Supporting Information

N-Methylation of ortho-Substituted Aromatic Amines with Methanol Catalyzed by 2-Arylbenzo[d]oxazole NHC-Ir(III) Complexes

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1. Characterization data of substrates

**N-methylaniline**

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (99%) *N*-methylaniline as yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (td, $J = 7.4$, 1.8 Hz, 2H), 6.84 (t, $J = 7.3$ Hz, 1H), 6.71 (d, $J = 7.7$ Hz, 2H), 3.57 (s, 1H), 2.91 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.45 (s), 129.28 (s), 117.28 (s), 112.50 (s), 30.76 (s) ppm. GC-MS (m/z): 107.07 (calc. 107.10).

**4-Methoxy-*N*-methylaniline**

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (89%) 4-methoxy-*N*-methylaniline as a oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.82 (d, $J = 8.7$ Hz, 2H), 6.60 (d, $J = 8.6$ Hz, 2H), 3.77 (s, 3H), 2.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.13 (s), 143.75 (s), 114.96 (s), 113.67 (s), 55.89 (s), 31.63 (s). GC-MS (m/z): 137.08 (calc. 137.10).

**4-(Methylamino)benzonitrile**

Followed the general procedure, purification by column chromatography (PE/EtOAc 10:1) gave product (98%), 4-(methylamino)benzonitrile as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (s, 2H), 6.46 (s, 2H), 4.34 (s, 1H), 2.78 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.30 (s), 133.66 (s), 120.63 (s), 111.84 (s), 98.37 (s), 29.95 (s). GC-MS (m/z): 132.07 (calc. 132.02).

**3-Methoxy-*N*-methylaniline**

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (92%) 3-methoxy-*N*-methylaniline as a oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (t, $J = 8.1$ Hz, 1H), 6.31 (dd, $J = 8.1$, 2.3 Hz, 1H), 6.26 (dd, $J = 8.0$, 2.1 Hz, 1H), 6.19 (t, $J = 2.2$ Hz, 1H), 3.81 (s, 4H), 2.85 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 129.79 (s), 105.58 (s), 102.21 (s), 98.23 (s), 54.96 (s), 30.60 (s), 29.58 (s). GC-MS (m/z): 137.08 (calc. 137.14).
3-Bromo-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave 89 mg (96%), 3-bromo-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (t, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 6.77 (t, $J = 1.9$ Hz, 1H), 6.55 (dd, $J = 8.2$, 1.8 Hz, 1H), 3.80 (s, 1H), 2.83 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.50 (s), 130.36 (s), 123.20 (s), 119.74 (s), 114.67 (s), 111.16 (s), 30.42 (s). GC-MS (m/z): 184.98(calc. 184.99).

2-Methoxy-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (86%) 2-methoxy-N-methylaniline as a oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.95 (t, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 7.4$ Hz, 1H), 6.72 (t, $J = 7.7$ Hz, 1H), 6.66 (d, $J = 7.7$ Hz, 1H), 4.28 (s, 1H), 3.89 (s, 3H), 2.91 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.80 (s), 139.29 (s), 121.25 (s), 116.19 (s), 109.18 (d, $J = 8.7$ Hz), 55.28 (s), 30.26 (s). GC-MS (m/z): 137.08 (calc. 137.11).

N,2-dimethylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (73 %), N,2-dimethylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.20 (m, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 6.75 (t, $J = 7.4$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 2.96 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.17 (s), 129.82 (s), 127.11 (s), 121.82 (s), 116.77 (s), 109.05 (s), 30.68 (s), 17.29 (s). GC-MS (m/z): 121.08 (calc. 121.15).

2-Bromo-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (83 %), 2-bromo-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.25 (s, 1H), 6.67 (dd, $J = 8.1$, 1.1 Hz, 1H), 6.64 – 6.57 (m, 1H), 4.39 (s, 1H), 2.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.97 (s), 132.28 (s), 128.56 (s), 117.60 (s), 110.74 (s), 109.62 (s), 30.61 (s). GC-MS (m/z): 184.98(calc. 185.15).
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (78%), 2-iodo-N-methylaniline as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.31 – 7.18 (m, 1H), 6.57 (dd, $J = 8.1$, 1.2 Hz, 1H), 6.46 (td, $J = 7.6$, 1.4 Hz, 1H), 4.21 (s, 1H), 2.90 (d, $J = 3.8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.16 (s), 138.86 (s), 129.47 (s), 118.47 (s), 109.99 (s), 30.97 (s). GC-MS (m/z): 232.97 (calc. 233.06).

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (75%), 2-chloro-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, $J = 7.2$ Hz, 1H), 7.24 – 7.16 (m, 1H), 6.67 (t, $J = 4.8$ Hz, 3H), 4.37 (s, 1H), 2.92 (d, $J = 4.8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 145.01 (s), 128.95 (s), 127.84 (s), 119.04 (s), 117.00 (s), 110.61 (s), 30.35 (s). GC-MS (m/z): 141.03 (calc. 141.23).

Followed the general procedure, purification by column chromatography (PE/EtOAc 10:1) gave product (88%) 4-ethoxy-N-methylaniline as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.84 (dd, $J = 11.0$, 6.6 Hz, 2H), 6.60 (d, $J = 7.8$ Hz, 2H), 3.99 (dt, $J = 11.2$, 4.7 Hz, 2H), 3.29 (s, 1H), 2.81 (d, $J = 3.9$ Hz, 3H), 1.41 (td, $J = 6.9$, 4.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.36 (s), 143.82 (s), 115.88 (s), 113.66 (s), 64.22 (s), 31.59 (s), 15.09 (s). GC-MS (m/z): 151.09 (calc. 151.11).

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (95%), 4-fluoro-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.01 – 6.87 (m, 2H), 6.56 (dd, $J = 6.8$, 5.1, 3.0 Hz, 2H), 3.40 (dd, $J = 57.2$, 12.0 Hz, 1H), 2.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.93 (s), 154.60 (s), 145.73 (s), 115.66 (s), 115.44 (s), 113.11 (d, $J = 7.4$ Hz), 31.25 (s). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -128.56 (s). GC-MS (m/z): 125.06 (calc. 125.36).
4-Chloro-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (99%), 4-chloro-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.11 (s, 2H), 5.50 (s, 2H), 2.70 (s, 1H), 1.79 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.91 (s), 129.01 (s), 121.81 (s), 113.44 (s), 30.79 (s). GC-MS (m/z): 141.03 (calc. 141.23).

4-Bromo-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (96%), 4-bromo-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.13 (d, $J = 7.9$ Hz, 2H), 6.34 (d, $J = 8.0$ Hz, 2H), 3.59 (s, 1H), 2.65 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.34 (s), 131.88 (s), 113.98 (s), 108.76 (s), 30.72 (s). GC-MS (m/z): 184.98(calc. 185.02).

4-Iodo-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (91%), 4-iodo-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 8.8$ Hz, 2H), 6.39 (d, $J = 8.8$ Hz, 2H), 3.52 (s, 1H), 2.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.92 (s), 137.76 (s), 129.30 (s), 114.74 (s), 30.67 (s). GC-MS (m/z): 232.97(calc. 232.99).

3-Chloro-N-methylaniline

Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (95%), 3-chloro-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.12 (t, $J = 8.0$ Hz, 1H), 6.70 (dt, $J = 19.9$, 10.0 Hz, 1H), 6.65 – 6.55 (m, 1H), 6.50 (dd, $J = 8.1$, 2.0 Hz, 1H), 3.82 (s, 1H), 2.84 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.33 (s), 134.90 (s), 130.02 (s), 116.86 (s), 111.76 (s), 110.73 (s), 30.41 (s). GC-MS (m/z): 141.03 (calc. 141.53).
3-Iodo-N-methylaniline  
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (95%), 3-iodo-N-methylaniline as a brown oil.  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07 (d, $J$ = 6.9 Hz, 1H), 7.01 – 6.88 (m, 2H), 6.63 – 6.55 (m, 1H), 3.75 (s, 1H), 2.82 (s, 3H).  
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.41 (s), 130.58 (s), 125.88 (s), 120.69 (s), 111.77 (s), 95.31 (s), 30.44 (s). GC-MS (m/z): 232.97 (calc. 233.03).

N,3-Dimethylaniline  
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (98%), N,3-dimethylaniline as a colourless oil.  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (s, 1H), 6.62 (d, $J$ = 7.4 Hz, 1H), 6.50 (d, $J$ = 6.5 Hz, 2H), 3.68 (s, 1H), 2.88 (s, 3H), 2.37 (s, 3H).  
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.34 (s), 138.88 (s), 129.00 (s), 118.12 (s), 113.10 (s), 109.56 (s), 30.69 (s), 21.56 (s). GC-MS (m/z): 121.08 (calc. 121.12).

(2-(Methylamino)phenyl)methanol  
Followed the general procedure, purification by column chromatography (PE/EtOAc 10:1) gave product (90%), (2-(methylamino)phenyl)methanol as a colourless oil.  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (t, $J$ = 7.7 Hz, 1H), 7.08 (d, $J$ = 7.6 Hz, 1H), 6.70 (t, $J$ = 7.0 Hz, 2H), 4.65 (s, 2H), 2.89 (d, $J$ = 0.7 Hz, 3H).  
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.46 (s), 129.59 (s), 128.84 (s), 124.23 (s), 116.26 (s), 109.99 (s), 64.59 (s), 30.20 (s). GC-MS (m/z): 137.08 (calc. 137.10).

N-Methyl-2-(methylthio)aniline  
Followed the general procedure, purification by column chromatography (PE/EtOAc 10:1) gave product (85 %), N-Methyl-2-(methylthio)aniline as a colourless oil.  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.40 (m, 1H), 7.25 (ddd, $J$ = 8.1, 7.4, 1.6 Hz, 1H), 6.69 (td, $J$ = 7.5, 1.3 Hz, 1H), 6.64 (dd, $J$ = 8.1, 1.0 Hz, 1H), 2.93 (s, 3H), 2.35 (s, 3H).  
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.13 (s), 133.64 (s), 129.32 (s), 119.55 (s), 116.72 (s), 109.39 (s), 30.48 (s), 17.88 (s). GC-MS (m/z): 153.06 (calc. 153.08).
4-Bromo-N,2-dimethylaniline
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (77 %), 4-bromo-N,2-dimethylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.23 (m, 1H), 7.18 (d, $J = 2.3$ Hz, 1H), 6.49 (d, $J = 8.6$ Hz, 1H), 2.89 (s, 3H), 2.12 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.14 (s), 132.15 (s), 129.56 (s), 123.87 (s), 110.46 (s), 108.31 (s), 30.64 (s), 17.04 (s). GC-MS (m/z): 198.99 (calc. 199.01).

2-Bromo-N,4-dimethylaniline
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (78 %), 2-bromo-N,4-dimethylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (t, $J = 4.1$ Hz, 1H), 7.08 – 7.03 (m, 1H), 6.61 – 6.56 (m, 1H), 2.91 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.67 (s), 132.53 (s), 128.93 (s), 127.02 (s), 110.65 (s), 109.41 (s), 30.73 (s), 19.89 (s). GC-MS (m/z): 198.99 (calc. 199.04).

4-Bromo-2-iodo-N-methylaniline
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (76 %), 4-bromo-2-iodo-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, $J = 2.0$ Hz, 1H), 7.39 – 7.31 (m, 1H), 6.40 (t, $J = 19.1$ Hz, 1H), 4.24 (s, 1H), 2.88 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.23 (s), 140.12 (s), 132.00 (s), 110.71 (s), 108.34 (s), 84.80 (s), 30.93 (s). GC-MS (m/z): 310.88 (calc. 310.95).

2-Chloro-4-fluoro-N-methylaniline
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (83 %), 2-chloro-4-fluoro-N-methylaniline as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 – 7.12 (m, 1H), 6.39 – 6.28 (m, 2H), 4.45 (s, 1H), 2.89 (d, $J = 5.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 129.49 (s), 129.49 (s), 103.26 (s), 103.03 (s), 98.04 (s), 97.76 (s), 30.22 (s). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -113.52 – -113.79 (m). GC-MS (m/z): 159.02 (calc. 159.11).
N-Methylquinolin-8-amine
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (92 %), N-methylquinolin-8-amine as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.73 (dd, $J = 4.1, 1.6$ Hz, 1H), 8.08 (dd, $J = 8.3, 1.6$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.42 – 7.37 (m, 2H), 7.07 (d, $J = 8.2$ Hz, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 6.16 (s, 1H), 3.07 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.81 (s), 135.99 (s), 127.86 (s), 121.38 (s), 113.69 (s), 104.13 (s), 30.07 (s). GC-MS (m/z): 158.08 (calc. 158.15).

N-Methylquinolin-5-amine
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (89 %), N-methylquinolin-5-amine as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.21 (d, $J = 18.1$ Hz, 1H), 6.55 (d, $J = 6.9$ Hz, 1H), 4.43 (s, 1H), 2.94 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.91 (s), 144.71 (s), 130.46 (s), 128.64 (s), 119.27 (s), 118.38 (s), 104.13 (s), 30.98 (s). GC-MS (m/z): 158.08 (calc. 158.14).

N-methylnaphthalen-1-amine
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (82 %), N-methylnaphthalen-1-amine as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (s, 2H), 7.45 – 7.22 (m, 3H), 7.17 (s, 1H), 6.53 (s, 1H), 4.43 (d, $J = 67.7$ Hz, 1H), 2.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.57 (s), 134.28 (s), 128.67 (s), 126.69 (s), 125.70 (s), 124.68 (s), 123.51 (s), 119.80 (s), 117.33 (s), 103.81 (s), 31.02 (s). GC-MS (m/z): 157.08 (calc. 157.12).

N,4-dimethylbenzenesulfonamide
Followed the general procedure, purification by column chromatography (PE/EtOAc 50:1) gave product (94 %), N,4-dimethylbenzenesulfonamide as white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.6$ Hz, 2H), 5.17 (s, 1H), 2.53 (d, $J = 4.2$ Hz, 3H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.46 (s), 135.75 (s), 129.72 (s), 127.25 (s), 29.22 (s), 21.47 (s). GC-MS (m/z): 185.05 (calc. 185.08).
2. Control experiments and kinetic experiments

2.1 Control experiments

Reaction under optimized conditions

A mixture of 2-bromoaniline (42.5 mg, 0.25 mmol), 4-bromoaniline (42.5 mg, 0.25 mmol), 7 (0.5 mol%) KO
Bu (56 mg, 1.0 equiv.), methanol (1 mL), in a 15 mL pressure tube with magnetic bar was stirred at 130 °C for 12 h. After cooling to the room temperature, the solvents were removed under vacuum, and the yields were determined by 1H NMR with 1,3,5-trimethoxybenzene as the internal standard.

![Chemical structure]

2.2 Kinetic experiments

Reaction under optimized conditions

A mixture of 2-bromoaniline (85 mg, 0.5 mmol), 5, and 6, or 7 (0.5 mol%) as catalyst, respectively, KO
Bu (56 mg, 1.0 equiv.), methanol (1 mL), in a 15 mL pressure tube with magnetic bar was stirred at 130 °C. After specific time, the reaction mixture was cooled to room temperature. The solvents were removed under vacuum, and the yields were determined by 1H NMR with 1,3,5-trimethoxybenzene as the internal standard.

The results are as following table.

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3. Deuteration experiments.

A mixture of 2-bromoaniline (85mg, 0.5 mmol), 7 (4.2 mg, 0.5 mol%) KOtBu (56 mg, 1.0 equiv.), CD3OD (1 mL), in a 15 mL pressure tube with magnetic bar was stirred at 130 °C for 12 h. The reaction mixture was cooled to room temperature. The solvents were removed under vacuum, and the yields were determined by 1H NMR with 1,3,5-trimethoxybenzene as the internal standard.

4. NMR spectra of compounds and substrates
$^{13}\text{C}$

$^1\text{H}$
[Chemical structures and NMR spectra]