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Supporting information for

Chemoselective Hydrogen Peroxide Oxidation of Allylic and Benzylic Alcohols under Mild Reaction Conditions Catalyzed by Simple Iron-picolinate Complexes

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Contents

General Procedure

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on JEOL 400 MHz NMR spectrometers. All spectra were recorded at 25 ± 1 ºC. Chemical shifts (δ) are in parts per million relative to residual $CHCl_3$ at 7.26 ppm for ^{1}H and at 77.0 ppm for ^{13}C or DMSO at 2.50 ppm for ^{1}H and at 39.52 ppm for ^{13}C unless otherwise noted. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 using an INERT CAP column (0.25 mm x 30 m, GL Sciences Inc.). All samples were analyzed and quantified by using biphenyl as an internal standard. Melting points were measured with a Mettler FP90 microscope on an object slide. Elemental analyses were measured on Thermo Fisher Scientific Inc. Flash2000. In X-ray crystallographic analyses, data were collected on a Bruker APEX-II CCD diffractometer using graphite-monochromated MoK_α radiation. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares techniques on F^2 (SHELXL-97).[1] The ORTEP-3 program was used to draw the molecule.[2]

Picolinic acid (picH), 6-methylpicolinic acid (Me-picH), 6-methoxypicolinic acid, 2,6-dicarboxypyridine, cinnamyl alcohol, cinnamaldehyde, allyl alcohol, acrolein, *trans*-crotyl alcohol β-methallyl alcohol, 3-methyl-2-buten-1-ol, 3-methyl-2-butenal, *trans*-2-octen-1-ol, *trans*-2-octenal, α-methylcinnamyl alcohol, α-methylcinnamaldehyde, citral, benzylalcohol, 2-octanol, n-octanal, 1,3-diphenyl-2-propen-1-ol, chalcone, 1-buten-3-ol, *trans*-3-octen-2-ol, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, 1-phenylethanol, acetophenone, 2-octanon, 1-phenyl-1,2-ethanediol, *β*-hydroxyacetophenone, and biphenyl were purchased from Tokyo Chemical Industry co., Ltd. Iron(II) acetate, 6-trifluoromethylpicolinic acid , methacrolein, benzaldehyde, methylvinylketone, 4-benzoylbenzoic acid, *N*-*tert*-butyl-α-phenylnitrone, and 4-chlorostyrene oxide were from Sigma-Aldrich. Iron(III) chloride, crotonaldehyde, *trans*-2-hexen-1-ol, *trans*-2-hexenal, geraniol, 1-octanol, 3-octen-2-one, 2,6-di-*tert*-butyl-4-methylphenol, cyclobutanol, cyclobutanone, duroquinone, toluene, THF, $CDCl_3$, and MeCN were from Wako Pure Chemical Industries, Ltd. 35% hydrogen peroxide aqueous solution was from Kanto Chemical Co., Inc. Iron(III) acetate hydroxide was form Kishida Inc., respectively. All chemicals were used as received. $[Fe(Me\text{-}pic)_2(pic)]$(**4**)[3] and 3-(hydroxylmethyl)phenyl]phenyl)methanol[4] were prepared according to literature. Oxidation reactions of alcohols in small scale were performed using ChemiStation (Tokyo Rika Inc.) equipped with thermostated apparatus.

Procedure for catalytic reaction

Preparation of catalyst solution.

$Fe(OAc)_2$ (9.0 mg, 0.052 mmol) and Me-PicH (21.0 mg, 0.153 mmol) were suspended in CH_3CN (3 mL). The mixture was warmed to 50 ºC with gentle stirring until almost all of iron acetate was dissolved (ca. 5 min), then the solution was filtered with membrane filter (pour size: 0.20 μm). The filtrate was diluted with CH_3CN, to adjust the total volume to 4 mL (the concentration of iron: 0.01 $mol \cdot L^{-1}$). The catalyst solutions with the different ligand ratio were also prepared in the same manner using the appropriate amount of PicH and Me-PicH. This procedure was also applied for preparation of catalyst solution with other iron salts such as $FeCl_3 \cdot 6H_2O$.

Typical procedure for the oxidation reaction.

Alcohol (1.0 mmol) was dissolved in 4 mL of the catalyst solution. 35% aqueous H_2O_2 (0.110 μL, 1.25 mmol) was added dropwise to the solution via a syringe pump for 10 min at 25 ºC, and the reaction solution was further stirred for 5 min at 25 ºC. To the resulting mixture was then added 6 mL of CH_3CN and measured amount of biphenyl (as an internal standard for GC analysis). The conversion of substrate and the yield of carbonyl compounds were determined by GC analysis. Products were identified by comparison to the GC retention time of authentic samples. The same reaction was performed twice for each substrate.

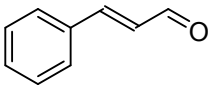
Oxidation of cinnamyl alcohol (10-g scale).

Cinnamyl alcohol (13.9 g, 0.100 mol) was dissolved in 400 mL of the catalyst solution prepared above. To the solution was added 35% aqueous H_2O_2 (11.1 mL, 125 mmol) dropwise via a dropping funnel for 30 min at 25 ºC, and the reaction solution was further stirred for 5 min at 25 ºC. Saturated sodium thiosulfate solution (25 mL) was added to the resulting solution, and the mixture was stirred for another 5 min at 25 ºC. The organic layer was separated, and CH_3CN was removed by rotary evaporator. The residual crude product was purified by distillation under reduced pressure, giving 11.1 g of cinnamaldehyde (84% yield).

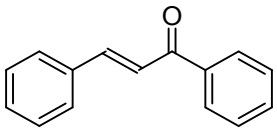
Synthesis of [Fe(Me-pic)$_3$](4).

$Fe(OAc)_2$ (200 mg, 1.15 mmol) and Me–PicH (790 mg, 5.76 mmol) were suspended in MeCN (60 mL). The mixture was warmed to 50 ºC with gentle stirring until almost all of the iron acetate was dissolved (ca. 15 min). The solution was then filtered. Recrystallization from MeCN afforded pure [Fe(Me-pic)$_3$](**4**) (277 mg, 0.596 mmol, 52% yield) as yellow crystals. M.p. 206-210 ºC (decomp.); Anal. Calcd for $C_{21}H_{18}FeN_3O_6$: C 54.33; H 3.91; N 9.05. Found: C 54.13; H 3.91; N 9.09.

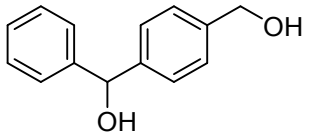
Spectral data of isolated compounds



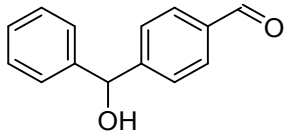
Cinnamaldehyde **2a** [5]: pale yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.72 (dd, *J* = 16, 7.8 Hz, 1H), 7.4-7.6 (m, 6H), 9.71 (d, *J* = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 128.4, 128.5, 129.0, 131.2, 133.9, 152.7, 193.6.



Chalcone **2k** [6]: Crude product was purified by silica gel column chromatography (EtOAc/Hexane). Pale yellow solid. Small amount of Z-isomer was contained (*E* : *Z* = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.45 (m, 3H), 7.48-7.68 (m, 6H), 7.82 (d, *J* = 15.8 Hz, 2H), 8.01-8.04 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 122.1, 128.4, 128.5, 128.6, 128.9, 130.5, 132.7, 134.8, 138.2, 144.8, 190.5.

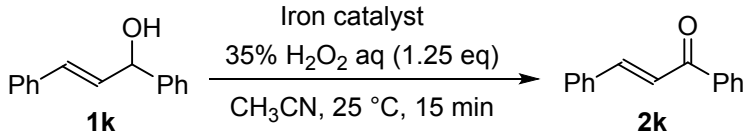


4-((Hydroxylmethyl)phenyl)benzylalcohol **10** [7]: This compound was prepared from 4-benzoylbenzoic acid according to the literature.[4] ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.45 (d, *J* = 5.7 Hz, 2H), 5.10 (t, *J* = 5.7 Hz, 6H), 5.69 (d, *J* = 4.0 Hz, 2H), 5.84 (d, *J* = 3.9 Hz, 2H); 7.15-7.38 (m, 9H), ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 62.8, 74.1, 125.9, 126.1$_8$, 126.2$_4$, 126.6, 128.0, 140.9, 144.1, 145.8.



4-((Hydroxylmethyl)phenyl)benzyaldehyde **11** [8]. Crude product was purified by silica gel column chromatography (EtOAc/Hexane), giving **1l** in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (br s, 1H), 5.91 (s, 1H) 7.27-7.37 (m, 5H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 9.99 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 126.6, 126.9, 128.1, 128.8, 129.9, 135.6, 143.0, 150.3, 191.9.

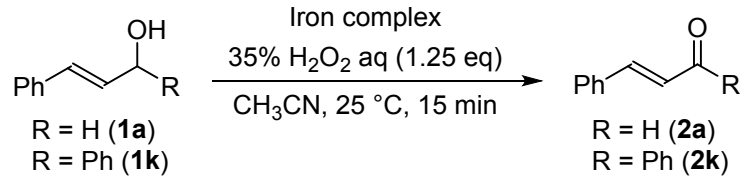
Table S1. Oxidation of 1,3-diphenyl-1-propen-3-ol **1k** by various catalysts[a]



Entry	Catalyst [mol%]			Conv. [%][b]	Yield [%][b]	Sel. [%][c]
	$Fe(OAc)_2$	PicH	Me-PicH			
1	5	15	0	80	49	61
2	5	5	5	99	93(91)[d]	93
3	5	0	15	88	78	89

[a] CH_3CN solution, 25 ºC, dropwise addition of 1.25 eq. of 35%H_2O_2 aq. for 10 min. and further stirring for 5 min., unless otherwise stated. [b] Determined by GC using biphenyl as an internal standard. Average of two runs. [c] yield / conversion x 100. [d] Isolated yield.

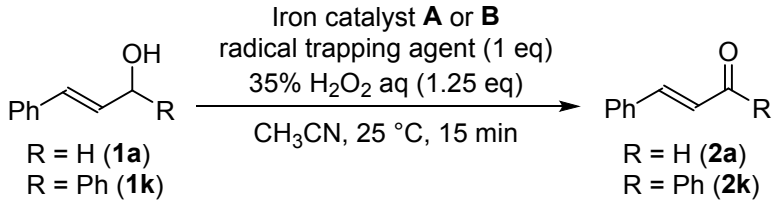
Table S2. Oxidation of **1a** and **1k** by iron complexes[a]



Entry	Substrate	Catalyst	Amount [mol%]	Conv. [%][b]	Yield [%][b]	Sel. [%][c]
1	**1a**	**3**	5	99	68	68
2	**1a**	**4**	5	98	90	92
3	**1k**	**3**	5	85	80	94
4	**1k**	**4**	5	80	69	87

[a] CH_3CN solution, 25 ºC, dropwise addition of 1.25 eq. of 35%H_2O_2 aq. for 10 min. and further stirring for 5 min., unless otherwise stated. [b] Determined by GC using biphenyl as an internal standard. Average of two runs. [c] yield / conversion x 100.

Table S3. Oxidation of **1a** and **1k** by in the presence of radical trapping agents[a]



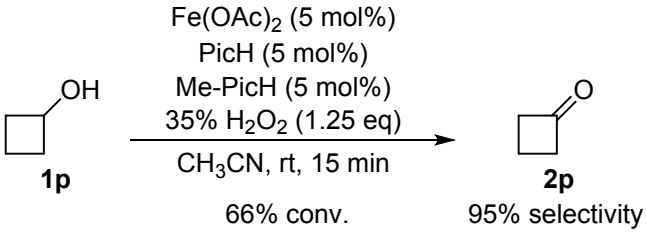
R = H (**1a**)
R = Ph (**1k**)

R = H (**2a**)
R = Ph (**2k**)

Entry	Substrate	Catalyst[b]	Radical trapping agent	Conv. [%][c]	Yield [%][c]	Sel. [%][d]
1	**1a**	**A**	duroquinone	96	91	95
2	**1a**	**A**	2,6-*tert*-butyl-4-methylphenol	37	32	86
3	**1a**	**A**	*N*-*tert*-butyl-α-phenylnitrone	59	54	92
4	**1k**	**B**	duroquinone	99	97	97
5	**1k**	**B**	2,6-*tert*-butyl-4-methylphenol	42	31	75
6	**1k**	**B**	*N*-*tert*-butyl-α-phenylnitrone	73	68	93

[a] CH_3CN solution, 25 ºC, dropwise addition of 1.25 eq. of 35%H_2O_2 aq. for 10 min. and further stirring for 5 min., unless otherwise stated. [b] catalyst **A** : $Fe(OAc)_2$ (5 mol%), Me-PicH (15 mol%); catalyst **B** : $Fe(OAc)_2$ (5 mol%), PicH (5 mol%), Me-PicH (5 mol%) [c] Determined by GC using biphenyl as an internal standard. . [d] yield / conversion x 100.

Scheme S1. Oxidation of Cyclobutanol **1p**



References

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