Synthesis of Quinolines through Copper-Catalyzed Intermolecular Cyclization Reaction from Anilines and Terminal Acetylene Esters

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research, Ministry of Education, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China;
Institute of Applied Chemistry, Central South University of Forestry and Technology, Changsha 410004, China

1) General Information S2
2) Synthesis of Starting Materials S2-S3
3) Typical Procedures S3-S4
4) Characterization Data S4-S13
5) References S13
6) Scanned $^1$H NMR and $^{13}$C NMR Spectra of All Compounds S13-S36
1) General Information

NMR spectra of the 3a-3w, 4a-4f were recorded using Bruker Avance-500 instruments, calibrated to TMS (1H NMR spectra) and CDCl₃ (13C NMR spectra) as the internal reference (0.00 ppm for 1H NMR spectra and 77.00 ppm for 13C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel (200-300 mesh).

2) Synthesis of Starting Materials

(i) General Procedure for the Synthesis of propargyl alcohol derivatives

To a freshly distilled THF solution (100 mL) of trimethylsilylacetylene (1.96 g, 20.0 mmol) in a glass flask that contained a magnetic stirring bar, n-BuLi (15 mL, 1.6 M in hexane) was dropwise added under a N₂ atmosphere at -90 °C. The mixture was stirred and slowly warmed to room temperature for 3 h. To the above reaction mixture was added an aldehyde (20.0 mmol) at -90 °C, and the mixture was slowly warmed to room temperature with stirring. After stirring for 16 h, the reaction was quenched with 2M-HCl aq. (20 mL), and then extracted with AcOEt, dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified via silica gel column chromatography (petroleum ether : AcOEt = 9 : 1) to give the corresponding propargyl alcohol derivative 1 (eq 1).

The propargyl alcohol derivative 1 was dissolved in distilled MeOH (10 mL)
containing K₂CO₃ (2.07 g, 15.0 mmol), and the mixture was stirred for 24 h at room temperature. To quench the reaction, AcOEt (10 mL) and H₂O (10 mL) were added. The organic layer was separated, washed with H₂O (10 mL), and dried over Na₂SO₄. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : AcOEt = 9 : 1) to give the corresponding propargyl alcohol derivative 2 (eq 2).

(ii) General Procedure to Synthesis of propargylic ester substrates

To a solution of 1-phenylprop-2-yn-1-ol (1.32 g, 10 mmol) in 15 mL CH₂Cl₂ at 0 °C was added DMAP (123 mg, 1 mmol), triethylamine (2.1 mL, 15 mmol), Ac₂O (2.0 mL, 15 mmol), and the reaction mixture was stirred for 2 h. After addition of an appropriate volume of aqueous water, the reaction was extracted with CH₂Cl₂. The combined organic layer was washed twice with saturated NaCl aqueous, dried over Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) to give the desired propargylic acetate 3 in almost quantitative yield as a yellow oil (eq 3).

3) Typical Procedures

(i) Partial Optimization of the Reaction Conditions for the Synthesis of Quinolines

S3
The stirred mixture of aromatic aniline 1a (0.2 mmol), propargylic acetate 2a (0.3 mmol, 1.5 equiv) and CuBr (0.04 mmol, 20%) in PhCl (2 mL) at 120 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 100:1) to provide the desired products 3a as a white solid.

4) Characterization Data

**2-phenylquinoline (3a):** white solid, isolated yield 60% (24.6 mg); ^1H NMR (CDCl₃, 500 MHz) 
δ = 8.23-8.18 (m, 4H), 7.88 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H),
7.56-7.52 (m, 3H), 7.48 (t, J = 7.5 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ = 157.3, 148.2, 139.6, 136.8, 129.7, 129.6, 129.3, 128.8, 127.6, 127.4, 127.1, 126.3, 119.0.

7-methyl-2-phenylquinoline (3b) and 5-methyl-2-phenylquinoline (3b’): pale yellow solid, isolated yield 76% (33.2 mg); $^1$H NMR (CDCl$_3$, 500 MHz) δ = 8.36 (d, J = 9.0 Hz, 1H), 8.20-8.15 (m, 5H), 8.06 (d, J = 8.5 Hz, 1H), 8.00 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.62 (t, J = 7.0 Hz, 1H), 7.56-7.52 (m, 4H), 7.49-7.46 (m, 2H), 7.36 (t, J = 7.0 Hz, 2H), 2.70 (s, 3H), 2.60 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ = 157.2, 156.7, 148.5, 148.4, 139.9, 139.7, 139.6, 136.4, 134.3, 133.2, 129.3, 129.2, 128.8, 128.7, 128.6, 128.5, 128.0, 127.5, 127.0, 126.7, 126.4, 125.2, 118.4, 118.1, 21.8, 18.5.

8-methyl-2-phenylquinoline (3c): pale yellow solid, isolated yield 61% (26.7 mg); $^1$H NMR (CDCl$_3$, 500 MHz) δ = 8.25 (d, J = 7.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 2.90 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ = 155.5, 147.2, 139.8, 137.7, 136.9, 129.6, 129.2, 128.7, 127.4, 127.1, 126.0, 125.4, 118.2, 17.9.
6-methyl-2-phenylquinoline (3d): white solid, isolated yield 53% (23.2 mg); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta = 8.16 (d, J = 7.5 \, \text{Hz}, 2H), 8.13-8.10 (m, 2H), 7.83 (d, J = 8.5 \, \text{Hz}, 1H), 7.58-7.52 (m, 4H), 7.47 (t, J = 7.5 \, \text{Hz}, 1H); ^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta = 156.5, 146.8, 139.7, 136.1, 136.1, 131.9, 129.3, 129.1, 128.8, 127.4, 127.2, 126.3, 119.0, 21.6.\)

\[
\begin{array}{c}
\text{MeO} \\
\end{array}
\]

6-methoxy-2-phenylquinoline (3e): pale yellow solid, isolated yield 46% (21.6 mg); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta = 8.12 (d, J = 7.5 \, \text{Hz}, 2H), 8.07 (t, J = 9.0 \, \text{Hz}, 2H), 7.81 (d, J = 8.5 \, \text{Hz}, 1H), 7.51 (t, J = 8.0 \, \text{Hz}, 2H), 7.43 (t, J = 7.5 \, \text{Hz}, 1H), 7.38 (dd, J = 9.0 \, \text{Hz}, 2.5 \, \text{Hz}, 1H), 7.07 (d, J = 2.5 \, \text{Hz}, 1H), 3.93 (s, 3H); ^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta = 157.6, 155.0, 144.3, 139.8, 135.5, 131.1, 128.9, 128.1, 127.3, 122.3, 119.2, 105.0, 55.5.\)

\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

5,7-dimethyl-2-phenylquinoline (3f): white solid, isolated yield 61% (28.4 mg); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta = 8.30 (d, J = 9.0 \, \text{Hz}, 1H), 8.18 (d, J = 7.5 \, \text{Hz}, 2H), 7.87 (s, 1H), 7.80 (d, J = 9.0 \, \text{Hz}, 1H), 7.54 (t, J = 7.5 \, \text{Hz}, 2H), 7.47 (t, J = 7.5 \, \text{Hz}, 1H), 7.20 (s, 1H), 2.65 (s, 3H), 2.54 (s, 3H); ^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta = 156.6, 148.7, 139.6, 139.5, 133.9, 133.0, 129.1, 128.7, 127.4, 126.8, 124.5, 117.6, 21.8, 18.4.\)
5,7-dimethoxy-2-phenylquinoline (3g): pale yellow solid, isolated yield 45% (23.9 mg); mp:
98.0-100.0 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta = 8.48 (d, J = 8.5 \text{ Hz}, 1H), 8.13 (d, J = 7.5 \text{ Hz}, 2H),
7.68 (d, J = 8.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.15 (s, 1H), 6.50 (s,
1H), 4.00 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta = 161.4, 158.0, 155.9, 150.3, 139.7, 131.5,
129.1, 128.7, 127.5, 115.9, 115.6, 99.9, 97.9, 55.7, 55.6; \) HRMS (ESI) m/z calcd for
C\(_{17}\)H\(_{16}\)NO\(_2\)(M+H)
\(^+\) 266.11756, found 266.11755.

5,8-dimethoxy-2-phenylquinoline (3h): pale yellow solid, isolated yield 67% (35.5 mg); \(^1\)H NMR
(CDCl\(_3\), 500 MHz) \(\delta = 8.60 (d, J = 8.5 \text{ Hz}, 1H), 8.20 (d, J = 7.5 \text{ Hz}, 2H), 7.90 (d, J = 8.5
Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.73 (d, J =
8.0 Hz, 1H), 4.1 (s, 3H), 4.0 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta = 156.5, 149.5, 148.7, 140.4,
139.5, 131.7, 129.2, 128.6, 127.6, 120.4, 118.4, 107.6, 103.5, 56.3, 55.7.

6-fluoro-2-phenylquinoline (3i): white solid, isolated yield 20% (9.0 mg); \(^1\)H NMR (CDCl\(_3\), 500
MHz) \(\delta = 8.21-8.14 (m, 4H), 7.89 (d, J = 8.5 \text{ Hz}, 1H), 7.55-7.43 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\), 125
MHz) \(\delta = 160.3 (d, J = 246.5 \text{ Hz}), 156.7 (d, J = 2.6 \text{ Hz}), 145.2, 139.2, 136.2 (d, J = 5.3 \text{ Hz}), 132.1
(d, J = 9.0 Hz), 129.4, 128.9, 127.7 (d, J = 10.0 Hz), 127.4, 119.9 (d, J = 25.5 Hz), 119.7, 110.5
6-iodo-2-phenylquinoline (3j): white solid, isolated yield 18% (12.0 mg); mp: 137.0-139.0 °C;  
$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ = 8.20 (s, 1H), 8.15 (d, $J$ = 7.0 Hz, 2H), 8.09 (d, $J$ = 9.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.87 (d, $J$ = 8.5 Hz, 1H), 7.54 (t, $J$ = 7.5 Hz, 2H), 7.48 (t, $J$ = 7.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ = 157.7, 147.0, 138.9, 138.4, 136.2, 135.7, 131.2, 129.7, 128.9, 128.8, 127.6, 119.6, 91.7; HRMS (ESI) m/z calcd for C$_{15}$H$_{11}$IN$^+(M+H)$=331.99307, found 331.99283.

N-(2-phenylquinolin-6-yl)acetamide (3k): yellow solid, isolated yield 40% (21.0 mg); mp: 163.0-165.1 °C; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ = 8.32 (s, 1H), 8.13-8.06 (m, 4H), 8.87 (s, 1H), 7.82 (d, $J$ = 9.0 Hz, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.51 (t, $J$ = 7.5 Hz, 2H), 7.45 (t, $J$ = 7.5 Hz, 1H), 2.22 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ = 168.8, 156.5, 145.4, 139.5, 136.6, 135.6, 130.2, 129.2, 128.8, 127.6, 127.4, 123.3, 119.6, 115.9, 24.6; HRMS (ESI) m/z calcd for C$_{17}$H$_{15}$N$_2$O$^+(M+H)$=263.11789, found 263.11789.

5-methyl-2-phenylquinoline-8-carboxylic acid (3l): yellow solid, isolated yield 40% (21.0 mg); mp: 172.5-174.8 °C; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ = 8.58-8.54 (m, 2H), 7.99-7.97 (m, 3H), 7.56-7.53 (m, 3H), 7.45 (d, $J$ = 7.5 Hz, 1H), 2.74 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ = 167.5,
HRMS (ESI) m/z calcd for C_{17}H_{14}NO_2^+(M+H)^+ 264.10191, found 264.10202.

4-nitro-N-(1-phenylprop-2-ynyl)benzenamine (3m): yellow solid, isolated yield 50% (25.2 mg); ¹H NMR (CDCl₃, 500 MHz) δ = 8.11 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H), 7.44-7.37 (m, 3H), 6.69 (d, J = 9.0 Hz, 2H), 5.38 (s, 1H), 4.88 (s, 1H), 2.56 (d, J = 2.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ = 151.2, 139.2, 137.3, 129.1, 128.8, 127.1, 126.1, 112.4, 81.1, 74.1, 49.3.

2-phenylbenzo[h]quinoline (3n): white solid, isolated yield 70% (35.7 mg); ¹H NMR (CDCl₃, 500 MHz) δ = 9.56 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 7.0 Hz, 2H), 8.19 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.81-7.78 (m, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ = 155.4, 146.2, 139.7, 136.5, 133.8, 131.8, 129.2, 128.8, 128.1, 127.7, 127.4, 126.8, 125.1, 125.0, 124.7, 118.8.

3-phenylbenzo[f]quinoline (3o): white solid, isolated yield 40% (20.4 mg); ¹H NMR (CDCl₃, 500 MHz) δ = 8.95 (d, J = 8.5 Hz, 1H), 8.59 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 7.5 Hz, 2H), 8.10 (d, J = 9.0 Hz, 1H), 7.99 (t, J = 8.5 Hz, 2H), 7.94 (d, J = 7.5 Hz, 1H), 7.70-7.63 (m, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ = 156.8, 148.1, 139.4, 131.6,
2-p-tolylbenzo[h]quinoline (3p): pale yellow solid, isolated yield 61% (32.8 mg); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta = 9.55$ (d, $J = 8.0$ Hz, 1H), 8.27 (d, $J = 8.0$ Hz, 2H), 8.18 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.80-7.78 (m, 2H), 7.72 (t, $J = 7.5$ Hz, 1H), 7.68 (d, $J = 9.0$ Hz, 1H), 7.39 (d, $J = 7.5$ Hz, 2H), 2.49 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta = 155.4$, 146.1, 139.2, 136.8, 136.4, 133.8, 131.7, 129.5, 128.0, 127.7, 127.3, 127.2, 126.8, 125.0, 124.9, 124.7, 118.6, 21.3.

2-(4-methoxyphenyl)benzo[h]quinoline (3q): pale yellow solid, isolated yield 59% (33.6 mg); mp: 110.9-112.7 °C; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta = 9.52$ (d, $J = 8.0$ Hz, 1H), $\delta = 8.32$ (d, $J = 9.0$ Hz, 2H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.92 (d, $J = 8.5$ Hz, 2H), 7.79-7.76 (m, 2H), 7.71 (t, $J = 7.5$ Hz, 1H), 7.66 (d, $J = 9.0$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 2H), 3.90 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta = 160.7$, 155.1, 146.0, 136.4, 133.8, 132.3, 131.7, 128.7, 128.0, 127.7, 126.9, 126.7, 125.1, 124.7, 118.2, 114.1, 55.3; HRMS (ESI) m/z calcd for C$_{20}$H$_{16}$NO$^+(M+H)^+$ 286.12264, found 286.12259.

2-(2-fluorophenyl)benzo[h]quinoline (3r): white solid, isolated yield 59% (32.3 mg); mp: 81.0-82.9 °C; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta = 9.43$ (d, $J = 8.0$ Hz, 1H), 8.40 (t, $J = 8.0$ Hz, 1H), 8.18
(d, \( J = 8.5 \) Hz, 1H), 8.04 (dd, \( J = 8.5 \) Hz, 2.0 Hz, 1H), 7.88 (d, \( J = 7.5 \) Hz, 1H), 7.78 (d, \( J = 8.5 \) Hz, 1H), 7.73 (t, \( J = 7.5 \) Hz, 1H), 7.70-7.65 (m, 2H), 7.44-7.40 (m, 1H), 7.35 (t, \( J = 7.5 \) Hz, 1H), 7.22-7.19 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta = 161.0 \) (d, \( J = 248.5 \) Hz), 151.9 (d, \( J = 1.8 \) Hz), 146.3, 136.0, 133.7, 131.8 (d, \( J = 2.8 \) Hz), 131.7, 130.6 (d, \( J = 8.5 \) Hz), 128.2, 127.9 (d, \( J = 11.3 \) Hz), 127.8, 126.9, 125.2, 125.0, 124.6, 124.6, 122.8 (d, \( J = 9.9 \) Hz), 116.3 (d, \( J = 22.9 \) Hz); HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{13}\)FN\(^{+}\)(M+H)\(^{+}\)274.10265, found 274.10263.

\[
\text{Cl} \quad \begin{array}{c}
\text{N} \\
\text{Cl}
\end{array}
\]

2-(2-chlorophenyl)benzo[h]quinoline (3s): white solid, isolated yield 62% (36.1 mg); mp: 121.6-124.1 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta = 9.43 \) (d, \( J = 7.5 \) Hz, 1H), 8.23 (d, \( J = 8.0 \) Hz, 1H), 7.96-7.90 (m, 3H), 7.85 (d, \( J = 8.5 \) Hz, 1H), 7.76-7.70 (m, 3H), 7.57 (d, \( J = 8.0 \) Hz, 1H), 7.47 (t, \( J = 7.5 \) Hz, 1H), 7.41 (t, \( J = 7.5 \) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta = 155.4, 146.2, 139.6, 135.4, 133.7, 132.5, 132.4, 131.6, 130.3, 129.7, 128.2, 128.0, 127.7, 127.0 \) (2C), 125.1, 125.0, 124.8, 123.1; HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{13}\)ClN\(^{+}\)(M+H)\(^{+}\)290.07310, found 290.07291.

\[
\text{Br} \quad \begin{array}{c}
\text{N} \\
\text{Br}
\end{array}
\]

2-(2-bromophenyl)benzo[h]quinoline (3t): pale yellow solid, isolated yield 68% (45.6 mg); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta = 9.42 \) (d, \( J = 8.5 \) Hz, 1H), 8.24 (d, \( J = 8.5 \) Hz, 1H), 7.93 (d, \( J = 7.5 \) Hz, 1H), 7.90 (d, \( J = 8.5 \) Hz, 1H), 7.85 (d, \( J = 9.0 \) Hz, 1H), 7.81 (d, \( J = 7.5 \) Hz, 1H), 7.77-7.70 (m, 4H), 7.50 (t, \( J = 7.5 \) Hz, 1H), 7.33 (t, \( J = 8.0 \) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta = 156.8, 146.1, 141.7, 135.4, 133.7, 133.5, 132.2, 131.6, 129.8, 128.2, 127.9, 127.7, 127.6, 127.0, 125.1, 125.0, 124.8, 123.0, 122.1.
2-(2-bromo-5-methoxyphenyl)benzo[h]quinoline (3u): pale yellow solid, isolated yield 64% (46.6 mg); mp: 91.0-93.2 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) \(\delta = 9.43\ (d, J = 7.5\ Hz, 1H), \delta = 8.23\ (d, J = 8.0\ Hz, 1H), 7.94-7.91\ (m, 2H), 7.85\ (d, J = 8.5\ Hz, 1H), 7.76-7.70\ (m, 3H), 7.64\ (d, J = 9.0\ Hz, 1H), 7.39\ (d, J = 3.0\ Hz, 1H), 6.91\ (dd, J = 9.0\ Hz, 3.0\ Hz, 1H), 3.88\ (s, 3H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz) \(\delta = 159.0, 156.6, 146.0, 142.3, 135.4, 134.2, 133.7, 131.5, 128.2, 128.0, 127.7, 127.0, 125.1, 125.0, 124.8, 123.0, 117.4, 116.0, 112.5, 55.6. HRMS (ESI) m/z calcd for C\textsubscript{20}H\textsubscript{15}BrNO\textsuperscript{+} (M+H)\textsuperscript{+} 364.03315, found 364.03268.

2-(thiophen-3-yl)benzo[h]quinoline (3v): pale yellow solid, isolated yield 64% (33.4 mg); mp: 106.0-108.1 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) \(\delta = 9.47\ (d, J = 8.5\ Hz, 1H), \delta = 8.15-8.11\ (m, 2H), 8.02\ (d, J = 5.0\ Hz, 1H), 7.91\ (d, J = 8.0\ Hz, 1H), 7.83\ (d, J = 8.5\ Hz, 1H), 7.79-7.76\ (m, 2H), 7.71\ (t, J = 7.5\ Hz, 1H), 7.64\ (d, J = 9.0\ Hz, 1H), 7.49-7.47\ (m, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz) \(\delta = 151.7, 146.1, 142.9, 136.4, 133.8, 131.6, 128.1, 127.7, 127.1, 126.8, 126.7, 126.2, 125.0, 124.9, 124.6, 124.1, 118.9; HRMS (ESI) m/z calcd for C\textsubscript{17}H\textsubscript{12}NS\textsuperscript{+} (M+H)\textsuperscript{+} 261.06850, found 261.06854.

2-(anthracen-10-yl)benzo[h]quinoline (3w): yellow solid, isolated yield 49% (34.8 mg); mp:
206.9-209.5 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) \( \delta = 9.36 \) (d, \( J = 8.5 \) Hz, 1H), 8.62 (s, 1H), 8.39 (d, \( J = 8.0 \) Hz, 1H), 8.12 (d, \( J = 8.5 \) Hz, 2H), 7.99-7.93 (m, 2H), 7.86 (d, \( J = 9.0 \) Hz, 1H), 7.77-7.71 (m, 4H), 7.66 (t, \( J = 7.5 \) Hz, 1H), 7.49 (t, \( J = 7.5 \) Hz, 2H), 7.36 (d, \( J = 8.0 \) Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz) \( \delta = 157.1, 146.6, 135.8, 133.8, 131.7, 131.5, 130.2, 128.5, 128.3, 128.0, 127.7, 127.6, 127.0, 126.4, 125.8, 125.3, 125.2, 125.1 \) (2C), 125.0; HRMS (ESI) m/z calcld for C\textsubscript{27}H\textsubscript{18}N\textsuperscript{+}(M+H)\textsuperscript{+} 356.14338, found 356.14316.

3x: yellow solid, isolated yield 58\% (23.8 mg); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) \( \delta = 8.24-8.22 \) (m, 0.57H), 8.19-8.16 (m, 3H), 7.89 (t, \( J = 4.5 \) Hz, 0.8H), 7.84 (d, \( J = 8.0 \) Hz, 1H), 7.75-7.72 (m, 1H), 7.55-7.52 (m, 3H), 7.49-7.45 (m, 1H).

5) References


6) Scanned \textsuperscript{1}H NMR and \textsuperscript{13}C NMR Spectra of All Compounds

\textsuperscript{1}H and \textsuperscript{13}C Spectrum of Compound 3a

![Spectrum Image]
$^1$H and $^{13}$C Spectrum of Compound 3b, 3b'
$^1$H and $^{13}$C Spectrum of Compound 3c
$^1$H and $^{13}$C Spectrum of Compound 3d
\(^1\)H and \(^{13}\)C Spectrum of Compound 3e
$^1$H and $^{13}$C Spectrum of Compound 3f
$^1$H and $^{13}$C Spectrum of Compound 3g
$^1$H and $^{13}$C Spectrum of Compound 3h
$^1$H and $^{13}$C Spectrum of Compound 3i
$\text{H and }^{13}\text{C Spectrum of Compound 3j}$

\[\text{Compound 3j} \begin{align*}
\text{H} & : 8.203, 8.098, 8.080, 7.961, 7.945, 7.926, 7.879, 7.820, 7.592, 7.559, 7.474, 7.451, 7.290 \\
\text{C} & : \text{Not present} \end{align*}\]
$^1$H and $^{13}$C Spectrum of Compound 3k
$^1$H and $^{13}$C Spectrum of Compound 3l
$^1$H and $^{13}$C Spectrum of Compound 3m
$^1$H and $^{13}$C Spectrum of Compound 3n
\(^1\text{H and }^{13}\text{C Spectrum of Compound }3\text{o}\)
1H and 13C Spectrum of Compound 3p
$^1$H and $^{13}$C Spectrum of Compound 3q
$^1$H and $^{13}$C Spectrum of Compound 3r
$^1$H and $^{13}$C Spectrum of Compound 3s
$^{1}$H and $^{13}$C Spectrum of Compound 3t
\( ^1\text{H} \) and \( ^{13}\text{C} \) Spectrum of Compound 3u
$\text{H and } ^{13}\text{C Spectrum of Compound 3v}$
$^{1}$H and $^{13}$C Spectrum of Compound 3w
$^1$H Spectrum of Compound 3a'