Electronic Supplementary Information

[Fe$^{III}$](TF$_4$DMAP)OTf] Catalysed Anti-Markovnikov Oxidation of Terminal Aryl Alkenes to Aldehydes and Transformation of Methyl Aryl Tertiary Amines to Formamides with H$_2$O$_2$ as Terminal Oxidant

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General Experimental: All experiments were performed using standard Schlenk techniques in flame-dried Schlenk tube under an atmosphere of argon unless otherwise specified. Solvents were dried by standard procedures [Dioxane, tetrahydrofuran (THF) and toluene were freshly distilled from Na/benzophenone; Dichloromethane (DCM), Dichloroethane (DCE), Acetonitrile (CH$_3$CN), tert-butyl alcohol (t-BuOH) and methanol (MeOH) were distilled from CaH$_2$] under argon and used immediately. Alkenes were obtained commercially and used directly or filtered through neutral Al$_2$O$_3$. $^1$H and $^{13}$C NMR were recorded on Varian Mercury 300 spectrometer with CDCl$_3$ as solvent (TMS as internal standard). Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet; dt = doublet of triplets, m = multiplet), coupling constants in Hertz (Hz), and integration. EI mass were determined on a HP5989A mass spectrometer. IR spectra (KBr) were measured on Bio-Rad FTS-185 spectrometer. UV-Visible absorption spectra were recorded on a CARY100 spectrophotometer in dichloromethane. GC analyses were performed on a Varian CP-3800, SPB$^\text{TM}$-5, FID and n-dodecane was used as the internal standard.
**Preparation of Fe(TF₄DMAP)Cl**

A mixture of H₂F₂₀TPP (380 mg, 0.39 mmol), FeCl₂ (494 mg, 3.9 mmol), and (CH₃)₂NH·HCl (954 mg, 11.7 mmol) in DMF (120 mL) was refluxed under argon for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on a neutral alumina column with CH₂Cl₂/PE 1:1 ~ CH₂Cl₂ as eluting solvent to give the desired product as a dark purple solid in 97% yield.

MS (MALDI) m/z: 1128.3 (100), 1129.4 (60); IR (KBr): νₘₐₓ 3446, 2892, 2812, 1682, 1647, 1538, 1506, 1479, 1436, 1419, 1334, 1209, 1075, 1048, 1002, 976, 948, 806, 771, 756, 707 cm⁻¹; UV-Vis (CH₂Cl₂, nm): λₘₐₓ = 347, 416, 505, 581, 635.

**Preparation of Fe(TF₄DMAP)OTf**

A mixture of [Fe(TF₄DMAP)Cl] (116 mg, 0.1 mmol) and AgOTf (26 mg, 0.1 mmol) in THF (6 mL) was refluxed gently under argon for 5 h. Upon cooling to room temperature, the reaction mixture was filtered through a pad of Celite under argon and then dried under vacuum to give the desired product.

HR-MS (MALDI) m/z: [C₅₂H₃₂N₈F₁₆Fe]⁺ cacld 1128.1838, found 1128.1901. IR (KBr): νₘₐₓ 3447, 2933, 2813, 1647, 1480, 1436, 1419, 1333, 1259, 1227, 1168, 1076, 1048, 1027, 975, 950, 807, 772, 756, 708, 636, 517 cm⁻¹; UV-Vis (CH₂Cl₂, nm): λₘₐₓ = 335, 409, 517, 646.
Preparation of Fe(TF₄DMAP)X (in situ, Table 1)

Fe(TF₄DMAP)Cl (4.65 mg, 0.004 mmol) and AgX or NaBArF (0.004 mmol) were added to 1.5 mL of dioxane and further stirred at room temperature under argon for 0.5 h. After adding styrene (0.2 mmol) to the mixture, H₂O₂ (0.4 mmol) diluted in dioxane (0.5 mL) was added via syringe pump.

Table S1 Solvent Effect of [Fe(TF₄DMAP)OTf] Catalysed E–I Reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>solvent</th>
<th>conversion (%)</th>
<th>Yield (%)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dioxane</td>
<td>100</td>
<td>84</td>
<td>0</td>
<td>5</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
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<td>11</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td></td>
</tr>
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<td>3</td>
<td>Toluene</td>
<td>31</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CH₃CN</td>
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<td>1</td>
<td>18</td>
<td>0</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Et₂O</td>
<td>42</td>
<td>13</td>
<td>0</td>
<td>25</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>MTBE</td>
<td>96</td>
<td>28</td>
<td>18</td>
<td>25</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CH₃OH/CH₂Cl₂</td>
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<td>9</td>
<td>0</td>
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<tr>
<td>8</td>
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<td>47</td>
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<td>38</td>
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<td></td>
</tr>
<tr>
<td>9</td>
<td>'BuOH</td>
<td>100</td>
<td>-</td>
<td>70</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
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<td>10</td>
<td>MeOH</td>
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<td>65</td>
<td>0</td>
<td>0</td>
<td>25</td>
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</tr>
<tr>
<td>11</td>
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<td>80</td>
<td>5</td>
<td>0</td>
<td>70</td>
<td>5</td>
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</tr>
</tbody>
</table>

* H₂O₂ (0.4 mmol, diluted in 0.5 mL solvent) was added to a mixture of styrene (0.2 mmol) and catalyst (2 mol%) in solvent (1.5 mL) at room temperature via syringe pump for 5 h, and then the mixture was further stirred for additional 15 h; * determined by GC; * the solvent itself was oxidized; * 5% (dimethoxy)methylbenzene and 3% 2-tert-butoxy-2-phenylethanol were also obtained; * CH₃OH/CH₂Cl₂ = 3/1, 0.05 mol% catalyst was used with 2.5 mmol of styrene; * ring-opening product 2-tert-butoxy-2-phenylethanol was obtained; * the products existed in the form of acetals. THF = tetrahydrofuran, MTBE = methyl tert-butyl ether, DME = 1,2-dimethoxyethane.
Table S2 The influence of the amount of H$_2$O$_2$

$$\text{Ph} + \text{H}_2\text{O}_2 \rightarrow \text{PhCHO} + \text{OH}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>H$_2$O$_2$ /eq.</th>
<th>Conversion (%)$^b$</th>
<th>Yield (%)$^b$</th>
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</thead>
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<tr>
<td></td>
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<td>c</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>40</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>100</td>
<td>41</td>
</tr>
</tbody>
</table>

$^a$ H$_2$O$_2$ (diluted in 0.5 mL of dioxane) was added to a mixture of styrene (0.2 mmol) and catalyst (2 mol%) in 1.5 mL of dioxane via syringe pump for 5 h; $^b$ determined by GC.

Table S3 Other Oxidants:

$$\text{Ph} + \text{Oxidant} \rightarrow \text{PhCHO} + \text{OH}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Conversion (%)$^b$</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>1</td>
<td>'BuOOBu$^f$</td>
<td>dioxane</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
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<td>'BuOOH</td>
<td>dioxane</td>
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<td>trace</td>
</tr>
<tr>
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<td>'BuOH</td>
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</tr>
<tr>
<td>4</td>
<td>H$_2$O$_2$</td>
<td>'BuOH</td>
<td>100</td>
<td>trace</td>
</tr>
</tbody>
</table>

$^a$ Oxidant (dissolved in 0.5 mL of solvent) was added to a mixture of styrene (0.2 mmol) and catalyst (0.5 mol%) in 1.5 mL of solvent via syringe pump for 5 h; $^b$ determined by GC; $^c$ one undefined structure with $m/z = 142$ was obtained; $^d$ determined by $^1$H NMR with PhTMS as internal standard.
**Table S4** Additive effect in iron porphyrin catalyzed formamide formation reactions

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Add. (eq.)</th>
<th>Cat.</th>
<th>Convn. (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TMSCF&lt;sub&gt;3&lt;/sub&gt; (1.2), AcOH (6)</td>
<td>RuCl&lt;sub&gt;3&lt;/sub&gt; (5%)</td>
<td>100</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>TMSCF&lt;sub&gt;3&lt;/sub&gt; (1.2), AcOH (6)</td>
<td>Fe(TDCDMAP)OTf</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>Fe(TDCDMAP)OTf</td>
<td>65</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>AcOH (1)</td>
<td>Fe(TPFPP)OTf</td>
<td>99.5</td>
<td>100</td>
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<tr>
<td>5</td>
<td>AcOH (1)</td>
<td>Fe(TF&lt;sub&gt;4&lt;/sub&gt;DMAP)OTf</td>
<td>91</td>
<td>100</td>
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<td>6</td>
<td>AcOH (1)</td>
<td>Fe(TDCDMAP)OTf</td>
<td>100</td>
<td>96 (80)</td>
</tr>
<tr>
<td>7</td>
<td>AcOH (0.2)</td>
<td>Fe(TF&lt;sub&gt;4&lt;/sub&gt;DMAP)OTf</td>
<td>80</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>AcOH (0.2)</td>
<td>Fe(TDCDMAP)OTf</td>
<td>82</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>AcOH (1)</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt; (5%)</td>
<td>47</td>
<td>49</td>
</tr>
<tr>
<td>10</td>
<td>AcOH (1)</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt; (5%)</td>
<td>19</td>
<td>37</td>
</tr>
</tbody>
</table>

<sup>a</sup> Fe(Por)OTf (3 µmol), substrate (1.0 mmol), and the additive were added successively to 1.2 mL of MeOH, and the mixture was stirred under argon at room temperature. H<sub>2</sub>O<sub>2</sub> (283.5 mg, 2.5 mmol) were added via syringe pump over 1 h. <sup>b</sup> Analysed by GC and GC-MS. <sup>c</sup> Determined by GC and GC-MS based on conversions, and the isolated yields were shown in brackets.

**Mechanism A) Control experiments:**

![Mechanism](image)

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>time (h)</th>
<th>Conversion (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>a</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>98</td>
<td>75</td>
<td>13</td>
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<tr>
<td>2</td>
<td>43</td>
<td>100</td>
<td>71</td>
<td>19</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> (0.4 mmol, diluted in 0.5 mL dioxane) was added to a mixture of styrene oxide (0.2 mmol) and catalyst (2 mol%) in 1.5 mL of dioxane via syringe pump for 5 h; <sup>b</sup> determined by GC.
B) $^{18}\text{O}$-Labelling:

$^{18}\text{O}$-H$_2$O (35 mg, diluted in 0.5 mL of dioxane) was added to a mixture of styrene oxide (0.2 mmol) and catalyst (2 mol%) in 1.5 mL of dioxane via syringe pump for 5 h. After stirring for another 5 h, the reaction mixture was analysed by GC-MS. No diol was obtained.

**Phenylacetaldehyde:** EI-MS $m/z$ (relative intensity): 120(M$^+$, 18), 122($^{18}$O-M$^+$, 6), 91 (100), 92 (31), 65 (27); **Styrene oxide:** EI-MS $m/z$ (relative intensity): 119(M-1, 54), 120(31), 121 ($^{18}$OM-1, 3), 91 (100), 89 (84), 90 (67), 92 (37), 63 (28), 51 (24), 65 (21).

The speculative mechanism on formation of diol:

Mass spectrometry analysis

Positive-ion ESI mass spectra were obtained on a Waters Micromass Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer. Typically, [Fe$^{III}$(Por)(OTf)] ($5 \times 10^{-4}$ M) was treated with H$_2$O$_2$ (5 equiv.) in acetonitrile. After reacting at room temperature for 30 s, the reaction mixture was introduced into the ESI source by a syringe pump operating at 5 μL min$^{-1}$. For accurate mass measurements, sodium formate was used as calibration reference. The mass resolution was fixed at about 8000 (full width at half-height) with mass accuracy limited within 10 ppm.
Fig. S1 ESI-MS spectrum of the reaction mixture of \([\text{Fe}^{\text{III}}(\text{TF}_4\text{DMAP})(\text{OTf})]\) (5 × 10\(^{-4}\) M in acetonitrile) with \(\text{H}_2\text{O}_2\) (5 equiv.)

Simulated
\([\text{Fe}(\text{TF}_4\text{DMAP})\text{O}]^+\)

Experimental
\([\text{Fe}(\text{TF}_4\text{DMAP})\text{O}]^+\)

Fig. S2 ESI-MS spectrum of \([\text{Fe}(\text{TF}_4\text{DMAP})(\text{O})]^+\): simulated isotopic pattern (top), experimentally observed (bottom)
Fig. S3 ESI-MS spectrum of [Fe(TF₄DMAP)O₂]⁺: simulated isotopic pattern (top), experimentally observed (bottom)

Fig. S4 Collision-induced dissociation spectrum of [Fe(TF₄DMAP)O]⁺
Fig. S5 Collision-induced dissociation spectrum of $[\text{Fe(TF}_4\text{DMAP)O}_2]^+$

Fig. S6 ESI-MS spectrum of the reaction mixture of $[\text{Fe}^{\text{III}}(\text{TF}_4\text{DMAP})(\text{OTf})] (5 \times 10^{-4} \text{ M in acetonitrile})$ with $\text{H}_2\text{O}_2$ (5 equiv., top) and in presence of styrene (50 equiv., bottom). Numbers in the brackets represent the signal intensity.
**Fig. S7** ESI-MS spectrum of [Fe(TF₄DMAP)O₂]⁺ in the absence (top) and presence of ¹⁸O-H₂O (500 equiv., bottom).

**Fig. S8** ESI-MS spectrum of [Fe(F₂₀TPP)(O)]⁺: simulated isotopic pattern (top), experimentally observed (bottom)
Fig. S9 ESI-MS spectrum of the reaction mixture of Fe(F$_2$0$_2$TPP)(OTf) (5 × 10$^{-4}$ M in acetonitrile) with H$_2$O$_2$ (5 equiv. top) and in presence of styrene (50 equiv. bottom). Numbers below m/z values represent the signal intensity.

Fig. S10 ESI-MS spectrum of [Fe(F$_2$0$_2$TPP)(O)]$^+$ in the absence (top) and presence of $^{18}$O-H$_2$O (500 equiv., bottom).
Fig. S11 UV-visible absorption spectra of [Fe(TF₄DMAP)OTf] with excess H₂O₂ in dichloromethane at room temperature.
Typical procedure for [Fe(TF₄DMAP)OTf]-catalysed oxidation of aryl alkenes to aldehydes:

To a solution of [Fe(TF₄DMAP)OTf] (1.3 mg, 1 μmol) and styrene (20.8 mg, 0.2 mmol) in dioxane (1.5 mL) was added H₂O₂ (30% aqueous solution, 45.4 mg, 0.4 mmol, diluted in 0.5 mL of dioxane) via syringe pump for 5 h. After stirring for additional 3 ~ 5 h at room temperature, the reaction mixture was filtered through a short column of silica (2 ~ 3 cm) and washed with EtOAc (50 mL). The product yields were determined by ^1H NMR with PhTMS as internal standard.

2-phenylacetaldehyde

![2-phenylacetaldehyde](image)

^1H NMR (300 MHz, CDCl₃): δ 9.75 (t, J = 2.4 Hz, 1H), 7.41-7.21 (m, 5H), 3.69 (d, J = 2.4 Hz, 2H); EI-MS m/z (relative intensity): 120(M⁺, 70), 91 (100), 44 (54), 107 (40), 77 (39), 79 (31), 105 (31), 45 (25).

2-p-tolylacetaldehyde

![2-p-tolylacetaldehyde](image)

^1H NMR (300 MHz, CDCl₃): δ 9.73 (t, J = 2.1 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 3.65 (d, J = 2.1 Hz, 2H), 2.35 (s, 3H); EI-MS m/z (relative intensity): 134 (M⁺, 25), 105 (100), 77 (22), 79 (21), 103 (13), 91 (11).

2-(4-methoxyphenyl)acetaldehyde

![2-(4-methoxyphenyl)acetaldehyde](image)

^1H NMR (300 MHz, CDCl₃): δ 9.72 (t, J = 2.4 Hz, 1H), 7.13 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.63 (d, J = 2.4 Hz, 2H); EI-MS m/z (relative intensity): 150 (M⁺, 13), 121 (100), 77 (18), 78 (14).

2-(4-(chloromethyl)phenyl)acetaldehyde

![2-(4-(chloromethyl)phenyl)acetaldehyde](image)

^1H NMR (300 MHz, CDCl₃): δ 9.72 (t, J = 2.4 Hz, 1H), 7.32-7.36 (m, 2H), 7.28-7.30 (m, 2H), 4.62 (s, 2H), 3.65 (d, J = 2.4 Hz, 2H); EI-MS m/z (relative intensity): 168 (M⁺, 28), 170 (^37Cl M⁺, 9), 139 (100), 103 (70), 104 (60), 77 (43), 105 (32), 141 (32), 78 (24), 91 (24).
2-(4-fluorophenyl)acetaldehyde

\[
\text{F} \quad \text{CHO} \\
\overset{2e}{\text{F}}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.75 (t, $J = 1.5$ Hz, 1H), 7.21-7.16 (m, 2H), 7.09-7.04 (m, 2H), 3.69 (d, $J = 1.5$ Hz, 2H); EI-MS $m/z$ (relative intensity): 138 (M$^+$, 19), 109(100), 83 (24), 110 (11).

2-(4-bromophenyl)acetaldehyde

\[
\text{Br} \quad \text{CHO} \\
\overset{2f}{\text{Br}}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$9.70 (t, $J = 1.9$ Hz,1H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.08 (d, $J = 8.2$ Hz, 2H), 3.66 (d, $J = 1.9$ Hz, 2H); EI-MS $m/z$ (relative intensity): 198 (M$^+$, 27), 200 ($^{81}\text{BrM}^+$, 28), 169 (100), 171 (93), 90 (93), 89 (78), 91 (54), 63 (49).

2-(4-(trifluoromethyl)phenyl)oxirane

\[
\overset{2g}{\text{H}} \quad \\
\overset{\text{F}_3\text{C}}{\text{O}}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$7.60 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 3.92 (dd, $J = 4.0$, 2.6 Hz, 1H), 3.19 (dd, $^1J = 5.6$ Hz, $^2J = 4.0$ Hz, 1H), 2.77 (dd, $^1J = 5.6$ Hz, $^2J = 2.6$ Hz, 1H), EI-MS $m/z$ (relative intensity): 188 (M$^+$, 6), 119 (100), 91 (42), 89 (28), 158 (24), 63 (21), 159 (19), 109 (18), 108 (13), 107 (11), 187 (9), 169 (5).

2-\text{m}-tolylacetaldehyde

\[
\overset{\text{Me}}{\text{CHO}} \\
\overset{2h}{\text{Me}}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.74 (t, $J = 2.4$ Hz, 1H), 7.26 (m, 1H), 7.12 (m, 1H), 7.02 (m, 2H), 3.64 (d, $J = 2.4$ Hz, 2H), 2.36 (s, 3H). EI-MS $m/z$ (relative intensity): 134 (M$^+$, 32), 105 (100), 106 (33), 91 (31), 77 (27), 79 (25), 103 (16).

2-(3-nitrophenyl)acetaldehyde

\[
\overset{\text{NO}_2}{\text{CHO}} \\
\overset{2i}{\text{NO}_2}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.84 (t, $J = 2.4$ Hz, 1H), 8.25-8.27 (m, 1H), 8.15-8.18 (m, 1H), 7.71-7.73 (m, 1H), 7.62-7.64 (m, 1H), 3.67 (d, $J = 2.4$ Hz, 2H); EI-MS $m/z$ (relative intensity): 165 (M$^+$, 22), 90 (100), 91 (80), 89 (80), 65 (56), 137 (50), 136 (50), 120 (27).
2-(3-fluorophenyl)acetaldehyde

![Chemical structure](Image)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 9.77 (t, $J = 3.0$ Hz, 1H), 7.33 (m, 1H), 6.98 (m, 3H), 3.69 (d, $J = 3.0$ Hz, 2H). EI-MS $m/z$ (relative intensity): 138 (M⁺, 29), 109 (100), 110 (43), 83 (33), 57 (10).

2-(3-chlorophenyl)acetaldehyde

![Chemical structure](Image)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 9.75 (t, $J = 1.8$ Hz, 1H), 7.34-7.28 (m, 2H), 7.23 (s, 1H), 7.12-7.10 (m, 1H), 3.69 (d, $J = 1.8$ Hz, 2H); EI-MS $m/z$ (relative intensity): 154 (M⁺, 29), 156 (ClM⁺, 9), 125 (100), 91 (92), 89 (51), 126 (36), 127 (35).

2-(3-bromophenyl)acetaldehyde

![Chemical structure](Image)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 9.78 (t, $J = 2.1$ Hz, 1H), 7.48 (d, $J = 8.1$ Hz, 1H), 7.42 (s, 1H), 7.26-7.23 (m, 1H), 7.18 (d, $J = 7.8$ Hz, 1H), 3.71 (d, $J = 2.1$ Hz, 2H); EI-MS $m/z$ (relative intensity): 198 (M⁺, 15), 200 (BrM⁺, 14), 125 (100), 91 (100), 90 (59), 89 (55), 63 (38), 169 (31), 171 (30), 170 (14), 172 (13).

2-(2-fluorophenyl)acetaldehyde

![Chemical structure](Image)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 9.76 (s, 1H), 7.34-7.07 (m, 4H), 3.73 (m, 2H); EI-MS $m/z$ (relative intensity): 138 (M⁺, 25), 109 (100), 83 (25), 110 (21).

2-(naphthalen-2-yl)acetaldehyde

![Chemical structure](Image)

$^1$H NMR (300 MHz, CDCl₃): $\delta$ 9.75 (t, $J = 2.1$ Hz, 1H), 7.86-7.79 (m, 3H), 7.69 (s, 1H), 7.50-7.47 (m, 2H), 7.52 (d, $J = 8.4$ Hz, 1H), 3.76 (d, $J = 2.1$ Hz, 2H); EI-MS $m/z$ (relative intensity): 170 (M⁺, 24), 141 (100), 115 (39), 142 (21), 139 (12).
2-phenylpropanal

\[
\begin{array}{c}
\text{Me} \\
\text{CHO} \\
\end{array}
\]

\(2\text{o}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 9.69\) (s, 1H), 7.42-7.21 (m, 5H), 3.64 (q, \(J = 7.2\) Hz, 1H), 1.45 (d, \(J = 7.2\) Hz, 3H); EI-MS \(m/z\) (relative intensity): 134(M\(^+\), 12), 105 (100), 79 (24), 77 (23), 103 (14), 106 (11), 91 (10).

2,2-diphenylacetaldehyde

\[
\begin{array}{c}
\text{Ph} \\
\text{CHO} \\
\end{array}
\]

\(2\text{p}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 9.94\) (d, \(J = 2.4\) Hz, 1H), 7.21-7.40 (m, 10H), 4.88 (d, \(J = 2.4\) Hz, 1H); EI-MS \(m/z\) (relative intensity): 196 (M\(^+\), 3), 167 (100), 165 (47), 152 (30).

3-bromo-2-phenylpropanal

\[
\begin{array}{c}
\text{Br} \\
\text{CHO} \\
\end{array}
\]

\(2\text{q}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 9.67\) (d, \(J = 2.4\) Hz, 1H), 7.33-7.45 (m, 5H), 4.39 (d, \(J = 4.5\) Hz, 2H), 3.67 (m, 1H).

EI-MS \(m/z\) (relative intensity): 212 (M\(^+\), 1), 214 (\(^{81}\)Br-M\(^+\), 1), 103 (100), 77 (27), 104 (16), 51 (15), 133 (12), 102 (12), 91 (7).

2-tert-butoxy-2-phenylethanol

\[
\begin{array}{c}
\text{OBU}^t \\
\text{OH} \\
\end{array}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.23-7.36\) (m, 5H), 4.62 (dd, \(^1\)\(J = 4.4\) Hz, \(^2\)\(J =8.2\) Hz, 1H), 3.43–3.57 (m, 2H), 2.27 (br, OH), 1.17 (s, 9H).

EI-MS \(m/z\) (relative intensity): 163 (22), 107 (100), 57 (60), 79 (24), 77 (16), 108 (9), 91 (9), 103 (8).
**Typical procedure** for [Fe(TF₄DMAP)OTf]-catalysed oxidation of methyl aryl tertiary amines to formamides:

To a solution of [Fe(TF₄DMAP)OTf] (3.9 mg, 3 μmol) and N,N-dimethyl aniline (121.2 mg, 1.0 mmol) and acetic acid (60.0 mg, 1.0 mmol) in dioxane (1.2 mL) was added H₂O₂ (30% aqueous solution, 283.5 mg, 2.5 mmol) via syringe pump for 1 h. After stirring for additional 1 h at room temperature, the reaction mixture was filtered through a short column of silica (2 ~ 3 cm) and washed with EtOAc (50 mL). The product yields were determined by GC and purified by column chromatography with PE/EA (10:1 ~ 2:1).

\[
\begin{align*}
\text{4a} & \\
\text{1H NMR (CDCl}_3, 300 MHz) & \delta 8.47 \text{ (s, 1H), 7.39-7.44 (m, 2H), 7.25-7.30 (m, 1H), 7.17 (d, 2H, } J = 7.5 \text{ Hz), 3.32 (s, 3H); 13C NMR (CDCl}_3, 75 MHz):} & \delta 162.2, 142.0, 129.4, 126.2, 122.1, 31.8.
\end{align*}
\]

\[
\begin{align*}
\text{4b} & \\
\text{1H NMR (CDCl}_3, 300 MHz): & \delta 8.43 \text{ (s, 1H), 6.91 (s, 1H), 6.78 (s, 2H), 3.28 (s, 3H), 2.33 (s, 6H); 13C NMR (CDCl}_3, 75 MHz):} & \delta 162.2, 142.0, 139.2, 127.9, 120.0, 31.9, 21.1.
\end{align*}
\]

\[
\begin{align*}
\text{4c} & \\
\text{1H NMR (CDCl}_3, 300 MHz): & \delta 7.98 \text{ (s, 1H), 6.93 (s, 2H), 3.09 (s, 3H), 2.28 (s, 3H), 2.16 (s, 6H); 13C NMR (CDCl}_3, 75 MHz):} & \delta 163.4, 138.2, 136.6, 136.2, 129.2, 31.7, 20.8, 17.5.
\end{align*}
\]

\[
\begin{align*}
\text{4d} & \\
\text{1H NMR (CDCl}_3, 300 MHz): & \delta 8.35 \text{ (s, 1H), 7.15 (d, 2H, } J = 8.2 \text{ Hz), 7.00 (d, 2H, } J = 8.2 \text{ Hz), 3.23 (s, 3H), 2.30 (s, 3H); 13C NMR (CDCl}_3, 75 MHz):} & \delta 162.1, 139.4, 136.0, 129.9, 122.2, 31.9, 20.6.
\end{align*}
\]
$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.30 (s, 1H), 7.05 (d, 2H, $J = 9.0$ Hz), 6.89 (d, 2H, $J = 9.0$ Hz), 3.78 (s, 3H), 3.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 162.4, 158.1, 134.8, 124.5, 114.6, 55.4, 32.5.

$^4$e

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.50 (s, 1H), 7.50 (d, 2H, $J = 7.6$ Hz), 7.10 (d, 2H, $J = 7.6$ Hz), 3.29 (s, 3H), 3.11 (s, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 161.8, 142.2, 133.3, 121.3, 119.8, 82.4, 78.0, 31.5.

$^4$f

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.42 (s, 1H), 7.48 (d, $J = 8.4$ Hz), 7.02 (d, $J = 8.4$ Hz), 3.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 161.7, 141.0, 132.5, 123.5, 119.4, 31.7.

$^4$g

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 10.00 (s, 1H), 8.72 (s, 1H), 7.96 (d, 2H, $J = 8.2$ Hz), 7.37 (d, 2H, $J = 8.2$ Hz), 3.39 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 190.6, 161.6, 147.0, 133.4, 131.1, 120.6, 31.1.