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 glassware. 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 capillaries 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 AVIII spectrometer in CDCl$_3$ using TMS as internal reference with chemical shifts (δ) are reported in ppm. All coupling constants (J) are reported in Hz. MS (EI) spectra were recorded on double focusing mass spectrometer. 18 W CFL (Compact fluorescent lamp; Philips, 6500 k, 1010 lm, 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$_3$(2; 10 mol%) in CH$_2$CN (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, 1 mmol) 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**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Colorless oil</th>
<th>$^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>89%</td>
<td>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);</td>
<td>129.86, 129.63, 134.41, 136.36, 192.31;</td>
<td>2819, 1698 cm$^{-1}$; HRMS (EI) calcd for C$_2$H$_5$OBr: 107.0452;</td>
<td>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);</td>
<td>185.9503, found 185.9506.</td>
</tr>
</tbody>
</table>

**Compound 3d**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>81%</td>
<td>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);</td>
<td>127.12, 127.89, 129.86, 133.49, 133.87, 135.34, 191.87;</td>
<td>2869, 1689 cm$^{-1}$; HRMS (EI) calcd for C$_2$H$_5$OBr: 185.9503, found 185.9503.</td>
<td></td>
</tr>
</tbody>
</table>

**Compound 3e**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>92%</td>
<td>7.47 (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);</td>
<td>21.83, 129.66, 129.77, 134.14, 145.49, 191.7;</td>
<td>2823, 1703 cm$^{-1}$; HRMS (EI) calcd for C$_2$H$_5$OBr: 121.0609, found 121.0605.</td>
<td></td>
</tr>
</tbody>
</table>

**Compound 3f**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>91%</td>
<td>7.27 (s, 3 H), 7.22 (d, J = 6.6 Hz, 1 H), 7.32 (d, J = 6.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 1 H), 7.77 (d, J = 7.8 Hz, 1 H), 10.25 (s, 1 H);</td>
<td>19.53, 126.24, 131.69, 131.97, 133.57, 134.09, 140.53, 192.7;</td>
<td>2865, 1693 cm$^{-1}$; HRMS (EI) calcd for C$_2$H$_5$OBr: 121.0609, found 121.0607.</td>
<td></td>
</tr>
</tbody>
</table>

**Compound 3g**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>80%</td>
<td>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);</td>
<td>116.29 (d, J$<em>{C,Br}$ = 22.9 Hz), 132.19 (d, J$</em>{C,Br}$ = 9.5 Hz), 132.93, 164.67 (d, J$_{C,Br}$ = 256.6 Hz), 190.45;</td>
<td>2829, 1695 cm$^{-1}$; HRMS (EI) calcd for C$_2$H$_5$OBr: 123.9241, found 123.9245.</td>
<td></td>
</tr>
</tbody>
</table>

**Compound 3i**

<table>
<thead>
<tr>
<th>Yield</th>
<th>White solid; m.p. 74–75 °C (lit. m.p. 73–75 °C); $^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>81%</td>
<td>7.92 (d, J = 8.2 Hz, 2 H), 9.96 (s, 1 H);</td>
<td>123.89, 130.91, 135.55, 138.49, 191.41;</td>
<td>23223.9421, found 232.9425.</td>
<td></td>
</tr>
</tbody>
</table>

**Compound 3j**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$); δ</th>
<th>$^1$C NMR (100 MHz, CDCl$_3$); δ</th>
<th>IR (neat): ν =</th>
<th>HRMS (EI) calcd for C$_2$H$_5$OBr:</th>
</tr>
</thead>
<tbody>
<tr>
<td>79%</td>
<td>7.82 (d, J = 8.1 Hz, 2 H), 8.01 (d, J = 8.1 Hz, 2 H), 10.13 (s, 1 H);</td>
<td>123.37 (q, J$<em>{C,Br} =$ 227.2 Hz), 126.01, 129.81, 135.48 (q, J$</em>{C,Br} =$ 32.4 Hz), 138.63, 191.00;</td>
<td>2837, 1707 cm$^{-1}$; HRMS (EI) calcd for C$_2$H$_5$OBr: 175.0326, found 175.0324.</td>
<td></td>
</tr>
</tbody>
</table>
Compound 3k \textsuperscript{7c}

Yield 90%; Light yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 31.01, 35.24, 125.89, 129.62, 133.98, 158.34, 191.97; IR (neat): \(v^\prime = 2964, 1696\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{11}H\textsubscript{14}O: 163.1078, found 163.1083.

Compound 3l \textsuperscript{7c}

Yield 96%; Colorless oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 55.53, 114.24, 129.86, 131.92, 164.56, 190.79; IR (neat): \(v^\prime = 2841, 2738, 1682\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{14}H\textsubscript{16}O:\n
\[
\text{137.0558, found 137.0554.}
\]

Compound 3m \textsuperscript{20b}

Yield 91%; White solid; m.p. 114-116 °C (lit. m.p. 115–116 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 55.96, 113.42, 113.67, 126.05, 131.04, 138.26, 160.69, 188.34; IR (KBr): \(v^\prime = 2981, 1682\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{15}H\textsubscript{18}O:\n
\[
\text{215.9609, found 215.9606.}
\]

Compound 3n \textsuperscript{7c}

Yield 78%; White solid; m.p. 155-157 °C (lit. m.p. 154–158 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 14.17, 61.53, 129.38, 130.05, 135.36, 139.01, 165.48, 191.59; IR (KBr): \(v^\prime = 2982, 1703\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{16}H\textsubscript{19}O:\n
\[
\text{179.0663, found 179.0667.}
\]

Compound 3o \textsuperscript{7c}

Yield 79%; White solid; m.p. 169-172 °C (lit. m.p. 165–173°C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 5.76 (br, 1 H), 6.12 (br, 1 H), 7.97 (m, 4 H), 10.09 (s, 1 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 128.16, 129.35, 137.81, 139.37, 167.08, 192.90; IR (KBr): \(v^\prime = 3360, 3178, 2833, 1657\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{16}H\textsubscript{15}N:\n
\[
\text{150.0510, found 150.0508.}
\]

Compound 3p \textsuperscript{7c}

Yield 78%; White solid; m.p. 65-66 °C (lit. m.p. 65–67 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 128.54, 129.48, 130.10, 130.31, 133.14, 136.73, 138.45, 142.57, 191.64, 195.81; IR (KBr): \(v^\prime = 2809, 1696, 1649\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{16}H\textsubscript{18}NO:\n
\[
\text{211.0714, found 211.1711.}
\]

Compound 3q \textsuperscript{7c}

Yield 91%; White solid; m.p. 58-60 °C (lit. m.p. 58–60 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 127.29, 127.59, 128.40, 128.96, 130.19, 135.11, 139.62, 147.09, 191.84; IR (KBr): \(v^\prime = 2836, 1695\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{16}H\textsubscript{17}NO:\n
\[
\text{183.0769, found 183.0762.}
\]

Compound 3r \textsuperscript{7c}

Yield 92%; Light yellow oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 124.87, 126.96, 128.45 (2 C), 129.04, 130.53, 131.39, 133.69, 135.27, 136.69, 193.50; IR (neat): \(v^\prime = 2981, 2738, 1682\) cm\(^{-1}\); HRMS (EI) caleld for C\textsubscript{16}H\textsubscript{18}O:\n
\[
\text{215.0305, found 151.0347.}
\]
Compound 3\textsuperscript{c}

Yield 91%; Light yellow solid; m.p. 58-60 °C (lit. m.p. 58–60 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 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); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 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\textsuperscript{-1}; HRMS (EI) calcd for C\textsubscript{11}H\textsubscript{8}O: 157.0609, found 157.0613.