Experimental Section

General Remarks

All commercially available reagents were obtained from commercial suppliers and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glass ware. Organic solutions were concentrated using a Buchi rotary evaporator. Flash chromatography was carried out over silica gel (Merck 200–300 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. IR spectra in KBr/neat were recorded on a Perkin-Elmer 993 IR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in $CDCl_3$ using TMS as internal reference with chemical shifts (δ) are reported in ppm. All coupling constants (J) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer. 18 W CFL (Compact fluorescent lamp; Philips, 6500 k, 1010 1m, 85 mA) was used as visible light source.

General procedure for the visible light-assisted aerobic oxidation of methylarenes to aromatic aldehydes 3a-z

The catalyst CBr_4 (**2**, 10 mol%) in CH_3CN (3 mL) was irradiated with 18 W CFL, at rt in a molecular oxygen atmosphere (O_2 balloon). After 15 min of irradiation, methylarene (**1**, 1mmol) was added to the reaction mixture under the same reaction condition and was irradiated under stirring for 2-4 h (Table 3). After completion of the reaction (indicated by TLC), the solvent was evaporated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (silica: 200~300; eluent: hexane/ethyl acetate (19:1) to afford an analytically pure sample of aromatic aldehyde **3** (Table 3).

Spectral data of isolated and purified compounds 3 are summarized below with relevant references:

Compound 3a [20i]

Yield 89%; Colorless oil; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.55 (t, J = 7.4 Hz, 2 H), 7.62 (t, J = 7.4 Hz, 1 H), 7.89 (d, J = 7.4 Hz, 2 H), 10.01 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.96, 129.63, 134.41, 136.36, 192.31; IR (neat): $\tilde{\nu}$ = 2819, 1698 cm^{-1}; HRMS (EI) calcd for C_7H_6O: 107.0452, found 107.0449.

Compound 3b [20d]

Yield 87%; White solid; m.p. 58-59 °C (lit. m.p. 58-60 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.6 Hz, 2 H), 7.73 (d, J = 8.6 Hz, 2 H), 9.97 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.9, 130.9, 132.5, 135.1, 191.2; IR (KBr): $\tilde{\nu}$ = 2861, 1687 cm^{-1}; HRMS (EI) calcd for C_7H_5OBr: 185.9503, found 185.9501.

Compound 3c [7c]

Yield 85%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, J = 7.9 Hz, 1 H), 7.76 (dd, J = 7.9, 1.8, 1.4 Hz, 1 H), 7.82 (dt, J = 7.9, 1.6 Hz, 1 H), 8.01 (t, J = 1.6 Hz, 1 H), 9.98 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.32, 128.35, 130.57, 132.31, 137.27, 137.94, 190.69; IR (neat): $\tilde{\nu}$ = 2879, 1668 cm^{-1}; HRMS (EI) calcd for C_7H_5OBr: 185.9503, found 185.9506.

Compound 3d [20d]

Yield 81%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.47 (m, 2 H), 7.64–7.67 (m, 1 H), 7.93–7.95 (m, 1 H), 10.39 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.12, 127.89, 129.86, 133.49, 133.87, 135.34, 191.87; IR (neat): $\tilde{\nu}$ = 2869, 1689 cm^{-1}; HRMS (EI) calcd for C_7H_5OBr: 185.9503, found 185.9503.

Compound 3e [20h]

Yield 92%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3 H), 7.35 (d, J = 7.9 Hz, 2 H), 7.76 (d, J = 7.9 Hz, 2 H), 9.95 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.83, 129.66, 129.77, 134.14, 145.49, 191.97; IR (neat): $\tilde{\nu}$ = 2823, 1703 cm^{-1}; HRMS (EI) calcd for C_8H_8O: 121.0609, found 121.0605.

Compound 3f [7c]

Yield 90%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3 H), 7.41–7.45 (m, 2 H), 7.67– 7.69 (m, 2 H), 9.97 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.03, 127.05, 128.71, 129.87, 135.13, 136.34, 138.77, 192.43; IR (neat): $\tilde{\nu}$ = 2819, 1701 cm^{-1}; HRMS (EI) calcd for C_8H_8O: 121.0609, found 121.0611.

Compound 3g [20c]

Yield 91%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 3 H), 7.23 (d, J = 8.2 Hz, 1 H), 7.36 (t, J = 7.6 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 1 H), 7.77 (d, J = 7.8 Hz, 1 H), 10.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.53, 126.24, 131.69, 131.97, 133.57, 134.09, 140.53, 192.73; IR (neat): $\tilde{\nu}$ = 2865, 1693 cm^{-1}; HRMS (EI) calcd for C_8H_8O: 121.0609, found 121.0607.

Compound 3h [7c]

Yield 80%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, J = 8.8 Hz, 2 H), 7.91 (dd, J = 5.5, 8.8 Hz, 2 H), 9.95 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.29 (d, $J_{C,F}$ = 22.9 Hz), 132.19 (d, $J_{C,F}$ = 9.5 Hz), 132.93, 166.47 (d, $J_{C,F}$ = 256.6 Hz), 190.45; IR (neat): $\tilde{\nu}$ = 2829, 1695 cm^{-1}; HRMS (EI) calcd for C_7H_5OF: 125.0358, found 125.0357.

Compound 3i [7c]

Yield 81%; White solid; m.p. 74-75 °C (lit. m.p.73–75 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.2 Hz, 2 H), 7.92 (d, J = 8.2 Hz, 2 H), 9.96 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.81, 130.79, 135.55, 138.40, 191.41; IR (KBr): $\tilde{\nu}$ = 2825, 1683 cm^{-1}; HRMS (EI) calcd for C_7H_5OI: 232.9421, found 232.9425.

Compound 3j [20f]

Yield 79%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.1 Hz, 2 H), 8.01 (d, J = 8.1 Hz, 2 H), 10.13 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.37 (q, $J_{C,F}$ = 272.7 Hz), 126.01, 129.81, 135.48 (q, $J_{C,F}$ = 32.4 Hz), 138.63, 191.00; IR (neat): $\tilde{\nu}$ = 2837, 1707 cm^{-1}; HRMS (EI) calcd for $C_8H_5OF_3$: 175.0326, found 175.0324.

Compound 3k [7c]
Yield 90%; Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9 H), 7.57 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 8.2 Hz, 2 H), 9.97 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.01, 35.24, 125.89, 129.62, 133.98, 158.34, 191.97; IR (neat): $\tilde{\nu}$ = 2964, 1696 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{14}O$: 163.1078, found 163.1083.

Compound 3l [7c]
Yield 96%; Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.91 (s, 3 H), 7.02 (d, J = 8.7 Hz, 2 H), 7.84 (d, J = 8.7 Hz, 2 H), 9.87 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.53, 114.24, 129.86, 131.92, 164.56, 190.79; IR (neat): $\tilde{\nu}$ = 2841, 2738, 1682 cm^{-1}; HRMS (EI) calcd for $C_8H_8O_2$: 137.0558, found 137.0554.

Compound 3m [20h]
Yield 91%; White solid; m.p. 114-116 °C (lit. m.p. 115–116 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3 H), 6.89 (d, J = 8.0 Hz, 1 H), 7.64 (dd, J = 2.6, 8.0 Hz, 1 H), 7.91 (d, J = 2.6 Hz, 1 H), 10.37 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.96, 113.42, 113.67, 126.05, 131.04, 138.28, 160.69, 188.34; IR (KBr): $\tilde{\nu}$ = 2831, 1682 cm^{-1}; HRMS (EI) calcd for $C_8H_7O_2Br$: 215.9609, found 215.9606.

Compound 3n [7c]
Yield 78%; White solid; m.p. 155-157 °C (lit. m.p. 154–158 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, J = 5.7 Hz, 3 H), 4.43 (q, J = 5.7 Hz, 2 H), 7.95 (d, J = 6.8 Hz, 2 H), 8.21 (d, J = 6.8 Hz, 2 H), 10.12 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.17, 61.53, 129.38, 130.05, 135.36, 139.01, 165.48, 191.59; IR (KBr): $\tilde{\nu}$ = 2982, 1703 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{10}O_3$: 179.0663, found 179.0667.

Compound 3o [7c]
Yield 79%; White solid; m.p. 169-172 °C (lit. m.p. 165–173 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (br., 1 H), 6.12 (br.,1 H), 7.97 (m, 4 H), 10.09 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.16, 129.35, 137.81, 139.37, 167.08, 192.90; IR (KBr): $\tilde{\nu}$ = 3360, 3178, 2833, 1657 cm^{-1}; HRMS (EI) calcd for $C_8H_7O_2N$: 150.0510, found 150.0508.

Compound 3p [7c]
Yield 78%; White solid; m.p. 65-66 °C (lit. m.p. 65–67 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (t, J = 7.2 Hz, 2 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.83 (d, J = 7.2 Hz, 2 H), 7.91 (d, J = 8.5 Hz, 2 H), 8.02 (d, J = 8.5 Hz, 2 H), 10.13 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.54, 129.48, 130.10, 130.31, 133.14, 136.73, 138.45, 142.57, 191.64, 195.81; IR (KBr): $\tilde{\nu}$ = 2809, 1696, 1649 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{10}O_2$: 211.0714, found 211.1711.

Compound 3q [7c]
Yield 91%; White solid; m.p. 58-60 °C (lit. m.p. 58–60 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (t, J = 7.5 Hz, 1 H), 7.47 (d, J = 7.5 Hz, 2 H), 7.64 (d, J = 7.5 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.95 (d, J = 8.4 Hz, 2 H), 10.09 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.29, 127.59, 128.40, 128.96, 130.19, 135.11, 139.62, 147.09, 191.84; IR (KBr): $\tilde{\nu}$ = 2836, 1695 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{10}O$: 183.0765, found 183.0762.

Compound 3r [7c]
Yield 79%; White solid; m.p. 158-160 °C (lit. m.p. 157–158 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.12 (s, 3 H), 8.09 (d, J = 8.6 Hz, 2 H), 8.14 (d, J = 8.6 Hz, 2 H), 10.13 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.29, 128.18, 130.33, 139.65, 145.35, 190.66; IR (KBr): $\tilde{\nu}$ = 2864, 1701 cm^{-1}; HRMS (EI) calcd for $C_8H_8O_3S$: 185.0228, found 185.0230.

Compound 3s [7c]
Yield 75%; White solid; m.p. 38-39 °C (lit. m.p. 37–39 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.06 (s, 2 H), 6.93 (d, J = 8.0 Hz, 1 H), 7.35 (d, J = 1.6 Hz, 1 H), 7.41 (dd, J = 8.0, 1.6 Hz, 1 H), 9.80 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.08, 106.89, 108.35, 128.65, 131.88, 148.69, 153.10, 190.27; IR (KBr): $\tilde{\nu}$ = 2726, 1684 cm^{-1}; HRMS (EI) calcd for $C_8H_6O_3$: 151.0350, found 151.0347.

Compound 3t [20e]
Yield 75%; Light yellow solid; m.p. 102-103 °C (lit. m.p. 103–104 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 9.0 Hz, 2 H), 8.39 (d, J = 9.0 Hz, 2 H), 10.16 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.28, 130.46, 140.02, 151.12, 190.27; IR (KBr): $\tilde{\nu}$ = 2849, 1702 cm^{-1}; HRMS (EI) calcd for $C_7H_5O_3N$: 152.0303, found 152.0306.

Compound 3u [20g]
Yield 77%; Yellow solid; m.p.55-57 °C (lit. m.p. 56-58 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, 1H, J=8.0 Hz), 8.24 (d, 1H, J=8.0 Hz), 8.48 (dd, 1H, J=2.0 Hz, J=8.0 Hz), 8.73 (s, 1H), 10.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.3, 128.8, 130.6, 134.9, 137.2, 148.9, 190.0; IR (KBr): $\tilde{\nu}$ = 2878, 2720, 1706 cm^{-1}; HRMS (EI) calcd for $C_7H_5O_3N$: 152.0303, found 152.0301.

Compound 3v [7c]
Yield 80%; White solid; m.p. 56-57 °C (lit. m.p. 55–58 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (t, J = 7.8 Hz, 1 H), 7.53 (t, J = 7.8 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 8.29 (s, 1 H), 8.67 (d, J = 7.8 Hz, 1 H), 10.12 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.39, 124.77, 126.09, 126.12, 135.11, 136.45, 140.42, 143.18, 185.39; IR (KBr): $\tilde{\nu}$ = 3078, 1664 cm^{-1}; HRMS (EI) calcd for C_9H_6OS: 163.0173, found 163.0168.

Compound 3w [7c]
Yield 75%; White solid; m.p. 156-159 °C (lit. m.p. 156–158 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.43 (m, 2 H), 7.48 (t, J = 7.6 Hz, 2 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.95–7.97 (m, 3 H), 8.24 (s, 1 H), 8.27 (d, J = 7.1 Hz, 1 H), 10.09 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.24, 122.57, 122.65, 125.12, 126.31, 126.39, 127.13, 129.69, 134.72, 135.27, 136.08, 137.45, 185.24; IR (KBr): $\tilde{\nu}$ = 2846, 1678 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{11}O_3NS$: 286.0493, found 286.0489.

Compound 3x [7c]
Yield 79%; White solid; m.p. 97-99 °C (lit. m.p. 98–100 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.6 Hz, 2 H), 8.02 (d, J = 8.6 Hz, 2 H), 10.13 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.55, 117.67, 129.84, 132.85, 138.68, 190.59; IR (KBr): $\tilde{\nu}$ = 2864, 2230, 1698 cm^{-1}; HRMS (EI) calcd for C_8H_5ON: 132.0405, found 132.0401.

Compound 3y [7c]
Yield 92%; Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.66 (m, 2 H), 7.71 (t, J = 8.5 Hz, 1 H), 7.93 (d, J = 8.5 Hz, 1 H), 7.98 (d, J = 8.3 Hz, 1 H), 8.09 (d, J = 8.3 Hz, 1 H), 9.24 (d, J = 8.5 Hz, 1 H), 10.39 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.87, 126.96, 128.45 (2 C), 129.04, 130.53, 131.39, 133.69, 135.27, 136.69, 193.50; IR (neat): $\tilde{\nu}$

= 2724, 1686 cm^{-1}; HRMS (EI) calcd for $C_{11}H_8O$: 157.0609, found 157.0611.

Compound 3z [7c]

Yield 91%; Light yellow solid; m.p. 58-60 °C (lit. m.p. 58–60 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (td, J = 6.9, 1.4 Hz, 1 H), 7.64 (td, J = 6.9, 1.4 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 1 H), 7.94 (s, 1 H), 7.95 (d, J = 1.4 Hz, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 8.34 (s, 1 H), 10.15 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.73, 127.10, 128.05, 129.09 (2 C), 129.52, 132.61, 134.08, 134.53, 136.41, 192.23; IR (KBr): $\tilde{\nu}$ = 2827, 1685 cm^{-1}; HRMS (EI) calcd for $C_{11}H_8O$: 157.0609, found 157.0613.