Supporting Information

Sc(OTf)₃-Catalyzed Cascade Reaction of 
{o-Aminoacetophenone with Methanamine: Construction of 
Dibenzo[b,h][1,6]naphthyridine Derivatives 

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General information

General Information. $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. Samples for IR were prepared as a thin film on a KBr plate. High Resolution Mass spectra (HRMS) were recorded on Micromass GCT with Electron Ionization (EI) resource. All reagents were obtained from commercial sources without further purification.
The detection of the intermediates

In order to explore the mechanism, we tried to capture the intermediates in the reaction mixture through atmospheric solids analysis probe (ASAP). Here we presented the spectra when the reaction had proceeded for 1 h.

Reaction condition: o-aminoacetophenone (1.25 mmol), benzylamine (0.5 mmol) and 5 mol% of Sc(OTf)$_3$ were added in a sealed tube, stirred in air atmosphere at 90 °C under solvent-free conditions for 1 h.

For the first proposed process (Scheme 4), we succeeded in detecting the masses of byproduct 4a or 5a (221.149 [M+1]), intermediates a (224.180 [M]), b or c (341.322 [M]), d (340.328 [M]), e, f or g (340.328 [M+1]) h (223.162 [M]) and the product 1a (322.257 [M]). As far as the second proposed mechanism (Scheme 6), the masses of intermediates l or m (340.328 [M]), j, k or 7 (223.162 [M]) and product 1a (322.257 [M]) were detected by ASAP.
General procedure for synthesis of 1a-p

To a mixture of o-aminoacetophenones (1.25 mmol) and methanamines (0.5 mmol) was added Sc(OTf)$_3$ (5 mol%). After being stirred at 90 °C in air atmosphere for 12 h, the mixture was extracted by CH$_2$Cl$_2$ and H$_2$O. The organic layer was dried with Na$_2$SO$_4$, and then concentrated in vacuo. The products 1a-p were obtained by column chromatography on silica gel with 5-10% ethyl acetate in petroleum ether as eluted.

Synthesis of compound 5

To a mixture of o-aminoacetophenones (1.25 mmol) and methanamines (0.5 mmol) was added Sc(OTf)$_3$ (5 mol%). After being stirred at 90 °C in O$_2$ atmosphere for 12 h, the mixture was extracted by CH$_2$Cl$_2$ and H$_2$O. The organic layer was dried with Na$_2$SO$_4$, and then concentrated in vacuo. The products 5 and 1 were obtained by column chromatography on silica gel with 2-10% ethyl acetate in petroleum ether as eluted.
The data of all products

7-Methyl-6-phenyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1a). Yellow power; 112.8 mg, 70% yield; mp: 232-234 °C; IR (KBr) ν 3886, 3282, 3059, 3013, 2913, 1607, 1582, 1505, 1489, 763, 749, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.57 (dd, J = 1.4 Hz, J = 7.8 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.70-7.66 (m, 1H), 7.49-7.45 (m, 1H), 7.21-7.15 (m, 6H), 6.93-6.89 (m, 1H), 6.53 (d, J = 7.6 Hz, 1H), 5.91 (s, 1H), 4.49 (br, 1H), 2.48 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 149.5, 147.5, 144.7, 143.2, 140.0, 131.1, 130.0, 128.9, 128.8, 127.6, 127.5, 126.5, 126.4, 125.9, 125.5, 123.6, 121.4, 119.1, 115.0, 56.8, 13.7. HRMS (EI) (m/z) calculated for C\(_{23}\)H\(_{18}\)N\(_2\) 322.1470, found 322.1471.

7-Methyl-6-(p-tolyl)-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1b). Yellow power; 131.2 mg, 78% yield; mp: 221-223 °C; IR (KBr) ν 3361, 3063, 3021, 2922, 2855, 1606, 1582, 1506, 1304, 1147, 757, 743 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.54 (dd, J = 1.2 Hz, J = 7.6 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.18-7.14 (m, 1H), 7.07-6.99 (m, 4H), 6.90 (t, J = 7.6 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 5.89 (s, 1H), 4.46 (br, 1H), 2.49 (s, 3H), 2.24 (s, 3H); \(^13\)C NMR (100 MHz, DMSO): δ 149.9, 147.2, 146.8, 141.2, 140.3, 136.8, 131.7, 129.8, 129.6, 129.4, 127.5, 127.1, 127.0, 126.0, 125.7, 124.7, 120.5, 117.5, 115.5, 54.7, 21.0, 14.0. HRMS (EI) (m/z) calculated for C\(_{24}\)H\(_{20}\)N\(_2\) 336.1626, found 336.1628.

6-(4-(Tert-butyl)phenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1c). Yellow power; 151.4 mg, 80% yield; mp: 236-241 °C IR (KBr) ν 3415, 3287, 3071, 3029, 2955, 2859, 2358, 2333 1608, 1585, 1507, 1489, 744 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.56 (dd, J = 1.2 Hz, J = 8.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.48-7.43 (m, 1H), 7.21-7.10 (m, 5H), 6.92-6.89 (m, 1H), 6.54 (d, J = 7.6 Hz, 1H), 5.89 (s, 1H), 4.49 (br,
1H), 2.50 (s, 3H), 1.22 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 149.5, 147.4, 144.9, 140.4, 140.0, 131.1, 130.0, 128.8, 127.5, 126.7, 126.1, 125.9, 125.6, 125.5, 123.6, 121.3, 118.9, 115.1, 56.5, 34.3, 31.1, 13.7. HRMS (EI) (m/z) calculated for C$_{27}$H$_{26}$N$_2$ 378.2096, found 378.2097.

6-(4-Chlorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1d). Yellow power; 128.5 mg, 72% yield; mp: 236-238 °C; IR (KBr) $\nu$ 3427, 3067, 2926, 1608, 1586, 1488, 1089, 1013, 762 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.54 (dd, $J = 1.2$ Hz, $J = 7.6$ Hz, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.70-7.66 (m, 1H), 7.53-7.46 (m, 1H), 7.20-7.15 (m, 3H), 7.11-7.09 (m, 2H), 6.94-6.90 (m, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 5.90 (s, 1H), 4.46 (br, 1H), 2.49 (s, 3H); $^{13}$C NMR (100 MHz, DMSO): $\delta$ 149.7, 146.5, 142.9, 140.6, 132.3, 131.8, 129.8, 129.7, 129.0, 128.9, 128.7, 126.6, 126.1, 125.8, 124.8, 120.4, 117.8, 115.5, 54.2, 14.0. HRMS (EI) (m/z) calculated for C$_{23}$H$_{17}$ClN$_2$ 356.1080, found 356.1081.

6-(4-Fluorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1e). Yellow power; 129.3 mg, 76% yield; mp: 210-211 °C; IR (KBr) $\nu$ 3295, 3075, 3029, 2918, 1605, 1506, 1229, 746 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.54 (d, $J = 8.0$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.20-7.13 (m, 3H), 6.94-6.86 (m, 3H), 6.55 (d, $J = 7.6$ Hz, 1H), 5.92 (s, 1H), 4.45 (br, 1H), 2.49 (s, 3H); $^{13}$C NMR (100 MHz, DMSO): $\delta$ 161.7 (d, $J = 241.1$ Hz), 149.7, 147.2, 146.6, 140.5, 140.3, 131.8, 129.7 (d, $J = 12.4$ Hz), 129.0 (d, $J = 8.1$ Hz), 127.5, 126.8, 126.1, 125.8, 124.8, 120.4, 117.7, 115.7, 115.5, 54.2, 14.0. HRMS (EI) (m/z) calculated for C$_{23}$H$_{17}$FN$_2$ 340.1376, found 340.1379.

6-(3-Fluorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1f). Yellow power; 129.3 mg, 76% yield; mp: 182-184 °C; IR (KBr) $\nu$ 3295, 3071, 3025, 2922, 1607, 1579, 1487, 1446, 1251, 756 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.57 (d, $J = 1.2$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.71-7.67 (m, 1H), 7.50-7.46 (m, 1H), 7.21-7.13 (m, 2H), 7.00-6.84 (m, 4H), 6.55 (d, $J = 8.0$ Hz, 1H), 5.88 (d, $J = 1.2$ Hz, 1H), 4.51 (br, 1H), 2.47 (s, 3H);
13C NMR (100 MHz, CDCl3): δ 163.0 (d, J = 247.4 Hz), 149.5, 147.6, 145.6 (d, J = 5.8 Hz), 144.4, 140.2, 131.4, 130.4 (d, J = 8.0 Hz), 130.1, 129.2, 127.5, 126.1, 126.0, 125.8, 123.7, d (122.3, 122.3), 121.5, 119.5, 115.2, 114.7 (d, J = 21.0 Hz), 113.7 (d, J = 21.4 Hz), 56.4, 13.9. HRMS (EI) (m/z) calculated for C23H17FN2 340.1376, found 340.1370.

6-(2-Fluorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1g). Yellow power; 136.2 mg, 80% yield; mp: 210-213 °C; IR (KBr) ν 3400, 3303, 2362, 2333, 1606, 1582, 1507, 1486, 1213, 749 cm⁻¹; ¹H NMR (400 MHz, CDCl3): δ 8.53 (d, J = 6.8 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.21-7.08 (m, 3H), 6.90 (t, J = 7.2 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 6.60 (dt, J = 1.2 Hz, J = 7.6 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.37 (s, 1H), 4.66 (br, 1H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl3): δ 159.7 (d, J = 242.9 Hz), 150.1, 147.7, 144.8, 140.4, 131.3, 130.2, 129.6, 129.4 (d, J = 8.2 Hz), 129.3, 129.1 (d, J = 3.7 Hz), 127.4, 126.0, 125.8, 125.0, 124.5 (d, J = 3.4 Hz), 123.8, 121.4, 119.4, 115.5 (d, J = 21.7 Hz), 115.2, 49.6 (d, J = 3.6 Hz), 13.6. HRMS (EI) (m/z) calculated for C23H17FN2 340.1370, found 340.1377.

6-(3,4-Difluorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1h). Yellow power; 146.9 mg, 82% yield; mp: 204-206 °C; IR (KBr) ν 3432, 3302, 1609, 1514, 1490, 1437, 1277, 1116, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl3): δ 8.54 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.02-6.90 (m, 4H), 6.56 (d, J = 8.0 Hz, 1H), 5.88 (s, 1H), 4.47 (br, 1H), 2.49 (s, 3H); ¹³C NMR (100 MHz, DMSO): δ 150.6 (dd, J = 12.6 Hz, 1H), 149.7, 148.1 (dd, J = 12.4 Hz, 72.5 Hz), 147.3, 146.3, 141.7, 140.8, 131.9, 129.8, 129.8, 127.5, 126.2, 126.2, 125.7, 124.8, 123.7 (d, J = 3.5 Hz), 120.5, 118.0, 117.8 (d, J = 16.9 Hz), 116.2 (d, J = 17.0 Hz), 115.6, 53.9, 14.0. HRMS (EI) (m/z) calculated for C23H16F2N2 358.1282, found 358.1272.

7-Methyl-6-(pyridin-2-yl)-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1i). Yellow power; 98.6 mg, 61% yield; mp: 93-95 ºC; IR (KBr) ν 3299, 3050, 2959, 2922, 1665, 1608, 1586, 1491,
7-Methyl-6-(5-methylthiophen-2-yl)-5,6-dihydrodibenzo[ bolster text]
(d, J = 8.0 Hz, 1H), 7.74 (dd, J = 4.0 Hz, J = 8.8 Hz, 1H), 7.26-7.20 (m, 4H), 7.14 (m, 2H), 6.42 (d, J = 8.4 Hz, 1H), 5.89 (s, 1H), 4.50 (br, 1H), 2.42 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.6, 146.0, 143.6, 142.8, 139.6, 134.0, 132.7, 131.8, 129.1, 128.9, 128.6, 128.1, 126.9, 126.5, 126.2, 122.7, 120.1, 116.8, 111.4, 56.9, 13.9. HRMS (EI) (m/z) calculated for C\(_{23}\)H\(_{14}\)Br\(_2\)N\(_2\) 477.9680, found 477.9682.

2,9-Dibromo-7-methyl-6-phenyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1m). Yellow powder; 108.0 mg, 45% yield; mp: 206-208 °C; IR (KBr) \(\nu\) 3417, 3064, 3018, 2917, 2860, 1600, 1578, 1498, 1293, 1067, 704 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.62 (d, J = 4.8 Hz, 1H), 8.07 (d, J = 4.0 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.74 (dd, J = 4.0 Hz, J = 8.8 Hz, 1H), 7.26-7.20 (m, 4H), 7.14 (m, 2H), 6.42 (d, J = 8.4 Hz, 1H), 5.89 (s, 1H), 4.50 (br, 1H), 2.42 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.6, 146.0, 143.6, 142.8, 139.6, 134.0, 132.7, 131.8, 129.1, 128.9, 128.6, 128.1, 126.9, 126.5, 126.2, 122.7, 120.1, 116.8, 111.4, 56.9, 13.9. HRMS (EI) (m/z) calculated for C\(_{23}\)H\(_{14}\)Br\(_2\)N\(_2\) 477.9680, found 477.9682.
2,9-Dibromo-6-(4-chlorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1o). Yellow powder; 128.7 mg, 50% yield; mp: 229-231 °C; IR (KBr) ν 3395, 2918, 2850, 1579, 1488, 1465, 1090, 1011, 829, 795 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(δ\) 8.62 (d, \(J = 4.0\) Hz, 1H), 8.09 (d, \(J = 4.0\) Hz, 1H), 7.99 (dd, \(J = 4.8\) Hz, \(J = 9.2\) Hz, 1H), 7.31-7.24 (m, 1H), 7.21-7.18 (m, 2H), 7.08-7.05 (m, 2H), 6.44 (d, \(J = 8.4\) Hz, 1H), 5.88 (s, 1H), 4.48 (br, 1H), 2.43 (s, 3H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(δ\) 147.4, 145.0, 142.2, 140.1, 138.5, 133.1, 132.9, 131.8, 130.8, 128.4, 127.8, 127.5, 126.8, 125.4, 119.3, 115.8, 110.6, 55.1, 13.1. HRMS (EI) (m/z) calculated for C\(_{23}\)H\(_{15}\)Br\(_2\)ClN\(_2\) 511.9291, found 511.9290.

2,9-Dibromo-6-(3,4-difluorophenyl)-7-methyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (1p). Yellow powder; 175.5 mg, 68% yield; mp: 248-250 °C; IR (KBr) ν 3258, 3030, 1601, 1571, 1510, 1480, 1434, 1282, 1206, 1145, 1114, 811, 765 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(δ\) 8.61 (d, \(J = 4.8\) Hz, 1H), 8.07 (d, \(J = 4.0\) Hz, 1H), 7.93 (d, \(J = 8.4\) Hz, 1H), 7.75 (dd, \(J = 4.0\) Hz, \(J = 8.8\) Hz, 1H), 7.25-7.18 (m, 2H), 7.05 (d, \(J = 8.8\) Hz, 2H), 6.42 (d, \(J = 8.4\) Hz, 1H), 5.86 (s, 1H), 4.48 (br, 1H), 2.41 (s, 3H); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \(δ\) 147.2, 145.1, 142.0, 138.5, 138.2, 133.2, 131.9, 130.8, 127.6, 125.2, 121.6, 119.4, 116.9, 116.7, 115.8, 114.7, 114.5, 113.0, 110.7, 54.7, 13.1. HRMS (EI) (m/z) calculated for C\(_{23}\)H\(_{14}\)Br\(_2\)F\(_2\)N\(_2\) 513.9492, found 513.9490.

2-(4-Methylquinolin-2-yl)aniline (4a). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(δ\) 8.05 (d, \(J = 8.4\) Hz, 1H), 7.98 (d, \(J = 8.4\) Hz, 1H), 7.71-7.67 (m, 3H), 7.53 (t, \(J = 7.6\) Hz, 1H), 7.23-7.19 (m, 1H), 6.84-6.79 (m, 2H), 6.15 (br, 2H), 2.75 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(δ\) 159.0, 147.6, 146.8, 144.7, 130.2, 129.8, 129.4, 129.3, 126.5, 125.9, 123.6, 121.7, 121.1, 117.4, 117.3, 19.0. HRMS (EI) (m/z) calculated for C\(_{16}\)H\(_{14}\)N\(_2\) 234.1157, found 234.1158.
4-Methyl-2-phenylquinazoline (5a).\textsuperscript{1} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.64-8.62 (m, 2H), 8.10-8.07 (m, 2H), 7.88-7.84 (m, 1H), 7.60-7.49 (m, 4H), 3.02 (s, 3H).

7-Methyl-6-phenylbenzo[\textit{b,h}][1,6]naphthyridine (6a). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.34 (dd, \(J = 1.2\) Hz, \(J = 8.0\) Hz, 1H), 8.36 (d, \(J = 8.4\) Hz, 1H), 8.35-8.15 (m, 2H), 7.91-7.87 (m, 1H), 7.84-7.80 (m, 1H), 7.75-7.71 (m, 1H), 7.63-7.60 (m, 3H), 7.56-7.50 (m, 3H), 2.53 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 160.3, 147.8, 147.6, 145.2, 143.3, 143.1, 130.2, 129.6, 129.1, 128.0, 127.8, 127.7, 127.5, 126.7, 126.3, 125.1, 123.8, 123.7, 123.5, 117.0, 19.2. HRMS (EI) (m/z) calculated for C\textsubscript{23}H\textsubscript{16}N\textsubscript{2} 320.1313, found 320.1314.

Reference
The $^1$H and $^{13}$C spectra of all products
X-Ray Structure of Compounds 1a

Figure S1. X-ray structure of 1a