Supporting Information

Gold(I) Catalyzed Oxidative Cleavage of C-C Double Bond in Air and Water

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General: All reagents were obtained commercially and used without further purification unless otherwise noted. The starting materials were synthesized by following previous procedures. Styrene, 2-vinylnaphthalene, α -methyl-styrene, 1, 1-diphenylethylene, 1-phenyl-1-propene, 4-vinylbenzyl acetate are commercial available and were used as starting materials without any further purification. Neocuproine, AuCl and AuCl₃ were obtained commercially from Aldrich Company and used without further purification. Flash chromatographic purification of products was performed on silica gel 200-300 mesh. Thin-layer chromatography (TLC) was visualized with UV light (254 and 365 nm) or by iodine vapor staining. Proton nuclear magnetic resonance (¹H NMR) spectra were acquired on a Varian YH200/300, and carbon nuclear magnetic resonance (¹³C NMR) spectra were acquired on a Varian YH200, respectively, and are referenced internally according to residual protio solvent signals or internal TMS standard. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), integration, coupling constant (Hz). Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). Infrared resonance (IR) spectra were acquired on a Nicolet AVATAR 330. Electron spray mass spectrascopy (ESI) was acquired on a LCQ

DECA XPplus (Thermo Finnigan). Low-resolution mass spectra were obtained from the Mass Spectrometry Facility, Peking University.

General procedure for preparation of the starting materials:

To a THF solution (30 mL) of phenylmagnesium bromide (6 mmol) under N₂, a THF solution (20 mL) of the substituted ketone (5 mmol) was added dropwise at room temperature. The reaction mixture was stirred at 60 °C overnight, monitored by TLC. Saturated aqueous NH₄Cl solution (80 mL) was added and the aqueous layer was extracted with diethyl ether (80 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. The residue was dehydrated by H₂SO₄/AcOH (1:4) without further purification.¹ after the dehydration, H₂O (100 mL) and diethyl ether (100 mL) were added and the aqueous layer was extracted with diethyl ether (100 mL x 3). The combined organic layer was washed with saturated aqueous NaHCO₃ solution, dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash chromatography afforded the product (table 2, entry 2-7, 9).

Procedure for preparation of 4-chloro-1-methoxy-2-(1-phenylvinyl)benzene by 1-(1,2-dibromoethyl)benzene and 5-chloro-2-methoxyphenylboronic acid ²:

A suspension of KOH (450 mg, 8 mmol) and 5-chloro-2-methoxyphenylboronic acid (450 mg, 3 mmol) in 5 mL of fresh dried THF under N₂ was stirred at 100°C for 1 h and then the reaction mixture was cooled to room temperature. 1-(1, 2-dibromoethyl)benzene (524 mg, 2 mmol), PPh₃ (42 mg, 0.16 mmol), Pd(OAc)₂ (18 mg, 0.08mmol) and 5 mL CH₃OH were added into the mixture and the reaction was maintained at 100°C for 5 h. The mixture was cooled to room temperature and diluted with 40 mL of diethyl ether. The solution was washed with 1 N NaOH solution and brine, dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash chromatography afforded the product (table 2, entry 8).

1-Phenyl-1-*p*-tolyl-ethylene (Table 2, entry 2, starting material): ¹H NMR (300MHz, CDCl₃, 25 °C, TMS) δ = 7.35-7.21 (m, 7H, 7CH), 7.11 (d, ³J(H-H) = 8.0 Hz, 2H, 2CH), 5.40 (s, 1H, CH₂), 5.38 (s, 1H, CH₂), 2.33 ppm (s, 3H, CH₃); ¹³C NMR (75M Hz, CDCl₃,

25 °C) δ = 149.9, 141.6, 138.6, 137.4, 128.8, 128.2, 128.1, 128.0, 127.6, 113.6, 21.1 ppm; MS (70eV): $m/z(100)$: 194(100) [M^+].

4-(1-Phenyl-vinyl)-anisole (Table 2, entry 3, starting material): ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS) δ 7.35-7.28 (m, 7H, 7CH), 6.88 (d, $^3J(\text{H-H}) = 9.0$ Hz, 2H, 2CH), 5.41 (s, 1H, CH_2), 5.37 (s, 1H, CH_2), 3.83 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ = 159.3, 149.5, 141.8, 134.0, 129.4, 128.3, 128.1, 127.6, 113.5, 112.9, 55.3; MS (70eV): $m/z(100)$: 210(100) [M^+].

1-Phenyl-1-o-tolyl-ethylene (Table 2, entry 4, starting material): ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS) δ = 7.26-7.18 (m, 9H, 9CH), 5.76 (s, 1H, CH_2), 5.19 (s, 1H, CH_2), 2.09 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ = 149.4, 141.6, 140.6, 136.1, 130.1, 130.0, 128.3, 127.5, 127.5, 126.5, 125.7, 114.8, 20.1 ppm; MS (70eV): $m/z(100)$: 194(100) [M^+].

1-(1-Phenyl-vinyl)-naphthylene (Table 2, entry 5, starting material): ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS) δ = 7.85 -7.74(m, 3H, 3CH), 7.50-7.40 (m, 3H, 3CH), 7.35-7.25 (m, 6H, 6CH), 5.98 (s, 1H, CH_2), 5.39 ppm (s, 1H, CH_2); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ = 148.3, 141.0, 139.8, 133.7, 131.8, 128.4, 128.2, 127.9, 127.7, 127.2, 126.6, 126.4, 125.9, 125.7, 125.4, 116.2 ppm; MS (70eV): $m/z(100)$: 230(100) [M^+].

1-(4-Fluoro-phenyl)-1-phenyl-ethylene (Table 2, entry 6, starting material): ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS) δ = 7.32-7.27 (m, 7H, 7CH), 7.00 (m, 2H, 2CH), 5.42 (s, 1H, CH_2), 5.40 ppm (s, 1H, CH_2); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ = 149.0, 129.9, 129.8, 128.7, 128.2, 128.2, 127.8, 115.2, 114.9, 114.2 ppm; MS (70eV): $m/z(100)$: 198(100) [M^+].

1-(4-Bromo-phenyl)-1-phenyl-ethylene (Table 2, entry 7, starting material): ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS) δ = 7.04 (d, $^3J(\text{H-H}) = 8.4$ Hz, 2H, 2CH), 6.98-6.82 (m, 5H, 5CH), 6.78 (d, $^3J(\text{H-H}) = 8.4$ Hz, 2H, 2CH), 5.05 (s, 1H, CH_2), 5.03 ppm (s,

1H, CH₂); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 149.0, 140.9, 140.4, 131.3, 129.9, 128.3, 128.2, 127.9, 121.8, 114.7 ppm; MS (70eV): m/z(100): 258(100, ⁷⁹Br) and 260(97, ⁸¹Br) [M⁺].

1-(5-Chloro-2-methoxy-phenyl)-1-phenyl-ethylene (Table 2, entry 8, starting material) ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS) δ = 7.27-7.22 (m, 7H, 7CH), 6.82 (d, ³J(H-H) = 8.4 Hz, 2H, 2CH), 5.72 (s, 1H, CH₂), 5.31 (s, 1H, CH₂), 3.60 ppm (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 155.8, 145.9, 140.4, 132.7, 128.6, 128.1, 127.5, 126.7, 126.3, 125.4, 116.1, 112.4, 55.9 ppm; MS (70eV): m/z(100): 244(100, ³⁵Cl) and 246 (34, ³⁷Cl) [M⁺].

2-(1-Phenyl-vinyl)-thiophene (Table 2, entry 9, starting material): ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS) δ = 7.45-7.20 (m, 6H, 6CH), 6.97-6.89 (m, 2H, 2CH), 5.57 (s, 1H, CH₂), 5.23 ppm (s, 1H, CH₂); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 143.3, 141.0, 128.3, 128.1, 128.1, 128.0, 127.2, 126.4, 125.0, 113.6 ppm; MS (70eV): m/z(100): 186(100) [M⁺].

General procedure for gold(I) catalyzed oxidative cleavage of C=C double bond in different solvents (Table 1).

A typical procedure is as following: To a solution mentioned in Table 1 (3 mL) containing AuCl (12 mg , 0.05 mmol) and ligand **1** (11 mg , 0.05 mmol), biphenyl ethylene (180 mg , 1 mmol) and TBHP (0.3 mL, 70% solution in *t*-BuOH, 2.1 mmol) were added at room temperature. The reaction mixture was stirred at 90 °C for the corresponding time listed in Table 1. The yield of benzophenone was determined by GC using dodecane as an internal standard and characterized by comparison with an authentic sample or purified by flash chromatography.

General procedure for the gold(I)-catalyzed oxidation of substituted styrenes in de-ionized water (Table 2)

A typical procedure is as following: To a de-ionized H₂O solvent (4 mL) containing AuCl₃ (12 mg, 0.05 mmol) and ligand **1** (11 mg, 0.05 mmol), the starting material (1 mmol) and TBHP (0.3 mL, 70% solution in *t*-BuOH, 2.1 mmol) were added at room temperature. The reaction mixture was stirred at 90 °C for the corresponding time listed in Table 2, monitored by TLC, diethyl ether (20 mL) and H₂O (15 mL) were added. The aqueous layer was extracted with diethyl ether (20 mL x 3). The combined organic layer was washed with saturated aqueous NaHSO₃ solution, dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash chromatography afforded the corresponding product **3**.

Benzophenone (3a)³: ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS) δ = 7.83–7.78 (m, 4H, 4CH), 7.59–7.48 ppm (m, 6H, 6CH); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 196.3, 137.9, 132.4, 130.1, 128.3 ppm; IR (KBr): 1658 cm⁻¹ (C=O); MS (70eV): *m/z*(100): 182(100) [M⁺].

4-Methyl-benzophenone (3b)⁴: ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS) δ = 7.82–7.72 (m, 4H, 4CH), 7.60–7.42 (m, 3H, 3CH), 7.29 (d, ³*J*(H-H) = 8.8 Hz, 2H, 2CH), 2.44 ppm (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ = 196.3, 143.2, 137.8, 134.8, 132.2, 130.0, 130.0, 128.9, 128.2, 21.7 ppm; IR (KBr): 1657 cm⁻¹ (C=O); MS (70eV): *m/z*(100): 196(100) [M⁺].

4-Methoxyl-benzophenone (3c)⁴: ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS) δ = 7.83 (d, ³*J*(H-H) = 8.8 Hz, 2H, 2CH), 7.75 (d, ³*J*(H-H) = 8.2 Hz, 2H, 2CH), 7.50–7.46 (m, 3H, 3CH), 6.96 (d, ³*J*(H-H) = 8.8 Hz, 2H, 2CH), 3.88 ppm (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 197.2, 163.2, 138.3, 132.5, 131.9, 130.1, 129.7, 128.2, 113.5, 55.5 ppm; IR (KBr): 1651 cm⁻¹ (C=O); MS (70eV): *m/z*(100): 212(100) [M⁺].

2-Methyl-benzophenone (3d)⁵: ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS) δ = 7.81 (d, ³*J*(H-H) = 7.8 Hz, 2H, 2CH), 7.60–7.25 (m, 7H, 7CH), 2.34 ppm (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 198.6, 138.5, 137.6, 136.6, 133.1, 130.9, 130.2, 130.1, 128.5,

128.4, 125.2, 19.9 ppm; IR (KBr): 1664 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 196(100) $[\text{M}^+]$.

1-Benzoyl-naphthylene (3e)⁵: ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 8.09 (d, $^3J(\text{H-H})$ = 7.5 Hz, 1H, CH), 7.99 (d, $^3J(\text{H-H})$ = 8.1 Hz, 1H, CH), 7.92-7.85 (m, 3H, 3CH), 7.61– 7.44 ppm (m, 7H, 7CH). ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 198.0, 138.3, 136.3, 133.7, 133.2, 131.2, 130.9, 130.4, 128.4, 128.4, 127.7, 127.2, 126.4, 125.7, 124.3 ppm; IR (KBr): 1658 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 232(100) $[\text{M}^+]$.

4-Fluoro-benzophenone (3f)⁴: ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 7.89-7.75 (m, 4H, 4CH), 7.61-7.46 (m, 3H, 3CH), 7.26-7.12 ppm (m, 2H, 2CH); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 195.3, 167.9, 132.7, 132.6, 132.4, 129.9, 128.3, 115.6, 115.2 ppm; IR (KBr): 1660 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 200(100) $[\text{M}^+]$.

4-Bromo-benzophenone (3g)⁶: ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 7.78 (d, $^3J(\text{H-H})$ = 8.6 Hz, 2H, 2CH), 7.70-7.57 (m, 5H, 5CH), 7.50 ppm (d, $^3J(\text{H-H})$ = 8.0 Hz, 2H, 2CH); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 195.6, 137.1, 136.3, 132.7, 131.6, 131.6, 130.0, 128.4, 127.5 ppm; IR (KBr): 1659 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 258(98) $[\text{M}^+, ^{79}\text{Br}]$ 260(100) $[\text{M}^+, ^{81}\text{Br}]$.

(5-Chloro-2-methoxyphenyl)-(phenyl)-methanone (3h): ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 7.78 (d, $J(\text{H-H})$ = 6.4 Hz, 2H, 2CH), 7.57-7.31 (m, 5H, 5CH), 6.91 (d, $^3J(\text{H-H})$ = 6.0 Hz, 2H, 2CH), 3.70 ppm (s, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 193.2, 155.8, 137.0, 133.2, 131.2, 129.7, 129.0, 128.2, 125.8, 115.7, 112.7, 55.8 ppm; IR (KBr): 1667 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 246(100) $[\text{M}^+]$.

Phenyl-(thiophen-2-yl)-methanone (3i)⁷: ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 7.90-7.74 (m, 2H, 2CH), 7.74-7.72 (m, 1H, CH), 7.67-7.48 (m, 4H, 4CH), 7.19-7.16 ppm (m, 1H, CH); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 188.2, 143.6, 138.1, 134.8, 134.2,

132.2, 129.1, 128.4, 128.0 ppm; IR (KBr): 1635 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 188(100) [M^+].

Acetophenone (3j)⁸: ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 7.98-7.93 (m, 2H, 2CH), 7.56-7.41 (m, 3H, 3CH), 2.59 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 198.0, 137.0, 133.0, 128.2, 128.2, 26.5 ppm; IR (KBr): 1683 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 120(100) [M^+].

Benzaldehyde (3k)⁸: ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 10.01 (s, 1H, CH), 7.90-7.85 (m, 2H, 2CH), 7.63-7.52 ppm (m, 3H, 3CH); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 192.3, 136.6, 134.4, 129.6, 129.0 ppm; IR (KBr): 1700 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 106(100) [M^+].

2-Naphthaldehyde (3l)⁹: ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 10.16 (s, 1H, CH), 8.34-7.58 ppm (m, 7H, 7CH); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 192.2, 134.6, 134.5, 132.4, 129.5, 129.1, 129.1, 128.0, 127.1, 122.9, 122.8 ppm; IR (KBr): 1691 cm^{-1} (C=O); MS (70eV): $m/z(100)$: 156(100) [M^+].

***p*-Acetoxymethyl-benzaldehyde (3m)**¹⁰: ^1H NMR (200 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS) δ = 10.01 (s, 1H, CH), 7.88 (d, $^3J(\text{H-H})$ = 8.2 Hz, 2H, 2CH), 7.53-7.49 (m, 2H, 2CH), 5.18 (s, 2H, CH_2), 2.14 ppm (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 191.7, 170.6, 142.7, 136.1, 130.0, 128.2, 65.4, 29.7 ppm; IR (KBr): 1739, 1704 cm^{-1} (C=O); MS (70eV): $m/z(\%)$: 178(100) [M^+].

Procedure for determining the gold(I) species in reaction solution.

To a solution of AuCl (12 mg, 0.05 mmol) and neocuproine **1** (11 mg, 0.05 mmol) in 2 mL of de-ionized H_2O was added biphenyl ethylene (180 mg, 1 mmol) and TBHP (0.3 mL, 70% solution in *t*-BuOH, 2.1 mmol). The reaction mixture was stirred at 90 $^\circ\text{C}$ for 10 min and diluted with methanol. ESI mass spectroscopy was determined on a LCQ DECA XPplus (Thermo Finnigan) directly. The gold(I) complex with styrene was observed clearly on this spectroscopy.

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