Supporting Information

Synthesis of 3-Aryl-2-Aminoquinolines: Palladium-Catalyzed Cascade Reactions of Gem-dibromovinylanilines with tert-Butyl Isocyanide and Arylboronic Acids

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Table of Contents

1. General Considerations .................................................................................................................S2
2. Preparation of Substrates I ..............................................................................................................S2
3. General Procedures and Characterization Data ..................................................................................S2
4. References .....................................................................................................................................S6
5. 1H and 13C NMR Spectra of Compounds .......................................................................................S7
1. General Considerations

All reagents were purchased from commercial suppliers and used without further purification. For flash column chromatography, silica gel (200-300 mesh) was applied. Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates (GF 254). Visualization of the developed plates was performed under UV lights (GF 254 nm). $^1$H and $^{13}$C NMR spectra were recorded on a 400 or 500 MHz spectrometer. Chemical shifts (δ) were reported in ppm referenced to an internal tetramethylsilane standard (δ 0.00) or the CDCl$_3$-d1 residual peak (δ 7.26) for $^1$H NMR. Chemical shifts of $^{13}$C NMR were reported relative to CDCl$_3$ (δ 77.0). The following abbreviations were used to describe peak splitting patterns when appropriate: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, J, was reported in Hertz unit (Hz). High resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS spectrometer.

2. Preparation of Substrates 1

2-(2,2-dibromovinyl)aniline 1 and derivatives, they were characterized in our previous work.

3. General Procedures and Characterization Data

1) Typical procedure for the cascade reaction

A mixture of gem-dibromovinylaniline 1 (0.2 mmol), arylboronic acid 2 (0.22 mmol), $t$-butyl isocyanide (0.22 mmol), Pd(dppf)Cl$_2$ (0.01 mmol), and Cs$_2$CO$_3$ (0.44 mmol) in 1,4-dioxane (2.0 mL) was stirred at 100°C for 8h in a sealed tube. Upon completion of the reaction, the mixture was concentrated under vacuum and the resulting residue was purified by flash chromatography on silica gel to give the desired product 3.

2) Product Characterization

$N$-(tert-butyl)-3-phenylquinolin-2-amine (3a)

Yellow oil, 43 mg, 78% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J$ = 8.4 Hz, 1H), 7.52 (s, 1H), 7.39 (m, 7H), 7.11 (t, $J$ = 7.4 Hz, 1H), 4.66 (s, 1H), 1.43 (s, 9H); $^{13}$C NMR (101 MHz, DMSO) δ 153.30, 146.55, 137.11, 135.30, 132.99, 132.79, 128.89, 128.65, 128.40, 128.35, 128.28, 127.80, 127.12, 125.70, 125.44, 122.46, 121.42, 50.92, 28.51. MS(ESI, m/z): 277.1[M+H]$^+$, HRMS (ESI): Exact mass calced for C$_{19}$H$_{21}$N$_2$ [M+H]$^+$ 277.1699, found 277.1704.

$N$-(tert-butyl)-6-chloro-3-phenylquinolin-2-amine (3b)
Yellow oil, 54 mg, 87% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (d, \(J = 8.8\) Hz, 1H), 7.40 (m, 4H), 7.34 (m, 4H), 4.67 (s, 1H), 1.40 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.31, 146.18, 137.94, 134.71, 129.51, 129.24, 129.05, 128.29, 128.09, 127.34, 127.01, 125.98, 123.83, 51.92, 29.24. MS(ESI, m/z): 311.1\([\text{M+H}]^+\); HRMS (ESI): Exact mass calcd for C\(_{19}\)H\(_{20}\)ClN\(_2\) [M+H]\(^+\) 311.1310, found 311.1312.

**N-(tert-butyl)-7-chloro-3-phenylquinolin-2-amine (3c)**

Yellow oil, 52 mg, 83% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (s, 1H), 7.46 (s, 1H), 7.37 (m, 6H), 7.03 (d, \(J = 8.4\) Hz, 1H), 4.71 (s, 1H), 1.40 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.75, 148.34, 138.01, 134.79, 129.24, 129.06, 128.74, 128.32, 128.23, 127.24, 127.20, 126.57, 125.71, 122.54, 121.57, 51.96, 29.21. MS(ESI, m/z): 311.1\([\text{M+H}]^+\); HRMS (ESI): Exact mass calcd for C\(_{19}\)H\(_{20}\)ClN\(_2\) [M+H]\(^+\) 311.1310, found 311.1313.

**N-(tert-butyl)-6-fluoro-3-phenylquinolin-2-amine (3d)**

Yellow oil, 50 mg, 85% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (m, 1H), 7.38 (m, 6H), 7.17 (t, \(J = 9.8\) Hz, 1H), 7.09 (d, \(J = 8.9\) Hz, 1H), 4.60 (s, 1H), 1.40 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.33, 156.94, 153.70, 144.52, 138.05, 135.06, 135.02, 129.20, 129.05, 128.74, 128.42, 128.33, 128.22, 127.32, 127.24, 127.19, 123.23, 118.28, 118.04, 110.68, 110.46, 51.80, 29.25. MS(ESI, m/z): 295.2\([\text{M+H}]^+\); HRMS (ESI): Exact mass calcd for C\(_{19}\)H\(_{20}\)FN\(_2\) [M+H]\(^+\) 295.1605, found 295.1608.

**N-(tert-butyl)-7-fluoro-3-phenylquinolin-2-amine (3e)**

Yellow oil, 51 mg, 86% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 7.5\) Hz, 1H), 7.46 (s, 1H), 7.36 (dd, \(J = 16.3, 6.9\) Hz, 5H), 7.26 (d, \(J = 11.1\) Hz, 1H), 6.84 (t, \(J = 8.6\) Hz, 1H), 4.70 (s, 1H), 1.40 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 164.94, 162.49, 154.81, 148.99, 148.86, 141.47, 138.16, 135.41, 129.21, 129.13, 128.93, 128.82, 128.74, 128.13, 127.24, 127.20, 125.58, 120.04, 111.42, 111.18, 110.74, 110.54, 51.92, 29.24. MS(ESI, m/z): 295.2\([\text{M+H}]^+\); HRMS (ESI): Exact mass calcd for C\(_{19}\)H\(_{20}\)FN\(_2\) [M+H]\(^+\) 295.1605, found 295.1609.
N-(tert-butyl)-6-methoxy-3-phenylquinolin-2-amine (3f)

![Chemical Structure](image)

Yellow oil, 48 mg, 79% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 9.0$ Hz, 1H), 7.45 (s, 1H), 7.36 (m, 5H), 7.11 (d, $J = 9.1$ Hz, 1H), 6.85 (s, 1H), 3.77 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.06, 153.02, 143.33, 138.66, 135.05, 129.16, 129.09, 128.74, 128.03, 127.95, 127.20, 126.68, 123.45, 120.30, 107.02, 55.69, 51.70, 29.39. MS(ESI, m/z): 307.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{20}$H$_{23}$N$_2$O [M+H]$^+$ 307.1805, found 307.1810.

N-(tert-butyl)-7-methoxy-3-phenylquinolin-2-amine (3g)

Yellow oil, 50 mg, 81% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (s, 1H), 7.35 (m, 6H), 7.03 (s, 1H), 6.75 (d, $J = 8.7$ Hz, 1H), 4.64 (s, 1H), 3.84 (s, 3H), 1.42 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.03, 154.60, 149.29, 138.70, 135.50, 129.24, 129.10, 128.74, 128.27, 127.79, 127.19, 123.92, 118.00, 113.76, 106.54, 55.38, 51.77, 29.39. MS(ESI, m/z): 307.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{20}$H$_{23}$N$_2$O [M+H]$^+$ 307.1805, found 307.1810.

N-(tert-butyl)-6,7-dimethoxy-3-phenylquinolin-2-amine (3h)

Yellow oil, 53 mg, 79% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (m, 6H), 7.06 (s, 1H), 6.82 (s, 1H), 4.52 (s, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 1.42 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.30, 151.85, 146.18, 143.85, 138.59, 134.66, 129.11, 129.03, 127.68, 123.84, 117.02, 106.66, 106.17, 77.25, 77.00, 76.74, 55.97, 55.92, 51.53, 29.30. MS(ESI, m/z): 337.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{21}$H$_{25}$N$_2$O$_2$ [M+H]$^+$ 337.1911, found 337.1913.

N-(tert-butyl)-7-phenyl-[1,3]dioxolo[4,5-g]quinolin-6-amine (3i)

White solid, 54 mg, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (m, 6H), 7.02 (s, 1H), 6.78 (s, 1H), 5.89 (s, 2H), 4.50 (s, 1H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.35, 150.15, 145.27, 144.35, 138.69, 135.15, 129.18, 129.07, 128.73, 127.76, 127.23, 127.18, 123.84, 118.38, 104.52, 103.27, 100.92, 51.66, 29.43. MS(ESI, m/z): 321.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{20}$H$_{21}$N$_2$O$_2$ [M+H]$^+$ 321.1598, found 321.1602.
methyl 2-(tert-butylamino)-3-phenylquinoline-6-carboxylate (3j)

White solid, 55 mg, 82% yield. \( ^1H \text{NMR} (400 \text{ MHz}, CDCl}_3 \) \( \delta \) 8.23 (s, 1H), 8.03 (d, \( J = 8.7 \text{ Hz}, 1H \), 7.62 (d, \( J = 8.6 \text{ Hz}, 1H \), 7.55 (s, 1H), 7.39 (m, 5H), 4.86 (s, 1H), 3.85 (s, 3H), 1.42 (s, 9H); \( ^{13}C \text{NMR} (101 \text{ MHz}, CDCl}_3 \) \( \delta \) 167.28, 155.54, 150.40, 137.72, 136.45, 130.46, 129.31, 129.12, 129.03, 128.36, 127.14, 126.42, 123.49, 122.24, 52.14, 51.73, 29.17. MS(ESI, m/z): 335.1[M+H]+, HRMS (ESI): Exact mass calcd for C\(_{22}\)H\(_{24}\)N\(_2\)O\(_2\) [M+H]+ 335.1754, found 335.1757.

methyl 2-(tert-butylamino)-3-phenylquinoline-7-carboxylate (3k)

White solid, 52 mg, 78% yield. \( ^1H \text{NMR} (400 \text{ MHz}, CDCl}_3 \) \( \delta \) 8.35 (s, 1H), 7.71 (d, \( J = 8.2 \text{ Hz}, 1H \), 7.60 (m, 2H), 7.38 (m, 5H), 4.72 (s, 1H), 3.89 (s, 3H), 1.42 (s, 9H); \( ^{13}C \text{NMR} (101 \text{ MHz}, CDCl}_3 \) \( \delta \) 167.54, 154.59, 147.09, 137.83, 135.25, 130.57, 129.25, 128.97, 128.91, 128.72, 128.38, 127.32, 127.17, 126.02, 121.74, 51.98, 51.93, 29.17. MS(ESI, m/z): 335.1[M+H]+, HRMS (ESI): Exact mass calcd for C\(_{22}\)H\(_{24}\)N\(_2\)O\(_2\) [M+H]+ 335.1754, found 335.1757.

N-(tert-butyl)-3-phenylbenzo[h]quinolin-2-amine (3l)

White solid, 50 mg, 77% yield. \( ^1H \text{NMR} (400 \text{ MHz}, CDCl}_3 \) \( \delta \) 9.07 (d, \( J = 7.9 \text{ Hz}, 1H \), 7.73 (d, \( J = 7.7 \text{ Hz}, 1H \), 7.52 (m, 3H), 7.39 (m, 6H), 7.32 (d, \( J = 6.0 \text{ Hz}, 1H \), 4.77 (s, 1H), 1.52 (s, 9H); \( ^{13}C \text{NMR} (101 \text{ MHz}, CDCl}_3 \) \( \delta \) 154.02, 145.33, 138.55, 136.55, 134.42, 131.26, 129.21, 129.17, 128.73, 127.95, 127.61, 127.18, 127.12, 125.81, 125.44, 125.12, 124.91, 122.53, 119.48, 51.80, 29.26. MS(ESI, m/z): 327.2[M+H]+, HRMS (ESI): Exact mass calcd for C\(_{23}\)H\(_{23}\)N\(_2\) [M+H]+ 327.1856, found 327.1857.

N-(tert-butyl)-3-(4-chlorophenyl)quinolin-2-amine (3m)

Yellow oil, 51 mg, 83% yield. \( ^1H \text{NMR} (500 \text{ MHz}, CDCl}_3 \) \( \delta \) 7.64 (d, \( J = 8.3 \text{ Hz}, 1H \), 7.46 (m, 3H), 7.37 (d, \( J = 8.4 \text{ Hz}, 2H \), 7.31 (d, \( J = 8.4 \text{ Hz}, 2H \), 7.10 (t, \( J = 7.4 \text{ Hz}, 1H \), 4.50 (s, 1H), 1.42 (s, 9H); \( ^{13}C \text{NMR} (101 \text{ MHz}, CDCl}_3 \) \( \delta \) 153.81, 147.81, 136.89, 135.99, 134.28, 130.55, 129.44, 129.22, 127.27, 126.70, 125.10, 123.08, 122.08, 51.95, 29.32. MS(ESI, m/z): 311.1[M+H]+,
HRMS (ESI): Exact mass calcd for C_{19}H_{20}ClN_{2} [M+H]^+ 311.1310, found 311.1314.

**N-(tert-butyl)-3-(4-fluorophenyl)quinolin-2-amine (3n)**

Yellow oil, 54 mg, 92% yield. ^1^H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, J = 8.2 Hz, 1H), 7.47 (m, 3H), 7.34 (m, 2H), 7.08 (m, 3H), 4.50 (s, 1H), 1.42 (s, 9H); ^1^C NMR (101 MHz, CDCl$_3$) δ 163.94, 161.48, 154.06, 147.75, 135.95, 134.30, 130.99, 130.91, 129.10, 127.23, 126.68, 125.31, 123.11, 122.01, 116.27, 116.06, 51.87, 29.30. MS(ESI, m/z): 295.1[M+H]^+, HRMS (ESI): Exact mass calcd for C$_{19}$H$_{20}$FN$_{2}$ [M+H]^+ 295.1605, found 295.1604.

**N-(tert-butyl)-3-(o-tolyl)quinolin-2-amine (3o)**

Yellow oil, 50 mg, 87% yield. ^1^H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, J = 8.3 Hz, 1H), 7.44 (m, 3H), 7.23 (m, 3H), 7.12 (m, 2H), 4.16 (s, 1H), 2.09 (s, 3H), 1.38 (s, 9H); ^1^C NMR (101 MHz, CDCl$_3$) δ 154.35, 147.88, 137.22, 137.01, 135.47, 130.58, 130.30, 128.83, 128.45, 127.20, 126.72, 126.57, 126.15, 123.07, 121.78, 51.60, 29.24, 19.52. MS(ESI, m/z): 291.2[M+H]^+, HRMS (ESI): Exact mass calcd for C$_{20}$H$_{23}$N$_{2}$ [M+H]^+ 291.1856, found 291.1855.

**3-(2-aminophenyl)-N-(tert-butyl)quinolin-2-amine (3p)**

Yellow oil, 48 mg, 83% yield. ^1^H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, J = 6.2 Hz, 1H), 7.50 (s, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.74 (d, J = 7.5 Hz, 1H), 6.63 (d, J = 8.4 Hz, 2H), 4.78 (s, 1H), 3.69 (s, 2H), 1.43 (s, 9H); ^1^C NMR (101 MHz, CDCl$_3$) δ 154.21, 147.60, 147.31, 139.49, 135.40, 130.01, 128.85, 127.22, 126.71, 126.55, 123.19, 121.79, 119.09, 115.74, 114.71, 51.78, 29.34. MS(ESI, m/z): 292.2[M+H]^+, HRMS (ESI): Exact mass calcd for C$_{19}$H$_{22}$N$_{3}$ [M+H]^+ 292.1808, found 292.1809.

**N-(tert-butyl)-3-(3-methoxyphenyl)quinolin-2-amine (3q)**

Yellow oil, 53 mg, 86% yield. ^1^H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, J = 8.3 Hz, 1H), 7.52 (s, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.42 (m, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.09 (dd, J = 10.9, 3.9 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.90 (m, 1H), 6.87 (dd, J = 8.3, 2.1 Hz, 1H), 4.72 (s, 1H), 3.77 (s,
\[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \text{)} \delta 160.48, 154.07, 147.73, 139.83, 135.66, 130.18, 129.69, 128.98, 127.26, 126.63, 126.29, 123.16, 121.89, 121.41, 114.96, 113.88, 55.39, 51.84, 29.34. \text{MS(ESI, m/z): 307.1[M+H]}^+, \text{HRMS (ESI): Exact mass calcd for C}_{20}\text{H}_{23}\text{N}_2\text{O [M+H]}^+ 307.1805, \text{found 307.1806.} \]

\text{N-(tert-butyl)-3-(4-(tert-butyl)phenyl)quinolin-2-amine (3r)}

![Chemical Structure](image)

Yellow oil, 52 mg, 79% yield. \(^1\text{H} \text{NMR (500 MHz, CDCl}_3 \text{)} \delta 7.64 (d, J = 8.3 \text{ Hz, 1H}), 7.50 (s, 1H), 7.45 (d, J = 7.9 \text{ Hz, 1H}), 7.41 (dd, J = 5.8, 2.2 \text{ Hz, 3H}), 7.31 (d, J = 8.0 \text{ Hz, 2H}), 7.08 (t, J = 7.4 \text{ Hz, 1H}), 4.74 (s, 1H), 1.43 (s, 9H), 1.30 (d, J = 0.4 \text{ Hz, 9H}); \(^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \text{)} \delta 154.33, 151.25, 147.66, 135.74, 135.40, 128.81, 127.21, 126.61, 126.39, 126.05, 123.34, 121.81, 51.81, 34.73, 31.38, 29.36. \text{MS(ESI, m/z): 333.2[M+H]}^+, \text{HRMS (ESI): Exact mass calcd for C}_{23}\text{H}_{29}\text{N}_2\text{[M+H]}^+ 333.2325, \text{found 333.2325.} \]

\text{3-([1,1'-biphenyl]-4-yl)-N-(tert-butyl)quinolin-2-amine (3s)}

![Chemical Structure](image)

White solid, 49 mg, 70% yield. \(^1\text{H} \text{NMR (400 MHz, CDCl}_3 \text{)} \delta 7.51 (m, 13H), 7.11 (dd, J = 15.3, 8.0 \text{ Hz, 1H}), 4.72 (s, 1H), 1.44 (s, 9H); \(^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \text{)} \delta 154.33, 151.25, 147.66, 135.74, 135.40, 128.81, 127.21, 126.61, 126.39, 126.05, 123.34, 121.81, 51.81, 34.73, 31.38, 29.36. \text{MS(ESI, m/z): 353.1[M+H]}^+, \text{HRMS (ESI): Exact mass calcd for C}_{25}\text{H}_{25}\text{N}_2\text{[M+H]}^+ 353.2012, \text{found 353.2012.} \]

\text{4-(2-(tert-butylamino)quinolin-3-yl)benzonitrile (3t)}

![Chemical Structure](image)

Yellow oil, 43 mg, 71% yield. \(^1\text{H} \text{NMR (400 MHz, CDCl}_3 \text{)} \delta 7.80 (d, J = 7.5 \text{ Hz, 2H}), 7.75 (d, J = 8.2 \text{ Hz, 1H}), 7.60 (m, 5H), 7.23 (t, J = 7.3 \text{ Hz, 1H}), 4.47 (s, 1H), 1.52 (s, 9H); \(^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \text{)} \delta 153.10, 148.01, 143.40, 136.44, 132.92, 129.98, 129.72, 127.42, 126.79, 124.39, 122.86, 122.38, 118.29, 112.30, 52.14, 29.29. \text{MS(ESI, m/z): 302.1[M+H]}^+, \text{HRMS (ESI): Exact mass calcd for C}_{20}\text{H}_{20}\text{N}_3\text{[M+H]}^+ 302.1652, \text{found 302.1655.} \]

\text{methyl 4-(2-(tert-butylamino)quinolin-3-yl)benzoate (3u)}

![Chemical Structure](image)
Yellow oil, 51 mg, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 7.4$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.63 (s, 1H), 7.55 (m, 4H), 7.21 (t, $J = 7.3$ Hz, 1H), 4.61 (s, 1H), 3.97 (s, 3H), 1.51 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.62, 153.55, 147.90, 143.22, 136.07, 130.45, 130.45, 129.36, 129.20, 127.36, 126.72, 125.33, 124.13, 52.06, 51.99, 29.30. MS(ESI, m/z): 335.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{21}$H$_{23}$N$_2$O$_2$[M+H]$^+$ 335.1754, found 335.1755.

N-(tert-butyl)-3-(4-(trifluoromethyl)phenyl)quinolin-2-amine (3v)

White solid, 50 mg, 72% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J = 7.9$ Hz, 3H), 7.49 (m, 5H), 7.11 (t, $J = 7.3$ Hz, 1H), 4.46 (s, 1H), 1.42 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.48, 147.95, 142.32, 136.32, 129.62, 129.48, 127.48, 127.37, 126.77, 126.17, 126.14, 124.86, 122.98, 122.22, 52.04, 29.31. MS(ESI, m/z): 345.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{20}$H$_{20}$F$_3$N$_2$[M+H]$^+$ 345.1573, found 345.1577.

N-(tert-butyl)-3-(thiophen-3-yl)quinolin-2-amine (3w)

Yellow oil, 43 mg, 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.3$ Hz, 1H), 7.59 (s, 1H), 7.47 (m, 3H), 7.34 (s, 1H), 7.17 (d, $J = 4.2$ Hz, 1H), 7.09 (t, $J = 7.3$ Hz, 1H), 4.82 (s, 1H), 1.45 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.25, 147.66, 138.75, 139.71, 129.02, 128.15, 127.18, 126.84, 126.65, 125.97, 123.65, 123.09, 121.95, 119.82, 51.85, 29.33. MS(ESI, m/z): 283.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{17}$H$_{19}$F$_3$N$_2$S[M+H]$^+$ 283.1263, found 283.1265.

N-cyclohexyl-3-phenylquinolin-2-amine (3x)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.3$ Hz, 1H), 7.62 (s, 1H), 7.58-7.40 (m, 7H), 7.18 (t, $J = 7.3$ Hz, 1H), 4.68 (d, $J = 7.5$ Hz, 1H), 4.27-4.17 (m, 1H), 2.08 (m, $J = 12.1$ Hz, 2H), 1.47 (m, $J = 24.1$, 11.6 Hz, 3H), 1.28-1.12 (m, 5H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ 153.62, 147.53, 137.56, 136.56, 129.67, 129.56, 129.16, 128.57, 127.98, 125.85, 125.73, 123.46, 122.01, 49.05, 32.53, 25.81, 24.99. MS(ESI, m/z): 303.2[M+H]$^+$, HRMS (ESI): Exact mass calcd for C$_{21}$H$_{22}$N$_2$[M+H]$^+$ 303.4202, found 303.4202.
7-chloro-3-phenylquinolin-2-amine (4c)

![Structural formula of 7-chloro-3-phenylquinolin-2-amine (4c)](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.68 (d, $J$ = 1.7 Hz, 1H), 7.59-7.53 (m, 1H), 7.50 (d, $J$ = 4.1 Hz, 4H), 7.45 (dd, $J$ = 9.0, 4.7 Hz, 1H), 7.22 (dd, $J$ = 8.5, 2.0 Hz, 1H), 5.30 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 155.80, 146.96, 137.03, 136.82, 135.53, 129.24, 128.74, 128.58, 128.48, 125.19, 124.20, 123.65, 122.28. MS(ESI, m/z): 254.1[M+H]$^+$ HRMS (ESI): Exact mass calcd for C$_{17}$H$_{19}$N$_2$S [M+H]$^+$ 255.0684, found 255.0688.

3-bromo-N-tert-butylquinolin-2-amine (5)$^2$

![Structural formula of 3-bromo-N-tert-butylquinolin-2-amine (5)](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (s, 1H), 7.61 (d, $J$ = 8.3 Hz, 1H), 7.42 (dd, $J$ = 19.4, 7.7 Hz, 2H), 7.11 (d, $J$ = 7.4 Hz, 1H), 5.22 (s, 1H), 1.50 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.70, 146.80, 138.34, 132.25, 132.16, 129.46, 128.54, 128.42, 126.71, 126.38, 123.86, 122.41, 108.96, 52.31, 29.03. MS(ESI, m/z): 279.0[M+H]$^+$ HRMS (ESI): Exact mass calcd for C$_{13}$H$_{15}$BrN$_2$ [M+H]$^+$ 279.0491, found 279.0495.

4. References

5. Copies of NMR Spectra

3a
3k