Supporting Information

Efficient and selective copper-catalyzed organic solvent-free and biphasic oxidation of aromatic gem-disubstituted alkenes to carbonyl compounds by tert-butyl hydroperoxide at room temperature

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1. General and Typical procedure for alkene oxidation………………….S2
2. NMR data…………………………………………………………………S5
3. Alkene oxidation with water……………………………………………..S13
4. Alkene oxidation without water………………………………………….S22
General

All chemicals were obtained from commercial sources and used without further purification. Phenanthroline, neocuproine, bipyridine, 4,4′-dimethyl-2,2′-bipyridine, α-methylstyrene, styrene, styrene oxide, 4-chloro-α-methylstyrene, α-4-dimethylstyrene, cis-stilbene, 1,1-diphenylethylene, 3-nitrostyrene, 3-nitrobenzaldehyde, 1,1-diphenylethylene oxide, valeraldehyde, benzaldehyde, 4-chloroacetophenone, acetophenone, 4-fluoroacetophenone, heptaldehyde, 1-octene and 2,6-di-tert-butyl-4-methylphenol were purchased from Across. Trans-5-decene, 3-methylstyrene, 4-fluoro-α-methylstyrene, 4-chloro-α-methylstyrene, 4-methylacetophenone, benzophenone, tert-butyl hydroperoxide 70% in aqueous solution (TBHP), 5-6 M TBHP solution in decane, m-tolualdehyde, cumene hydroperoxide (80%), 2,3-dihydrofuran, ammonium chloride, and cupric chloride dihydrate were purchased from Alfa Aesar. H$_2$O$_2$ (34.5-36.5 wt. % aqueous solution) and 2-methyl-1,1-heptene were purchased from Aldrich. [(phen)Cu(μ-Cl)(Cl)]$_2$ and 2-hydroperoxytetrahydrofuran were synthesized according to literature.$^{1,2}$ Gas chromatographic analyses were performed on an Agilent 6890 instrument with a FID detector and an Agilent 30 m x 0.53 mm x 3.0 μm HP-1 capillary column. Product isolation was carried out by TLC (Merck, TLC silica gel 60 F$_{254}$ 25 Aluminium sheets 20x20 cm). NMR spectra were recorded in CDCl$_3$ on a Bruker AV 300 MHz, at room temperature.


Typical procedure for alkene oxidation

A stock solution of CuCl₂·2H₂O in water (0.0171 g/cc) was prepared (by dissolving 0.171 g in 10 mL H₂O). To 5 mL flask, catalyst A (100 µL of the stock solution, 0.01 mmol of CuCl₂) or B (100 µL of a stock solution; 0.01 mmol of CuCl₂, 2.1 mg, 0.01 mmol of neocuproine) was added. Then 700 µL of H₂O, 0.2 mmol of alkene, and tert-butyl hydroperoxide (200 µL, 1.55 mmol) were added in each case. The mixture was stirred vigorously at room temperature till to its reaction time specified in the Table 2. The reaction mixture was then diluted with ethyl acetate and the products dissolved in ethyl acetate layer were analysed by GC. For product separation, the aqueous phase was extracted with ethyl acetate (3x5 mL). The combined extracts were dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated and product isolation was carried out by TLC. Similar procedure was followed for the control reactions of styrene epoxide (23.0 µL, 0.2 mmol), 1,1-diphenylethylene oxide (39.4 mg, 0.2 mmol), and 2,6-di-tert-butyl-4-methylphenol (412 mg, 2 mmol). Products were characterized by ¹H NMR and ¹³C NMR. For reaction without addition of H₂O, to a solid mixture of CuCl₂·2H₂O (1.71 mg, 0.01 mmol) and neocuporine (2.1 mg, 0.01 mmol), TBHP (200 uL, 1.55 mmol in 70 % aq. solution) and 1,1 diphenylethylene (35.7 uL, 0.2 mmol) were added and the reaction run as above. Similarly, a solution of TBHP (240 uL, 1.5 mmol in decane) and 1,1 diphenylethylene (35.7 uL, 0.2 mmol) were added to a solid mixture of CuCl₂·2H₂O (1.71 mg, 0.01 mmol) and neocuproine (2.1 mg, 0.01 mmol). Then the reaction was continued as above and products identified by GC diluting with ethyl acetate.

Benzenaldehyde: TLC (hexane/ethyl acetate = 1:0.5) gave benzaldehyde as a colorless liquid; yield: 7.8 mg (37%). ¹H NMR (300 MHz, CDCl₃) δ ppm 9.79 (s, 1H), 7.67-7.24 (m, 5H); ¹³C NMR (300 MHz, CDCl₃) δ ppm 192.0, 136.0, 134.1, 129.2, 128.6.

m-Tolualdehyde: TLC (hexane/ethyl acetate = 1:0.5) gave m-tolualdehyde as a colorless liquid; yield: 5.8 mg (24%). ¹H NMR (300 MHz, CDCl₃) δ ppm 9.72 (s, 1H), 7.44-7.40 (m, 2H), 7.16-7.14 (m, 2H), 2.14 (s, 3H); ¹³C NMR (300 MHz, CDCl₃) δ ppm 191.8, 138.4, 136.2, 134.7, 129.5, 128.4, 126.6, 20.5.

3-Nitrobenzaldehyde: TLC (hexane/dichloromethane = 1:1) gave 3-nitrobenzaldehyde as a colorless solid; yield: 6.9 mg (23%). ¹H NMR (300 MHz, CDCl₃) δ ppm 10.09 (s, 1H), 8.68-8.67 (m, 1H), 8.47-8.43 (m, 1H), 8.21 (d, J = 7.8, 1H), 7.75 (t, J = 7.8 Hz, 1H); ¹³C NMR (300 MHz, CDCl₃) δ ppm 189.9, 148.9, 137.5, 134.8, 130.6, 128.7, 124.6.
Benzophenone: TLC (hexane/ethyl acetate = 1:0.5) gave benzophenone as a colorless solid; yield: 31.7 mg (87%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.59-7.57 (m, 4H), 7.56-7.54 (m, 2H), 7.48-7.43 (m, 4H), $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ ppm 196.9, 137.8, 132.6, 130.2, 128.4.

Acetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave acetophenone as a colorless liquid; yield: 21.8 mg (91%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.68 (d, $J$ = 7.5, Hz, 2H), 7.27 (t, $J$ = 7.5, 1H), 7.16 (t, $J$ = 8.1, 2H), 2.29 (s, 3H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ ppm 197.2, 136.6, 132.6, 128.1, 127.8, 26.0.

4-Methylacetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave 4-methylacetophenone as a colorless liquid; yield: 23.9 mg (89%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.57 (d, $J$ = 8.4, Hz, 2H), 6.94 (d, $J$ = 8.1, 2H), 2.26 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ ppm 196.8, 143.2, 134.2, 128.7, 127.9, 25.8, 20.9.

4-Fluoroacetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave 4-fluoroacetophenone as a colorless liquid; yield: 23.7 mg (86%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.88–7.83 (d,d, $J$ = 5.4, 2H), 6.99 (t, $J$ = 8.4, 2H), 2.46 (s, 3H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ ppm 196.3, 167.3, 164.0, 133.6, 133.5, 130.9, 130.8, 115.7, 115.4, 26.4.

4-Chloroacetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave 4-chloroacetophenone as a colorless liquid; yield: 28.3 mg (92%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.57 (d, $J$ = 7.6, 2H), 7.09 (d, $J$ = 8.4, 2H), 2.28 (s, 3H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ ppm 196.0, 138.8, 135.0, 129.3, 128.3, 25.9.
NMR data

Fig. S1 $^1$H NMR spectrum of Benzaldehyde

Fig. S2 $^{13}$C NMR spectrum of Benzaldehyde
Fig. S3 $^1$H NMR spectrum of $m$-Tolualdehyde

Fig. S4 $^{13}$C NMR spectrum of $m$-Tolualdehyde
Fig. S5 $^1$H NMR spectrum of 3-Nitrobenzaldehyde

Fig. S6 $^{13}$C NMR spectrum of 3-Nitrobenzaldehyde
Fig. S7 $^1$H NMR spectrum of Benzophenone

Fig. S8 $^{13}$C NMR spectrum of Benzophenone
Fig. S9 $^1$H NMR spectrum of Acetophenone

Fig. S10 $^{13}$C NMR spectrum of Acetophenone
Fig. S11 $^1$H NMR spectrum of 4-methylacetophenone

Fig. S12 $^{13}$C NMR spectrum of 4-methylacetophenone
Fig. S13 $^1$H NMR spectrum of 4-Fluoroacetophenone

Fig. S14 $^{13}$C NMR spectrum of 4-Fluoroacetophenone
Fig. S15 $^1$H NMR spectrum of 4-Chloroacetophenone

Fig. S16 $^{13}$C NMR spectrum of 4-Chloroacetophenone
Alkene oxidation with water

Fig. S17 GC Spectra of the catalytic cycles using 1,1-diphenylethylene
Fig. S18 The reaction was carried out using styrene (23.2 μL, 0.2 mmol) and catalyst A (100 μL stock solution, 0.01 mmol of CuCl₂) following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (43%) of cleavage product benzaldehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.15).
The reaction was carried out using 3-methylstyrene (26.8 μL, 0.2 mmol) and catalyst A (100 μL stock solution, 0.01 mmol of CuCl₂) following the above typical procedure. The compound 3-methylbenzaldehyde was identified by GC with standard sample. The yield (30%) of cleavage product m-tolualdehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.4).
The reaction was carried out using 3-nitrostyrene (28.7 μL, 0.2 mmol) and catalyst A (100 μL stock solution, 0.01 mmol of CuCl₂) following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (29%) of cleavage product 3-nitrobenzaldehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.9).
Fig. S21 The reaction was carried out using $\alpha$-4-dimethylstyrene (30.3 $\mu$L, 0.2 mmol) and catalyst B (100 $\mu$L stock solutions, 0.01 mmol of CuCl$_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The compound 4-methylacetophenone was identified by GC with standard sample. The yield (91%) of the cleavage product 4-methylacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor $=1.8$).

Fig. S22 The reaction was carried out using 4-fluoro-$\alpha$-methylstyrene (28.4 $\mu$L, 0.2 mmol) and catalyst B (100 $\mu$L stock solution, 0.01 mmol of CuCl$_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The compound 4-fluoroacetophenone was identified by GC with standard sample. The yield (89%) of the cleavage product 4-fluoroacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor $=2.2$).
The reaction was carried out using 4-chloro-α-methylstyrene (29.6 µL, 0.2 mmol) and catalyst B (100 µL stock solutions, 0.01 mmol of CuCl₂; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The compound 4-chloroacetophenone was identified by GC with standard sample. The yield (98%) of the cleavage product 4-chloroacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.26).
Fig. S24 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol), tert-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) and 2,6-di-tert-butyl-4-methylphenol (440.7 mg, 2 mmol) following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (2%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.07).
Fig. S25 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), Neocuporine (2.1 mg, 5 mol%), tert-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) and H₂O (700 μL) following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (3%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.07).
Fig. S26 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), cis-stilbene (36.8 μL, 0.2 mmol), catalyst B (100 mL stock solution, 0.01 mmol of CuCl$_2$; 0.01 mmol, 2.1 mg of neocuproine), tert-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) and H$_2$O (700 μL) following the above typical procedure. The compound benzophenone and benzaldehyde was identified by GC with standard sample. The yield (84%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.07) and the yield (8%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.99).
Alkene oxidation without water

**Fig. S27** The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), Neocuporine (2.1 mg, 5 mol%) and *tert*-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) without addition of water following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (4%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07).
**Fig. S28** The reaction was carried out using 1,1-diphenylethylen (35.7 µL, 0.2 mmol), Neocuporine (2.1 mg, 5 mol%) and tert-butyl hydroperoxide (240 µL, 1.55 mmol, 5M-6M decane solution) without addition of water following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (3%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.07).

**Fig. S29** The reaction was carried out using styrene oxide (23.0 µL, 0.2 mmol) and catalyst B (100 µL stock solutions, 0.01 mmol of CuCl₂; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The starting material styrene oxide was identified by GC with standard sample. The yield (96%) was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.35).
Fig. 30 The reaction was carried out using styrene oxide (23.0 μL, 0.2 mmol) and catalyst A (100 μL stock solution, 0.01 mmol of CuCl₂) following the above typical procedure. The starting material styrene oxide was identified by GC with standard sample. The yield (93%) was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.35).

Fig. S31 The reaction was carried out using 1,1-diphenylethylene oxide (39.4 mg, 0.2 mmol) and catalyst B (100 μL stock solutions, 0.01 mmol of CuCl₂; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The starting material 1,1-diphenylethylene oxide was identified by GC with standard sample. The yield (95%) was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.6).
**Fig. S32** The reaction was carried out using 1,1-diphenylethylene oxide (39.4 mg, 0.2 mmol) and catalyst A (100 μL stock solution, 0.01 mmol of CuCl$_2$) following the above typical procedure. The starting material 1,1-diphenylethylene oxide was identified by GC with standard sample. The yield (90%) was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.6).

**Fig. S33** The reaction was carried out using styrene (23.2 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (16.9%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.99).
The reaction was carried out using 3-methylstyrene (27.1 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl₂·2H₂O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound \( m \)-tolualdehyde was identified by GC with standard sample. The yield (12.4%) of the cleavage product \( m \)-tolualdehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.97).
The reaction was carried out using 3-nitrostyrene (28.7 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 3-nitrobenzaldehyde was identified by GC with standard sample. The yield (11.5%) of the cleavage product 3-nitrobenzaldehyde was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.26).
Fig. S36 The reaction was carried out using 1,1-diphenylethylene (35.7 µL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl₂·2H₂O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (95.2%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.07).
The reaction was carried out using isopropenylbenzene (26.3 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound acetophenone was identified by GC with standard sample. The yield (99.5%) of the cleavage product acetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.44).

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Fig. S38 The reaction was carried out using 1-isopropenyl-4-methylbenzene (26.3 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 4-methylacetophenone was identified by GC with standard sample. The yield (84.1%) of the cleavage product 4-methylacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.65).
Fig. S39 The reaction was carried out using 1-fluoro-4-isopropenylbenzene (25.19 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 4-fluoroacetophenone was identified by GC with standard sample. The yield (93.4%) of the cleavage product 4-fluoroacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.96).
The reaction was carried out using 1-chloro-4-isopropenylbenzene (29.9 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl$_2$·2H$_2$O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 4-chloroacetophenone was identified by GC with standard sample. The yield (93.0%) of the cleavage product 4-chloroacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.99).

**Fig. S40**
The reaction was carried out using cis-stilbene (36.8 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid CuCl₂·2H₂O (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (9.9%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-tert-butyldibenzene (conversion factor = 1.99).

Fig. S41
Fig. S42 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), 
cis-stilbene (36.8 μL, 0.2 mmol), neocuproine (2.1 mg, 0.01 mmol), solid CuCl₂·2H₂O 
(1.71 mg, 0.01 mmol) and tert-butyl hydroperoxide (200 μL, 1.55 mmol, 70% 
aqueous solution) without addition of water following the above typical procedure. 
The compound benzophenone and benzaldehyde was identified by GC with standard 
Sample. The yield (88%) of the cleavage product Benzophenone was calculated with 
the internal standard 1,4-di-tert-butylbenzene (conversion factor = 1.07) and the yield 
(8%) of the cleavage product benzaldehyde was calculated with the internal standard 
1,4-di-tert-butylbenzene (conversion factor = 1.99).