocycles via intramolecular cyclization.[1,6] For example, Lautens et al. reported the intramolecular amination of amino-containing *gem*-dibromoolefins to provide the brominated indoles, in which the remaining C–Br bond could further undergo Suzuki coupling.[2b] Xu et al. reported a palladium-catalyzed intermolecular amidation reaction of *gem*-dihaloolefins with aryl amines yielding acyclic carboxamides upon hydrolysis.[7]

Our group has been interested in the preparation and synthetic applications of polyhalo conjugated compounds.[8a,9,10] Herein, we report an intermolecular amination between amines and *gem*-dibromoenynes that efficiently yields quinolines and quinolinones. Mechanistic investigations have revealed that a domino process involving palladium-catalyzed amination of the alkenyl bromide, 1,5-H transfer, annulation via 6-*exo*-*dig* electrophilic cyclization, and palladium-catalyzed etherification took place, resulting in the formation of C^{sp2}–C^{sp}, C^{sp2}–N, and C^{sp2}–O bonds. The quinoline unit is an important skeleton found in a variety of bioactive compounds.[11] Most of the known synthetic methods for accessing functionalized quinolines are based on the reaction of substituted anilines with carbonyl compounds.[12–14] Synthesis of N-heterocycles via intermolecular amination between amines and *gem*-dihaloolefins is rare.[6f,8] This palladium-catalyzed intermolecular domino reaction between amines and *gem*-dibromoenynes thus provides an efficient alternative synthesis of quinolines and quinolinones.

First, we investigated the model reaction between aniline and compound **1a** (Table 1). The reaction was initially carried out in toluene at 110 °C for two hours with NaO*t*-Bu as the base. Various palladium catalysts (Table 1, entries 1–4) and a series of ligands (Table 1, entries 5–15) were examined. Although the Buchwald biaryl phosphine ligands showed better activity than Ph_3P and Cy_3P, the bidentate ligand DPEPhos [bis(2-diphenylphosphinophenyl)ether] proved to be more efficient in this reaction. It was also noticed that the reactivity diminished when the solvent was changed from toluene to 1,4-dioxane or DME. Notably, the choice of base seems crucial for this transformation; NaO*t*-Bu was found to be the most effective base, whereas other bases such as LiO*t*-Bu or KO*t*-Bu did not afford any expected products. After extensive screening, optimal reaction conditions were established {[$Pd_2(dba)_3$] (2.5 mol%), DPEPhos (10 mol%), NaO*t*-Bu (5 equiv), toluene, 110 °C, 2 h} with which polysubstituted quinoline **3a** was obtained in 68% isolated yield (Table 1, entry 12).

Because the substituents on the quinoline has such a great influence on its properties, the scope of this domino reaction was studied by testing various substituted anilines **2b**–**k**, with the aim of synthesizing a diverse range of quinolines. As shown in Table 2, various quinolines **3d**–**m** could be obtained in moderate to high isolated yields under the above optimized reaction conditions. Anilines substituted with either electron-withdrawing or electron-donating groups could both be applied in this reaction. Naphthylamine (**2h**) and the heteroaromatic amine (**2i**) could also be used to provide the corresponding quinoline derivatives.

It is noteworthy that, along with the formation of quinolines **3**, a small amount of the corresponding quinolinones **4** were formed, which could be separated from quinolines **3**. It became clear that quinolinone **4** was formed through hydrolysis of quinoline **3**. Quantitative transformation of quinoline **3** into quinolinone **4** was observed when pure

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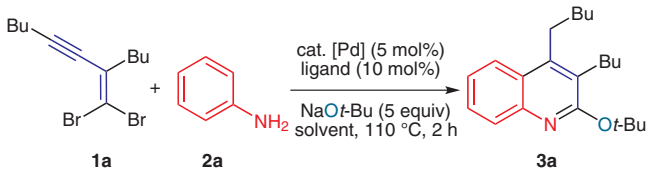
Table 1 Reaction Optimization[a]



1a 2a 3a

Entry	[Pd]	Ligand	Base	Solvent	Yield (%)[a]
1	$PdCl_2$		NaO*t*-Bu	toluene	trace
2	$Pd(OAc)_2$		NaO*t*-Bu	toluene	trace
3	$Pd_2(dba)_3$		NaO*t*-Bu	toluene	trace
4	$Pd(PPh_3)_4$		NaO*t*-Bu	toluene	9
5	$Pd(OAc)_2$	XPhos	NaO*t*-Bu	toluene	53
6	$Pd_2(dba)_3$	XPhos	NaO*t*-Bu	toluene	65 (61)
7	$Pd_2(dba)_3$	SPhos	NaO*t*-Bu	toluene	57
8	$Pd_2(dba)_3$	RuPhos	NaO*t*-Bu	toluene	47
9	$Pd_2(dba)_3$	DavePhos	NaO*t*-Bu	toluene	57
10	$Pd_2(dba)_3$	PPh_3	NaO*t*-Bu	toluene	33
11	$Pd_2(dba)_3$	PCy_3	NaO*t*-Bu	toluene	trace
12	$Pd_2(dba)_3$	DPEPhos	NaO*t*-Bu	toluene	72 (68)
13	$Pd_2(dba)_3$	XantPhos	NaO*t*-Bu	toluene	31
14	$Pd_2(dba)_3$	DPPF	NaO*t*-Bu	toluene	51
15	$Pd_2(dba)_3$	DPPP	NaO*t*-Bu	toluene	52
16	$Pd_2(dba)_3$	DPEPhos	LiO*t*-Bu	toluene	trace
17	$Pd_2(dba)_3$	DPEPhos	KO*t*-Bu	toluene	trace
18	$Pd_2(dba)_3$	DPEPhos	NaO*t*-Bu	1,4-dioxane	66[b]
19	$Pd_2(dba)_3$	DPEPhos	NaO*t*-Bu	DME	24[b]

[a] GC yields. Isolated yields given in parentheses.
[b] Heated to reflux.

quinoline **3** was treated with aqueous 3 M HCl. Accordingly, as shown in Table 2, quinolinones **4d**–**m** were isolated in moderate to high yields as the sole products when the one-pot reaction mixture was quenched with aqueous 3 M HCl.

We also investigated other *gem*-dibromoenynes with different substituents on the unsaturated skeleton. As summarized in Table 2 (entries 2 and 3), derivatives **3** and **4** were obtained in moderate isolated yields from propyl-substituted enyne (**1b**) and hexyl-substituted enyne (**1c**), respectively, with aniline **2a**.

Two plausible catalytic pathways for the formation of quinolines **3** from *gem*-dihaloenyne **1** are presented in Scheme 1. The first pathway (**I**) might involve four subsequent steps: palladium-catalyzed amination of the alkenyl bromides,[15–17] 1,5-H transfer,[18] annulation via 6-*exo*-*dig* electrophilic cyclization,[19] and palladium-catalyzed etherification.[20,21] The second pathway might involve: palladium-catalyzed etherification, amination, 1,5-H shift, and 6-*exo*-*dig* electrophilic cyclization.

To gain a better understanding of the present reaction mechanism, three different experiments were carried out. First, the two-component coupling between the conjugated *cis*-bromo alkenyne **5** and aniline **2a** was carried out under the above reaction conditions, providing quinoline **6** in 57% isolated yield as well as pyrrole **7** in 16% isolated yield (Scheme 2).[22,23] The formation of **6** presumably arises from 6-*exo*-*dig* electrophilic cyclization of the alkynylenamine intermediate **8**, whereas pyrrole derivative **7** should be generated via 5-*endo*-*dig* hydroamination of **8**. This result clearly shows the prior palladium-catalyzed amination with one bromine is reasonable and should result in the formation of quinoline **6**, which strongly supports Step 1 of the proposed pathway **I** shown in Scheme 1.

A deuterium-labeling experiment using aniline-D_2 and **1a** was carried out in the presence of anhydrous NaO*t*-Bu (Scheme 3). The *gem*-dihaloenyne **1a** was converted completely in refluxing toluene within two hours, resulting in the formation of the product **3a**-D/H in 65% isolated yield. The deuterium on the C5 position of quinoline **3a**-D/H originates from aniline-D_2, which strongly supports the proposed 1,5-H shift shown in Scheme 1.

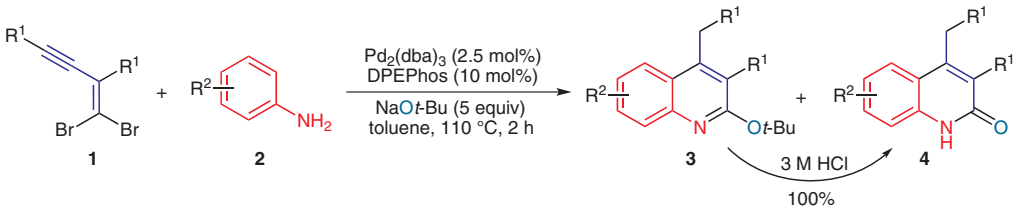
Finally, an experiment was designed to investigate at which step the etherification reaction occurs; either the first step in pathway **II** or in the last step in pathway **I**. No reaction took place when 2-bromoquinoline **9** was treated with three equivalents of NaO*t*-Bu without the palladium catalyst. Under the optimized reaction conditions used above, as shown in Scheme 4, the ether-containing quinoline **10** was obtained in 70% isolated yield, along with formation of the corresponding quinolinone **11** in 21% isolated yield. This result and other experimental observations show that pathway **I** (Scheme 1) is more likely.

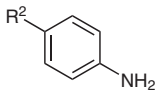
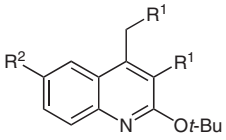
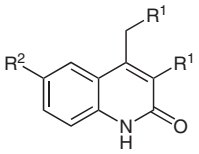
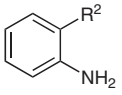
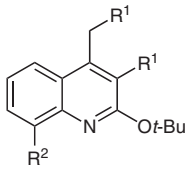
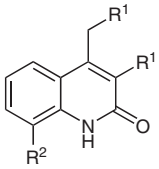
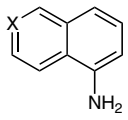
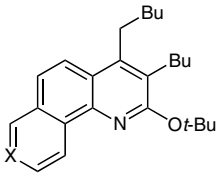
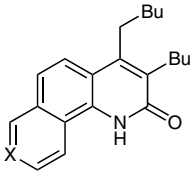
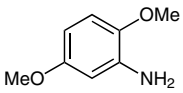
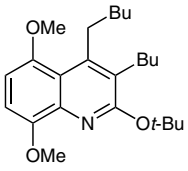
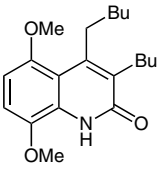
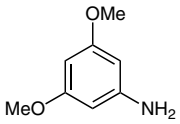
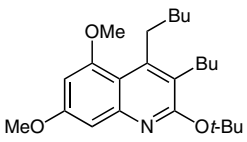
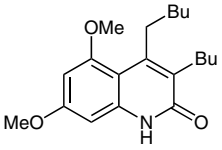
In summary, we have developed a domino palladium-catalyzed amination, C–C bond formation, and C–O coupling process. This method provides an efficient synthesis of multi-substituted quinolines and quinolinones from *gem*-dibromoenynes and anilines.

Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions were carried out either using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2 Combi-Analyzer to ensure both were always below 1 ppm. Solvents were purified by a Solvent Purification System and dried over fresh Na chips in the glovebox.

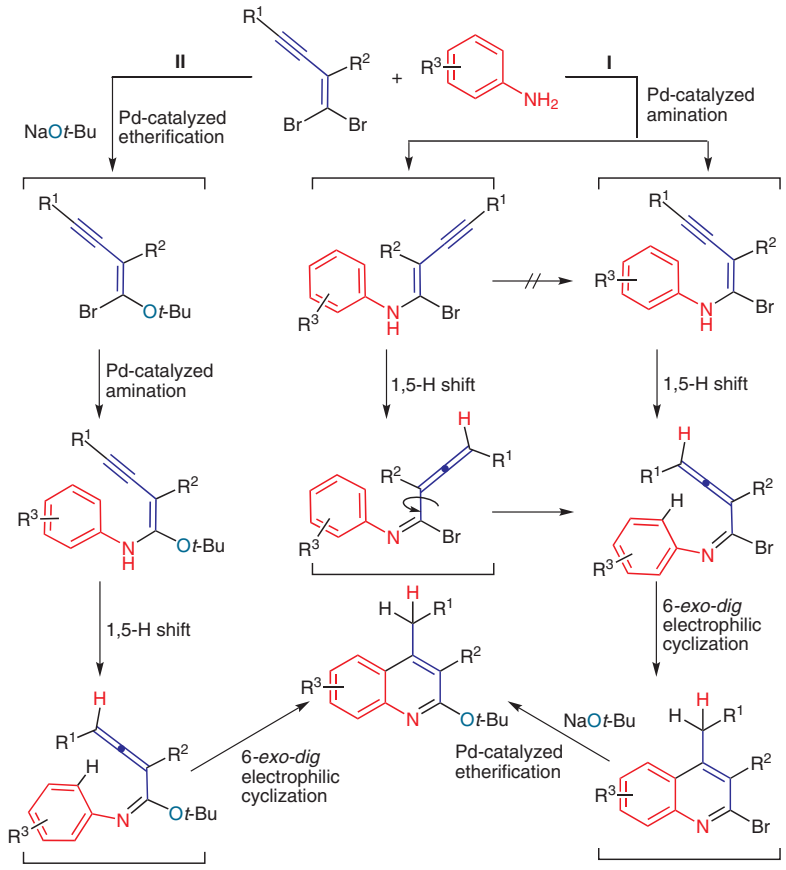
^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-AL 300 spectrometer (FT, 300 MHz for ^1H; 75 MHz for ^{13}C), a Bruker DMX 300 spectrometer (FT, 300 MHz for ^1H; 75 MHz for ^{13}C), a Bruker ARX 400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C), a Bruker AVANCE 400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) or a Bruker AVANCE III 500 spectrometer (FT,

Table 2 Domino Three-Component Synthesis of Quinolines **3** and Quinolinones **4**

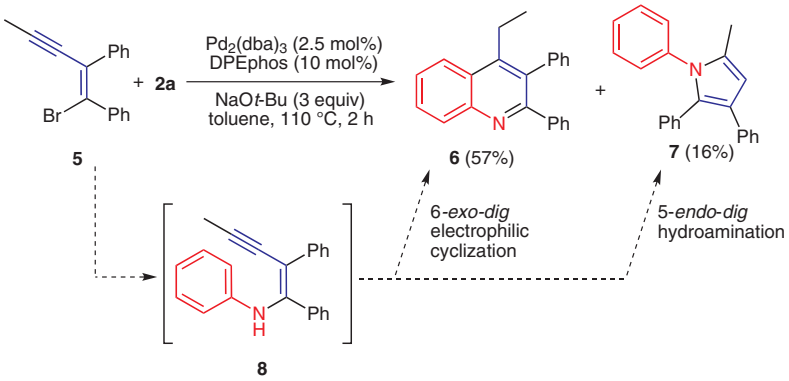


Entry	Amines **2**	Quinolines **3** (Yield) [%][a]	Quinolinones **4** (Yield) [%][b]
			
1	**2a**: R^2 = H	**3a**: R^1 = Bu (68%)	**4a**: R^1 = Bu (74%)
2		**3b**: R^1 = Pr (52%)	**4b**: R^1 = Pr (61%)
3		**3c**: R^1 = Hex (63%)	**4c**: R^1 = Hex (70%)
4	**2b**: R^2 = F	**3d**: R^1 = Bu (50%)	**4d**: R^1 = Bu (64%)
5	**2c**: R^2 = OMe	**3e**: R^1 = Bu (59%)	**4e**: R^1 = Bu (65%)
6	**2d**: R^2 = Bn	**3f**: R^1 = Bu (47%)	**4f**: R^1 = Bu (63%)
			
7	**2e**: R^2 = *i*-Pr	**3g**: R^1 = Bu (66%)	**4g**: R^1 = Bu (73%)
8	**2f**: R^2 = OMe	**3h**: R^1 = Bu (72%)	**4h**: R^1 = Bu (81%)
9	**2g**: R^2 = Ph	**3i**: R^1 = Bu (62%)	**4i**: R^1 = Bu (70%)
			
10	**2h**: X = C	**3j** (60%)	**4j** (71%)
11	**2i**: X = N	**3k** (32%)	**4k** (43%)
			
12	**2j**	**3l** (50%)	**4l** (63%)
			
13	**2k**	**3m** (45%)	**4m** (63%)

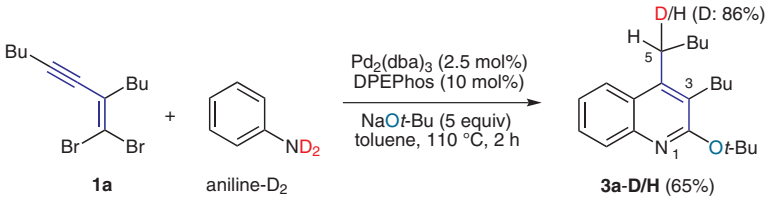
[a] Isolated yields of quinolines **3**.
[b] An 3 M HCl was added to the crude mixture and stirred for 30 min; isolated yields of quinolinones **4** are given in parentheses.



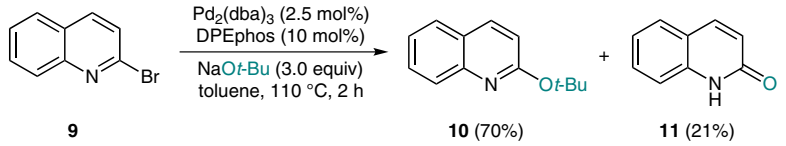
Scheme 1 Proposed reaction mechanism



Scheme 2 Palladium-catalyzed amination of monohaloenyne **5** affording quinoline **6** and pyrrole **7**



Scheme 3 Deuterium-labeling experiment confirming the 1,5-H-shift



Scheme 4 Control experiment used to investigate the etherification reaction

500 MHz for ^{1}H; 125 MHz for ^{13}C) at r.t. in $CDCl_3$ solutions and with tetramethylsilane (δ = 0.00 ppm) as internal standard, unless otherwise noted. Infrared spectra (IR) were recorded with a Thermo Nicolet Avatar 330 FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were recorded with a Bruker Apex IV FTMS mass spectrometer using electrospray ionization (ESI) and FT-ICR mass analyser or a Waters Micromass GCT mass spectrometer using electron-ionization (EI) and a TOF mass analyzer. The *gem*-dihaloenynes **1** were prepared from 1,1,4,4-tetrahalo-1,3-butadienes through the Fritsch–Buttenberg–Wiechell (FBW) rearrangement mediated by an organolithium compound.[10b]

Preparation of Quinolines 3 and Quinolinones 4; General Procedure

$[Pd_2(dba)_3]$ (4.6 mg, 0.005 mmol), DPEPhos (10.2 mg, 0.02 mmol) and toluene (2.0 mL) were placed in an oven-dried 25 mL flask, and the mixture was stirred at r.t. for 15 min, then *gem*-dihaloenyne **1** (0.2 mmol), aniline **2** (0.24 mmol), and NaO*t*-Bu (96 mg, 1.0 mmol) were added. The flask was then placed in a preheated oil bath (110 °C) and stirred for 2 h. After cooling to r.t., the solvent was evaporated under vacuum and the residue was purified by chromatography (EtOAc–pentane, 0→10%) to give the quinoline product **3**. To obtain the corresponding quinolinone product **4**, excess 3 M HCl was added and the solution was stirred for 1 h. The reaction mixture was neutralized with $NaHCO_3$ and extracted with EtOAc (3 × 3 mL). The solvent was then evaporated in vacuo and the crude product was purified by column chromatography over silica gel (EtOAc–pentane, 50→100%).

2-*tert*-Butoxy-3-butyl-4-pentylquinoline (3a)

Yield: 68% (45 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.99 (m, 6 H, CH_3), 1.38–1.53 (m, 10 H, CH_2), 1.69 (s, 9 H, CH_3), 2.69 (t, *J* = 8.3 Hz, 2 H, CH_2), 2.96 (t, *J* = 7.8 Hz, 2 H, CH_2), 7.31 (t, *J* = 7.5 Hz, 1 H, CH), 7.49 (t, *J* = 7.2 Hz, 1 H, CH), 7.73–7.83 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.1, 26.7, 28.2, 28.7 ($3CH_3$), 30.3, 31.9, 32.4, 79.5, 123.1, 123.4, 124.2, 125.5, 127.5, 127.9, 145.0, 145.8, 160.4.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{34}NO^+$: 328.2635; found: 328.2629.

2-*tert*-Butoxy-4-butyl-3-propylquinoline (3b)

Yield: 52% (31 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98–1.03 (m, 6 H, CH_3), 1.49–1.60 (m, 6 H, CH_2), 1.69 (s, 9 H, CH_3), 2.67 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.97 (t, *J* = 7.5 Hz, 2 H, CH_2), 7.32 (t, *J* = 7.5 Hz, 1 H, CH), 7.49 (t, *J* = 7.5 Hz, 1 H, CH), 7.75 (d, *J* = 8.4 Hz, 1 H, CH), 7.83 (d, *J* = 8.4 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.6, 23.1, 23.3, 27.9, 28.7 ($3CH_3$), 29.1, 32.7, 79.4, 123.1, 123.5, 124.2, 125.4, 127.5, 127.9, 145.1, 145.9, 160.4.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{30}NO^+$: 300.2322; found: 300.2316.

2-*tert*-Butoxy-4-heptyl-3-hexylquinoline (3c)

Yield: 63% (48 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88–0.92 (m, 6 H, CH_3), 1.31–1.63 (m, 18 H, CH_2), 1.69 (s, 9 H, CH_3), 2.68 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.95 (t, *J* = 8.1 Hz, 2 H, CH_2), 7.31 (t, *J* = 7.5 Hz, 1 H, CH), 7.49 (t, *J* = 7.5 Hz, 1 H, CH), 7.75 (d, *J* = 8.2 Hz, 1 H, CH), 7.82 (d, *J* = 8.2 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 ($2CH_3$), 22.7 ($2CH_2$), 27.1, 28.2, 28.7 ($3CH_3$), 29.1, 29.7, 29.8, 30.2, 30.6, 31.7, 31.8, 79.5, 123.1, 123.5, 124.2, 125.6, 127.5, 127.9, 145.0, 145.8, 160.4.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{42}NO^+$: 384.3261; found: 384.3258.

2-*tert*-Butoxy-3-butyl-6-fluoro-4-pentylquinoline (3d)

Yield: 50% (35 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91–1.00 (m, 6 H, CH_3), 1.37–1.53 (m, 10 H, CH_2), 1.68 (s, 9 H, CH_3), 2.68 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.89 (t, *J* = 8.1 Hz, 2 H, CH_2), 7.21–7.28 (m, 1 H, CH), 7.40–7.45 (m, 1 H, CH), 7.68–7.73 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.98, 14.03, 22.5, 23.1, 26.8, 28.4, 28.6 ($3CH_3$), 30.0, 31.8, 32.4, 79.6, 107.4 (d, J_{C-F} = 22.3 Hz), 116.8 (d, J_{C-F} = 24.7 Hz), 124.7 (d, J_{C-F} = 8.6 Hz), 126.5, 129.7 (d, J_{C-F} = 8.7 Hz), 141.8, 145.2 (d, J_{C-F} = 4.3 Hz), 159.0 (d, J_{C-F} = 239.3 Hz), 160.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{33}FNO^+$: 346.2541; found: 346.2538.

2-*tert*-Butoxy-3-butyl-6-methoxy-4-pentylquinoline (3e)

Yield: 59% (42 mg); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92–0.99 (m, 6 H, CH_3), 1.38–1.53 (m, 8 H, CH_2), 1.59–1.65 (m, 2 H, CH_2), 1.67 (s, 9 H, CH_3), 2.68 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.92 (t, *J* = 8.2 Hz, 2 H, CH_2), 3.90 (s, 3 H, CH_3), 7.16–7.19 (m, 2 H, CH), 7.67 (d, *J* = 9.4 Hz, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.00, 14.05, 22.5, 23.1, 26.8, 28.3, 28.7 ($3CH_3$), 29.8, 31.9, 32.4, 55.5, 79.1, 103.7, 118.1, 124.7, 125.8, 129.2, 140.4, 144.8, 155.5, 159.2.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{36}NO_2^+$: 358.2741; found: 358.2737.

6-Benzyl-2-*tert*-butoxy-3-butyl-4-pentylquinoline (3f)

Yield: 47% (39 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89–0.98 (m, 6 H, CH_3), 1.34–1.55 (m, 10 H, CH_2), 1.67 (s, 9 H, CH_3), 2.67 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.89 (t, *J* = 8.0 Hz, 2 H, CH_2), 4.12 (s, 2 H, CH_2), 7.19–7.34 (m, 6 H, CH), 7.56 (s, 1 H, CH), 7.66 (d, *J* = 8.4 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.01, 14.04, 22.5, 23.1, 26.7, 28.1, 28.7 ($3CH_3$), 30.2, 31.9, 32.3, 42.1, 79.3, 123.1, 124.1, 125.6, 126.0, 128.0, 128.4 (2CH), 128.9 (2CH), 129.0, 135.7, 141.4, 143.7, 145.5, 160.2.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{40}NO^+$: 418.3104; found: 418.3107.

2-*tert*-Butoxy-3-butyl-8-isopropyl-4-pentylquinoline (3g)

Yield: 66% (49 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92–1.00 (m, 6 H, CH_3), 1.34–1.53 (m, 16 H, CH_2, CH_3), 1.71 (s, 9 H, CH_3), 2.70 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.96 (t, *J* = 6.8 Hz, 2 H, CH_2), 4.15–4.23 (m, 1 H, CH), 7.31 (t, *J* = 7.8 Hz, 1 H, CH), 7.45 (d, *J* = 6.3 Hz, 1 H, CH), 7.70 (d, *J* = 8.4 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.1, 23.6 ($2CH_3$), 26.8, 27.3, 28.4, 28.6 ($3CH_3$), 30.3, 31.9, 32.5, 78.8, 121.2, 123.0, 123.3, 124.1, 125.1, 142.7, 145.6, 146.3, 159.3.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{40}NO^+$: 370.3104; found: 370.3103.

2-*tert*-Butoxy-3-butyl-8-methoxy-4-pentylquinoline (3h)

Yield: 72% (51 mg); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91–0.98 (m, 6 H, CH_3), 1.37–1.53 (m, 8 H, CH_2), 1.58–1.64 (m, 2 H, CH_2), 1.71 (s, 9 H, CH_3), 2.69 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.94 (t, *J* = 8.3 Hz, 2 H, CH_2), 3.99 (s, 3 H, CH_3), 6.93 (d, *J* = 7.2 Hz, 1 H, CH), 7.22 (t, *J* = 8.1 Hz, 1 H, CH), 7.42 (d, *J* = 7.7 Hz, 1 H, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.00, 14.04, 22.5, 23.1, 26.8, 28.6, 28.7 ($3CH_3$), 30.3, 31.9, 32.4, 56.7, 79.5, 108.1, 115.9, 122.9, 125.5, 125.7, 136.8, 146.0, 155.1, 159.6.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{36}NO_2^+$: 358.2741; found: 358.2746.

2-*tert*-Butoxy-3-butyl-4-pentyl-8-phenylquinoline (3i)
Yield: 62% (50 mg); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.98 (m, 6 H, CH_3), 1.41–1.55 (m, 17 H, CH_2, CH_3), 1.62–1.70 (m, 2 H, CH_2), 2.69 (t, *J* = 7.7 Hz, 2 H, CH_2), 3.00 (t, *J* = 8.2 Hz, 2 H, CH_2), 7.32–7.43 (m, 4 H, CH), 7.50–7.55 (m, 3 H, CH), 7.86 (d, *J* = 9.7 Hz, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.1, 26.8, 28.3 ($3CH_3$), 28.5, 30.4, 31.9, 32.5, 79.1, 122.7, 123.1, 124.6, 125.4, 126.4, 127.3 (2CH), 128.5, 130.7 (2CH), 139.7, 141.2, 143.0, 146.0, 159.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{38}NO^+$: 404.2948; found: 404.2949.

2-*tert*-Butoxy-3-butyl-4-pentylbenzo[*h*]quinoline (3j)
Yield: 60% (45 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92–1.02 (m, 6 H, CH_3), 1.40–1.59 (m, 10 H, CH_2), 1.80 (s, 9 H, CH_3), 2.75 (t, *J* = 7.7 Hz, 2 H, CH_2), 3.02 (t, *J* = 8.1 Hz, 2 H, CH_2), 7.57–7.66 (m, 3 H, CH), 7.83 (t, *J* = 8.9 Hz, 2 H, CH), 9.08 (d, *J* = 7.8 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.1, 26.7, 28.4, 28.7 ($3CH_3$), 30.6, 32.0, 32.4, 79.3, 120.7, 121.9, 123.7, 124.6, 125.0, 125.9, 126.8, 127.3, 131.6, 133.1, 142.4, 146.8, 160.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{36}NO^+$: 378.2791; found: 378.2794.

2-*tert*-Butoxy-3-butyl-4-pentyl-1,9-phenanthroline (3k)
Yield: 32% (24 mg); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.00 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.40–1.68 (m, 10 H, CH_2), 1.80 (s, 9 H, CH_3), 2.77 (t, *J* = 7.9 Hz, 2 H, CH_2), 3.04 (t, *J* = 8.3 Hz, 2 H, CH_2), 7.74 (d, *J* = 9.0 Hz, 1 H, CH), 7.93 (d, *J* = 9.1 Hz, 1 H, CH), 8.72 (d, *J* = 5.7 Hz, 1 H, CH), 8.77 (d, *J* = 5.6 Hz, 1 H, CH), 9.24 (s, 1 H, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.01, 14.05, 22.5, 23.2, 26.8, 28.5, 28.7 ($3CH_3$), 30.5, 31.8, 32.4, 79.9, 117.6, 121.7, 123.0, 123.5, 127.4, 128.1, 135.6, 140.9, 144.3, 147.0, 151.0, 160.6.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{35}N_2O^+$: 379.2744; found: 379.2744.

2-*tert*-Butoxy-3-butyl-5,8-dimethoxy-4-pentylquinoline (3l)
Yield: 50% (39 mg); yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91–0.99 (m, 6 H, CH_3), 1.38–1.50 (m, 10 H, CH_2), 1.70 (s, 9 H, CH_3), 2.69 (t, *J* = 7.2 Hz, 2 H, CH_2), 3.18 (t, *J* = 6.5, 2 H, CH_2), 3.86 (s, 3 H, CH_3), 3.94 (s, 3 H, CH_3), 6.59 (d, *J* = 8.7 Hz, 1 H, CH), 6.86 (d, *J* = 8.7 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.2, 22.5, 23.1, 26.1, 28.6 ($3CH_3$), 31.2, 31.3, 32.0, 32.8, 55.6, 57.6, 79.4, 102.6, 108.7, 117.3, 125.8, 138.6, 147.6, 149.3, 151.3, 159.6.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{38}NO_3^+$: 388.2846; found: 388.2836.

2-*tert*-Butoxy-3-butyl-5,7-dimethoxy-4-pentylquinoline (3m)
Yield: 45% (35 mg); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91–0.98 (m, 6 H, CH_3), 1.38–1.55 (m, 10 H, CH_2), 1.67 (s, 9 H, CH_3), 2.64 (t, *J* = 7.6 Hz, 2 H, CH_2), 3.12 (t, *J* = 8.1 Hz, 2 H, CH_2), 3.87–3.90 (m, 6 H, CH_3), 6.35 (d, *J* = 2.5 Hz, 1 H, CH), 6.74 (d, *J* = 2.4 Hz, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.2, 22.5, 23.1, 26.0, 28.8 ($3CH_3$), 31.1, 31.2, 32.2, 32.8, 55.3, 55.4, 79.2, 96.2, 100.2, 111.6, 123.0, 147.5, 148.4, 158.0, 159.2, 160.9.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{38}NO_3^+$: 388.2846; found: 388.2848.

3-Butyl-4-pentylquinolin-2(1*H*)-one (4a)
Yield: 74% (40 mg); colorless solid; mp 147.5–149.2 °C.

IR (film): 1654 (C=O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92–1.01 (m, 6 H, CH_3), 1.37–1.70 (m, 10 H, CH_2), 2.76 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.88 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.17–7.22 (m, 1 H, CH), 7.39–7.46 (m, 2 H, CH), 7.67 (d, *J* = 8.2 Hz, 1 H, CH), 12.08 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.1, 26.7, 28.8, 29.7, 31.6, 32.4, 116.3, 120.1, 122.1, 124.2, 128.9, 131.2, 137.3, 147.5, 164.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{26}NO^+$: 272.2009; found: 272.2014.

4-Butyl-3-propylquinolin-2(1*H*)-one (4b)
Yield: 61% (30 mg); colorless solid; mp 135.2–136.9 °C.

IR (film): 1650 (C=O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99–1.08 (m, 6 H, CH_3), 1.51–1.66 (m, 6 H, CH_2), 2.74 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.90 (t, *J* = 7.9 Hz, 2 H, CH_2), 7.21 (t, *J* = 7.4 Hz, 1 H, CH), 7.38–7.46 (m, 2 H, CH), 7.69 (d, *J* = 8.2 Hz, 1 H, CH), 11.94 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.6, 22.7, 23.3, 28.6, 29.0, 32.1, 116.3, 120.1, 122.2, 124.3, 129.0, 130.9, 137.2, 147.8, 164.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{22}NO^+$: 244.1696; found: 244.1701.

4-Heptyl-3-hexylquinolin-2(1*H*)-one (4c)
Yield: 70% (46 mg); colorless solid; mp 145.6–147.4 °C.

IR (film): 1654 (C=O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.93 (m, 6 H, CH_3), 1.32–1.62 (m, 18 H, CH_2), 2.74 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.88 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.20 (t, *J* = 7.6 Hz, 1 H, CH), 7.32 (d, *J* = 8.1 Hz, 1 H, CH), 7.42 (t, *J* = 7.6 Hz, 1 H, CH), 7.68 (d, *J* = 8.2 Hz, 1 H, CH), 11.42 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.7 ($2CH_2$), 27.0, 28.9, 29.1, 29.3, 29.7, 30.0, 30.2, 31.8 ($2CH_2$), 116.1, 120.2, 122.1, 124.4, 128.9, 131.3, 137.1, 147.5, 163.7.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{34}NO^+$: 328.2635; found: 328.2633.

3-Butyl-6-fluoro-4-pentylquinolin-2(1*H*)-one (4d)
Yield: 64% (37 mg); colorless solid; mp 133.3–135.3 °C.

IR (film): 1654 (C=O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92–1.01 (m, 6 H, CH_3), 1.37–1.58 (m, 10 H, CH_2), 2.74–2.85 (m, 4 H, CH_2), 7.16–7.42 (m, 3 H, CH), 12.67 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.1, 26.8, 29.0, 29.5, 31.5, 32.3, 109.4 (d, J_{C-F} = 22.8 Hz), 117.1 (d, J_{C-F} = 24.2 Hz), 117.8 (d, J_{C-F} = 8.1 Hz), 121.0 (d, J_{C-F} = 8.0 Hz), 132.4, 133.8, 146.8 (d, J_{C-F} = 3.7 Hz), 158.1 (d, J_{C-F} = 238.1 Hz), 163.9.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{25}FNO^+$: 290.1915; found: 290.1915.

3-Butyl-6-methoxy-4-pentylquinolin-2(1*H*)-one (4e)
Yield: 65% (39 mg); colorless solid; mp 101.3–103.0 °C.

IR (film): 1646 (C=O) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93–1.01 (m, 6 H, CH_3), 1.39–1.65 (m, 10 H, CH_2), 2.76 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.85 (t, *J* = 7.8 Hz, 2 H, CH_2), 3.86 (s, 3 H, CH_3), 7.07–7.11 (m, 2 H, CH), 7.32 (d, *J* = 8.8 Hz, 1 H, CH), 12.14 (s, 1 H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.2, 26.9, 29.0, 29.4, 31.7, 32.4, 55.8, 107.1, 117.4 (2CH), 120.9, 131.8, 132.0, 146.8, 154.9, 163.6.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{28}NO_2^+$: 302.2115; found: 302.2115.

6-Benzyl-3-butyl-4-pentylquinolin-2(1*H*)-one (4f)
Yield: 63% (46 mg); colorless solid; mp 124.4–126.2 °C.

IR (film): 1654 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.89–0.99 (m, 6 H, CH_3), 1.31–1.56 (m, 10 H, CH_2), 2.71–2.83 (m, 4 H, CH_2), 4.06 (s, 2 H, CH_2), 7.18–7.33 (m, 7 H, CH), 7.41 (s, 1 H, CH), 12.12 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.4, 23.1, 26.7, 28.7, 29.6, 31.6, 32.2, 41.6, 116.4, 120.0, 124.1, 126.1, 128.5 (2CH), 128.9 (2CH), 130.0, 131.2, 134.7, 135.7, 141.0, 147.3, 163.9.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{32}NO^+$: 362.2478; found: 362.2482.

3-Butyl-8-isopropyl-4-pentylquinolin-2(1*H*)-one (4g)
Yield: 73% (46 mg); colorless solid; mp 114.3–115.8 °C.

IR (film): 1630 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.92–0.99 (m, 6 H, CH_3), 1.34–1.62 (m, 16 H, CH_2, CH_3), 2.72 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.87 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.43–3.51 (m, 1 H, CH), 7.16–7.20 (m, 1 H, CH), 7.38 (t, *J* = 5.4 Hz, 1 H, CH), 7.56 (t, *J* = 6.3 Hz, 1 H, CH), 10.08 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 22.9 ($2CH_3$), 23.3, 26.6, 27.0, 29.1, 29.7, 31.5, 32.4, 120.1, 121.8, 122.3, 125.3, 130.9, 133.4, 134.3, 147.7, 163.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{32}NO^+$: 314.2478; found: 314.2479.

3-Butyl-8-methoxy-4-pentylquinolin-2(1*H*)-one (4h)
Yield: 81% (49 mg); colorless solid; mp 113.2–115.1 °C.

IR (film): 1633 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.91–0.98 (m, 6 H, CH_3), 1.36–1.64 (m, 10 H, CH_2), 2.70 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.84 (t, *J* = 8.1 Hz, 2 H, CH_2), 3.95 (s, 3 H, CH_3), 6.91 (d, *J* = 7.8, 1 H, CH), 7.12 (t, *J* = 8.3, 1 H, CH), 7.27 (d, *J* = 8.4, 1 H, CH), 9.15 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.00, 14.02, 22.4, 23.1, 26.9, 29.1, 29.6, 31.5, 32.3, 55.9, 108.5, 116.4, 120.4, 121.4, 127.2, 132.2, 145.5, 147.1, 161.8.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{28}NO_2^+$: 302.2115; found: 302.2114.

3-Butyl-4-pentyl-8-phenylquinolin-2(1*H*)-one (4i)
Yield: 70% (49 mg); yellow oil.

IR (film): 1640 (C=O) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.2 Hz, 6 H, CH_3), 1.41–1.55 (m, 8 H, CH_2), 1.63–1.70 (m, 2 H, CH_2), 2.70 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.91 (t, *J* = 8.3 Hz, 2 H, CH_2), 7.25 (t, *J* = 7.8 Hz, 1 H, CH), 7.34 (d, *J* = 7.3 Hz, 1 H, CH), 7.40–7.41 (m, 2 H, CH), 7.45 (t, *J* = 7.4 Hz, 1 H, CH), 7.51 (t, *J* = 7.3 Hz, 2 H, CH), 7.70 (d, *J* = 8.2 Hz, 1 H, CH), 8.67 (s, 1 H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.5, 23.1, 26.9, 29.1, 29.7, 31.5, 32.4, 120.4, 121.8, 124.1, 128.5, 128.6, 129.4 (2CH), 129.5 (2CH), 129.9, 131.7, 134.1, 136.5, 147.3, 162.2.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{24}H_{30}NO^+$: 348.2322; found: 348.2322.

3-Butyl-4-pentylbenzo[*h*]quinolin-2(1*H*)-one (4j)
Yield: 71% (46 mg); colorless solid; mp 165.3–167.0 °C.

IR (film): 1636 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.95–1.06 (m, 6 H, CH_3), 1.44–1.69 (m, 10 H, CH_2), 2.89–3.01 (m, 4 H, CH_2), 7.60–7.88 (m, 5 H, CH), 9.08 (t, *J* = 6.6 Hz, 1 H, CH), 12.76 (s, 1 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.05, 14.13, 22.5, 23.5, 27.2, 29.3, 29.9, 31.5, 32.4, 116.1, 121.8, 122.3, 122.5, 122.6, 126.4, 127.3, 128.1, 131.0, 133.2, 134.1, 148.5, 164.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{22}H_{28}NO^+$: 322.2165; found: 322.2163.

3-Butyl-4-pentyl-1,9-phenanthrolin-2(1*H*)-one (4k)
Yield: 43% (28 mg); colorless solid; mp 118.2–120.2 °C.

IR (film): 1643 (C=O) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.3 Hz, 3 H), 1.04 (t, *J* = 7.2 Hz, 3 H), 1.42–1.70 (m, 10 H), 2.89 (t, *J* = 7.9 Hz, 2 H), 3.02 (t, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.9 Hz, 1 H), 7.88 (d, *J* = 8.9 Hz, 1 H), 8.73 (d, *J* = 5.9 Hz, 1 H), 8.88 (d, *J* = 5.9 Hz, 1 H), 9.28 (s, 1 H), 13.00 (br, 1 H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 23.4, 27.3, 29.3, 29.9, 31.5, 32.3, 115.1, 119.0, 121.4, 123.4, 126.2, 127.8, 132.7, 133.6, 144.3, 148.6, 152.1, 164.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{27}N_2O^+$: 323.2118; found: 323.2120.

3-Butyl-5,8-dimethoxy-4-pentylquinolin-2(1*H*)-one (4l)
Yield: 63% (42 mg); colorless solid; mp 130.3–132.1 °C.

IR (film): 1630 (C=O) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.98 (m, 6 H, CH_3), 1.37–1.56 (m, 10 H, CH_2), 2.70 (t, *J* = 7.8 Hz, 2 H, CH_2), 3.07 (t, *J* = 7.8 Hz, 2 H, CH_2), 3.85 (s, 3 H, CH_3), 3.90 (s, 3 H, CH_3), 6.52 (d, *J* = 8.8 Hz, 1 H, CH), 6.81 (d, *J* = 8.8 Hz, 1 H, CH), 9.18 (s, 1 H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.04, 14.15, 22.5, 23.2, 26.5, 30.5, 31.7, 31.9, 32.7, 55.8, 56.3, 102.4, 108.8, 111.6, 128.9, 132.1, 139.8, 148.8, 151.4, 161.5.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{30}NO_3^+$: 332.2220; found: 332.2222.

3-Butyl-5,7-dimethoxy-4-pentylquinolin-2(1*H*)-one (4m)
Yield: 63% (42 mg); colorless solid; mp 166.8–168.3 °C.

IR (film): 1600 (C=O) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.98 (m, 6 H, CH_3), 1.38–1.56 (m, 10 H, CH_2), 2.71 (t, *J* = 7.8 Hz, 2 H, CH_2), 3.05 (t, *J* = 7.7 Hz, 2 H, CH_2), 3.86–3.87 (m, 6 H, CH_3), 6.24 (d, *J* = 2.3 Hz, 1 H, CH), 6.51 (t, *J* = 2.5 Hz, 1 H, CH), 12.34 (s, 1 H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 14.2, 22.6, 23.2, 26.1, 30.6, 31.9 ($2CH_2$), 32.7, 55.3, 55.5, 91.2, 94.7, 106.1, 127.7, 140.7, 149.6, 158.6, 160.7, 164.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{30}NO_3^+$: 332.2220; found: 332.2222.

(*Z*)-(1-Bromopent-1-en-3-yne-1,2-diyl)dibenzene (5)[24]
Yield: 70% (884 mg); yellow solid; mp 83.2–84.9 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, CH_3), 7.12–7.19 (m, 10 H, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.9, 81.8, 93.7, 126.7, 127.4, 127.9 (2CH), 128.0 (2CH), 128.2, 128.3, 129.4 (2CH), 130.1 (2CH), 138.2, 139.5.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{14}Br^+$: 297.0273; found: 297.0277.

Pd-Catalyzed Amination of Monohaloenyne 5 Affording Quinoline 6 and Pyrrole 7
$[Pd_2(dba)_3]$ (4.6 mg, 0.005 mmol), DPEPhos (10.8 mg, 0.02 mmol), and toluene (2.0 mL) were placed in an oven-dried 25 mL Schlenk

tube, and the mixture was stirred at r.t. for 15 min, then monohaloenyne **5** (59 mg, 0.2 mmol), aniline **2a** (22 mg, 0.24 mmol), and NaO*t*-Bu (58 mg, 0.6 mmol) were added. The tube was placed in a preheated oil bath (110 °C) and stirred for 2 h. After cooling to r.t., the solvent was evaporated in vacuo and the crude product was purified by column chromatography over silica gel (EtOAc–pentane, 1→10%).

4-Ethyl-2,3-diphenylquinoline (6)
Yield: 57% (35 mg); yellow solid; mp 68.8–70.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.4 Hz, 3 H), 2.97 (q, *J* = 7.2 Hz, 2 H), 7.11–7.31 (m, 10 H), 7.56–7.74 (m, 2 H), 8.09–8.23 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 22.6, 124.1, 125.9, 126.4, 126.9, 127.3, 127.5 (2CH), 127.9 (2CH), 129.0, 129.6 (2CH), 130.5 (3CH), 133.4, 138.8, 141.3, 147.3, 148.1, 159.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{20}N^+$: 310.1590; found: 310.1590.

5-Methyl-1,2,3-triphenyl-1*H*-pyrrole (7)
Yield: 16% (10 mg); yellow solid; mp 88.7–90.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.16 (s, 3 H, CH_3), 6.29 (s, 1 H, CH), 7.00–7.27 (m, 15 H, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.1, 108.0, 122.5, 125.2, 126.5, 127.3, 127.8 (2CH), 128.1 (2CH), 128.2 (2CH), 128.6 (2CH), 128.7 (2CH), 130.4, 131.1 (2CH), 133.0, 133.6, 136.6, 139.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{20}N^+$: 310.1590; found: 310.1592.

Control Experiment Confirming the Etherification
$[Pd_2(dba)_3]$ (4.6 mg, 0.005 mmol), DPEPhos (10.8 mg, 0.02 mmol), and toluene (2.0 mL) were placed in an oven-dried 25 mL Schlenk tube, and the mixture was stirred at r.t. for 15 min, then 2-bromoquinoline **9** (42 mg, 0.2 mmol) and NaO*t*-Bu (58 mg, 0.6 mmol) were added. The tube was placed in a preheated oil bath (110 °C) and stirred for 2 h. After cooling to r.t., the solvent was evaporated under vacuum and the residue was purified by chromatography (EtOAc–pentane, 10→100%) to give quinoline **10** and quinolinone **11**.

2-*tert*-Butoxyquinoline (10)[25]
Yield: 70% (28 mg); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (s, 9 H, CH_3), 6.79 (d, *J* = 8.7 Hz, 1 H, CH), 7.32 (s, 1 H, CH), 7.57 (s, 1 H, CH), 7.65 (d, *J* = 8.4 Hz, 1 H, CH), 7.79 (d, *J* = 8.4 Hz, 1 H, CH), 7.89 (d, *J* = 8.7 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.6 ($3CH_3$), 80.1, 115.0, 123.6, 124.5, 127.2, 127.5, 129.0, 138.0, 146.4, 161.8.

Quinolin-2(1*H*)-one (11)[26]
Yield: 21% (6 mg); colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (d, *J* = 9.4 Hz, 1 H, CH), 7.20–7.24 (m, 1 H, CH), 7.47–7.57 (m, 3 H, CH), 7.83 (d, *J* = 9.4 Hz, 1 H, CH), 12.81 (s, 1 H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.3, 120.0, 121.4, 122.7, 127.7, 130.7, 138.6, 141.0, 164.8.

4-(1-Deuterium)-2-*tert*-butoxy-3-butylquinoline (3a-D/H)
Yield: 65% (43 mg); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.99 (m, 6 H, CH_3), 1.38–1.54 (m, 8 H, CH_2), 1.59–1.64 (m, 2 H, CH_2), 1.69 (s, 9 H, CH_3), 2.69 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.92–2.97 (m, 1.14 H, CH_2), 7.30 (t, *J* = 7.6 Hz, 1 H, CH), 7.48 (t, *J* = 7.6 Hz, 1 H, CH), 7.74 (d, *J* = 8.3 Hz, 1 H, CH), 7.81 (d, *J* = 8.3 Hz, 1 H, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.00, 14.04, 22.5, 23.2, 26.8, 27.9 (t, J_{C-D} = 19.3 Hz), 28.2, 28.7 ($3CH_3$), 30.2, 30.3, 32.0, 32.4, 32.5, 79.5, 123.1, 123.5, 124.3, 125.6, 127.5, 128.0, 145.2, 145.8, 145.9, 160.5.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{34}NO^+$: 328.2635; found: 328.2638.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{33}DNO^+$: 329.2698; found: 329.2701.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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