Chemoselective Iron(II) Catalyzed Oxidation of a Variety of Secondary Alcohols Over Primary Alcohols Utilizing H$_2$O$_2$ as the Oxidant

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1. Experimental procedures for the synthesis of the diols

**General.** Chemicals were treated as follows: toluene, diethyl ether, distilled from Na/benzophenone; CH$_2$Cl$_2$, MeOH distilled from CaH$_2$, and CHCl$_3$, silica (Aldrich) were used as received. H$_2$O$_2$ (30 wt% in H$_2$O, Aldrich), were used as received.

The diols utilized for the oxidation reactions were either commercially available (6, 8, 16, 18, 20, 22, all Sigma-Aldrich) or synthesized by reduction of the corresponding commercially available keto esters. The synthesized diols 10, 12, and 14 are known, and spectroscopic data matched literature values.$^{1-3}$ The syntheses of the diols 10, 12, and 14 were carried out under nitrogen employing standard Schlenk techniques, and workups were carried out in the air.

The catalytic experiments were carried out in the air. The products were known and spectroscopic data matched those reported in the literature.$^{4-10}$

NMR spectra were obtained at room temperature on a Bruker Avance 300 MHz or a Varian Unity Plus 300 MHz instrument and referenced to a residual solvent signal; all assignments are tentative. IR spectra were recorded on a Thermo Nicolet 360 FT-IR spectrometer.

2-hydroxycyclohexane-1-methanol (10).$^1$

![Chemical Structure](image)

To a 100 mL Schlenk flask, lithium aluminum hydride (LiAlH$_4$, 1.67 g, 44.1 mmol) was added followed by diethyl ether (30 mL). The slurry was stirred for 5 min at room temperature
and the flask was then lowered into an ice bath. Then ethyl-2-cyclohexanonecarboxylate (2.50 g, 14.7 mmol), suspended in diethyl ether (20 mL), was added dropwise. After the addition was complete, the flask was removed from the ice bath and allowed to warm to room temperature. The reaction mixture was stirred for 12 hours at room temperature. Ethyl acetate (30 mL) was added to the reaction mixture to quench unreacted lithium aluminum hydride and allowed to stir for one hour. A saturated solution of aqueous sodium sulfate (40 mL) was added to precipitate the aluminum side products. The white slurry was then filtered through a coarse fritted glass funnel containing 2 inch of celite. The filtrate was transferred to a separatory funnel; the organic phase was separated, and the aqueous phase was washed with ethyl acetate (3 × 20 mL) to extract the product from the aqueous layer. All organic extracts were combined, dried using Na₂SO₄ and evaporated to dryness yielding a light yellow, clear oil. The crude oil was then purified via column chromatography using ethyl acetate as eluent and 2-hydroxycyclohexane-1-methanol (10, 0.993 g, 7.63 mmol, 52 %) was isolated as a colorless oil as a mixture of two diastereomers, for which the NMR data are listed separately below. IR (neat solid) νmax/cm⁻¹ 3332s (OH), 2926s, 2855s.

Diastereomer 1: ¹H-NMR δH (300.13 MHz; CDCl₃; Me₄Si; 298 K) 4.35-3.89 (2H, m, 2OH), 3.64-3.45 (3H, CHOCH₂CH₂OH), 2.00-1.03 (8H, m, 4CH₂), 0.93-0.81 (1H, m, CHCH₂OH); ¹³C{¹H}-NMR δC (75.5 MHz; CDCl₃; Me₄Si; 298 K) 75.9 (s, CHO), 69.1 (s, CHCH₂OH), 45.9 (s, CHCH₂OH), 35.1 (s, CH₂CHOH), 27.2 (s, CH₂), 24.9 (s, CH₂), 23.5 (s, CH₂).

Diastereomer 2: ¹H-NMR δH (300.13 MHz; CDCl₃; Me₄Si; 298 K) 4.35-3.89 (2H, m, 2OH), 3.64-3.45 (3H, CHOCH₂CH₂OH), 2.00-1.03 (8H, m, 4CH₂), 0.93-0.81 (1H, m,
$CHCH_2OH); ^{13}C\{^1H\}$-NMR $\delta_C$ (75.5 MHz; CDCl$_3$; Me$_4$Si; 298 K) 68.2 (s, CHO), 65.5 (s, CHCH$_2$OH), 42.4 (s, CHCH$_2$OH), 32.7 (s, CH$_2$CHOH), 25.1 (s, CH$_2$), 24.4 (s, CH$_2$), 20.5 (s, CH$_2$).

3-hydroxycyclohexane-1-methanol (12).$^2$

![Diagram of the reaction](image)

To a 100 mL Schlenk flask, lithium aluminum hydride (LiAlH$_4$, 1.32 g, 34.8 mmol) was added followed by diethyl ether (30 mL). The slurry was stirred for 5 min at room temperature and the flask was then lowered into an ice bath. Then ethyl-3-hydroxycyclohexanecarboxylate (2.00 g, 11.6 mmol), suspended in diethyl ether (20 mL), was added dropwise. After addition was complete, the flask was removed from the ice bath and allowed to warm to room temperature. The reaction mixture was stirred for 12 hours at room temperature. Ethyl acetate (30 mL) was added to reaction mixture to quench the unreacted LiAlH$_4$ and allowed to stir for one hour. Finally, a saturated solution of aqueous Na$_2$SO$_4$ (40 mL) was added to precipitate aluminum side products. The white slurry was then filtered through a coarse fritted glass funnel containing 2 inch of celite. The filtrate was then transferred to a separatory funnel; the organic phase was separated, and the aqueous phase was washed with ethyl acetate (3 × 20 mL) to extract the product from the aqueous layer. All organic extracts were combined, dried using Na$_2$SO$_4$ and evaporated to dryness yielding a light yellow, clear oil. The crude oil was then purified via column chromatography using ethyl acetate as eluent and 3-hydroxycyclohexane-1-methanol (0.818 g, 6.28 mmol, 54%) was isolated as a colorless oil as a mixture of two
diastereomers. The NMR data of the two diastereomers are listed below separately. IR (neat solid) $\nu_{\text{max}}$/cm$^{-1}$ 3311 (OH), 2927s, 2855s.

Diastereomer 1: $^1$H-NMR $\delta$H (300.13 MHz; CDCl$_3$; Me$_4$Si; 298 K) 3.61-3.54 (1H, m, CHOH), 3.51-3.37 (2H, m, CH$_2$OH), 3.26 (2H, s, 2OH), 2.04-1.47 (5H, m, CH$_2$CHOHCH$_2$CHCH$_2$OH), 1.30-1.13 (2H, m, CH$_2$), 0.98-0.81 (2H, m CH$_2$); $^{13}$C$\{^1$H$\}$-NMR $\delta$C (75.5 MHz; CDCl$_3$; Me$_4$Si; 298 K) 70.3 (s, COH), 67.6 (s, CHCH$_2$OH), 39.2 (s, CHCH$_2$OH), 35.5 (s, CHOCH$_2$CH), 34.4 (s, CH$_2$CHOH), 28.3 (s, CH$_2$CHCH$_2$OH), 23.7 (s, CH$_2$).

Diastereomer 2: $^1$H-NMR $\delta$H (300.13 MHz; CDCl$_3$; Me$_4$Si; 298 K) 3.61-3.54 (1H, m, CHOH), 3.51-3.37 (2H, m, CHCH$_2$OH), 3.26 (2H, s, 2OH), 2.04-1.47 (5H, m, CH$_2$CHOHCH$_2$CHCH$_2$OH), 1.30-1.13 (2H, m, CH$_2$), 0.98-0.81 (2H, m CH$_2$); $^{13}$C$\{^1$H$\}$-NMR $\delta$C (75.5 MHz; CDCl$_3$; Me$_4$Si; 298 K) 67.6 (s, CH$_2$OH), 66.1 (s, CH$_2$OH), 67.6 (s, CH$_2$OH), 38.7 (s, CHCH$_2$OH), 35.9 (s, CHOCH$_2$CH), 32.9 (s, CH$_2$CHOH), 28.7 (s, CH$_2$CHCH$_2$OH), 19.7 (s, CH$_2$CH$_2$CH$_2$).

2-hydroxycyclopentane-1-methanol (14).³

To a 100 mL Schlenk flask, lithium aluminum hydride (LiAlH$_4$, 1.46 g, 38.4 mmol) was added followed by diethyl ether (30 mL). The slurry was stirred for 5 min at room temperature and the flask was then lowered into an ice bath. Then ethyl-2-cyclopentanonecarboxylate (2.00 g, 12.8 mmol), suspended in diethyl ether (20 mL), was added dropwise. After addition was
complete, the flask was removed from the ice bath and allowed to warm to room temperature. The reaction mixture was stirred for 12 hours at room temperature. Ethyl acetate (30 mL) was added to the reaction mixture to quench the unreacted LiAlH₄ and allowed to stir for one hour. A saturated solution of aqueous Na₂SO₄ (40 mL) was added to precipitate aluminum side products. The white slurry was then filtered through a coarse fritted glass funnel containing 2 inch of celite. The filtrate was then transferred to a separatory funnel; the organic phase was separated, and the aqueous phase was washed with ethyl acetate (3 × 20 mL) to extract the product from the aqueous layer. All organic extracts were combined, dried using Na₂SO₄ and evaporated to dryness yielding a light yellow, clear oil. The crude oil was then purified via column chromatography using ethyl acetate as eluent and 2-hydroxycyclopentane-1-methanol (14, 1.07 g, 9.21 mmol, 72%) was isolated as a colorless oil as a single diastereomer.

1H-NMR δH (300.13 MHz; CDCl₃; Me₄Si; 298 K) 4.31 (1H, q, JHH = 5.2 Hz, CHOH), 3.67 (2H, m, CH₂OH), 3.83 (2H, s, 2OH), 3.01 (2H, br s, 2OH), 2.00-1.94 (1H, m, CH), 1.82-1.71 (2H, m, CH₂), 1.52-1.44 (4H, m, 2CH₂); 13C{1H}-NMR δC (75.5 MHz; CDCl₃; Me₄Si; 298 K) 75.1 (CHOH) 62.8 (s, CH₂OH), 45.7 (s, CHCH₂OH), 35.2 (s, CH₂CHOH), 24.4 (s, CH₂), 22.3 (s, CH₂); IR (neat solid) νmax/cm⁻¹ 3364s (OH), 2958m, 2921s, 2852m.

2. Experimental procedures for the isolated yields in Table 2

2-octanone-1-ol (7). The substrate 1,2-octanediol (6, 0.062 g, 0.424 mmol) and the catalyst [Fe(5)₂]²⁺OTf₂ (0.010 g, 0.012 mmol) were dissolved in CH₃CN (2 mL). The oxidant H₂O₂ (0.109 mL, 30 wt % in H₂O, 1.06 mmol) was added dropwise via syringe (0.027
mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. To avoid overoxidation, the reaction mixture was immediately worked up. The CH₃CN was removed under vacuum and CH₂Cl₂ (10 mL) was added. The reaction mixture was dried with Na₂SO₄ and subsequently filtered through a 1 inch pad of silica. The product 2-octanone-1-ol was isolated by column chromatography as colorless oil (7, 0.046 g, 0.318 mmol, 75 %) using silica gel and EtOAc as eluent.

¹H-NMR δₜ (300.13 MHz; CDCl₃; Me₄Si; 298 K) 4.18 (2H, s, C=OCH₂OH), 3.09 (1H, bs, OH), 2.34 (2H, t, J_HH = 7.4 Hz, CH₂C=O), 1.2-1.52 (2H, m, CH₂), 1.22-1.18 (6H, m, 3CH₂); 0.81 (3H, t, J_HH = 6.3 Hz, CH₃); ¹³C{¹H}-NMR δ_C (75.5 MHz; CDCl₃; Me₄Si; 298 K) 209.9 (s, C=O), 68.1 (s, CH₂OH), 38.4 (s, CH₂C=O), 31.5 (s, CH₂CH₂C=O), 28.9 (s, CH₂), 23.7 (s, CH₂), 22.4 (s, CH₂), 14.0 (s, CH₃); IR (neat solid) ν_max/cm⁻¹ 3370m (OH), 3255m (OH), 2950m, 2918m, 2854m, 1723m (C=O).

2-butanone-1-ol (9).⁵ The substrate 1,2-butanediol (8, 0.120 g, 1.33 mmol), utilizing the oxidant H₂O₂ (0.343 mL, 30 wt % in H₂O, 3.33 mmol) and catalyst [Fe(5)₂]²⁺(OTf)₂ (0.031 g, 0.039 mmol), was converted to 2-butanone-1-ol as a colorless oil (9, 0.099 g, 1.12 mmol, 84 %) as described above for 2-octanone-1-ol, using silica gel and EtOAc as eluent.

¹H-NMR δₜ (300.13 MHz; CDCl₃; Me₄Si; 298 K) 4.27 (2H, s, C=OCH₂OH), 3.35 (1H, bs, OH), 2.45 (2H, q, J_HH = 7.4, CH₃CH₂), 1.14 (3H, t, J_HH = 7.4, CH₃CH₂); ¹³C{¹H}-NMR δ_C (75.5 MHz; CDCl₃; Me₄Si; 298 K) 210.4 (s, C=O), 68.0 (s, CH₂OH), 31.6 (s, CH₂C=O), 7.45 (s, CH₃); IR (neat solid) ν_max/cm⁻¹ 3435m (OH), 3370m (OH), 2979m, 2942m, 2885m, 1717s (C=O).
2-cyclohexanone-1-methanol (11). The substrate 2-hydroxycyclohexane-1-methanol (10, 0.136 g, 1.04 mmol) and the catalyst [Fe(5)2]2+OTf2 (0.024 g, 0.031 mmol) were dissolved in CH3CN (2 mL). The oxidant H2O2 (0.269 mL, 30 wt % in H2O, 2.61 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH3CN was removed under vacuum and CH2Cl2 (10 mL) was added. The reaction mixture was dried with sodium sulfate and subsequently filtered through a 1 inch pad of silica. The product 2-cyclohexanone-1-methanol was isolated by column chromatography as colorless oil (11, 0.078 g, 0.608 mmol, 58 %) using silica gel and EtOAc as eluent.

1H-NMR δH (300.13 MHz; CDCl3; Me4Si; 298 K) 3.74 (1H, dd, JHH = 7.3 Hz, JHH = 12.0 Hz, CHH’OH), 3.60 (1H, dd, JHH = 3.9 Hz, JHH = 11.7 Hz, CHH’OH), 3.36 (1H, br s, OH), 2.57–2.27 (3H, m, CH+CH2), 2.14–1.99 (2H, m, CH2), 1.94–1.88 (1H, m, CH), 1.74–1.60 (2H, m, CH2), 1.53–1.44 (1H, m, CH); 13C{1H} δC (75.5 MHz; CDCl3; Me4Si; 298 K) 214.9 (s, C=O), 62.8 (s, CH2OH), 52.2 (s, CHCH2OH), 42.2 (s, CH2C=O), 30.0 (s, CH2), 27.5 (s, CH2), 24.7 (s, CH2); IR (neat solid) νmax/cm–1 3404m (OH), 2935m, 2864m, 1704s (C=O).

3-cyclohexanone-1-methanol (13). The substrate 3-hydroxycyclohexane-1-methanol (12, 0.081 g, 0.622 mmol), utilizing the oxidant H2O2 (0.160 mL, 30 wt % in H2O, 1.56 mmol) and catalyst [Fe(5)2]2+OTf2 (0.014 g, 0.018 mmol), was converted to 3-cyclohexanone-1-methanol as a colorless oil (13, 0.043 g, 0.335 mmol, 54 %) as described above for 2-octanone-1-ol, using silica gel and EtOAc as eluent.
\(^1\)H-NMR \(\delta_H\) (300.13 MHz; CDCl\(_3\); Me\(_4\)Si; 298 K) 3.52 (2H, d, \(J_{HH} = 4.6\) Hz, C=OCH\(_2\)CH), 2.40–2.18 (2H, m, CH\(_2\)), 2.15–1.81 (4H, m, 2CH\(_2\)), 1.74–1.51 (2H, m, CH\(_2\)), 1.40 (1H, dq, \(J_{HH} = 3.4\) Hz, \(J_{HH} = 12.0\) Hz, CH); \(^{13}\)C\(^{1}\)H\(-\)NMR \(\delta_C\) (75.5 MHz; CDCl\(_3\); Me\(_4\)Si; 298 K) 211.7 (s, C=O), 66.9 (s, CH\(_2\)OH), 44.4 (s, CHCH\(_2\)OH), 41.5 (s, CH\(_2\)C=O), 41.4 (s, C=OCH\(_2\)), 27.7 (s, CH\(_2\)), 25.0 (s, CH\(_2\)); IR (neat solid) \(\nu_{max}/\text{cm}^{-1}\) 3404m (OH), 2930m, 2868m, 1706s (C=O).

2-cyclopentanone-1-methanol (15).\(^8\) The substrate 2-hydroxycyclopentane-1-methanol (14, 0.060 g, 0.516 mmol), utilizing the oxidant H\(_2\)O\(_2\) (0.133 mL, 30 wt \% in H\(_2\)O, 1.29 mmol) and catalyst [Fe(5)\(_2\)]\(^{2+}\)OTf\(_2\) (0.012 g, 0.015 mmol), was converted to 2-cyclopentanone-1-methanol as a colorless oil (15, 0.037 g, 0.324 mmol, 63 \%) as described above for 2-octanone-1-ol, using silica gel and EtOAc as eluent.

\(^1\)H-NMR \(\delta_H\) (300.13 MHz; CDCl\(_3\); Me\(_4\)Si; 298 K) 3.77 (2H, qd, \(J_{HH} = 5.5\) Hz, \(J_{HH} = 11.5\) Hz, CHCH\(_2\)OH), 2.41-2.29, 2.24-1.98, 1.92-1.68, 1.25 (8H, 3m, 1s, 3CH\(_2\), CH, OH); \(^{13}\)C\(^{1}\)H\(-\)NMR \(\delta_C\) (75.5 MHz; CDCl\(_3\); Me\(_4\)Si; 298 K) 222.5 (s, C=O), 62.0 (s, CH\(_2\)OH), 50.6 (s, CH\(_2\)C=O), 38.5 (s, CHCH\(_2\)OH), 26.1 (s, CH\(_2\)CHCH\(_2\)OH), 20.8 (s, CH\(_2\)CH\(_2\)CH\(_2\)); IR (neat solid) \(\nu_{max}/\text{cm}^{-1}\) 3440m (OH), 2993s, 2853s, 1730s (C=O).

2-ethyl-3-hexanone-1-ol (17).\(^9\) The substrate 2-ethyl-1,3-hexanediol (16, 0.200 g, 1.37 mmol), utilizing the oxidant H\(_2\)O\(_2\) (0.352 mL, 30 wt \% in H\(_2\)O, 3.42 mmol) and catalyst [Fe(5)\(_2\)]\(^{2+}\)OTf\(_2\) (0.030 g, 0.041 mmol), was converted to 2-ethyl-3-hexanone -1-ol as a colorless
oil (17, 0.164 g, 1.14 mmol, 83 %) as described above for 2-octanone-1-ol, using silica gel and EtOAc : CH₂Cl₂ (1:1) as eluent.

\(^1\)H-NMR δ\(H\) (300.13 MHz; CDCl₃; Me₄Si; 298 K) 3.80 (1H, dd, \(J_{HH} = 7.3\) Hz, \(J_{HH} = 11.1\) Hz, HOCH\(\text{H}^\prime\)), 3.70 (1H, dd, \(J_{HH} = 4.0\) Hz, \(J_{HH} = 11.0\) Hz, HOCH\(\text{H}^\prime\)), 2.63 (1H, qd, \(J_{HH} = 4.0\) Hz, \(J_{HH} = 6.9\) Hz, HOCH₂CH₂CH₂CH₃), 2.48 (2H, t, \(J_{HH} = Hz, C=OCH₂CH₂\)), 1.71-1.46 (4H, m, 2CH₂CH₃), 0.93 (3H, t, \(J_{HH} = 7.4\) Hz, \(CH₃\)), 0.93 (3H, t, \(J_{HH} = 7.4\) Hz, \(CH₃\)); \(^{13}\)C\{\(^1\)H\}\)-NMR δ\(C\) (75.5 MHz; CDCl₃; Me₄Si; 298 K) 215.2 (s, \(C=O\)), 62.4 (s, \(CH₂OH\)), 54.8 (s, CH₂CH(CH₂CH₃)C=O), 44.7 (s, \(C=OCH₂CH₂\)), 21.2 (s, CHCH₂CH₃C=O), 16.8 (s, CH₂CH₂CH₃), 13.7 (s, \(CH₃\)), 11.8 (s, \(CH₃\)); IR (neat solid) \(ν_{\text{max}}/\text{cm}^{-1}\) 3338m (OH), 2962m, 2923m, 1706m (C=O).

**3-hexanone-1-ol (19).** The substrate 1,3-hexanediol (18, 0.094 g, 0.795 mmol), utilizing the oxidant H₂O₂ (0.204 mL, 30 wt % in H₂O, 1.99 mmol) and catalyst [Fe(5)₂]²⁺(OTf)₂ (0.018 g, 0.023 mmol), was converted to 3-hexanone-1-ol as a colorless oil (19, 0.066 g, 0.588 mmol, 71 %) as described above 2-octanone-1-ol, using silica gel and EtOAc as eluent.

\(^1\)H-NMR δ\(H\) (300.13 MHz; CDCl₃; Me₄Si; 298 K) 3.84 (2H, t, \(J = 5.6\), \(CH₂OH\)), 2.66 (2H, t, \(J_{HH} = 5.4\), \(C=OCH₂\)), 2.42 (2H, t, \(J_{HH} = 7.2\) Hz, \(CH₂C=O\)), 1.61 (2H, q, \(J_{HH} = 7.2\) Hz, \(CH₃CH₂CH₂\)), 0.91 (3H, t, \(J_{HH} = 7.5\) Hz, \(CH₃\)); \(^{13}\)C\{\(^1\)H\}\)-NMR δ\(C\) (75.5 MHz; CDCl₃; Me₄Si; 298 K) 211.8 (s, \(C=O\)), 57.8 (s, \(CH₂OH\)), 45.2 (s, \(C=OCH₂\)), 44.3 (s, \(CH₂C=O\)), 17.1 (s, \(CH₃\)).
CH$_3$CH$_2$), 13.6 (s, CH$_3$); IR (neat solid) $\nu_{\text{max}}$ cm$^{-1}$ 3454w (OH), 2958s, 2924s, 2853s, 1706m (C=O).

**2-hydroxy-1-phenylethanone (21).**

The substrate 1-phenyl-1,2-ethanediol (20, 0.116 g, 0.839 mmol), utilizing the oxidant H$_2$O$_2$ (0.216 mL, 30 wt % in H$_2$O, 2.10 mmol) and catalyst $[\text{Fe(5)}_2]^{2+}$OTf$_2$ (0.019 g, 0.025 mmol), was converted to 2-hydroxy-1-phenylethanone as a colorless oil (21, 0.061 g, 0.448 mmol, 53 %) as described above for 2-octanone-1-ol, using silica gel and EtOAc as eluent.

$^1$H-NMR $\delta_H$ (300.13 MHz; CDCl$_3$; Me$_4$Si; 298 K) 7.90 (2H, d, $J_{HH} = 5.6$, Ph), 7.61 (1H, t, $J_{HH} = 7.4$, Ph), 7.48 (2H, t, $J_{HH} = 7.4$, Ph), 4.86 (2H, s, CH$_2$), 3.50 (1H, br s, OH); $^{13}$C{$_^1$H} NMR $\delta_C$ (75.5 MHz; CDCl$_3$; Me$_4$Si; 298 K) 198.4 (s, C=O), 134.3, 133.3, 129.0, 127.7 (4s, Ph), 65.5 (s, CH$_2$OH); IR (neat solid) $\nu_{\text{max}}$ cm$^{-1}$ 3423s (OH), 3066w, 2929m, 2852w, 1682s (C=O).

**3. Experimental procedures for the complex screening in Table 1**

Standard procedure: The substrate 1,2-octanediol (6, 0.050 g, 0.341 mmol) and the complex (0.01 mmol) was placed in a 7 mL vial with screw cap and CH$_3$CN was added (1.0 mL; all complexes tested for the study are depicted in Figure 1). Then H$_2$O$_2$ (0.088 mL, 30 wt % in H$_2$O, 0.854 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH$_3$CN was removed under vacuum and CH$_2$Cl$_2$ (5.0 mL) was added. The reaction mixture was dried with Na$_2$SO$_4$ and subsequently filtered through short pad of silica (1 inch). The reaction mixture was analyzed using Gas Chromatography (FID). Two 0.150 mL
fractions of the reaction mixture were taken at 2 different time intervals. The first one after 10 minutes and the second after 24 hours. In all cases except for the catalyst \([\text{Fe(5)}_2]^{2+}\text{OTf}_2\), after 10 minutes there was no product and after 24 hours only a mixture of oxidation products was observed (no selectivity) and there was still 90% of the 1,2-octanediol starting material remaining.

4. Experimental procedure for the radical scavenger experiments

Radical Scavenger Investigation (Phenol)

The substrate 1,2-octanediol (6, 0.050 g, 0.341 mmol), the radical scavenger phenol (0.016 g, 0.170 mmol) and catalyst \([\text{Fe(5)}_2]^{2+}\text{OTf}_2\) (0.007 g, 0.010 mmol) was placed into a 7 mL vial with screw cap and CH\(_3\)CN (1.0 mL) was added. Then H\(_2\)O\(_2\) (0.088 mL, 30 wt % in H\(_2\)O, 0.854 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH\(_3\)CN was removed under vacuum and CH\(_2\)Cl\(_2\) (5.0 mL) was added. The reaction mixture was dried with sodium sulfate and subsequently filtered through short pad of silica (1 inch). The reaction mixture was analyzed using Gas Chromatography (FID). Results: After a total of 9 minutes reaction time, the GC chromatogram showed that only very small amount of 2-octanone-1-ol (7, <5 %) had been produced and a remainder was unoxidized 1,2-octanediol (95 %).

Radical Scavenger Investigation (2,4,6-tri-tert-butylphenol)

A. The substrate 1,2-octanediol (0.050 g, 0.341 mmol), the radical scavenger 2,4,6-tri-tert-butylphenol (0.005 g, 0.020 mmol) and catalyst \([\text{Fe(5)}_2]^{2+}\text{OTf}_2\) (0.007 g, 0.010 mmol)
were placed into 7 mL vial with screw cap and CH₃CN (1.0 mL) was added. Then H₂O₂ (0.088 mL, 30 wt % in H₂O, 0.854 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH₃CN was removed under vacuum and CH₂Cl₂ (5.0 mL) was added. The reaction mixture was dried with sodium sulfate and subsequently filtered through short pad of silica (1 in). The reaction mixture was analyzed using Gas Chromatography (FID).

**Results:** After a total of 9 minutes reaction time, the GC chromatogram showed that all of the 1,2-octanediol had been oxidized to 2-octanone-1-ol and the remaining peaks were identified as various oxidized forms of 2,4,6-tri tert butylphenol.

**B.** The substrate 1,2-octanediol (0.050 g, 0.341 mmol), the radical scavenger 2,4,6-tri tert butylphenol (0.045 g, 0.170 mmol) and catalyst [Fe(5)₂]²⁺OTf₂ (0.007 g, 0.010 mmol) were placed into 7 mL vial with screw cap and CH₃CN (1.0 mL) was added. Then H₂O₂ (0.088 mL, 30 wt % in H₂O, 0.854 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH₃CN was removed under vacuum and CH₂Cl₂ (5.0 mL) was added. The reaction mixture was dried with sodium sulfate and subsequently filtered through short pad of silica (1 in). The reaction mixture was analyzed using Gas Chromatography (FID).

**Results:** After a total of 9 minutes reaction time, the GC chromatogram showed that most of the 1,2-octanediol had been oxidized to 2-octanone-1-ol (7) and the remaining peaks were identified as various oxidized forms of 2,4,6-tri tert butylphenol.

**C.** The substrate 1,2-octanediol (0.050 g, 0.341 mmol), the radical scavenger 2,4,6-tri tert butylphenol (0.089 g, 0.341 mmol) and catalyst [Fe(5)₂]²⁺OTf₂ (0.007 g, 0.010 mmol) were placed into 7 mL vial with screw cap and CH₃CN (1.0 mL) was added. Then H₂O₂ (0.088 mL, 30 wt % in H₂O, 0.854 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH₃CN was removed under vacuum and CH₂Cl₂ (5.0 mL) was added. The reaction mixture was dried with sodium sulfate and subsequently filtered through short pad of silica (1 in). The reaction mixture was analyzed using Gas Chromatography (FID).

**Results:** After a total of 9 minutes reaction time, the GC chromatogram showed that most of the 1,2-octanediol had been oxidized to 2-octanone-1-ol (7) and the remaining peaks were identified as various oxidized forms of 2,4,6-tri tert butylphenol.
mmol) were placed into 7 mL vial with screw cap and CH$_3$CN (1.0 mL) was added. Then H$_2$O$_2$ (0.088 mL, 30 wt % in H$_2$O, 0.854 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH$_3$CN was removed under vacuum and CH$_2$Cl$_2$ (5.0 mL) was added. The reaction mixture was dried with sodium sulfate and subsequently filtered through short pad of silica (1 inch). The reaction mixture was analyzed using Gas Chromatography (FID). Results: After a total of 9 minutes reaction time, the GC chromatogram showed that only half of the 1,2-octanediol (6) had been oxidized to 2-octanone-1-ol (7) while other half remained 1,2-octanediol (6) and the remaining peaks were identified as various oxidized forms of 2,4,6-tri-tert-butylphenol.

5. Experimental procedures for the competition experiments in Scheme 1

The substrates 1-decanol (24, 0.050 g, 0.315 mmol) and 2-decanol (26, 0.050 g, 0.315 mmol) were placed into 7 mL vial with screw cap and CH$_3$CN (1.0 mL) was added. Then H$_2$O$_2$ (0.033 mL, 30 wt % in H$_2$O, 0.315 mmol) was added dropwise via syringe (0.027 mL/min) at room temperature with stirring until addition was complete. The reaction was stirred for additional 5 minutes at room temperature. The CH$_3$CN was removed under vacuum and CH$_2$Cl$_2$ (5.0 mL) was added. The reaction mixture was dried with Na$_2$SO$_4$ and subsequently filtered through short pad of silica (1 inch). The reaction mixture was analyzed using Gas Chromatography (FID). Results: After a total of 7 minutes reaction time, The GC chromatogram showed that only 2-decanol (26) had been oxidized to 2-decananone (27, 15 %). The only other two peaks were identified as the 1-decanol and 2-decanol starting materials.
6. References


2-hydroxycyclohexane-1-methanol (10)
3-hydroxycyclohexane-1-methanol (12)
2-hydroxycyclopentane-1-methanol (14)

H$_2$O
2-octanone-1-ol (7)
2-butanone-1-ol (9)
2-cyclohexanone-1-methanol (11)
3-cyclohexanone-1-methanol (13)
2-cyclopentanone-1-methanol (15)
2-ethyl-3-hexanone-1-ol (17)
3-hexanone-1-ol (19)
2-hydroxy-1-phenylethanone (21)
Screening experiment Table 1, entry 5 ([Fe(5)$_2$]OTf$_2$ catalyst, H$_2$O$_2$, after 15 min)
Screening experiment Table 1, entry 6 (Fe(OTf)$_2$ as catalyst, H$_2$O$_2$, after 15 min)
Screening experiment Table 1, entry 7 (no catalyst, H\textsubscript{2}O\textsubscript{2}, after 15 min)
GC experiment 1-decanol oxidation (Scheme 1, left)

\[
\begin{align*}
\text{8-OH} & \quad \begin{array}{c}
\text{[Fe(5)]_2OTf}_2 \\
\text{24} \quad \text{CH}_3\text{CN} \\
\text{rt, H}_2\text{O}_2
\end{array} \\
\rightarrow & \quad \begin{array}{c}
\text{8-O} \\
\text{25}
\end{array}
\end{align*}
\]

After 2 hours

After 24 hours
Competition Experiment (Scheme 1, right) after 15 minutes

\[
\text{CH}_3\text{CN, rt} \quad \text{H}_2\text{O}_2 (0.5 \text{ equiv.})
\]

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Radical scavenger experiment with phenol

\[
\begin{align*}
\text{OH} & \quad \text{[Fe(5)_{2}]OTf}_2 \\
\text{CH}_3\text{CN} & \quad \text{rt, } H_2O_2, \text{ 10 minutes} \\
\text{phenol (0.5 equiv.)} & \quad \text{24} \quad \text{25}
\end{align*}
\]
9. UV-vis spectra of $[\text{Fe}(\text{5})(\text{OTf})_2]$ in CH$_3$CN before (dotted line) and after addition (solid line) of 1-decanol (top), 2-decanol (middle) and 1,2-octanediol (bottom). The spectra indicate an interaction of the alcohol with the iron complex.