Supporting Information

Metal-Free Oxidative Olefination of Primary Amines with Benzylic
C-H Bonds through Direct Deamination and C-H Bond Activation

Liang Gong+, Li-Juan Xing+, Tong Xu, Xue-Ping Zhu, Wen Zhou, Ning
Kang and Bin Wang*

State Key Laboratory of Medicinal Chemical Biology and College of Pharmacy,
Nankai University, Tianjin 300071, China.

E-mail: wangbin@nankai.edu.cn

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General information

$^1$H NMR spectra were recorded on AVANCE 400 spectrometer and the chemical shifts were reported in parts per million (ppm) relative to internal standard TMS (0 ppm) for CDCl$_3$ or DMSO. The peak patterns are indicated as follows: s, singlet; d, doublet; bs, broad singlet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). $^{13}$C NMR spectra were obtained on the same spectrometer and referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl$_3$ and 39.6 ppm in DMSO-$d_6$). CDCl$_3$ and DMSO-$d_6$ were used as the NMR solvents. Mass spectra were determined with Agilent 6450 spectrometer for ESI-MS. Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air at room temperature. Unless otherwise noted, all reagents were purchased from commercial suppliers. NBS was purchased from Alfa Aesar and used without further purification.

General procedure for products 3

An oven-dried Schlenk tube covered by silver paper was charged with 2-methylquinolines 1 (0.5 mmol) and N-bromosuccinimide (NBS, 17.8 mg, 0.1 mmol) under air at room temperature, then benzylamines 2 (0.6 mmol), tert-butyl hydroperoxide (TBHP, 1.0 mmol, 70% aqueous solution) and CH$_3$CN (1.0 mL) were added. The resulting mixture was stirred at 100 °C for 48 h. The resulting reaction mixture was mixed with few silica gel and concentrated, then purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (1:50) as eluent to give the desired product 3.

Characterization Data of Products

(E)-2-Styrylquinoline (3a)$^{[1]}$. White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13-8.09 (m, 2H), 7.78 (d, $J$ = 8.0 Hz, 1H), 7.73-7.64 (m, 5H), 7.49 (t, $J$ = 8.0 Hz, 1H), 7.45-7.39 (m, 3H), 7.35-7.31 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.9, 148.2, 136.5, 136.3, 134.5, 129.7, 129.1, 128.9, 128.8, 128.6, 127.5, 127.3, 127.2, 126.1, 119.2.
(E)-6-methyl-2-styrylquinoline (3b) \([2]\). White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 8.0\) Hz, 1H), 7.76 (d, \(J = 8.0\) Hz, 1H), 7.48-7.44 (m, 3H), 7.38-7.30 (m, 2H), 7.25-7.21 (m, 3H), 7.16-7.15 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.9, 146.6, 136.5, 135.8, 135.4, 133.6, 131.8, 129.0, 128.7, 128.6, 128.3, 127.2, 127.0, 126.3, 119.0, 21.4.

(E)-4-methyl-2-styrylquinoline (3c). Light yellow solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 8.0\) Hz, 1H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.57-7.49 (m, 4H), 7.37-7.33 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.18 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 155.6, 148.1, 144.3, 136.6, 134.2, 129.8, 129.4, 129.2, 128.8, 128.6, 127.5, 127.3, 125.9, 123.7, 119.9, 18.9. HRMS m/z (ESI) calcd. for C\(_{18}\)H\(_{15}\)N (M\(^{+}\)+H): 250.1277, found: 246.1275.

(E)-6-methoxy-2-styrylquinoline (3d) \([1]\). White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (t, \(J = 8.8\) Hz, 2H), 7.64-7.60 (m, 4H), 7.40-7.35 (m, 4H), 7.33-7.31 (m, 1H), 7.06 (d, \(J = 2.4\) Hz, 1H), 3.93 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.7, 153.6, 144.2, 136.7, 135.1, 133.3, 130.6, 128.9, 128.7, 128.4, 128.3, 127.1, 122.3, 119.5, 105.3, 55.5.

(E)-7-chloro-2-styrylquinoline (3e) \([1]\). White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (s, 1H), 7.95 (d, \(J = 8.0\) Hz, 1H), 7.65-7.56 (m, 4H), 7.50 (d, \(J = 8.0\) Hz, 1H), 7.38-7.34 (m, 3H), 7.31-7.27 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.7, 148.5, 136.2, 135.9, 135.3, 135.0, 128.7, 128.5, 128.3, 128.0, 127.2, 126.9, 125.5, 119.4.
(E)-4-chloro-2-styrylquinoline (3f). Light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 8.0$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.76-7.72 (m, 2H), 7.68-7.61 (m, 3H), 7.59-7.55 (t, 1H), 7.42-7.38 (t, 2H), 7.34-7.30 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.9, 148.9, 142.7, 136.1, 135.4, 130.6, 129.5, 128.9, 127.8, 127.4, 127.1, 125.4, 124.0, 119.3. HRMS m/z (ESI) calcd. for C$_{17}$H$_{12}$ClN (M$^+$+H): 266.0732, found: 266.0731.

(E)-8-chloro-2-styrylquinoline (3g) $^{[1]}$. White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 16.0$ Hz 1H), 7.70-7.63 (m, 4H), 7.45 (d, $J = 16.0$ Hz 1H), 7.41-7.31 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.7, 144.5, 136.7, 136.4, 135.4, 133.3, 129.9, 128.9, 128.8, 128.6, 127.5, 126.6, 125.9, 120.0. HRMS m/z (ESI) calcd. for C$_{17}$H$_{12}$ClN (M$^+$+H): 266.0732, found: 266.0729.

(E)-6-fluoro-2-styrylquinoline (3h) $^{[5]}$. Light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04-8.00 (m, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.61-7.51 (m, 4H), 7.43-7.26 (m, 6H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 161.5, 159.0, 155.4, 145.3, 136.4, 135.6, 134.4, 131.7, 131.6, 128.8, 128.7, 128.6, 127.9, 127.8, 120.0, 119.9, 119.7, 110.7, 110.5. HRMS m/z (ESI) calcd. for C$_{17}$H$_{12}$FN (M$^+$+H): 250.1027, found: 250.1026.

(E)-6-bromo-2-styrylquinoline (3i) $^{[2]}$. White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97-7.89 (m, 3H), 7.76-7.73 (m, 1H), 7.69-7.60 (m, 4H), 7.41-7.32 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.2, 146.7, 136.3, 135.2, 134.9, 133.1, 130.8, 129.5, 128.8, 128.4, 128.3, 127.3, 120.1, 119.8.
(E)-8-nitro-2-styrylquinoline (3j). Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 8.0$ Hz, 1H), 7.96-7.91 (m, 2H), 7.80-7.76 (m, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.40-7.37 (m, 2H), 7.35-7.28 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.9, 148.0, 139.5, 136.7, 136.1, 136.0, 131.4, 129.1, 128.8, 128.0, 127.7, 127.5, 124.3, 123.7, 121.4. HRMS m/z (ESI) calcd. for C$_{17}$H$_{12}$N$_2$O$_2$ (M$^+$+H): 277.0972, found: 277.0966.

(E)-3-styrylbenzo[f]quinoline (3k) $^{[2]}$. Light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (d, $J = 8.0$ Hz, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 7.99-7.93 (m, 2H), 7.89-7.87 (m, 1H), 7.74-7.68 (m, 2H), 7.65-7.57 (m, 4H), 7.42-7.37 (m, 3H), 7.32-7.29 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.3, 148.1, 143.2, 136.6, 134.0, 131.5, 131.0, 129.6, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 127.2, 127.0, 124.2, 122.5, 119.5.

(E)-1-styrylisoquinoline (3l) $^{[1]}$. Light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J = 5.6$ Hz, 1H), 8.36 (d, $J = 8.0$ Hz, 1H), 8.00 (s, 2H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.71-7.60 (m, 4H), 7.56 (d, $J = 5.6$ Hz, 1H), 7.43-7.40 (m, 2H), 7.35-7.32 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.6, 142.5, 137.0, 136.8, 135.9, 129.9, 128.8, 128.6, 127.5, 127.3, 127.2, 126.8, 124.5, 122.8, 120.0.

(E)-2-styrylquinoxaline (3m) $^{[1]}$. White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.03 (s,
1H), 8.07 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 16.0 Hz, 1H), 7.77-7.69 (m, 2H), 7.66 (d, J = 7.2 Hz, 2H), 7.44-7.34 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.6, 144.4, 142.5, 141.6, 136.5, 136.0, 130.3, 129.3, 129.2, 128.9, 127.5, 125.3.

(E)-2-methyl-3-styrylquinoxaline (3n) [3]. Light yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06-7.95 (m, 3H), 7.66-7.65 (m, 4H), 7.47-7.32 (m, 4H), 2.86 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.5, 149.7, 141.5, 141.3, 137.5, 136.5, 129.1, 129.1, 129.0, 128.8, 127.6, 122.6, 23.1. HRMS m/z (ESI) calcd. for C$_{17}$H$_{14}$N$_2$ (M$^+$+H): 247.1230, found: 247.1226.

(E)-2-(4-methylstyryl)quinoline (3o) [2]. White solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.70-7.61 (m, 3H), 7.52 (d, J = 8.0 Hz, 2H), 7.48-7.44 (m, 1H), 7.35 (d, J = 16.0Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.2, 148.3, 138.8, 136.3, 134.5, 133.8, 129.7, 129.6, 129.2, 128.1, 127.5, 127.3, 127.2, 126.1, 119.2, 21.4.

(E)-2-(4-methoxystyryl)quinoline (3p) [1]. White solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07-8.01 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.68-7.54 (m, 5H), 7.46-7.42 (t, 1H), 7.25 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 8.0Hz, 2H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.1, 156.3, 148.3, 136.2, 134.1, 129.7, 129.3, 129.1, 128.7, 127.5, 127.2, 126.9, 125.9, 119.2, 114.3, 55.3.

(E)-2-(4-fluorostyryl)quinoline (3q). White solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.71-7.55 (m, 5H), 7.47 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 16.0 Hz, 1H), 7.06 (t, J = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.2, 161.7, 155.8, 148.2, 136.4, 133.2, 132.7, 129.8, 129.2, 128.9, 128.8, 128.7, 127.5, 127.4, 126.2, 119.3, 115.9, 115.7.
(E)-2-(4-chlorostyryl)quinoline (3r) \[^1\]. White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (t, \(J = 8.0\) Hz, 2H), 7.73 (d, \(J = 8.0\) Hz, 1H), 7.68 (t, \(J = 8.0\) Hz, 1H), 7.61-7.55 (m, 2H), 7.51-7.45 (m, 3H), 7.34-7.30 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 155.6, 148.2, 136.4, 135.0, 134.3, 133.0, 129.8, 129.5, 129.2, 129.0, 128.4, 127.5, 127.4, 126.3, 119.4.

(E)-4-(2-(quinolin-2-yl)vinyl)phenol (3s) \[^4\]. Light yellow solid; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 9.79 (s, 1H), 8.30 (d, \(J = 8.0\) Hz, 1H), 7.96 (d, \(J = 8.0\) Hz, 1H), 7.91 (d, \(J = 8.0\) Hz, 1H), 7.81 (d, \(J = 8.0\) Hz, 1H), 7.77-7.71 (m, 2H), 7.58 (d, \(J = 8.0\) Hz, 2H), 7.55-7.51 (m, 1H), 7.26 (d, \(J = 16.0\) Hz, 1H), 6.84 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 158.8, 156.6, 148.2, 136.7, 134.8, 130.2, 129.3, 129.0, 128.2, 127.8, 127.3, 126.3, 125.9, 120.2, 116.2.

(E)-2-(2, 4-dimethoxystyryl)quinoline (3t) \[^2\]. Bright yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06-8.04 (m, 2H), 7.93 (d, \(J = 16.0\) Hz, 1H), 7.74-7.63 (m, 4H), 7.44 (t, \(J = 8.0\) Hz, 1H), 7.35 (d, \(J = 16.0\) Hz, 1H), 6.55-6.52 (m, 1H), 6.48 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.5, 158.7, 157.1, 136.1, 129.5, 129.3, 129.0, 128.3, 127.5, 127.3, 127.1, 125.8, 118.9, 118.7, 105.2, 98.5.

(E)-2-(4-(trifluoromethyl)styryl)quinoline (3u) \[^2\]. White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.13-8.08 (m, 2H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.73-7.67 (m, 4H), 7.63-7.61 (m, 3H), 7.52-7.48 (t, 1H), 7.44 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 155.2, 148.3, 140.0, 136.6, 132.7, 131.3, 130.3, 129.9, 129.3, 127.6, 127.3, 126.5, 125.7, 122.8, 119.5.
(E)-2-(2-(naphthalen-1-yl)vinyl)quinoline (3v) [2]. Yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J$ = 8.0 Hz, 1H), 8.31 (d, $J$ = 8.0 Hz, 1H), 8.13-8.08 (m, 2H), 7.88-7.81 (m, 3H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.71-7.67 (m, 2H), 7.57-7.42 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.9, 148.3, 136.3, 134.0, 133.7, 131.7, 131.4, 131.3, 129.7, 129.3, 128.9, 128.6, 127.5, 127.4, 126.3, 126.2, 125.9, 125.6, 124.1, 123.7, 119.5.

(E)-2-(2-(thiophen-2-yl)vinyl)quinoline (3w) [1]. Light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (t, $J$ = 8.0 Hz, 2H), 7.83 (d, $J$ = 16.0 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.49-7.45 (m, 1H), 7.28-7.18 (m, 3H), 7.05-7.03 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.6, 148.3, 142.1, 136.3, 129.8, 129.1, 128.2, 128.1, 127.9, 127.5, 127.3, 126.1, 126.1, 125.9, 119.4.

(E)-2-(2-(furan-2-yl)vinyl)quinoline (3x) [2]. Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10-8.05 (t, 2H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.71-7.67 (m, 1H), 7.58-7.52 (m, 2H), 7.49-7.46 (t, 2H), 7.28 (d, $J$ = 16.0 Hz, 1H), 6.54 (d, 1H), 6.47-6.46 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.6, 152.9, 148.3, 143.2, 136.4, 129.8, 129.1, 127.5, 127.3, 126.7, 126.1, 121.8, 120.0, 112.0, 111.2.

(E)-2-(2-cyclohexylvinyl)quinoline (3y) [2]. Light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08-8.04 (t, 2H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.49-7.45 (m, 1H), 6.79 (dd, $J_1$ = 16.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.70 (d, $J$ = 16.0 Hz, 1H), 2.30-2.23 (m, 1H), 1.91-1.68 (m, 4H), 1.37-1.23 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.7, 143.7, 136.3, 129.6, 128.9, 128.4, 127.4, 127.1, 125.9, 118.7, 41.2, 32.5, 30.9, 26.1, 26.0.
References


$^1$H NMR and $^{13}$C NMR spectra

(*E*)-2-Styrylquinoline (3a)
(E)-6-methyl-2-styrylquinoline (3b)
(E)-4-methyl-2-styrylquinoline (3c)
(E)-6-methoxy-2-styrylquinoline (3d)
(E)-7-chloro-2-styrylquinoline (3e)
(E)-4-chloro-2-styrylquinoline (3f)
(E)-8-chloro-2-styrylquinoline (3g)
(E)-6-fluoro-2-styrylquinoline (3h)
(E)-6-bromo-2-styrylquinoline (3i)
(E)-8-nitro-2-styrylquinoline (3j)
(E)-3-styrylbenzo[f]quinoline (3k)
(E)-1-styrylisoquinoline (3l)
(E)-2-styrylquinoxaline (3m)
(E)-2-methyl-3-styrylquinoxaline (3n)
(E)-2-(4-methylstyryl)quinoline (3o)
(E)-2-(4-methoxystyryl)quinoline (3p)
(E)-2-(4-fluorostyryl)quinoline (3q)
(E)-2-(4-chlorostyryl)quinoline (3r)
(E)-4-(2-(quinolin-2-yl)vinyl)phenol (3s)
(E)-2-(2,4-dimethoxystyryl)quinoline (3t)
(E)-2-(4-(trifluoromethyl)styryl)quinoline (3u)
(E)-2-(2-(naphthalen-1-yl)vinyl)quinoline (3v)
(E)-2-(2-(thiophen-2-yl)vinyl)quinoline (3w)
(E)-2-(2-(furan-2-yl)vinyl)quinoline (3x)
(E)-2-(2-cyclohexylvinyl)quinoline (3y)
Characterization data and NMR spectra of N-benzylbenzamide
N-benzylbenzamide. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.2$ Hz, 2H), 7.52-7.48 (m, 1H), 7.44-7.41 (m, 2H), 7.36-7.35 (m, 4H), 7.32-7.30 (m, 1H), 6.52 (s, 1H), 4.65-4.64 (d, $J = 6.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 138.1, 134.3, 131.5, 128.8, 128.6, 127.9, 127.6, 126.9, 44.1.