

Supporting Information

I₂-Promoted oxidative annulation of three different amines to access diverse biheteroaryls

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1. General

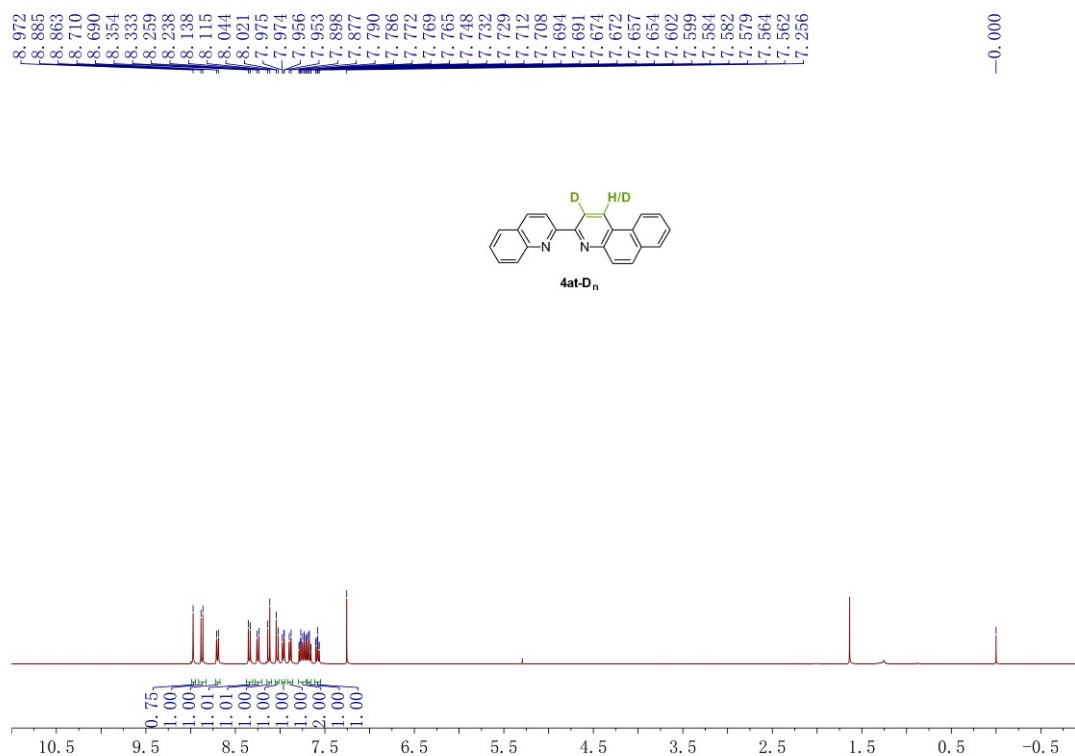
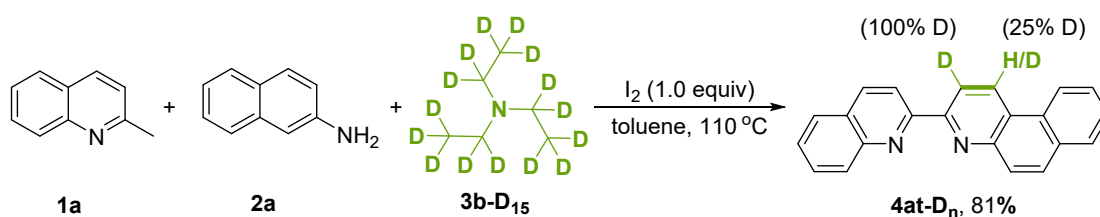
All substrates methylazaarenes (**1**), arylamines (**2**), tertiary alkylamines (**3**) and reagents were commercially available and used without further purification. All methylazaarenes (**1**), arylamines (**2**) and tertiary alkylamines (**3**) are known compounds. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^1H spectra were recorded in CDCl_3 on 400 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in CDCl_3 on 100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS analysis of compounds was performed with a time-of-flight mass spectrometer (micrOTOF-Q, Bruker Daltonik, Germany) equipped with an electrospray ionization source. The X-ray crystal-structure determinations of **4an** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected. All reactions were heated by a metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>).

2. General procedure for the synthesis of compounds 4 (4a as an example)

2-Methyl quinoline **1a** (43.0 mg, 0.3 mmol), naphthalen-2-amine **2a** (28.7 mg, 0.2 mmol), tripropylamine **3a** (28.7 mg, 0.2 mmol), I_2 (50.8 mg, 0.2 mmol) and toluene (2.0 mL) were charged into a pressure tube (35 mL) and were stirred at 110 °C for 20 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3×50 mL). The extract was washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution (w/w), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 12:1) to afford the product **4a** as a light yellow solid (54.5 mg, 85% yield).

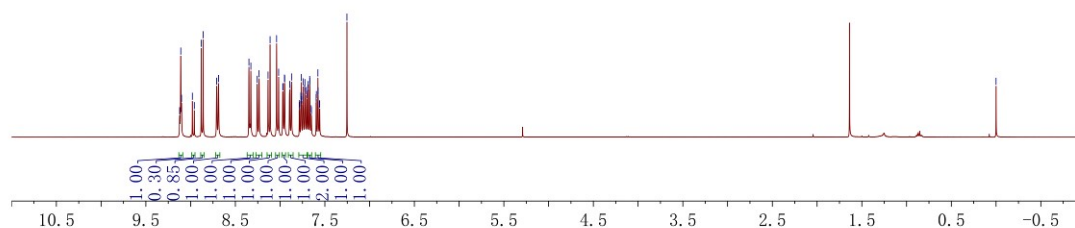
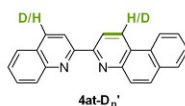
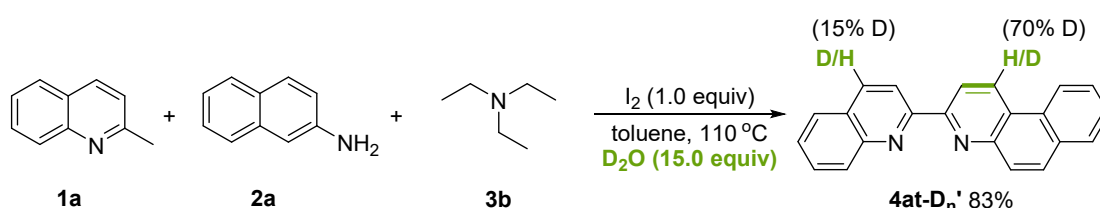
3. The D-labeling experiments and the spectrogram

2-Methyl quinoline **1a** (43.0 mg, 0.3 mmol), naphthalen-2-amine **2a** (28.7 mg, 0.2 mmol), **3b-D₁₅** (23.2 mg, 0.2 mmol), I₂ (50.8 mg, 0.2 mmol) and toluene (2.0 mL) were charged into a pressure tube (35 mL) and were stirred at 110 °C for 20 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na₂S₂O₃ solution (w/w), dried over anhydrous Na₂SO₄ and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to afford the product **4at-D_n**. Then, the product was monitored by ¹H NMR (400 MHz), the spectral copies of ¹H NMR was listed in the following. This result reveals that deuteration grade at the β-position and γ-position of 3-(quinolin-2-yl)benzo[*f*]quinoline scaffold was 100% and 25%, respectively.



4. The H/D exchange experiment and the spectrogram

2-Methyl quinoline **1a** (43.0 mg, 0.3 mmol), naphthalen-2-amine **2a** (28.7 mg, 0.2 mmol), triethylamine **3b** (20.2 mg, 0.2 mmol), I₂ (50.8 mg, 0.2 mmol), D₂O (60.1 mg, 3.0 mmol) and toluene (2.0 mL) were charged into a pressure tube (35 mL) and were stirred at 110 °C for 20 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na₂S₂O₃ solution (w/w), dried over anhydrous Na₂SO₄ and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to afford the product **4at-D_n'**. Then, the product was monitored by ¹H NMR (400 MHz), the spectral copies of ¹H NMR was listed in the following. NMR analysis of the isolated product revealed that significant H/D exchange was detected at the γ-selective deuteration reactions of two pyridine rings.



5. Experimental details

(1) The scale-up synthesis (**4a** as an example)

2-Methyl quinoline **1a** (214.8 mg, 1.5 mmol), naphthalen-2-amine **2a** (143.2 mg, 1.0 mmol), tripropylamine **3a** (143.3 mg, 1.0 mmol), I₂ (253.8 mg, 1.0 mmol) and toluene (10.0 mL) were charged into a pressure tube (150 mL) and were stirred at 110 °C for 20 h. After disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na₂S₂O₃ solution (w/w), dried over anhydrous Na₂SO₄ and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 12:1) to afford the product **4a** as a light yellow solid (249.9 mg, 78% yield).

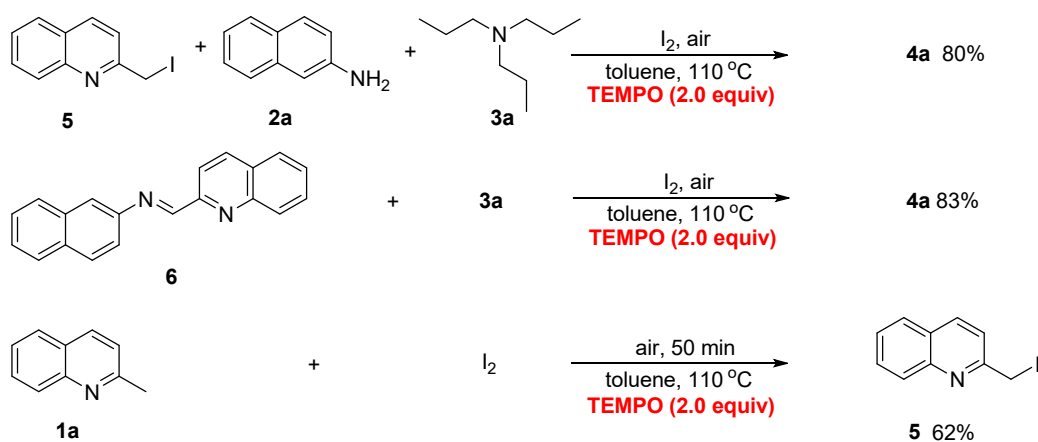
(2) Experimental procedure for the synthesis of compound **6**

A round bottom flask equipped with stir bar was charged with quinoline-2-carbaldehyde (377.2 mg, 2.4 mmol), naphthalen-2-amine (286.4 mg, 2.0 mmol) and anhydrous DCM (5.0 mL), followed by addition of anhydrous MgSO₄ (1820.0 mg, 15.1 mmol). The mixture was stirred at room temperature overnight. After filtration of MgSO₄, the filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography to obtain the corresponding imines **6**.¹

(3) Experimental procedure for the synthesis of compound **7**

Phenylacetaldehyde (600.8 mg, 5.0 mmol, commercial sources) was charged into a 50 mL RB flask containing 35.0 mL THF at room temperature. Diethylamine (731.4 mg, 10.0 mmol), MgSO₄ (9g, 74.8 mmol) were added sequentially, and the reaction was stirred at room temperature for 24 h. The solution was diluted with EtOAc (50 mL), filtration, then concentrated in vacuo to give the product **7**.²

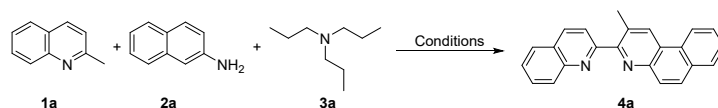
(4) Radical inhibition experiments



Scheme S1

When adding TEMPO in the reaction of 2-(iodomethyl)quinoline (**5**) with naphthalen-2-amine (**2a**) and tripropylamine (**3a**), the yield of **4a** was obtained in 80%; Also, adding TEMPO in the reaction of imine (**6**) and **3a** under the standard conditions did not inhibit the production of **4a**; Ultimately, the iodination reaction of **1a** went smoothly with TEMPO. These results ruled out the possibility of a free-radical pathway in this reaction.

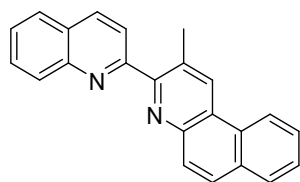
6. Optimization of the reaction conditions^a



entry	[I]	oxidant	acid	solvent	temp. (°C)	yield (%) ^b
1	I ₂	—	—	toluene	110	85
2	KI	—	—	toluene	110	0
3	TBAI	—	—	toluene	110	25
4	NIS	—	—	toluene	110	37
5	NH ₄ I	—	—	toluene	110	52
6	—	—	—	toluene	110	0
7	I ₂	CHP	—	toluene	110	26
8	I ₂	TBHP	—	toluene	110	35
9	I ₂	TBPB	—	toluene	110	40
10	I ₂	DCP	—	toluene	110	47
11	I ₂	K ₂ S ₂ O ₈	—	toluene	110	53
12	I ₂	DMSO	—	toluene	110	66
13	I ₂	DTBP	—	toluene	110	70
14	I ₂	—	CF ₃ SO ₃ H	toluene	110	55
15	I ₂	—	CH ₃ SO ₃ H	toluene	110	71
16	I ₂	—	CH ₃ COOH	toluene	110	77
17	I ₂	—	PhCOOH	toluene	110	79
18	I ₂	—	—	<i>o</i> -DCB	110	63
19	I ₂	—	—	PhCl	110	74
20	I ₂	—	—	<i>o</i> -Xylene	110	81
21	I ₂	—	—	DCE	110	18
22	I ₂	—	—	THF	110	23
23	I ₂	—	—	DMSO	110	27
24	I ₂	—	—	CH ₃ CN	110	33
25	I ₂	—	—	DMF	110	37
26	I ₂	—	—	NMP	110	43
27	I ₂	—	—	toluene	120	71
28	I ₂	—	—	toluene	100	78
29	I ₂	—	—	toluene	80	62
30	I ₂	Ar	—	toluene	110	45
31	I ₂	O ₂	—	toluene	110	87
32 ^c	I ₂	—	—	toluene	110	50
33 ^d	I ₂	—	—	toluene	110	86
34 ^e	I ₂	—	—	toluene	110	64
35 ^f	I ₂	—	—	toluene	110	77
36 ^g	I ₂	—	—	toluene	110	45

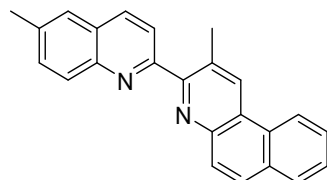
^aReaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (0.2 mmol), [I] (0.2 mmol), oxidant (0.6 mmol), acid (0.2 mmol), solvent (2.0 mL) in the 35 mL sealed tube at 110 °C for 20 h. ^bIsolated yields. ^c**3a** (0.4 mmol). ^d**1a** (0.4 mmol). ^e**1a** (0.2 mmol). ^fI₂ (0.3 mmol). ^gI₂ (0.1 mmol).

7. Characterization data for compounds



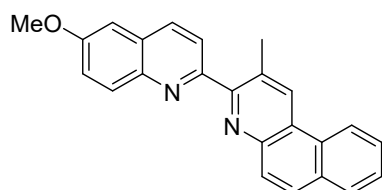
2-methyl-3-(quinolin-2-yl)benzo[f]quinoline (4a):

Yield 85% (54.5 mg; petroleum ether/EtOAc = 12:1); light yellow solid; mp 174–176 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.90 (s, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.98–7.94 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.77–7.75 (m, 1H), 7.75–7.70 (m, 1H), 7.69–7.64 (m, 1H), 7.61 (t, J = 7.6 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.8, 156.6, 147.3, 146.1, 136.6, 133.2, 132.0, 130.8, 130.1, 129.7, 129.6, 129.2, 128.7, 128.2, 127.6, 127.4, 127.3, 126.9, 126.8, 125.1, 122.9, 122.2, 21.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2$: 321.1386; found: 321.1390.



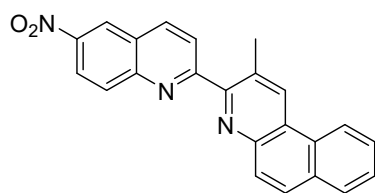
2-methyl-3-(6-methylquinolin-2-yl)benzo[f]quinoline (4b):

Yield 80% (53.5 mg; petroleum ether/EtOAc = 12:1); white solid; mp 179–181 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.86 (s, 1H), 8.67 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 8.13–8.07 (m, 2H), 8.05 (d, J = 9.2 Hz, 1H), 7.96–7.91 (m, 2H), 7.72–7.67 (m, 1H), 7.67–7.62 (m, 2H), 7.58 (dd, J = 8.4, 2.0 Hz, 1H), 2.85 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 157.9, 156.7, 146.0, 145.9, 136.8, 135.9, 133.1, 132.0, 131.8, 130.8, 130.0, 129.4, 129.2, 128.7, 128.2, 127.4, 127.2, 126.9, 126.4, 125.0, 122.8, 122.1, 21.6, 21.0; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2$: 335.1543; found: 335.1549.



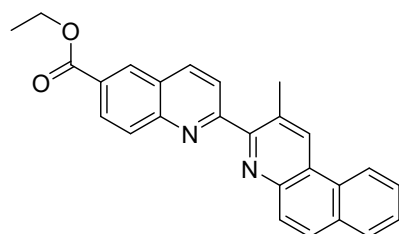
3-(6-methoxyquinolin-2-yl)-2-methylbenzo[f]quinoline (4c):

Yield 83% (58.2 mg; petroleum ether/EtOAc = 12:1); white solid; mp 181–183 °C; ^1H NMR (400 MHz, CDCl_3): 8.86 (s, 1H), 8.67 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 9.2 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.96–7.91 (m, 2H), 7.72–7.67 (m, 1H), 7.67–7.61 (m, 1H), 7.41 (dd, J = 9.2, 2.8 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 3.96 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.1, 156.7, 156.4, 146.0, 143.4, 135.3, 133.1, 131.9, 131.1, 130.7, 130.0, 129.2, 128.6, 128.4, 128.1, 127.2, 126.9, 124.9, 122.8, 122.4, 122.3, 105.0, 55.5, 21.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}$: 351.1492; found: 351.1496.



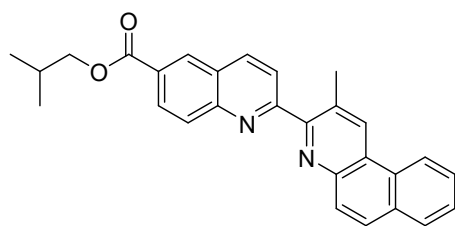
2-methyl-3-(6-nitroquinolin-2-yl)benzo[f]quinoline (4d):

Yield 71% (51.9 mg; petroleum ether/EtOAc = 10:1); white solid; mp 237–239 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.92 (s, 1H), 8.87 (d, *J* = 2.4 Hz, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.54–8.51 (m, 1H), 8.50 (s, 1H), 8.46 (d, *J* = 8.8 Hz, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.99 (s, 1H), 7.97–7.94 (m, 1H), 7.77–7.71 (m, 1H), 7.69 (td, *J* = 7.6, 1.2 Hz, 1H), 2.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.2, 154.9, 149.3, 146.2, 145.6, 138.1, 133.6, 132.2, 131.4, 131.1, 130.5, 129.0, 128.8, 128.0, 127.6, 127.1, 126.2, 125.4, 124.4, 124.2, 123.0, 21.4. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆N₃O₂: 366.1237; found: 366.1244.



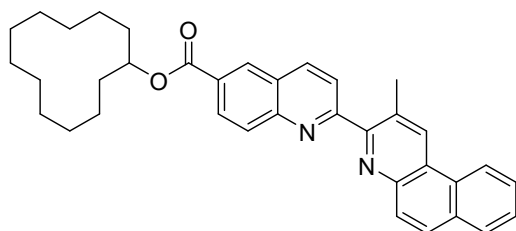
ethyl 2-(2-methylbenzo[f]quinolin-3-yl)quinoline-6-carboxylate (4e):

Yield 82% (64.4 mg; petroleum ether/EtOAc = 15:1); white solid; mp 193–195 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.88 (s, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 2.0 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.35 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.97–7.92 (m, 2H), 7.74–7.69 (m, 1H), 7.69–7.64 (m, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 2.90 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 166.2, 160.8, 155.8, 149.1, 146.1, 137.8, 133.3, 132.1, 130.9, 130.6, 130.3, 129.9, 129.1(0), 129.0(8), 128.7, 128.6, 128.1, 127.4, 127.0, 126.5, 125.2, 123.0, 122.9, 61.4, 21.2, 14.4; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₂₁N₂O₂: 393.1598; found: 393.1603.



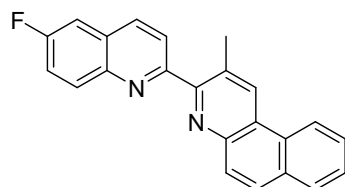
isobutyl 2-(2-methylbenzo[f]quinolin-3-yl)quinoline-6-carboxylate (4f):

Yield 88% (74.0 mg; petroleum ether/EtOAc = 15:1); white solid; mp 146–148 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.88 (s, 1H), 8.71–8.64 (m, 2H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.36 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.98–7.91 (m, 2H), 7.75–7.69 (m, 1H), 7.69–7.63 (m, 1H), 4.21 (d, *J* = 6.8 Hz, 2H), 2.90 (s, 3H), 2.22–2.12 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 166.3, 160.8, 155.9, 149.2, 146.2, 137.8, 133.4, 132.1, 131.0, 130.6, 130.3, 130.0, 129.2, 129.1, 128.8, 128.7, 128.1, 127.5, 127.0, 126.6, 125.3, 123.0(2), 122.9(8), 71.5, 28.0, 21.2, 19.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₈H₂₅N₂O₂: 421.1911; found: 421.1903.



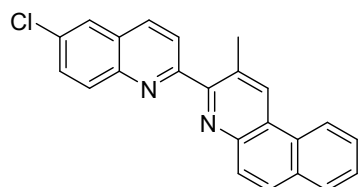
cyclododecyl 2-(2-methylbenzo[f]quinolin-3-yl)quinoline-6-carboxylate (4g):

Yield 81% (86.0 mg; petroleum ether/EtOAc = 8:1); light yellow solid; mp 170–172 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.89 (s, 1H), 8.69 (d, $J = 8.0$ Hz, 1H), 8.64 (d, $J = 1.6$ Hz, 1H), 8.44 (d, $J = 8.4$ Hz, 1H), 8.35 (dd, $J = 8.8, 1.6$ Hz, 1H), 8.28 (d, $J = 8.8$ Hz, 1H), 8.22 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 9.2$ Hz, 1H), 7.98–7.93 (m, 2H), 7.75–7.69 (m, 1H), 7.69–7.64 (m, 1H), 5.39–5.32 (m, 1H), 2.90 (s, 3H), 1.96–1.86 (m, 2H), 1.77–1.70 (m, 2H), 1.56–1.45 (m, 8H), 1.44–1.33 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 165.8, 160.7, 155.9, 149.1, 146.1, 137.8, 133.3, 132.0, 130.9, 130.5, 130.3, 129.8, 129.2, 129.1, 129.0, 128.7, 128.1, 127.4, 127.0, 126.5, 125.2, 122.9(2), 122.8(9), 73.5, 29.1, 24.2, 24.0, 23.3, 23.1, 21.2, 20.9; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{39}\text{N}_2\text{O}_2$: 531.3006; found: 531.3002.



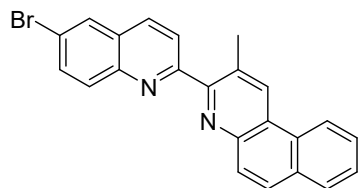
3-(6-fluoroquinolin-2-yl)-2-methylbenzo[f]quinoline (4h):

Yield 80% (54.1 mg; petroleum ether/EtOAc = 20:1); white solid; mp 212–214 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.88 (s, 1H), 8.69 (d, $J = 8.0$ Hz, 1H), 8.29 (d, $J = 8.8$ Hz, 1H), 8.23–8.16 (m, 2H), 8.04 (d, $J = 9.2$ Hz, 1H), 7.98–7.93 (m, 2H), 7.74–7.69 (m, 1H), 7.69–7.63 (m, 1H), 7.56–7.49 (m, 2H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 161.9, 159.5, 158.1(9), 158.1(6), 156.1, 146.1, 144.4, 136.0, 135.9, 133.2, 132.2, 132.1, 132.0, 130.8, 130.2, 129.2, 128.7, 128.1, 128.0, 127.3, 127.0, 125.1, 122.9(2), 122.8(9), 119.9, 119.6, 110.7, 110.5, 21.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{16}\text{FN}_2$: 339.1292; found: 339.1299.



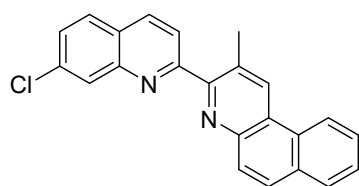
3-(6-chloroquinolin-2-yl)-2-methylbenzo[f]quinoline (4i):

Yield 82% (58.2 mg; petroleum ether/EtOAc = 20:1); white solid; mp 229–231 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.90 (s, 1H), 8.69 (d, $J = 8.4$ Hz, 1H), 8.28–8.21 (m, 2H), 8.13 (d, $J = 8.8$ Hz, 1H), 8.04 (d, $J = 9.2$ Hz, 1H), 7.99–7.93 (m, 2H), 7.89 (d, $J = 2.0$ Hz, 1H), 7.75–7.65 (m, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.0, 156.0, 146.1, 145.7, 135.7, 133.3, 132.6, 132.0, 131.3, 130.8, 130.5, 130.3, 129.1, 128.7, 128.1, 128.0, 127.4, 127.0, 126.3, 125.2, 123.1, 122.9, 21.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{16}\text{ClN}_2$: 355.0997; found: 355.0999.



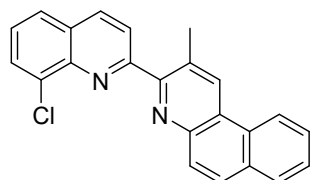
3-(6-bromoquinolin-2-yl)-2-methylbenzo[f]quinoline (4j):

Yield 78% (62.3 mg; petroleum ether/EtOAc = 20:1); white solid; mp 216–218 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.90 (s, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.28–8.21 (m, 2H), 8.08–8.02 (m, 3H), 7.99–7.94 (m, 2H), 7.85–7.81 (m, 1H), 7.75–7.70 (m, 1H), 7.70–7.65 (m, 1H), 2.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.2, 156.0, 146.1, 145.9, 135.6, 133.3, 133.0, 132.0, 131.4, 130.8, 130.3, 129.6, 129.1, 128.7, 128.5, 128.1, 127.4, 127.0, 125.2, 123.1, 122.9, 120.8, 21.1; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆BrN₂: 399.0491; found: 399.0485.



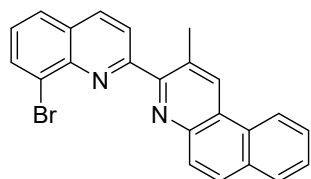
3-(7-chloroquinolin-2-yl)-2-methylbenzo[f]quinoline (4k):

Yield 82% (58.2 mg; petroleum ether/EtOAc = 20:1); white solid; mp 209–211 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.88 (s, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.26–8.16 (m, 2H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.98–7.92 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.74–7.64 (m, 2H), 7.58–7.51 (m, 1H), 2.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.7, 155.9, 147.6, 146.1, 136.4, 135.4, 133.3, 132.0, 130.9, 130.2, 129.1, 128.8, 128.7(1), 128.6(6), 128.0, 127.9, 127.4, 127.0, 125.8, 125.2, 122.9, 122.4, 21.2; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆ClN₂: 355.0997; found: 355.0999.



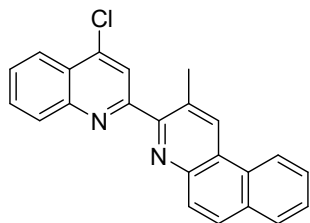
3-(8-chloroquinolin-2-yl)-2-methylbenzo[f]quinoline (4l):

Yield 80% (56.8 mg; petroleum ether/EtOAc = 20:1); white solid; mp 219–221 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.89 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.98–7.91 (m, 2H), 7.90–7.85 (m, 1H), 7.83–7.78 (m, 1H), 7.74–7.64 (m, 2H), 7.52–7.46 (m, 1H), 3.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.1, 155.0, 146.0, 143.4, 136.9, 134.2, 133.7, 132.1, 131.9, 130.1, 129.5, 129.2, 128.8, 128.7, 128.1, 127.4, 127.0, 126.7, 126.6, 125.2, 123.0(0), 122.9(7), 22.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆ClN₂: 355.0997; found: 355.0995.

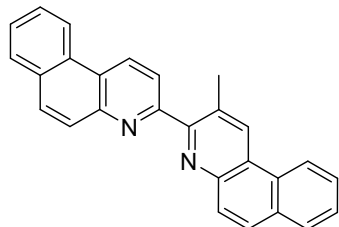


3-(8-bromoquinolin-2-yl)-2-methylbenzo[f]quinoline (4m):

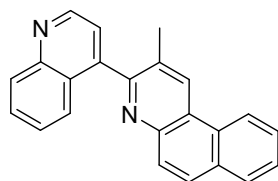
Yield 78% (62.3 mg; petroleum ether/EtOAc = 30:1); white solid; mp 225–227 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.91 (s, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.01–7.92 (m, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.75–7.64 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 3.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 159.3, 154.9, 146.0, 144.3, 137.0, 133.7, 133.1, 132.1, 132.0, 130.1, 129.2, 128.8, 128.7, 128.1, 127.4(1), 127.3(9), 127.2, 127.0, 125.6, 125.2, 123.0, 22.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆BrN₂: 399.0491; found: 399.0497.

**3-(4-chloroquinolin-2-yl)-2-methylbenzo[f]quinoline (4n):**

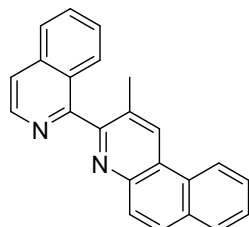
Yield 43% (30.5 mg; petroleum ether/EtOAc = 30:1); white solid; mp 189–191 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.91 (s, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.38 (s, 1H), 8.33 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 8.00–7.94 (m, 2H), 7.85–7.80 (m, 1H), 7.76–7.72 (m, 1H), 7.72–7.70 (m, 1H), 7.70–7.65 (m, 1H), 2.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.6, 155.1, 148.1, 146.1, 143.0, 133.5, 132.1, 131.0, 130.4(2), 130.3(6), 130.0, 129.1, 128.8, 128.0, 127.8, 127.5, 127.0, 125.7, 125.3, 124.0, 123.0, 122.3, 21.2; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆ClN₂: 355.0997; found: 355.1006.

**2-methyl-3,3'-bibenzo[f]quinoline (4o):**

Yield 85% (63.0 mg; petroleum ether/EtOAc = 10:1); white solid; mp 245–247 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.15 (d, *J* = 8.8 Hz, 1H), 8.91 (s, 1H), 8.75–8.68 (m, 2H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.12–8.02 (m, 3H), 8.00–7.93 (m, 3H), 7.77–7.65 (m, 4H), 2.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.4, 156.5, 147.2, 146.2, 133.2, 132.0(1), 131.9(5), 131.4, 131.0, 130.8, 130.2, 129.6, 129.2, 128.7(3), 128.7(2), 128.5, 128.2, 127.4, 127.3, 127.1, 126.9, 125.1, 124.6, 122.9(1), 122.8(8), 122.3, 21.2; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₇H₁₉N₂: 371.1543; found: 371.1538.

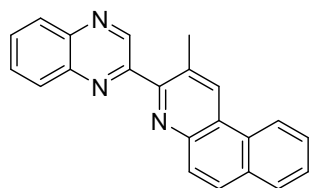
**2-methyl-3-(quinolin-4-yl)benzo[f]quinoline (4p):**

Yield 88% (56.4 mg; petroleum ether/EtOAc = 5:1); white solid; mp 212–214 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.06 (d, $J = 4.4$ Hz, 1H), 8.89 (s, 1H), 8.68 (d, $J = 8.0$ Hz, 1H), 8.23 (d, $J = 8.8$ Hz, 1H), 8.03–7.96 (m, 2H), 7.96–7.93 (m, 1H), 7.75–7.70 (m, 2H), 7.69–7.65 (m, 1H), 7.49–7.42 (m, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 156.3, 150.1, 148.5, 146.6, 146.1, 131.9, 131.8, 130.6, 129.8, 129.5, 129.0, 128.7, 127.8, 127.4, 127.1, 127.0, 126.4, 125.4, 125.0, 122.6, 120.9, 19.6; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2$: 321.1386; found: 321.1376.



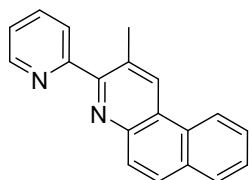
3-(isoquinolin-1-yl)-2-methylbenzo[f]quinoline (4q):

Yield 83% (53.2 mg; petroleum ether/EtOAc = 8:1); white solid; mp 98–100 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.92 (s, 1H), 8.68 (d, $J = 6.0$ Hz, 2H), 8.04 (d, $J = 8.8$ Hz, 1H), 7.97–7.91 (m, 2H), 7.91–7.87 (m, 1H), 7.75 (d, $J = 5.6$ Hz, 1H), 7.72–7.63 (m, 4H), 7.49–7.44 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.0, 157.0, 145.8, 142.0, 136.7, 132.2, 131.9, 130.5, 130.23(X2), 129.1, 128.6, 128.0, 127.5, 127.2, 127.0, 126.9(0), 126.8(9), 126.8, 125.1, 122.7, 120.8, 19.4; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2$: 321.1386; found: 321.1390.



2-methyl-3-(quinoxalin-2-yl)benzo[f]quinoline (4r):

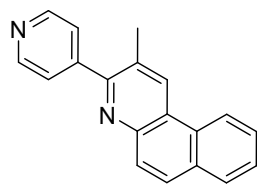
Yield 70% (45.0 mg; petroleum ether/EtOAc = 8:1); white solid; mp 174–176 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.73 (s, 1H), 8.89 (s, 1H), 8.69 (d, $J = 8.0$ Hz, 1H), 8.23–8.16 (m, 2H), 8.07 (d, $J = 8.8$ Hz, 1H), 8.00–7.94 (m, 2H), 7.85–7.79 (m, 2H), 7.75–7.70 (m, 1H), 7.70–7.65 (m, 1H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 153.4, 153.1, 146.6, 146.2, 141.5, 141.0, 133.5, 132.2, 131.5, 130.5, 130.1(4), 130.0(6), 129.6, 129.2, 129.0, 128.8, 128.0, 127.6, 127.1, 125.3, 123.0, 21.2; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{16}\text{N}_3$: 322.1339; found: 322.1338.



2-methyl-3-(pyridin-2-yl)benzo[f]quinoline (4s):

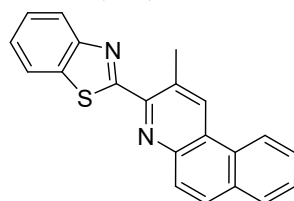
Yield 85% (46.0 mg; petroleum ether/EtOAc = 5:1); brownish-yellow solid; mp 124–126 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.79 (s, 1H), 8.74 (d, $J = 4.4$ Hz, 1H), 8.62 (d, $J = 8.0$ Hz, 1H), 8.01 (d, $J = 9.2$ Hz, 1H), 7.94 (d, $J = 7.6$ Hz, 1H), 7.93–7.88 (m, 2H), 7.88–7.83 (m, 1H), 7.69–7.64 (m, 1H), 7.64–7.59 (m, 1H), 7.33 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 1H), 2.72 (s, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.9, 156.7, 148.5, 145.9, 136.7, 132.9, 131.8, 130.2, 130.0, 129.1, 128.6, 128.0, 127.2, 126.8, 124.9, 124.4, 122.8, 122.7, 20.6; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2$: 271.1230; found: 271.1222.



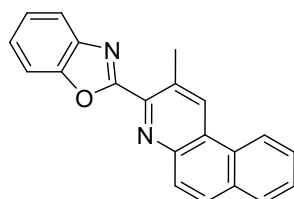
2-methyl-3-(pyridin-4-yl)benzo[f]quinoline (4t):

Yield 87% (47.0 mg; petroleum ether/EtOAc = 2:1); white solid; mp 190–192 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.82 (s, 1H), 8.77 (dd, J = 4.4, 1.6 Hz, 2H), 8.63 (d, J = 8.4 Hz, 1H), 8.01–7.94 (m, 2H), 7.94–7.91 (m, 1H), 7.73–7.68 (m, 1H), 7.68–7.64 (m, 1H), 7.59 (dd, J = 4.4, 1.6 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 156.3, 149.9, 148.2, 146.3, 132.7, 131.9, 130.6, 129.0, 128.72(X2), 127.8, 127.4, 127.1, 124.9, 123.8, 122.7, 20.5; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2$: 271.1230; found: 271.1236.



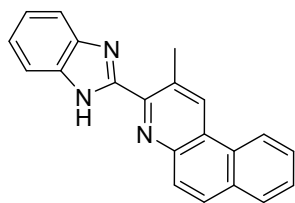
2-(2-methylbenzo[f]quinolin-3-yl)benzo[d]thiazole (4u):

Yield 74% (48.3 mg; petroleum ether/EtOAc = 50:1); white solid; mp 183–185 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.84 (s, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 9.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.97–7.90 (m, 2H), 7.73–7.64 (m, 2H), 7.53–7.48 (m, 1H), 7.46–7.40 (m, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.1, 154.9, 149.0, 145.9, 136.2, 133.7, 132.2, 130.8, 130.6, 129.0, 128.8, 127.7(4), 127.7(0), 127.1, 125.8, 125.7, 125.6, 124.0, 123.0, 121.6, 21.9; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{S}$: 327.0950; found: 327.0944.



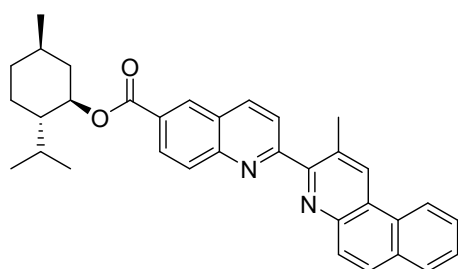
2-(2-methylbenzo[f]quinolin-3-yl)benzo[d]oxazole (4v):

Yield 49% (30.4 mg; petroleum ether/EtOAc = 15:1); light brown solid; mp 187–189 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.92 (s, 1H), 8.67 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 9.2 Hz, 1H), 7.97–7.89 (m, 2H), 7.78–7.67 (m, 3H), 7.48–7.40 (m, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 161.4, 150.5, 146.3, 144.4, 142.0, 133.8, 132.3, 132.2, 131.0, 128.8(1), 128.7(8), 128.0(3), 128.0(1), 127.2, 126.1, 126.0, 124.7, 123.1, 120.8, 111.4, 21.9; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}$: 311.1179; found: 311.1186.



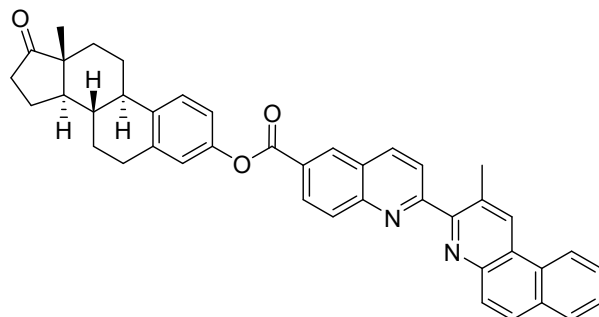
3-(1*H*-benzo[*d*]imidazol-2-yl)-2-methylbenzo[*f*]quinoline (4w):

Yield 78% (48.3 mg; petroleum ether/EtOAc = 3:1); light brown solid; mp 178–180 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 11.02 (s, 1H), 8.70 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 7.94–7.88 (m, 1H), 7.87–7.82 (m, 3H), 7.67–7.62 (m, 1H), 7.62–7.57 (m, 1H), 7.44 (s, 1H), 7.30–7.25 (m, 2H), 3.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.6, 145.8, 145.5, 133.6, 131.9, 131.4, 130.6, 129.5, 128.9, 128.6, 127.5, 127.3, 127.1, 125.7, 125.4, 124.0, 122.8, 122.2, 120.5, 110.9, 21.8; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₁H₁₆N₃: 310.1339; found: 310.1344.



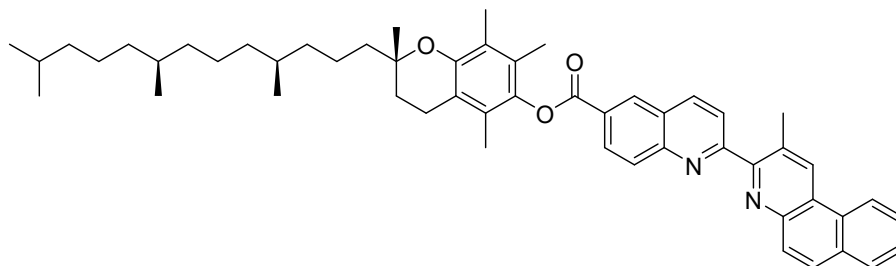
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(2-methylbenzo[*f*]quinolin-3-yl)quinoline-6-carboxylate (4x):

Yield 81% (81.4 mg; petroleum ether/EtOAc = 20:1); white solid; mp 125–127 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.92 (s, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 1.6 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.36 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 8.00–7.94 (m, 2H), 7.76–7.71 (m, 1H), 7.71–7.66 (m, 1H), 5.05 (td, *J* = 10.8, 4.4 Hz, 1H), 2.91 (s, 3H), 2.24–2.17 (m, 1H), 2.09–2.01 (m, 1H), 1.81–1.73 (m, 2H), 1.69–1.62 (m, 2H), 1.21–1.14 (m, 2H), 0.97 (d, *J* = 6.8 Hz, 7H), 0.85 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 165.7, 160.7, 155.9, 149.1, 146.1, 137.8, 133.4, 132.1, 131.0, 130.6, 130.3, 129.9, 129.2, 129.1, 129.0, 128.7, 128.1, 127.4, 127.0, 126.6, 125.2, 123.0, 122.9, 75.3, 47.3, 41.0, 34.3, 31.5, 26.5, 23.6, 22.1, 21.2, 20.8, 16.5; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₃₄H₃₅N₂O₂: 503.2693; found: 503.2682.



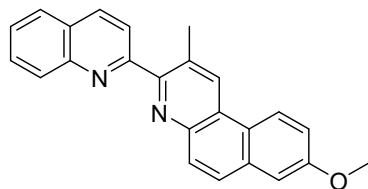
(8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 2-(2-methylbenzo[*f*]quinolin-3-yl)quinoline-6-carboxylate (4y):

Yield 80% (98.7 mg; petroleum ether/EtOAc = 10:1); white solid; mp 277–279 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.92 (s, 1H), 8.84 (d, *J* = 2.0 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.51–8.46 (m, 2H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 8.00–7.94 (m, 2H), 7.76–7.71 (m, 1H), 7.71–7.66 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.09–7.02 (m, 2H), 3.01–2.95 (m, 2H), 2.94 (s, 3H), 2.51–2.49 (m, 1H), 2.49–2.42 (m, 1H), 2.38–2.31 (m, 1H), 2.22–2.14 (m, 1H), 2.10–1.96 (m, 3H), 1.71–1.67 (m, 1H), 1.63–1.56 (m, 2H), 1.56–1.44 (m, 3H), 0.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 220.9, 165.1, 161.2, 155.7, 149.4, 148.8, 146.2, 138.2, 137.9, 137.6, 133.4, 132.1, 131.5, 131.0, 130.4, 130.2, 129.3, 129.1, 128.8, 128.1, 127.7, 127.5, 127.0, 126.58(X2), 125.3, 123.2, 123.0, 121.7, 118.8, 50.4, 48.0, 44.2, 38.0, 35.9, 31.5, 29.4, 26.4, 25.8, 21.6, 21.2, 13.8; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₄₂H₃₇N₂O₃: 617.2799; found: 617.2798.



(S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl 2-(2-methylbenzo[quinolin-3-yl]quinoline-6-carboxylate (4z):

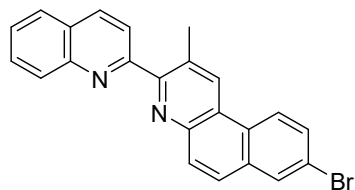
Yield 78% (121.2 mg; petroleum ether/EtOAc = 30:1); white solid; mp 111–113 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.93 (s, 1H), 8.89 (d, *J* = 2.0 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.57–8.52 (m, 1H), 8.52–8.48 (m, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 8.00–7.95 (m, 2H), 7.77–7.72 (m, 1H), 7.71–7.67 (m, 1H), 2.94 (s, 3H), 2.68–2.62 (m, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 1.89–1.78 (m, 2H), 1.58–1.48 (m, 3H), 1.46–1.35 (m, 4H), 1.32–1.22 (m, 10H), 1.18–0.99 (m, 7H), 0.89–0.84 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 164.9, 161.1, 155.8, 149.6, 149.4, 146.2, 140.6, 137.9, 133.4, 132.1, 131.4, 131.0, 130.4, 130.2, 129.5, 129.1, 128.8, 128.1, 127.7, 127.5, 127.0, 126.9, 126.7, 125.3, 125.1, 123.2(3), 123.1(5), 123.0, 117.6, 75.1, 39.4, 37.4(4), 37.3(8), 37.3, 32.7(9), 32.7(8), 28.0, 24.8(2), 24.8(1), 24.4, 22.7, 22.6, 21.2, 21.0, 20.6, 19.8, 19.6(9), 19.6(7), 19.6(4), 19.6(0), 13.2, 12.3, 11.9; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₅₃H₆₅N₂O₃: 777.4990; found: 777.4985.



8-methoxy-2-methyl-3-(quinolin-2-yl)benzo[quinoline (4aa):

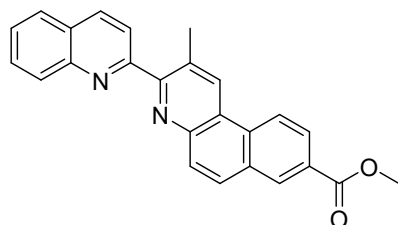
Yield 90% (63.1 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 182–184 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.56 (d, *J* = 9.2 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.91–7.85 (m, 2H), 7.78–7.73 (m, 1H), 7.61–7.56 (m, 1H), 7.35–7.28 (m, 2H), 3.98 (s, 3H), 2.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.9, 158.8, 155.7, 147.3, 145.2, 136.6, 133.5, 132.6, 130.9, 129.7, 129.6, 129.5, 128.7, 127.6, 127.4, 126.8, 125.2, 124.5, 123.3, 122.1, 117.5,

108.7, 55.5, 21.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{24}H_{19}N_2O$: 351.1492; found: 351.1487.



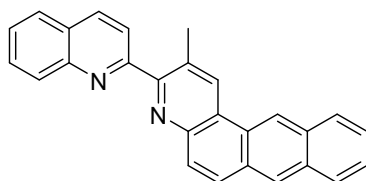
8-bromo-2-methyl-3-(quinolin-2-yl)benzo[f]quinoline (4ab):

Yield 78% (62.3 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 234–236 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.84 (s, 1H), 8.55 (d, J = 8.8 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 8.08 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.81–7.75 (m, 2H), 7.64–7.59 (m, 1H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.5, 157.0, 147.3, 145.9, 136.7, 133.4, 133.0, 131.4, 130.9, 130.0, 129.7, 129.6, 129.5, 128.9, 127.9, 127.6, 127.4, 127.0, 124.8, 124.6, 122.1, 121.4, 21.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{16}BrN_2$: 399.0491; found: 399.0482.



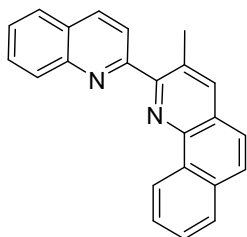
methyl 2-methyl-3-(quinolin-2-yl)benzo[f]quinoline-8-carboxylate (4ac):

Yield 75% (56.8 mg; petroleum ether/EtOAc = 12:1); white solid; mp 256–258 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.91 (s, 1H), 8.74 (d, J = 8.8 Hz, 1H), 8.67 (d, J = 1.6 Hz, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.33–8.29 (m, 1H), 8.22–8.16 (m, 2H), 8.11 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.80–7.75 (m, 1H), 7.64–7.59 (m, 1H), 4.03 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.0, 158.5, 157.6, 147.3, 146.8, 136.7, 133.7, 132.3, 131.4(2), 131.3(9), 130.9, 130.4, 129.7(4), 129.6(5), 129.1, 128.6, 127.6, 127.5, 127.0, 126.8, 124.6, 123.2, 122.1, 52.4, 21.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{19}N_2O_2$: 379.1441; found: 379.1450.



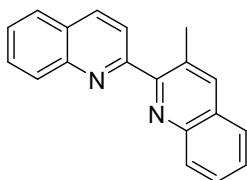
2-methyl-3-(quinolin-2-yl)naphtho[2,3-f]quinoline (4ad):

Yield 55% (40.8 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 258–260 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.20 (s, 1H), 9.05 (s, 1H), 8.45 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.26–8.17 (m, 3H), 8.13–8.09 (m, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.98–7.92 (m, 2H), 7.83–7.77 (m, 1H), 7.67–7.59 (m, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.8, 156.2, 147.4, 146.6, 136.6, 133.4, 132.3, 132.0, 131.0, 130.7, 130.2, 129.7, 129.6, 128.4, 128.3, 127.9, 127.6(1), 127.5(9), 127.4, 127.2, 126.8, 126.3, 126.2, 125.6, 122.2, 122.1, 21.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{19}N_2$: 371.1543; found: 371.1547.



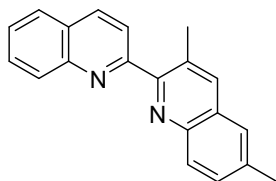
3-methyl-2-(quinolin-2-yl)benzo[*h*]quinoline (4ae):

Yield 82% (52.5 mg; petroleum ether/EtOAc = 30:1); white solid; mp 130–132 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.41–9.35 (m, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.11 (s, 1H), 7.94–7.89 (m, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.79–7.74 (m, 1H), 7.74–7.65 (m, 3H), 7.62–7.57 (m, 1H), 2.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.2, 155.0, 147.2, 144.2, 138.2, 136.3, 133.4, 131.61(X2), 129.7, 129.4, 128.2, 127.7(8), 127.7(6), 127.6, 127.4, 126.9, 126.8, 126.1, 124.8, 124.4, 122.6, 21.0; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₇N₂: 321.1386; found: 321.1384.



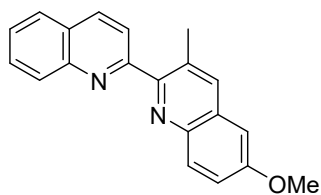
3-methyl-2,2'-biquinoline (4af):

Yield 74% (40.0 mg; petroleum ether/EtOAc = 20:1); white solid; mp 133–135 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.34 (d, *J* = 8.4 Hz, 1H), 8.20–8.14 (m, 2H), 8.10 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.79–7.74 (m, 1H), 7.71–7.66 (m, 1H), 7.62–7.57 (m, 1H), 7.57–7.53 (m, 1H), 2.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.8, 157.8, 147.3, 146.4, 137.6, 136.7, 130.5, 129.7, 129.6, 129.4, 128.8, 128.1, 127.6, 127.4, 126.8(9), 126.8(6), 126.8, 122.0, 20.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₉H₁₅N₂: 271.1230; found: 271.1233.



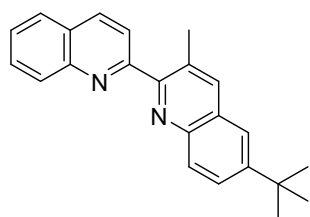
3,6-dimethyl-2,2'-biquinoline (4ag):

Yield 83% (47.2 mg; petroleum ether/EtOAc = 50:1); light yellow solid; mp 121–123 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.26 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.93 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.71–7.66 (m, 1H), 7.55–7.49 (m, 2H), 7.46–7.42 (m, 1H), 2.65 (s, 3H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.9, 156.9, 147.3, 145.1, 137.0, 136.8, 136.6, 131.1, 130.4, 129.7, 129.5, 129.0, 128.1, 127.6, 127.4, 126.8, 125.6, 122.1, 21.7, 20.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₁₇N₂: 285.1386; found: 285.1382.



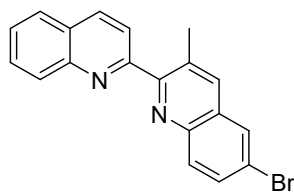
6-methoxy-3-methyl-2,2'-biquinoline (4ah):

Yield 72% (43.3 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 124–126 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.26 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.04–7.98 (m, 2H), 7.93 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.71–7.66 (m, 1H), 7.54–7.49 (m, 1H), 7.27 (dd, J = 9.2, 2.8 Hz, 1H), 7.01 (d, J = 2.8 Hz, 1H), 3.89 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.2, 155.1, 147.2, 142.4, 136.7, 130.8, 130.7, 129.6(3), 129.5(6), 129.2, 127.6, 127.4, 126.8, 122.1, 121.7, 104.1, 55.5, 20.7; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$: 301.1335; found: 301.1333.



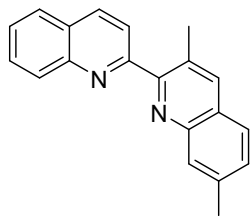
6-(*tert*-butyl)-3-methyl-2,2'-biquinoline (4ai):

Yield 80% (52.2 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 135–137 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.31 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 7.6 Hz, 1H), 7.79–7.71 (m, 3H), 7.60–7.55 (m, 1H), 2.72 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.9, 157.0, 149.7, 147.2, 145.0, 137.6, 136.6, 130.3, 129.6, 129.5, 128.8, 127.8, 127.6, 127.4, 126.7, 122.1, 121.7, 34.9, 31.2, 20.6; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{N}_2$: 327.1856; found: 327.1858.



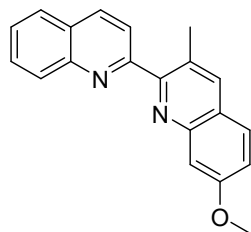
6-bromo-3-methyl-2,2'-biquinoline (4aj):

Yield 53% (37.0 mg; petroleum ether/EtOAc = 30:1); white solid; mp 167–169 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.35 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H), 8.01 (s, 1H), 7.98 (d, J = 2.4 Hz, 1H), 7.93–7.89 (m, 1H), 7.80–7.73 (m, 2H), 7.64–7.59 (m, 1H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.2, 158.0, 147.2, 144.9, 136.9, 136.6, 132.3, 131.7, 131.1, 129.8, 129.6, 129.1, 128.8, 127.6, 127.5, 127.1, 121.9, 120.9, 20.8; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{14}\text{BrN}_2$: 349.0335; found: 349.0337.



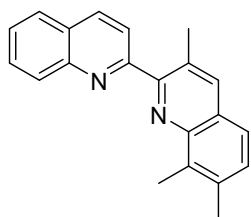
3,7-dimethyl-2,2'-biquinoline (4ak):

Yield 82% (46.5 mg; petroleum ether/EtOAc = 30:1); white solid; mp 123–125 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.32 (d, $J = 8.4$ Hz, 1H), 8.18 (d, $J = 8.4$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 8.04 (s, 1H), 7.94 (s, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.75 (t, $J = 7.2$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.61–7.56 (m, 1H), 7.38 (d, $J = 8.4$ Hz, 1H), 2.72 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.0, 157.7, 147.3, 146.7, 138.9, 137.3, 136.6, 129.7, 129.6, 129.5, 129.2, 128.4, 127.6, 127.4, 126.8, 126.4, 126.2, 122.1, 21.9, 20.6; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2$: 285.1386; found: 285.1389.



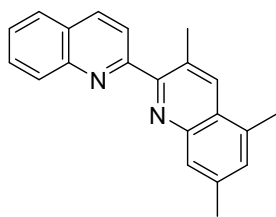
7-methoxy-3-methyl-2,2'-biquinoline (4al):

Yield 50% (30 mg; petroleum ether/EtOAc = 15:1); light yellow solid; mp 126–128 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.33 (d, $J = 8.4$ Hz, 1H), 8.18 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 8.8$ Hz, 1H), 8.03 (s, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.79–7.73 (m, 1H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.62–7.57 (m, 1H), 7.49 (d, $J = 2.0$ Hz, 1H), 7.22 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.95 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 160.2, 159.0, 157.9, 148.0, 147.3, 137.5, 136.7, 129.7, 129.6, 128.0, 127.8, 127.6, 127.4, 126.8, 123.4, 122.0, 120.3, 107.2, 55.5, 20.3; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$: 301.1335; found: 301.1328.



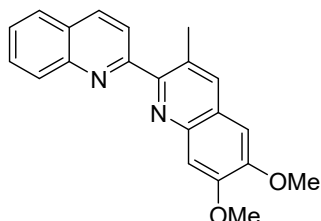
3,7,8-trimethyl-2,2'-biquinoline (4am):

Yield 83% (49.5 mg; petroleum ether/EtOAc = 50:1); light yellow solid; mp 128–130 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.29 (s, 2H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.99 (s, 1H), 7.89–7.85 (m, 1H), 7.76–7.71 (m, 1H), 7.59–7.53 (m, 2H), 7.35 (d, $J = 8.4$ Hz, 1H), 2.82 (s, 3H), 2.81 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.5, 155.6, 147.1, 145.4, 137.9, 136.2, 136.1, 134.5, 129.8, 129.7, 129.3, 127.5, 127.4, 126.6, 126.3, 123.6, 122.6, 20.9, 20.6, 13.3; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2$: 299.1543; found: 299.1549.



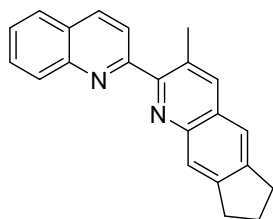
3,5,7-trimethyl-2,2'-biquinoline (4an):

Yield 85% (50.7 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 104–106 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.31 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 5.6 Hz, 2H), 8.08 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.77–7.72 (m, 1H), 7.60–7.55 (m, 1H), 7.21 (s, 1H), 2.75 (s, 3H), 2.67 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.0, 157.0, 147.2, 146.9, 138.4, 136.6, 134.1, 133.2, 129.7, 129.6, 129.5, 129.0, 127.5, 127.4, 126.7, 126.5, 125.4, 122.1, 21.7, 20.8, 18.5; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2$: 299.1543; found: 299.1547.



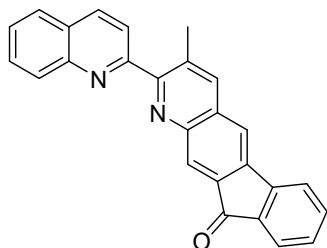
6,7-dimethoxy-3-methyl-2,2'-biquinoline (4ao):

Yield 76% (50.2 mg; petroleum ether/EtOAc = 5:1); white solid; mp 152–154 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.32 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.78–7.73 (m, 1H), 7.62–7.56 (m, 1H), 7.50 (s, 1H), 7.05 (s, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.0, 155.4, 152.0, 150.2, 147.3, 143.3, 136.6, 136.2, 129.7, 129.5, 128.5, 127.6, 127.3, 126.7, 123.8, 122.0, 108.0, 104.1, 56.1, 56.0, 20.4; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_2$: 331.1441; found: 331.1435.



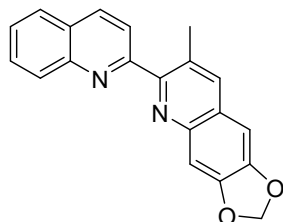
3-methyl-2-(quinolin-2-yl)-7,8-dihydro-6H-cyclopenta[g]quinoline (4ap):

Yield 79% (49.0 mg; petroleum ether/EtOAc = 15:1); white solid; mp 146–148 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.31 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 16.8 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.78–7.72 (m, 1H), 7.61–7.55 (m, 2H), 3.14–3.09 (m, 2H), 3.08–3.04 (m, 2H), 2.70 (s, 3H), 2.21–2.13 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.1, 156.5, 147.2, 146.9, 146.3, 144.6, 137.2, 136.6, 129.6, 129.5, 129.2, 127.6, 127.4, 127.3, 126.7, 123.5, 122.2, 120.7, 32.8, 32.6, 26.1, 20.6; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2$: 311.1543; found: 311.1545.



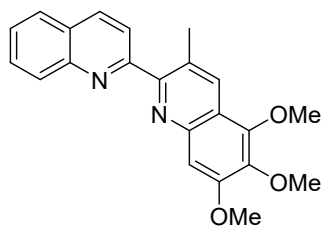
3-methyl-2-(quinolin-2-yl)-10H-indeno[1,2-g]quinolin-10-one (4aq):

Yield 67% (49.9 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 246–248 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.42 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.18–8.14 (m, 2H), 8.05 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.80–7.75 (m, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.63–7.60 (m, 1H), 7.60–7.56 (m, 1H), 7.40–7.35 (m, 1H), 2.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.5, 158.1, 157.8, 147.3, 147.2, 144.3, 139.4, 138.2, 136.7, 136.2, 135.5, 135.2, 133.5, 132.0, 129.7, 129.64, 129.56, 127.6, 127.5, 127.0, 126.8, 124.6, 122.0, 121.2, 117.7, 21.1; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₁₇N₂O: 373.1335; found: 373.1340.



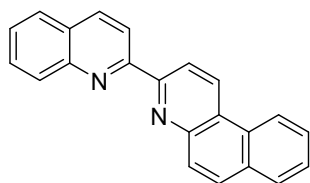
7-methyl-6-(quinolin-2-yl)-[1,3]dioxolo[4,5-g]quinoline (4ar):

Yield 75% (47.2 mg; petroleum ether/EtOAc = 8:1); white solid; mp 153–155 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.31 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.90–7.87 (m, 1H), 7.78–7.72 (m, 1H), 7.61–7.56 (m, 1H), 7.44 (s, 1H), 7.06 (s, 1H), 6.11 (s, 2H), 2.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.0, 155.3, 150.2, 148.2, 147.3, 144.5, 136.8, 136.6, 129.7, 129.5, 128.7, 127.6, 127.3, 126.7, 125.2, 122.1, 105.8, 101.8, 101.6, 20.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₁₅N₂O₂: 315.1128; found: 315.1118.



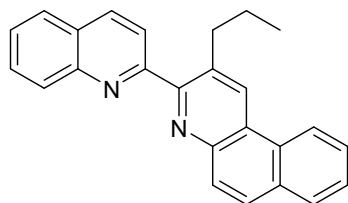
5,6,7-trimethoxy-3-methyl-2,2'-biquinoline (4as):

Yield 62% (44.7 mg; petroleum ether/EtOAc = 8:1); light yellow solid; mp 121–123 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.32 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.78–7.73 (m, 1H), 7.62–7.57 (m, 1H), 7.32 (s, 1H), 4.09 (s, 3H), 4.02 (s, 3H), 4.00 (s, 3H), 2.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.0, 157.1, 155.4, 147.4, 146.3, 144.2, 141.3, 136.7, 132.0, 129.8, 129.6, 128.0, 127.6, 127.4, 126.8, 122.0, 119.2, 104.3, 61.7, 61.3, 56.1, 20.5; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₂₁N₂O₃: 361.1547; found: 361.1555.



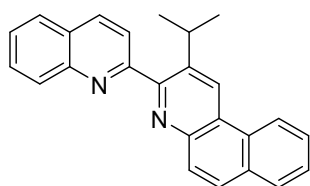
3-(quinolin-2-yl)benzo[f]quinoline (4at):

Yield 88% (53.9 mg; petroleum ether/EtOAc = 10:1); white solid; mp 205–207 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.14 (d, J = 8.4 Hz, 1H), 8.99 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.8 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.80–7.72 (m, 2H), 7.71–7.66 (m, 1H), 7.63–7.56 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 156.2, 155.7, 148.0, 147.8, 136.8, 132.0, 131.6, 131.0, 129.9, 129.7, 129.6, 128.7, 128.6, 128.4, 127.7, 127.4, 127.1, 126.9, 125.7, 123.0, 119.6, 119.3; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2$: 307.1230; found: 307.1232.



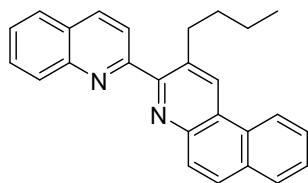
2-propyl-3-(quinolin-2-yl)benzo[f]quinoline (4au):

Yield 85% (59.2 mg; petroleum ether/EtOAc = 20:1); white solid; mp 130–132 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.89 (s, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.99–7.92 (m, 2H), 7.91–7.87 (m, 1H), 7.79–7.73 (m, 1H), 7.73–7.68 (m, 1H), 7.68–7.63 (m, 1H), 7.62–7.56 (m, 1H), 3.28–3.20 (m, 2H), 1.78–1.68 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.8, 156.6, 147.3, 146.0, 136.6, 135.3, 132.4, 132.0, 130.2, 129.8, 129.5, 129.3, 128.7, 128.1, 127.6, 127.4, 127.2, 126.9, 126.8, 125.0, 122.9, 122.2, 35.5, 24.6, 14.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2$: 349.1699; found: 349.1701.



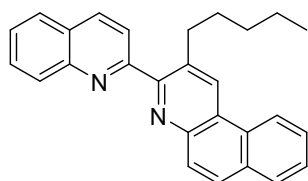
2-isopropyl-3-(quinolin-2-yl)benzo[f]quinoline (4av):

Yield 77% (53.7 mg; petroleum ether/EtOAc = 30:1); white solid; mp 117–119 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.04 (s, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 8.00–7.93 (m, 3H), 7.92 (d, J = 8.0 Hz, 1H), 7.80–7.71 (m, 2H), 7.70–7.64 (m, 1H), 7.63–7.57 (m, 1H), 3.88–3.77 (m, 1H), 1.41 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.9, 156.9, 147.4, 145.7, 141.1, 136.6, 132.0, 130.3, 129.8, 129.6, 129.4, 128.8, 128.4, 128.1, 127.6, 127.4, 127.3, 126.9, 126.8, 125.2, 122.8, 122.3, 29.1, 24.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2$: 349.1699; found: 349.1702.



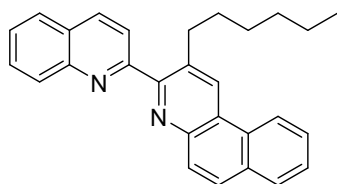
2-butyl-3-(quinolin-2-yl)benzo[f]quinoline (4aw):

Yield 82% (59.4 mg; petroleum ether/EtOAc = 20:1); white solid; mp 111–113 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.90 (s, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.98–7.92 (m, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.79–7.74 (m, 1H), 7.74–7.69 (m, 1H), 7.69–7.63 (m, 1H), 7.63–7.56 (m, 1H), 3.30–3.22 (m, 2H), 1.73–1.64 (m, 2H), 1.40–1.30 (m, 2H), 0.89–0.81 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.8, 156.6, 147.3, 146.0, 136.6, 135.6, 132.3, 132.0, 130.2, 129.7, 129.5, 129.3, 128.7, 128.1, 127.6, 127.4, 127.3, 126.9, 126.8, 125.1, 122.9, 122.2, 33.6, 33.1, 22.6, 13.9; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{N}_2$: 363.1856; found: 363.1864.



2-pentyl-3-(quinolin-2-yl)benzo[f]quinoline (4ax):

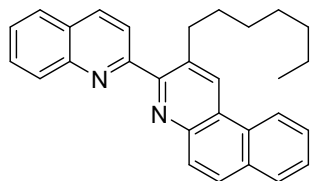
Yield 81% (61.0 mg; petroleum ether/EtOAc = 20:1); white solid; mp 88–90 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.88 (s, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.96–7.91 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.78–7.73 (m, 1H), 7.73–7.68 (m, 1H), 7.67–7.62 (m, 1H), 7.61–7.55 (m, 1H), 3.28–3.21 (m, 2H), 1.75–1.65 (m, 2H), 1.30–1.24 (m, 4H), 0.83–0.75 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.8, 156.6, 147.3, 146.0, 136.6, 135.6, 132.3, 131.9, 130.1, 129.7, 129.5, 129.2, 128.7, 128.1, 127.6, 127.4, 127.2, 126.9, 126.8, 125.0, 122.9, 122.2, 33.4, 31.8, 31.1, 22.4, 13.9; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{N}_2$: 377.2012; found: 377.2013.



2-hexyl-3-(quinolin-2-yl)benzo[f]quinoline (4ay):

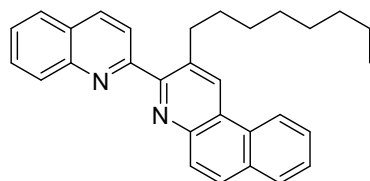
Yield 82% (64.0 mg; petroleum ether/EtOAc = 20:1); white solid; mp 85–87 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.90 (s, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.97–7.92 (m, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.79–7.74 (m, 1H), 7.74–7.69 (m, 1H), 7.68–7.64 (m, 1H), 7.62–7.57 (m, 1H), 3.28–3.22 (m, 2H), 1.73–1.64 (m, 2H), 1.35–1.27 (m, 6H), 0.82–0.75 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.8, 156.7, 147.3, 146.0, 136.6, 135.6, 132.3, 132.0, 130.2, 129.7, 129.5, 129.3, 128.7, 128.2, 127.6, 127.4, 127.2, 126.9, 126.8, 125.1, 122.9,

122.2, 33.4, 31.6, 31.4, 29.2, 22.5, 14.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{28}H_{27}N_2$: 391.2169; found: 391.2169.



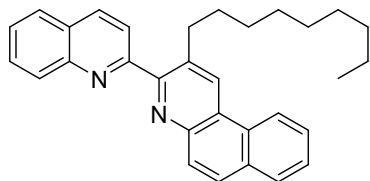
2-heptyl-3-(quinolin-2-yl)benzo[f]quinoline (4az):

Yield 80% (64.7 mg; petroleum ether/EtOAc = 20:1); white solid; mp 79–81 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.91 (s, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.98–7.94 (m, 2H), 7.92 (dd, J = 8.0, 0.8 Hz, 1H), 7.80–7.75 (m, 1H), 7.75–7.70 (m, 1H), 7.69–7.65 (m, 1H), 7.63–7.58 (m, 1H), 3.28–3.22 (m, 2H), 1.71–1.64 (m, 2H), 1.33–1.26 (m, 2H), 1.25–1.13 (m, 6H), 0.83–0.77 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.9, 156.8, 147.4, 146.0, 136.7, 135.7, 132.4, 132.0, 130.2, 129.8, 129.6, 129.3, 128.8, 128.2, 127.6, 127.5, 127.3, 127.0, 126.8, 125.1, 123.0, 122.3, 33.4, 31.7, 31.5, 29.6, 29.0, 22.6, 14.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{29}H_{29}N_2$: 405.2325; found: 405.2320.



2-octyl-3-(quinolin-2-yl)benzo[f]quinoline (4aaa):

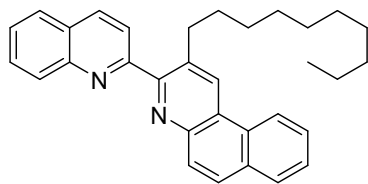
Yield 82% (68.6 mg; petroleum ether/EtOAc = 20:1); white solid; mp 85–87 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.89 (s, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.98–7.91 (m, 2H), 7.91–7.87 (m, 1H), 7.79–7.73 (m, 1H), 7.73–7.68 (m, 1H), 7.68–7.62 (m, 1H), 7.62–7.56 (m, 1H), 3.30–3.19 (m, 2H), 1.74–1.62 (m, 2H), 1.34–1.26 (m, 2H), 1.24–1.09 (m, 8H), 0.88–0.77 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.9, 156.7, 147.4, 146.0, 136.7, 135.7, 132.4, 132.0, 130.2, 129.8, 129.6, 129.3, 128.8, 128.2, 127.6, 127.5, 127.3, 127.0, 126.8, 125.2, 123.0, 122.3, 33.4, 31.8, 31.5, 29.6, 29.4, 29.2, 22.6, 14.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{31}N_2$: 419.2482; found: 419.2478.



2-nonyl-3-(quinolin-2-yl)benzo[f]quinoline (4aab):

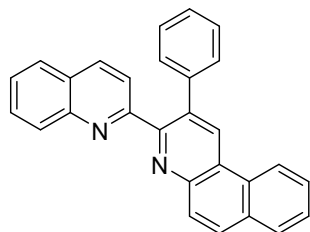
Yield 80% (69.2 mg; petroleum ether/EtOAc = 20:1); white solid; mp 82–84 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.90 (s, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.98–7.92 (m, 2H), 7.92–7.88 (m, 1H), 7.79–7.74 (m, 1H), 7.74–7.69 (m, 1H), 7.68–7.63 (m, 1H), 7.62–7.57 (m, 1H), 3.29–3.21 (m, 2H), 1.72–1.64 (m, 2H), 1.35–1.27 (m, 2H), 1.25–1.12 (m, 10H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.8, 156.7, 147.3, 146.0, 136.6, 135.6,

132.3, 132.0, 130.2, 129.7, 129.5, 129.3, 128.7, 128.1, 127.6, 127.4, 127.3, 126.9, 126.8, 125.1, 122.9, 122.2, 33.4, 31.8, 31.4, 29.5, 29.4, 29.3, 29.2, 22.6, 14.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{31}H_{33}N_2$: 433.2638; found: 433.2635.



2-decyl-3-(quinolin-2-yl)benzo[f]quinoline (4aac):

Yield 78% (69.7 mg; petroleum ether/EtOAc = 20:1); white solid; mp 68–70 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.90 (s, 1H), 8.72 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.98–7.93 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.79–7.70 (m, 2H), 7.69–7.64 (m, 1H), 7.63–7.58 (m, 1H), 3.30–3.20 (m, 2H), 1.73–1.67 (m, 2H), 1.35–1.24 (m, 4H), 1.22–1.10 (m, 10H), 0.89–0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.8, 156.7, 147.4, 146.0, 136.6, 135.6, 132.4, 132.0, 130.2, 129.8, 129.6, 129.3, 128.7, 128.2, 127.6, 127.4, 127.3, 126.9, 126.8, 125.1, 122.9, 122.2, 33.4, 31.9, 31.4, 29.52(X2), 29.5, 29.3(3), 29.2(6), 22.6, 14.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{32}H_{35}N_2$: 447.2795; found: 447.2803.



2-phenyl-3-(quinolin-2-yl)benzo[f]quinoline (8):

Yield 65% (49.7 mg; petroleum ether/EtOAc = 12:1); white solid; mp 197–199 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.07 (s, 1H), 8.72 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 9.2 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 2.8 Hz, 1H), 8.04 (d, J = 3.2 Hz, 1H), 8.00–7.97 (m, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.76–7.72 (m, 1H), 7.71–7.67 (m, 2H), 7.57–7.51 (m, 2H), 7.39–7.34 (m, 2H), 7.31–7.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.2, 156.1, 147.9, 147.2, 139.9, 135.8, 134.9, 133.1, 132.1, 131.2, 130.0, 129.8, 129.4, 128.8, 128.4, 128.3, 127.6, 127.4, 127.2(3), 127.1(7), 126.8, 125.0, 123.0, 122.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{28}H_{19}N_2$: 383.1543; found: 383.1535.

8. Crystallographic data and molecular structure of 4ap

The crystal of **4ap** for X-ray diffraction study has been obtained through the dissolving of compound in CHCl_3 , followed by slow evaporation of the solvent at room temperature. The crystal was kept at 296(2) during data collection. CCDC 2384037 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

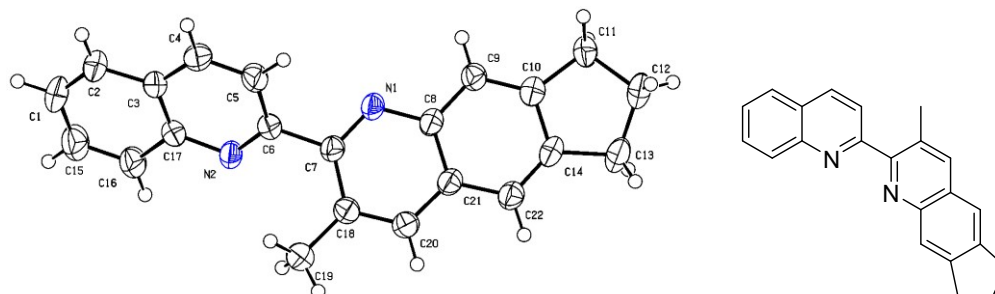


Figure S1. X-ray crystal structure of **4ap**; the ellipsoids depicted at the 50% probability level.

Empirical formula	$\text{C}_{22}\text{H}_{18}\text{N}_2$		Density (calculated)	1.312 g/cm^3
Formula weight	310.38		Absorption coefficient	0.077 mm^{-1}
Temperature	296(2) K		F(000)	656.0
Crystal system	monoclinic		Crystal size	$0.19 \times 0.16 \times 0.1 \text{ mm}^3$
Space group	$\text{P2}_1/\text{c}$		Theta range for data collection	2.526 to 55.196°
Unit cell dimensions	a = 3.989(3) Å	$\alpha = 90^\circ$	Reflections collected	3510
	b = 12.220(9) Å	$\beta = 92.740(11)^\circ$	Data / restraints / parameters	3510/0/219
	c = 32.27(2) Å	$\gamma = 90^\circ$	Goodness-of-fit on F^2	1.182
Volume	$1571(2) \text{ Å}^3$		Final R indices [I>2sigma(I)]	$R_1 = 0.1161$, $wR_2 = 0.3128$
Z	4		R indices (all data)	$R_1 = 0.1590$, $wR_2 = 0.3406$

9. References

1. Hu, Y.; Nan, J.; Yin, J.; Huang, G.; Ren, X.; Ma, Y. Rhodium-Catalyzed Dehydrogenative Annulation of N-Arylmethanimines with Vinylene Carbonate for Synthesizing Quinolines. *Org. Lett.* **2021**, *23*, 8527–8532.
2. Wang, L.-C.; Geng, H.-Q.; Peng, J.-B.; Wu, X.-F. Iron-Catalyzed Synthesis of 2-Aminofurans from 2-Haloketones and Tertiary Amines or Enamines. *Eur. J. Org. Chem.* **2020**, *2020*, 2605–2616.

10. NMR spectra

