Highly Efficient Oxidation of Alcohols
Catalyzed by a Porphyrin-inspired Manganese Complex

Wen Dai, Ying Lv, Lianyue Wang, Sensen Shang, Bo Chen, Guosong Li, and Shuang Gao*

Dalian Institute of Chemical Physics, the Chinese Academy of Sciences, Dalian, 116023, P. R. China

Supporting Information

Table of content
1. Representative procedures for the oxidation of alcohols.........................S2-S8
2. Experimental procedure for the Gram-Scale reactions.........................S10-S11
3. Determination of the KIE value ..........................................................S11-S11
4. Screening the ratio of metal and ligand .............................................S11-S11
5. Oxidative kinetic resolution of the secondary alcohols ......................S12-S12
6. NMR spectra ..................................................................................S13-S34
Representative Procedure for the oxidation of alcohols.

A solution of Mn(OTf)$_2$ (0.008 M solution in CH$_3$CN, 0.25 mL, 0.002 mmol) was added to L2 (0.008 M solution in CH$_3$CN, 0.25 mL, 0.002 mmol) at room temperature. The reaction mixture was stirred at room temperature for 8 h. To the solution of manganese complex was directly added substrate (0.2 mmol) and CH$_3$CN (0.5 mL) and the mixture was cooled to 0 °C. Then 47% H$_2$O$_2$ (86.8 mg, 1.2 mmol, diluted with 1.0 mL CH$_3$CN) was added through syringe pump over 1 h and the mixture was stirred at 0 °C for another 1.0 h. At this point, a saturated aqueous solution of NaHCO$_3$ (8 mL) was added and the resulting mixture was extracted with EtOAc (10 mL× 3). The organic layer was combined and washed with brine, dried over MgSO$_4$ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding aldehydes or ketones.

Chalcone (Table 3, entry 2). Yellow solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (38.3 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 – 8.00 (m, 2H), 7.82 (m, 1H), 7.65 (m, 2H), 7.58 (m, 2H), 7.51 (m, 2H), 7.41 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.5, 162.9, 158.8, 134.8, 132.3, 130.8, 128.4, 113.7, 113.5, 55.5, 55.3.

1-(4-Methoxyphenyl)ethanone (Table 3, entry 6). White solid, purified by column
chromatography on silica gel (10% EtOAc in petroleum ether) (28.5 mg, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (m, 2H), 7.00 – 6.83 (m, 2H), 3.94 – 3.78 (m, 3H), 2.62 – 2.49 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.3.

1-(3-Methoxyphenyl)ethanone (Table 3, entry 7). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (25.2 mg, 84% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (m, 2H), 7.40 – 7.31 (m, 1H), 7.15 – 7.01 (m, 1H), 4.00 – 3.73 (m, 3H), 2.70 – 2.50 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.9, 159.8, 138.4, 129.5, 121.1, 119.5, 112.6, 55.6, 26.7.

1-(O-tolyl)ethanone (Table 3, entry 8). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (23.3 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J$ = 7.7 Hz, 1H), 7.37 (t, $J$ = 7.5 Hz, 1H), 7.25 (m, 2H), 2.57 (d, $J$ = 0.6 Hz, 3H), 2.53 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 201.7, 138.4, 137.6, 132.1, 131.5, 129.4, 125.7, 29.5, 21.6.

1-(4-Chlorophenyl)ethanone (Table 3, entry 9). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (21.7 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 – 7.76 (m, 2H), 7.39 (m, 2H), 2.76 – 2.38 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.7, 139.4, 135.8, 129.7, 128.8, 26.5.
2,3-Hydro-1H-inden-1-one (Table 3, entry 10). Brown solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (24.3 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 7.6 Hz, 1H), 7.59 (m, 1H), 7.48 (dd, $J$ = 7.7, 0.7 Hz, 1H), 7.37 (m, 1H), 3.21 – 3.09 (m, 2H), 2.75 – 2.65 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.1, 155.2, 137.1, 134.6, 127.3, 126.7, 123.7, 36.2, 25.8.

3,4-Hydroronaphthalen-1(2H)-one (Table 3, entry 11). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (25.2 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J$ = 7.6 Hz, 1H), 7.43 (m, 1H), 7.26 (m, 2H), 3.04 – 2.89 (m, 2H), 2.61 (m, 2H), 2.10 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.3, 144.5, 133.4, 132.6, 128.8, 127.1, 126.6, 39.1, 29.7, 23.3.

9H-fluoren-9-one (Table 3, entry 12). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (32.4 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J$ = 7.3 Hz, 2H), 7.49 (m, 4H), 7.28 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.9, 144.4, 134.7, 134.2, 129.1, 124.3, 120.3.

10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-one (Table 3, entry 13). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (38.7 mg, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (dd, $J$ = 7.9, 1.3 Hz, 2H), 7.42 (m, 2H), 7.31 (m, 2H), 7.21 (d, $J$ = 7.6 Hz, 2H), 3.19 (s, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.8, 142.0, 138.6, 132.4, 130.6, 129.3,
1-(Naphthalen-2-yl)ethanone (Table 3, entry 14). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (31.3 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.46 (s, 1H), 8.03 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.96 (d, $J$ = 7.9 Hz, 1H), 7.93 – 7.82 (m, 2H), 7.65 – 7.46 (m, 2H), 2.72 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.1, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 127.8, 126.8, 123.9, 26.7.

Benzophenone (Table 3, entry 15). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (32.4 mg, 89% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.76 (m, 4H), 7.62 – 7.55 (m, 2H), 7.52 – 7.44 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.8, 137.6, 132.4, 130.1, 128.3.

Benzil (Table 3, entry 16). Yellow solid, purified by column chromatography on silica gel (30% EtOAc in petroleum ether) (20.2 mg, 48% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (m, 4H), 7.70 – 7.62 (m, 2H), 7.55 – 7.44 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.6, 134.9, 133.0, 129.9, 129.0.

Phenyl(pyridin-2-yl)methanone (Table 3, entry 17). White solid, purified by column chromatography on silica gel (30% EtOAc in petroleum ether) (29.3 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ...
9H-xanthen-9-one (Table 3, entry 18). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (35.3 mg, 90% yield). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.35 (dd, \( J = 8.0, 1.5 \) Hz, 2H), 7.73 (t, \( J = 7.8 \) Hz, 2H), 7.50 (d, \( J = 8.5 \) Hz, 2H), 7.39 (t, \( J = 7.5 \) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 177.2, 156.2, 134.8, 127.2, 121.4, 117.9, 67.0, 37.8.

Chroman-4-one (Table 3, entry 19). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (26.0 mg, 88% yield). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.16 – 7.83 (m, 1H), 7.47 (m, 1H), 7.12 – 6.80 (m, 2H), 4.68 – 4.41 (m, 2H), 2.93 – 2.71 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 191.8, 161.9, 136.0, 127.2, 121.4, 117.9, 67.0, 37.8.

3,4-Dimethoxybenzaldehyde (Table 3, entry 23). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (25.6 mg, 74% yield). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.06 – 9.76 (m, 1H), 7.45 (m, 2H), 6.98 (m, 1H), 3.96 (m, 6H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 190.9, 154.5, 149.6, 130.2, 126.9, 110.4, 108.9, 56.1.

3,4,5-Trimethoxybenzaldehyde (Table 3, entry 24). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (29.4 mg, 75% yield). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.06 – 9.76 (m, 1H), 7.45 (m, 2H), 6.98 (m, 1H), 3.96 (m, 6H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 190.9, 154.5, 149.6, 130.2, 126.9, 110.4, 108.9, 56.1.
MHz, CDCl$_3$) $\delta$ 9.88 (d, $J = 2.3$ Hz, 1H), 7.14 (s, 2H), 3.94 (d, $J = 2.8$ Hz, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.1, 153.7, 143.6, 131.7, 106.7, 61.0, 56.3.

![Structural formula of 1-Phenylhex-1-yn-3-one](image)

1-Phenylhex-1-yn-3-one (Table 3, entry 25). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (24.1 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.55 (m, 2H), 7.48 – 7.42 (m, 1H), 7.41 – 7.34 (m, 2H), 2.65 (t, $J = 7.3$ Hz, 2H), 1.84 – 1.71 (m, 2H), 1.00 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.2, 133.0, 130.7, 128.6, 120.1, 90.5, 87.9, 47.4, 17.7, 13.6.

![Structural formula of 1,3-Diphenylprop-2-yn-1-one](image)

1,3-Diphenylprop-2-yn-1-one (Table 3, entry 26). White solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (37.5 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (dd, $J = 8.3$, 1.3 Hz, 2H), 7.71 – 7.67 (m, 2H), 7.63 (m, 1H), 7.54 – 7.46 (m, 3H), 7.45 – 7.39 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.1, 136.9, 134.2, 133.1, 130.8, 129.6, 128.7, 127.8, 120.2, 93.2, 86.9.

![Structural formula of 1-Phenylprop-2-yn-1-one](image)

1-Phenylprop-2-yn-1-one (Table 3, entry 28). Yellow solid, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (21.8 mg, 85% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 – 8.12 (m, 2H), 7.75 – 7.59 (m, 1H), 7.55 – 7.45 (m, 2H), 3.45 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.4, 136.2, 134.6, 129.7, 128.7, 80.8, 80.3.

![Structural formula of 3-Phenylpropionaldehyde](image)

3-Phenylpropionaldehyde (Table 3, entry 29). Colorless oil, purified by column chromatography on silica gel (10% EtOAc in petroleum ether) (39.6 mg, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.88 (d, $J = 2.3$ Hz, 1H), 7.75 – 7.59 (m, 1H), 7.55 – 7.45 (m, 2H), 3.45 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.4, 136.2, 134.6, 129.7, 128.7, 80.8, 80.3.
chromatography on silica gel (10% EtOAc in petroleum ether) (10.4 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.43 (s, 1H), 7.65 – 7.58 (m, 2H), 7.53 – 7.46 (m, 1H), 7.41 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.8, 133.3, 131.3, 128.8, 119.5, 95.2, 88.4.

2-hydroxy-1-phenylethanone (Table 3, entry 30). Yellow solid, purified by column chromatography on silica gel (30% EtOAc in petroleum ether) (15.2 mg, 56% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 – 7.86 (m, 2H), 7.68 – 7.60 (m, 1H), 7.51 ($J$ = 7.7 Hz, 2H), 4.89 (s, 2H), 3.43 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.4, 134.3, 133.4, 129.0, 127.7, 65.5.
Experimental Procedure for the Gram Scale Synthesis of 2b.

A mixture of Mn(OTf)$_2$ (23.3 mg, 0.066 mmol) and L$_2$ (0.066 mmol) in CH$_3$CN (10 mL) was stirred at room temperature for 12 h. To the solution of manganese complex was added 1b (1000 mg, 6.6 mmol) and adamantane carboxylic acid (594 mg, 3.3 mmol) and the temperature was cooled to 0 °C. Then 47 % H$_2$O$_2$ (2865 mg, 39.6 mmol, diluted with 10 mL CH$_3$CN) was added dropwise to the stirring reaction over 1 h and the mixture was stirred at room temperature for another 2 h, the reaction was quenched by adding the sat. aq. NaHCO$_3$ (20 mL), and extracted with EtOAc (20 mL×5). The organic layer was separated and washed with brine, dried over MgSO$_4$ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the 2b (890 mg, 90% yield).

Experimental Procedure for the Gram Scale Synthesis of 2c.

A mixture of Mn(OTf)$_2$ (17.8 mg, 0.05 mmol) and L$_2$ (0.05 mmol) in CH$_3$CN (10 mL) was stirred at room temperature for 12 h. To the solution of manganese complex was added 1c (1000 mg, 5.0 mmol) and adamantane carboxylic acid (450 mg, 2.5 mmol) and the temperature was cooled to 0 °C. Then 47 % H$_2$O$_2$ (2170 mg, 30.0 mmol, diluted with 10 mL CH$_3$CN) was added dropwise
to the stirring reaction over 1 h and the mixture was stirred at room temperature for another 2 h, the reaction was quenched by adding the sat. aq. NaHCO$_3$ (20 mL), and extracted with EtOAc (20 mL×5). The organic layer was separated and washed with brine, dried over MgSO$_4$ and concentrated at reduced pressure. The residue was purified by silica gel column chromatography to afford the 2c (872 mg, 88% yield).

**Determination of the KIE value.**

A solution of Mn(OTf)$_2$ (0.008 M solution in CH$_3$CN, 0.25 mL, 0.002 mmol) was added to L2 (0.008 M solution in CH$_3$CN, 0.25 mL, 0.002 mmol) at room temperature. The reaction mixture was stirred at room temperature for 8 h. To the solution of manganese complex was directly added 1-phenylethanol or (0.2 mmol) and CH$_3$CN (0.5 mL) and the mixture was cooled to 0 °C. Then 47% H$_2$O$_2$ (86.8 mg, 1.2 mmol, diluted with 1.0 mL CH$_3$CN) was directly added and the mixture was stirred at 0 °C for 10 min. At this point, decane was added to the mixture as the internal standard. Then the result was determined by GC and the $k_H$ value could be calculated. The $k_D$ was calculated by the same method as $k_H$. Finally, the KIE value was calculate by using the equations: KIE= $k_H$/

$k_D$.

**Screening the ratio of Mn(OTf)$_2$ and ligand.**

**Table S1 Screening the ratio of Mn(OTf)$_2$ and ligand.**

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Oxidative kinetic resolution of the secondary alcohols.

Table S2 Oxidative kinetic resolution of the secondary alcohol

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<sup>a</sup>Determined by GC.  <sup>b</sup>Determined by chiral HPLC analysis.