Supporting Information

Aryne triggered dearomatization reaction of isoquinolines and quinolines with chloroform

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I. General Information

Unless stated otherwise, all reactions were carry out with distilled and dried solvents under an atmosphere of N\textsubscript{2}, oven (100 °C) dried glassware with standard vacuum line techniques were used. Organic solvents used for carrying out reactions were dry using standard methods. The reactions were monitored either by thin-layer chromatography on silica Gel 60-F254 coated 0.2mm plates (Yantai Chemical Industry Research Institute) or by GC-MS (Thermo Fisher Trace1300ISQ). Visualization was accomplished by UV light (254nm). The crude products were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical).

\textsuperscript{1} H NMR spectra was recorded on a 400 MHz spectrometer at ambient temperature. Data were report as follows: (1) chemical shift in parts per million (δ, ppm) from CDCl\textsubscript{3} (7.26 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintet and m = multiplet); (3) coupling constants (Hz). \textsuperscript{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were report in ppm from CDCl\textsubscript{3} (77.00 ppm). All commercial materials were use as received unless otherwise noted. Aryne precursors are all prepared following the literature procedures\textsuperscript{[1]}. Isoquinoline 2b, 2c, 2d, 2g, 2h, 2j, and quinoline 2n\textsuperscript{[5]} are prepared following the literature procedures. Compound 9 is prepared following the literature procedures\textsuperscript{[6]}. CsF was dried in vacuum at 130°C for 2h before use.

II. Substrates Preparation

Synthesis of 2f:

\[ \text{4-phenylisoquinoline (2f)} \]

4-Phenylisoquinoline 2f was prepared according to the modified literature procedure\textsuperscript{[3]}.

In an oven-dried round-bottom flask, 4-idoisoquinoline 2d (62mg, 0.25 mmol, 1.0 equiv.) was taken in a mixture of 0.25mL EtOH, 0.5 mL water and 1mL toluene and degassed for 20 min. To the resulting mixture, phenylboronic acid (50 mg, 0.375mmol, 1.5 equiv.), K\textsubscript{2}CO\textsubscript{3} (138mg, 1 mmol, 4.0 equiv.) and Pd(PPh\textsubscript{3})\textsubscript{4} (14mg, 0.0125 mmol, 0.05 equiv.) were added successively at r.t. The resulting mixture was stirred at 95°C under positive argon pressure for 24h. The reaction mixture was cooled to r.t. quenched.
with sat. NH₄Cl solution, extracted with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄, concentrated in vacuo to obtain a black oil which was purified by silica gel column chromatography (PE: EA = 5:1 as the eluent) to give 4-phenylisoquinoline 2f (95% yield) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 8.50 (s, 1H), 8.07 – 8.02 (m, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.56 – 7.44 (m, 5H).

Synthesis of (2g)

4-(p-tolyl)isoquinoline(2g)

Following the procedure of 2f, the crude product was purified by silica gel chromatography (PE: EA = 5:1 as the eluent) to give 2g (98% yield) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.23 (s, 1H), 8.48 (s, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.72 – 7.53 (m, 2H), 7.40 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H).
III. General procedure for the three-component reaction

1) Scope of Aryne:

General procedure: To a 10 mL flame-dried schlenk tube containing CsF (0.5 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added aryne precursor (1) (0.18 mmol), (iso)quinolone (2) (0.15 mmol), acetonitrile (0.4 ml) and chloroform (0.4 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours (general procedure A) or 24 hours (general procedure B). The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (20 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE:EA).

2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (4a)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4a (91% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J$ = 7.6 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.29 – 7.19 (m, 4H), 7.05 (t, $J$ = 7.2 Hz, 1H), 6.78 (dd, $J$ = 7.3, 1.2 Hz, 1H), 6.12 (d, $J$ = 7.3 Hz, 1H), 5.81 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.69, 133.14, 129.98, 129.25, 129.13, 129.12, 125.79, 124.19, 123.41, 122.55, 118.52, 108.75, 104.78, 74.54. HR-MS (ESI): Calcd for C$_{16}$H$_{13}$Cl$_3$N$^+$ [M+H$^+$] requires 324.0108; found 324.0106.

2-(3,4-dimethylphenyl)-1-(trichloromethyl) Naphthalene (4b)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4b (85% yield) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J$ = 7.5 Hz, 1H), 7.36 (dd, $J$ = 10.8, 4.1 Hz, 1H), 7.28 – 7.17 (m, 2H), 7.15 – 7.05 (m, 1H), 7.03 (s, 2H), 6.75 (dd, $J$ = 7.3, 1.0 Hz, 1H), 6.05 (d, $J$ = 7.3 Hz, 1H), 5.77 (s, 1H), 2.26 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.05, 137.55, 133.40, 131.12, 130.30, 130.07, 129.99, 129.05, 125.59, 124.07, 123.16, 120.51, 116.46, 107.74, 105.05, 75.01, 20.14, 18.91. HR-MS (ESI): Calcd for C$_{18}$H$_{17}$Cl$_3$N$^+$ [M+H$^+$] requires 352.0421; found 352.0417.
2-(naphthalen-2-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4c)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: DCM = 30:1 as the eluent) to give 4c (81% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.8$ Hz, 1H), 7.78 – 7.69 (m, 2H), 7.53 (dd, $J = 17.1$, 5.4 Hz, 3H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.37 (q, $J = 7.7$ Hz, 2H), 7.25 (dd, $J = 15.4$, 7.8 Hz, 2H), 6.90 (d, $J = 7.2$ Hz, 1H), 6.15 (d, $J = 7.3$ Hz, 1H), 5.96 (s, 1H). 13C NMR (100 MHz, CDCl$_3$) δ 144.46, 134.02, 133.27, 130.14, 129.75, 129.56, 129.26, 129.24, 127.52, 127.14, 126.74, 125.89, 124.66, 124.28, 123.42, 119.24, 115.34, 108.86, 104.84, 74.80. HR-MS (ESI): Calcd for C$_{20}$H$_{15}$Cl$_3$N$^+$ [M+H]$^+$ requires 374.0265; found 374.0261.

2-(3,4-difluorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4d)

Following the general procedure with 0.25mmol 4,5-difluoro-2-(trimethylsilyl)phenyltrifluoromethanesulfonate instead of 0.15 mmol, for 24h. The crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4d (90% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.3$ Hz, 1H), 7.30 (dt, $J = 8.2$, 6.0 Hz, 2H), 7.21 – 7.07 (m, 2H), 7.05 – 6.90 (m, 1H), 6.67 (d, $J = 7.5$ Hz, 1H), 6.20 (d, $J = 7.3$ Hz, 1H), 5.68 (s, 1H). 13C NMR (100 MHz, CDCl$_3$) δ 149.39 (dd, $J = 247.9$, 13.4 Hz), 145.20 (dd, $J = 244.5$, 12.8 Hz), 142.60 (d, $J = 7.6$ Hz), 131.75, 129.07, 128.37, 127.57, 125.23, 123.47, 122.31, 116.51 (d, $J = 18.0$ Hz), 113.22 (dd, $J = 5.3$, 3.2 Hz), 108.95, 107.23 (d, $J = 20.9$ Hz), 103.35, 74.00. HR-MS (ESI): Calcd for C$_{16}$H$_{11}$Cl$_3$F$_2$N$^+$ [M+H]$^+$ requires 359.9920; found 359.9917.

2-(benzo[d][1,3]dioxol-5-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4e)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4e (85% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 7.6$ Hz, 1H), 7.29 (td, $J = 7.5$, 1.2 Hz, 1H), 7.18 (dd, $J = 7.6$, 1.3 Hz, 1H), 7.14 (dd, $J = 11.5$, 4.4 Hz, 1H), 6.80 (d, $J = 2.3$ Hz, 1H), 6.70 – 6.65 (m, 1H), 6.55 (dd, $J = 7.3$, 1.3 Hz, 1H), 5.94 (d, $J = 7.5$ Hz, 1H), 5.85 (t, $J = 4.8$ Hz, 2H), 5.58 (d, $J = 1.0$ Hz, 1H). 13C NMR (100 MHz, CDCl$_3$) δ 148.33, 143.74, 142.59, 133.32, 130.78, 130.19, 129.15, 125.66, 124.10, 122.78, 113.32, 108.28, 107.56, 104.87, 102.52, 101.38, 76.08. HR-MS (ESI): Calcd for C$_{17}$H$_{13}$Cl$_3$O$_2$N$^+$ [M+H]$^+$ requires 368.0006; found 368.0002.

3-(naphthalen-2-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4f) and 2-(naphthalen-1-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4f')

Following the general procedure A, the crude product was
purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4f and 4f’ (4:1, 85% yield) as a black solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J = 9.0$ Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 4H), 7.78 – 7.70 (m, 8H), 7.62 – 7.47 (m, 14H), 7.43 (dd, $J = 15.5$, 7.5 Hz, 6H), 7.41 – 7.32 (m, 8H), 7.32 – 7.12 (m, 12H), 6.90 (d, $J = 7.3$ Hz, 4H) (major), 6.72 (d, $J = 7.4$ Hz, 1H), 6.15 (d, $J = 7.3$ Hz, 4H) (major), 5.96 (s, 4H) (major), 5.80 (d, $J = 7.2$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.46 (major), 134.14, 134.02 (major), 133.27 (major), 131.11, 130.14 (major), 129.74, 129.56 (major), 129.41, 129.26 (major), 129.24 (major), 127.52 (major), 127.14 (major), 126.74 (major), 126.26, 125.89 (major), 125.23, 124.66 (major), 124.28 (major), 124.03, 123.42 (major), 119.24 (major), 115.34 (major), 108.86 (major), 104.84 (major), 102.96, 74.79 (major).

HR-MS (ESI): Calcd for C$_{20}$H$_{15}$Cl$_3$N$^+$ [M+H$^+$] requires 374.0265; found 374.0261.

2-(4-methoxyphenyl)-1-(trichloromethyl)-1, 2-dihydroisoquinoline (4g) and 3-(4-methoxyphenyl) -1-(trichloromethyl)-1, 2-dihydroisoquinoline (4g’)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4g and 4g’ (1:1.15, 97% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (t, $J = 7.3$ Hz, 2H), 7.36 (ddd, $J = 7.5$, 2.3, 1.2 Hz, 2H), 7.31 – 7.14 (m, 7H), 6.94 – 6.82 (m, 3H), 6.80 (t, $J = 2.3$ Hz, 1H), 6.76 (dd, $J = 7.3$, 1.1 Hz, 1H), 6.68 (dd, $J = 7.3$, 1.0 Hz, 1H), 6.60 (dd, $J = 8.2$, 2.1 Hz, 1H), 6.12 (d, $J = 7.3$ Hz, 1H), 6.01 (d, $J = 7.3$ Hz, 1H) (major), 5.79 (s, 1H), 5.70 (s, 1H) (major), 3.81 (s, 3H), 3.78 (s, 3H) (major). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.49, 155.73, 148.03, 141.08, 133.45, 133.12, 130.82, 130.19, 129.98, 129.15, 129.09, 128.98, 125.88, 125.52, 124.26, 124.01, 123.63, 122.68, 121.44, 114.52, 110.96, 109.09, 107.39, 107.06, 105.14, 105.05, 102.69, 75.81 (major), 74.57, 55.54 (major), 55.34. HR-MS (ESI): Calcd for C$_{17}$H$_{14}$Cl$_3$NO$^+$ [M+H$^+$] requires 354.0141; found 354.0211.

2-(3-fluorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4h) and 2-(4-fluorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4h’)

Following the general procedure A, the crude product with 0.25 mmol 4-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate instead of 0.15 mmol, for 24h. The crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4h and 4h’ (1:2.5, 88% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (t, $J = 7.6$ Hz, 4H), 7.41 – 7.34 (m, 4H), 7.30 – 7.25 (m, 4H), 7.25 - 7.20 (m, $J = 6.9$, 5.2, 2.5 Hz, 9H), 7.07 – 6.99
(m, 6H), 6.96 (dt, J = 11.5, 2.3 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.67 (dd, J = 7.3, 1.3 Hz, 2H), 6.17 (d, J = 7.3 Hz, 1H), 6.08 (d, J = 7.3 Hz, 2H) (major), 5.74 (d, J = 1.0 Hz, 1H), 5.70 (d, J = 1.0 Hz, 2H) (major). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.43 (d, J = 245.2 Hz), 157.76 (d, J = 242.9 Hz) (major), 147.17 (d, J = 10.0 Hz), 142.44 (d, J = 2.6 Hz) (major), 132.12 (major), 131.82, 129.35 (d, J = 9.7 Hz), 129.12 (major), 128.99, 128.85 (major), 128.29, 128.23 (major), 127.12, 125.18, 124.85 (major), 123.47, 123.21 (major), 122.78, 121.98, 119.93 (d, J = 8.0 Hz) (major), 114.93 (d, J = 22.6 Hz) (major), 112.44 (d, J = 2.6 Hz), 109.14, 108.05 (d, J = 21.4 Hz), 107.37 (major), 104.57, 104.32, 103.79, 74.41 (major), 73.28. HR-MS (ESI): Calcd for C$_{16}$H$_{11}$Cl$_3$FN$^+$ [M+H]$^+$ requires 342.0014; found 342.0010.

**2-(p-tolyl)-1-(trichloromethyl)-1, 2-dihydroisoquinoline (4i) and 2-(m-tolyl)-1-(trichloromethyl)-1, 2-dihydroisoquinoline (4i')**

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4i and 4i’ (1:1.5, 93% yield) as a pale yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.34 (m, 3H), 7.33 – 7.25 (m, 3H), 7.22 – 7.08 (m, 7H), 6.85 – 6.74 (m, 4H), 6.73 (s, 2H), 6.68 (dd, J = 7.3, 1.0 Hz, 1H), 6.60 (dd, J = 7.3, 0.9 Hz, 1H), 6.52 (dd, J = 8.2, 2.2 Hz, 1H), 6.04 (d, J = 7.3 Hz, 1H) (major), 5.94 (d, J = 7.3 Hz, 1H), 5.71 (s, 1H) (major), 5.63 (s, 1H), 3.73 (s, 4H), 3.70 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.85 (major), 144.68, 139.18 (major), 133.34, 133.25 (major), 132.30, 130.05 (major), 130.02, 129.82 (major), 129.78, 129.43, 129.09 (major), 125.75 (major), 125.64, 124.17 (major), 124.10, 123.49 (major), 123.43, 123.17, 119.46, 118.96 (major), 115.78, 108.53 (major), 107.91, 104.98, 104.87 (major), 74.95, 74.66 (major), 21.68 (major), 20.56 HR-MS (ESI): Calcd for C$_{17}$H$_{11}$Cl$_3$FN$^+$ [M+H]$^+$ requires 338.0265; found 338.0262.

**2-(3-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4j) and 2-(2-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4j')**

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 4j and 4j’ (13:1, 89% yield) as a yellow solid.

For major isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, J = 7.7 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.28 – 7.23 (m, 1H), 7.23 – 7.18 (m, 2H), 6.86 (dd, J = 8.2, 2.1 Hz, 1H), 6.80 (t, J = 2.3 Hz, 1H), 6.75 (dd, J = 7.3, 1.1 Hz, 1H), 6.59 (dd, J = 8.2, 2.1 Hz, 1H), 6.11 (d, J = 7.3 Hz, 1H), 5.79 (s, 1H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.49, 148.02, 133.11, 129.98, 129.14, 128.97, 125.88, 124.26, 123.62, 110.96, 109.08, 107.39, 105.14, 104.69, 74.56, 55.33. HR-MS (ESI):
Calcd for C$_{17}$H$_{14}$Cl$_3$NO$^+$ [M+H]$^+$ requires 354.0141; found 354.0210.

2) Scope of (Iso)quinolines:

5-nitro-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5b)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5b (76% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (dd, $J$ = 8.3, 1.1 Hz, 1H), 7.69 (dd, $J$ = 19.6, 4.6 Hz, 1H), 7.41 - 7.37 (m, $J$ = 4.0, 2.0 Hz, 2H), 7.35 - 7.30 (m, $J$ = 8.6, 7.9 Hz, 3H), 7.14 (t, $J$ = 7.3 Hz, 1H), 7.04 (dd, $J$ = 7.8, 1.5 Hz, 1H), 6.87 (d, $J$ = 7.8 Hz, 1H), 5.89 (d, $J$ = 1.3 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.06, 143.68, 135.58, 134.45, 129.65, 128.49, 126.27, 125.04, 124.99, 124.10, 119.69, 103.73, 102.42, 74.73. HR-MS (ESI): Calcd for C$_{16}$H$_{12}$Cl$_3$N$_2$O$_2^+$ [M+H]$^+$ requires 368.9959; found 368.9959.

5-bromo-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5c)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5c (70% yield) as a pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (dd, $J$ = 8.0, 0.9 Hz, 1H), 7.40 (t, $J$ = 8.1 Hz, 1H), 7.36 (dd, $J$ = 8.6, 7.4 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.09 (q, $J$ = 7.7 Hz, 2H), 6.88 (dd, $J$ = 7.5, 1.4 Hz, 1H), 6.44 (d, $J$ = 7.5 Hz, 1H), 5.78 (d, $J$ = 1.0 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.26, 133.22, 132.73, 130.96, 129.39, 126.50, 124.84, 123.14, 119.75, 118.90, 107.44, 104.29, 74.66. HR-MS (ESI): Calcd for C$_{16}$H$_{11}$BrCl$_3$N$^+$ [M+H]$^+$ requires 401.9213; found 401.9214.

4-iodo-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5d)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5d (96% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J$ = 7.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.40 – 7.30 (m, 4H), 7.27 – 7.24 (m, 2H), 7.19 (d, $J$ = 1.2 Hz, 1H), 7.09 (t, $J$ = 7.3 Hz, 1H), 5.75 (d, $J$ = 8.1 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.47, 140.42, 129.32, 129.25, 128.57, 126.50, 125.09, 124.97, 122.60, 119.61, 103.81, 74.91. HR-MS (ESI): Calcd for C$_{16}$H$_{11}$ICl$_3$N$^+$ [M+H]$^+$ requires 449.9075; found 449.9073.
5,8-dibromo-2-phenyl-1-(trichloromethyl)-1,2-dihydronaphthalene (5e)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5e (94% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 8.5$ Hz, 1H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.34 – 7.27 (m, 3H), 7.12 (t, $J = 7.3$ Hz, 1H), 6.92 (dd, $J = 7.5, 1.2$ Hz, 1H), 6.46 (d, $J = 1.2$ Hz, 1H), 6.36 (d, $J = 7.5$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.01, 135.02, 133.90, 132.38, 130.88, 129.64, 123.84, 122.72, 119.80, 119.79, 118.42, 106.64, 103.98, 73.38. HR-MS (ESI): Calcd for C$_{16}$H$_{11}$Br$_2$Cl$_3$N + [M+H]$^+$ requires 481.8298; found 481.8293.

1,4-diphenyl-2-(trichloromethyl)-1,2-dihydroisoquinoline (5f)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5f (92% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (dd, $J = 10.8, 4.9$ Hz, 1H), 7.49 – 7.40 (m, 4H), 7.39 – 7.26 (m, 8H), 7.08 – 7.02 (m, 1H), 6.84 (d, $J = 1.4$ Hz, 1H), 5.85 (d, $J = 1.0$ Hz, 1H).$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.12, 137.52, 133.70, 130.17, 129.31, 128.95, 128.91, 128.68, 127.18, 126.80, 126.40, 124.55, 123.63, 123.11, 122.40, 117.98, 103.93, 74.34. HR-MS (ESI): Calcd for C$_{22}$H$_{16}$Cl$_3$N $^+ [M+H]^+$ requires 440.0421; found 440.0423.

2-phenyl-4-(p-tolyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5g)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5g (79% yield) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.47 (m, 1H), 7.36 (dt, $J = 6.9, 5.5$ Hz, 4H), 7.32 – 7.29 (m, 4H), 7.24 (dd, $J = 13.3, 5.4$ Hz, 3H), 7.03 (dd, $J = 9.9, 4.2$ Hz, 1H), 6.80 (d, $J = 1.4$ Hz, 1H), 5.83 (d, $J = 1.2$ Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.13, 136.90, 134.53, 133.82, 130.13, 129.37, 129.28, 128.90, 128.78, 126.43, 126.34, 124.59, 123.70, 123.11, 122.28, 117.86, 103.95, 74.32, 21.21 HR-MS (ESI): Calcd for C$_{23}$H$_{19}$Cl$_3$N$^+ [M+H]$^+$ requires 414.0578; found 417.0572.

6,7-dimethoxy-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5h)

Following the general procedure A, reacted for 1h. the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5h (90% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (t, $J = 7.9$ Hz, 2H), 7.26 (s, 1H), 7.04 (t, $J = 7.2$ Hz, 2H), 6.99 (s, 1H), 6.73 (s, 1H), 6.69 (dd, $J = 7.3, 1.0$ Hz, 1H), 6.06 (d, $J = 7.3$ Hz, 1H), 5.74 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.86, 147.47, 146.88, 129.29, 127.63, 126.90, 122.45, 118.40, 115.83, 113.28, 108.80, 106.91, 105.34, 77.36, 56.22, 55.89. HR-MS (ESI): Calcd for C$_{18}$H$_{17}$Cl$_3$NO$_2$ $^+ [M+H]^+$ requires 384.0319; found 384.0315.
5-phenyl-6-(trichloromethyl)-5,6-dihydrophenanthridine (5i)

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5i (46% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.8$ Hz, 1H), 7.88 (dd, $J = 7.8$, 1.1 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.37 – 7.29 (m, 4H), 7.29 – 7.19 (m, 3H), 7.19 – 7.12 (m, 1H), 6.98 (t, $J = 7.2$ Hz, 1H), 5.53 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.97, 139.21, 132.45, 130.55, 129.38, 129.07, 128.69, 128.36, 128.33, 126.90, 124.33, 123.46, 123.42, 123.14, 122.62, 120.47, 103.86, 76.67. HR-MS (ESI): Calcd for C$_{20}$H$_{15}$Cl$_3$N$^+$ [M+H]$^+$ requires 374.0265; found 374.0263.

1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5j)

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5j (95% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 7.6$ Hz, 2H), 7.31 (dd, $J = 10.6$, 5.2 Hz, 2H), 7.18 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.02 (d, $J = 8.1$ Hz, 1H), 6.98 – 6.91 (m, 2H), 6.15 (dd, $J = 9.5$, 5.9 Hz, 1H), 4.99 (d, $J = 5.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.90, 141.79, 130.27, 129.18, 128.73, 127.04, 125.36, 124.81, 124.66, 121.68, 121.42, 118.35, 104.16, 75.00. HR-MS (ESI): Calcd for C$_{16}$H$_{13}$Cl$_3$N$^+$ [M+H]$^+$ requires 324.0108; found 324.0108.

4-methyl-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5k)

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give 5k (40% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.18 – 7.12 (m, 1H), 7.12 – 7.09 (m, 1H), 7.06 (dd, $J = 8.1$, 1.1 Hz, 1H), 6.99 (td, $J = 7.5$, 1.2 Hz, 1H), 5.99 (dd, $J = 6.1$, 1.3 Hz, 1H), 4.92 (d, $J = 6.0$ Hz, 1H), 2.25 (s, 3H). $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 149.97, 141.44, 135.81, 129.14, 128.43, 127.32, 124.17, 123.87, 123.78, 122.18, 121.76, 115.82, 104.54, 74.84, 18.96. HR-MS (ESI): Calcd for C$_{17}$H$_{15}$Cl$_3$N$^+$ [M+H]$^+$ requires 338.0265; found 338.0263.

8-methoxy-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5l)

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give 5l (48% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.14 (ddd, $J = 8.9$, 5.4, 1.9 Hz, 2H), 7.10 – 7.05 (m, 2H), 6.99 (ddd, $J = 8.5$, 2.3, 1.1 Hz, 1H), 6.93 (ddd, $J = 6.9$, 2.5, 1.2 Hz, 1H), 6.87 (d, $J = 9.5$ Hz, 1H), 6.82 (dd, $J$
= 7.5, 1.2 Hz, 1H), 6.76 (dd, J = 8.1, 1.2 Hz, 1H), 6.09 (ddd, J = 9.3, 6.0, 1.3 Hz, 1H), 4.88 – 4.84 (m, 1H), 3.54(s, 3H). 13C NMR (100 MHz, CDCl3) δ 152.78, 149.66, 129.98, 129.39, 128.62, 128.57, 123.95, 122.79, 120.16, 119.97, 119.60, 113.69, 103.30, 75.08, 56.51. HR-MS (ESI): Calcd for C17H15OCl3N+ [M+H]+ requires 354.0214; found 354.0214.

6-chloro-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5m)
Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give 5m (86% yield) as a yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.31 – 7.26 (m, 2H), 7.26 – 7.19 (m, 2H), 7.11 – 7.04 (m, 2H), 6.98 (dd, J = 8.7, 2.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 1H), 6.10 (dd, J = 9.6, 5.9 Hz, 1H), 4.90 (dd, J = 5.9 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 152.78, 149.66, 129.98, 129.39, 128.62, 128.57, 123.95, 122.79, 120.16, 119.97, 119.60, 113.69, 103.30, 75.08, 56.51. HR-MS (ESI): Calcd for C17H15OCl3N+ [M+H]+ requires 354.0214; found 354.0214.

6-bromo-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5n)
Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give 5n (86% yield) as a yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.33 – 7.27 (m, 3H), 7.19 – 7.12 (m, 2H), 6.88 (dd, J = 3.9 Hz, 1H), 6.86 (d, J = 2.9 Hz, 1H), 6.16 (dd, J = 9.6, 5.9 Hz, 1H), 4.98 (d, J = 5.9 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 152.78, 149.66, 129.98, 129.39, 128.62, 128.57, 123.95, 122.79, 120.16, 119.97, 119.60, 113.69, 103.30, 75.08, 56.51. HR-MS (ESI): Calcd for C16H12Cl4BrN+ [M+H]+ requires 401.9213; found 401.9215.

8-phenoxy-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5o)
Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give 5o (70% yield) as a yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.26 – 7.22 (m, 3H), 7.16 – 7.11 (m, 4H), 7.11 – 7.05 (m, 3H), 7.04 – 7.00 (m, 1H), 6.98 – 6.93 (m, 2H), 6.54 (dd, J = 8.6, 0.9 Hz, 2H), 6.17 (dd, J = 9.5, 5.9 Hz, 1H), 4.76 (dd, J = 6.0, 0.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 157.59, 149.51, 148.20, 132.94, 129.85, 129.77, 129.33, 129.15, 128.69, 123.70, 122.91, 122.34, 122.24, 121.59, 120.13, 117.24, 102.95, 75.46. HR-MS (ESI): Calcd for C22H17Cl3NO+ [M+H]+ requires 416.0370; found 416.0373.

2-methyl-5-nitro-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5p)
Following the general procedure B, reacted for 24h, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give 5p (46% yield) as a yellow liquid.
1H NMR (400 MHz, DMSO) 1H NMR (400 MHz, DMSO) δ 8.15 (d, J = 2.7 Hz, 1H), 7.86 (dd, J = 9.2, 4.5 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 7.20 – 7.15 (m, 2H), 6.21 – 6.07 (m, 2H), 1.65 (s, 3H). 13C NMR (100 MHz, DMSO) 13C NMR (100 MHz, DMSO) δ 150.80, 140.72, 138.51, 133.79, 131.56, 130.18, 128.80, 127.02, 125.64, 124.68, 122.99, 115.37, 72.05, 40.15, 39.94, 39.73, 39.53, 39.32, 39.11, 38.90, 24.60. HR-MS (ESI): Calcd for C17H14Cl3N2O2+ [M+H]+ requires 383.0115; found 383.0109.

1-phenyl-2-(trichloromethyl)-1,2-dihydro-1,10-phenanthroline (5q)

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give 5q (43% yield) as a yellow solid. 1H NMR (400 MHz, CDCl3) δ 8.68 (d, J = 2.6 Hz, 1H), 8.03 (dd, J = 8.2, 1.2 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.20 – 7.09 (m, 5H), 6.98 (t, J = 6.7 Hz, 1H), 6.31 (dd, J = 9.3, 6.0 Hz, 1H), 5.13 (d, J = 6.0 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 151.18, 149.46, 142.74, 136.51, 135.84, 129.88, 129.20, 128.72, 127.59, 125.26, 123.24, 122.85, 121.04, 120.90, 120.78, 103.16, 75.57. HR-MS (ESI): Calcd for C19H12Cl3N2+ [M+H]+ requires 357.0217; found 357.0213.

3) Substrate Scope with CDCl3

General procedure C: To a 10 mL flame-dried schlenk tube containing CsF (0.5 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added aryn precursor (1) (0.18 mmol), (iso)quinoline (0.15 mmol), acetonitrile (0.4 ml) and deuterated chloroform (0.4 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours. The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (20 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA). Percentage of exchanged protons at the specified position are determined by 1H NMR.

2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5a-D1)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5a-D1 (73% yield) as a white solid. 1H NMR (400 MHz, CDCl3) δ 7.46 (t, J = 7.9 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.29 – 7.20 (m, 3H), 7.04 (tt, J = 7.8, 3.9 Hz, 1H), 6.78 (dd, J = 7.3, 1.3 Hz, 1H), 6.12 (d, J = 7.3 Hz, 1H), 5.81 (d, J = 1.1 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 146.75, 133.25, 130.07, 129.33, 129.22(three carbon), 125.88, 124.28, 123.54, 122.62, 118.60, δ 118.21 (m).108.86, 104.86, 74.66. HR-MS (ESI): Calcd for C16H12DCl3N2+[M+H]+ requires 325.0171; found 325.0168.

5-bromo-2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5c-D1)
Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5c-D₁ (90% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 7.9 Hz, 1H), 7.40 (t, J = 8.1 Hz, 1H), 7.33 (dd, J = 16.2, 14.4 Hz, 2H), 7.29 – 7.20 (m, 1H), 7.09 (q, J = 7.7 Hz, 2H), 6.88 (dd, J = 7.5, 1.0 Hz, 1H), 6.44 (d, J = 7.5 Hz, 1H), 5.78 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 146.20, 133.22, 132.72, 130.94, 129.39, 129.39, 129.28, 126.50, 124.84, 123.12, 119.75, 118.86, 118.48 (m), 107.45, 104.30, 74.66.

4-iodo-2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5d-D₁)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5d-D₁ (79% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.39 – 7.29 (m, 4H), 7.24 (d, J = 6.8 Hz, 1H), 7.19 (d, J = 0.9 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 5.76 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.42, 135.41, 133.21, 130.02, 129.83, 129.45, 129.35, 128.22, 127.36, 124.22, 123.35, 118.56, 118.40 (m), 103.74, 76.55, 74.82.

5,8-dibromo-2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5e-D₁)

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5e-D₁ (74% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.5 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 (dd, J = 12.3, 8.4 Hz, 2H), 7.12 (dd, J = 14.8, 7.5 Hz, 1H), 6.93 (dd, J = 7.5, 0.8 Hz, 1H), 6.45 (d, J = 0.8 Hz, 1H), 6.36 (d, J = 7.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.95, 135.02, 133.91, 132.36, 130.89, 129.64, 129.54, 123.83, 122.73, 119.79, 119.75, 119.36 (m), 118.43, 106.67, 103.98, 73.38.

1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline (5j-D₁)

Following the general procedure C, reacted for 24h. The crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5j-D₁ (90% yield) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.19 – 7.16 (m, 1H), 7.15 – 7.08 (m, 2H), 7.02 (d, J = 8.1 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.13 (dd, J = 9.5, 5.9 Hz, 1H), 4.99 (d, J = 5.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.87, 141.80, 130.31, 129.24, 129.13, 128.78, 127.10, 125.41, 124.59 (m), 124.76, 124.68, 121.75, 121.49, 118.42, 104.21, 75.02.

4-methyl-1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline (5k-D₁)
Following the general procedure C, reacted for 24h. The crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give $5k$-$D_1$ (40% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 (dd, $J = 7.3, 1.0$ Hz, 1H), 7.13 – 7.09 (m, 1H), 7.07 – 7.00 (m, 1H), 6.01 (dd, $J = 6.1, 1.1$ Hz, 1H), 4.96 (d, $J = 5.9$ Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.94, 141.37, 135.77, 129.09, 128.98, 128.39(m), 127.29, 124.10, 123.74, 122.15, 121.73, 115.79, 104.53, 18.93.

6-chloro-1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline ($5m$-$D_1$)

Following the general procedure C, reacted for 24h the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give $5m$-$D_1$ (86% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H), 7.21 – 7.12 (m, 2H), 6.91 (dd, $J = 17.3, 9.1$ Hz, 2H), 6.18 (dd, $J = 9.6, 5.9$ Hz, 1H), 4.98 (d, $J = 5.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.40, 140.40, 129.31, 129.24, 129.20, 128.56, 126.49, 126.46, 125.06, 124.90(m), 122.60, 119.61, 103.80, 74.90.

6-bromo-1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline ($5n$-$D_1$)

Following the general procedure C, reacted for 24h the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give $5n$-$D_1$ (86% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.34 (m, 1H), 7.34 – 7.27 (m, 3H), 7.21 – 7.12 (m, 2H), 6.87 (dd, $J = 9.1, 3.5$ Hz, 2H), 6.17 (dd, $J = 9.6, 5.9$ Hz, 1H), 4.98 (d, $J = 5.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.35, 141.05, 131.50, 129.52, 129.40, 129.23, 126.97, 125.26, 125.19(m), 122.88, 119.60, 113.90, 103.90, 74.96.

1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydro-1,10-phenanthroline ($5q$-$D_1$)

Following the general procedure C, reacted for 24h the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give $5q$-$D_1$ (43% yield) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.04 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.43 (d, $J = 8.3$ Hz, 1H), 7.27 – 7.23 (m, 1H), 7.19 – 7.10 (m, 1H), 6.32 (dd, $J = 9.3, 6.0$ Hz, 1H), 5.05 (dd, $J = 63.4, 8.5$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.16, 149.50, 142.79, 136.54, 135.86, 129.91, 129.24, 128.74, 128.64, 127.62, 125.28, 123.29, 122.86, 121.05, 121.03, 120.94, 120.81, 75.61.
4) Reaction of benzyne precursor 1a, Isoquinoline 2a, and Nucleophile

General procedure D: To a 10 mL flame-dried schlenk tube containing CsF (0.5 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added 1a (0.18 mmol), isoquinoline (0.15 mmol), acetonitrile (0.4 ml) and nucleophile (0.4 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours (general procedure A) or 24 hours (general procedure B). The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (20 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE:EA).

1-(dibromomethyl)-2-phenyl-1,2-dihydroisoquinoline (7)

Following the procedure D, using dibromomethane as nucleophile, the crude product was further purified by silica gel flash chromatography (PE: EA = 200:1 as the eluent) to give 5f (52% yield) as a maroon solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.27 (m, 4H), 7.16 - 7.19 (m, 4H), 7.02 (t, \(J = 7.3\) Hz, 1H), 6.66 (dd, \(J = 7.2, 1.5\) Hz, 1H), 6.07 (d, \(J = 7.3\) Hz, 1H), 5.69 (d, \(J = 8.3\) Hz, 1H), 5.49 (dd, \(J = 8.3, 1.3\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.96, 131.08, 129.32, 129.22, 128.66, 127.50, 125.77, 125.18, 123.96, 122.09, 117.53, 107.25, 67.27, 49.12. HR-MS (ESI): Calcd for C\(_{16}\)H\(_{13}\)Br\(_2\)N\(^+\) [M+H]\(^+\) requires 378.9467; found 379.9463.

1-(dichloromethyl)-2-phenyl-1,2-dihydroisoquinolin (8)

Following the procedure D, using dichloromethane as nucleophile, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 8 (50% yield) as a yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.27 (m, 4H), 7.23 – 7.13 (m, 4H), 7.08 – 6.92 (m, 1H), 6.66 (dd, \(J = 7.3, 1.5\) Hz, 1H), 6.07 (d, \(J = 7.3\) Hz, 1H), 5.77 (d, \(J = 8.1\) Hz, 1H), 5.35 (dd, \(J = 8.1, 1.3\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.13, 131.35, 129.27, 129.11, 128.75, 127.84, 125.87, 125.07, 123.85, 122.13, 117.63, 107.13, 73.17, 67.34. Calcd for C\(_{16}\)H\(_{13}\)Cl\(_2\)N\(^+\) [M+H]\(^+\) requires 290.0498; found 290.0494.

5) Synthetic Applications

2-phenylisoquinolin-1(2H)-one (10)
To stirred a suspension of 4a (0.0323g, 0.1mmol) in MeOH (1.5ml), a solution of KOH (0.023g, 5equiv.) in MeOH (2ml) was cautiously added over a period of 30min. The reaction mixture was heated at 90°C for 24h with intensive stirring. Cooled to room temperature. The reaction mixture was then treated with water (10 mL), extracted, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give 10 (yield=62%) as a purple liquid. 1H NMR (400 MHz, CDCl3) δ 8.48 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.59 – 7.47 (m, 4H), 7.47 – 7.38 (m, 3H), 7.19 (d, J = 7.4 Hz, 1H), 6.57 (d, J = 7.4 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 162.01, 141.38, 137.06, 132.53, 132.16, 129.26, 128.28, 128.06, 127.14, 126.84, 126.58, 125.92, 106.16.

6) Gram-scale reaction

To a 50 mL flame-dried schlenk tube containing CsF (10 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added 1a (3.6 mmol), isoquinoline (3 mmol), acetonitrile (8 ml) and chloroform (8 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours (general procedure A) or 24 hours (general procedure B). The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (40 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA =200: 1 as the eluent) to give 4a (0.8772g, 89%) as a white solid.
IV. Spectrum
Reference:


