

Electronic Supplementary Information

Ethylene carbonate as a unique solvent for palladium catalyzed Wacker oxidation using oxygen as the sole oxidant

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List of Contents

(1) General information	S2
(2) Optimizing the reaction conditions	S2
(3) The ¹ H NMR and ¹³ C NMR data for products	S5
(4) The ¹ H NMR and ¹³ C NMR charts for products	S7

(1) General information

All the alkenes were commercially available and were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz or Bruker 300 MHz, and at 100.4 or 75 MHz respectively in the CDCl_3 . Chemical shifts (δ) are given in ppm relative to TMS. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl_3 : δ_{C} 77.0 ppm; residual CHCl_3 in CDCl_3 : δ_{H} 7.26 ppm). Column chromatography was performed by using silica gel 200-300 mesh with ethyl acetate/petroleum (1:20-1:10) as eluent to obtain the desired product. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-5, 30 m \times 0.25 μm) using a flame ionization detector.

Transmission Electron Microscopic (TEM) Measurements: A 50 μL portion of sample solution was dropped on a copper grid. The grid was then air-dried. The samples were examined by a high-resolution transmission electron microscope (TEM) (Philips Tecnaï G2 20 S-TWIN microscope) operating at an accelerating voltage of 200 keV.

(2) Optimizing the reaction conditions

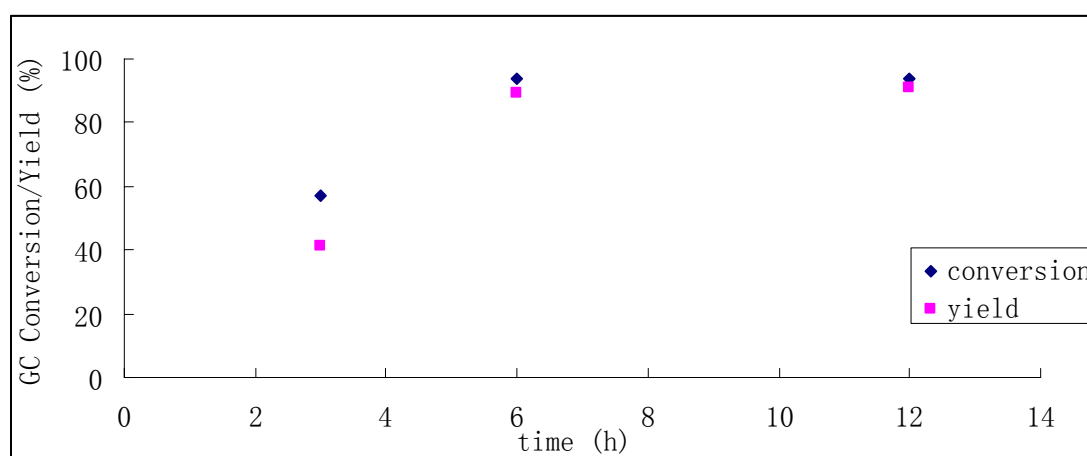


Figure S1. Effect of the reaction time on the Wacker oxidation of 1-dodecene in EC.

Reaction conditions: 1-dodecene (0.5 mmol, 0.11 mL), PdCl_2 (0.01 mmol, 1.77 mg), NaOAc (10 mol %, 4.1 mg), EC (3 mL), Temp. 80 $^\circ\text{C}$, P_{O_2} (10 atm).

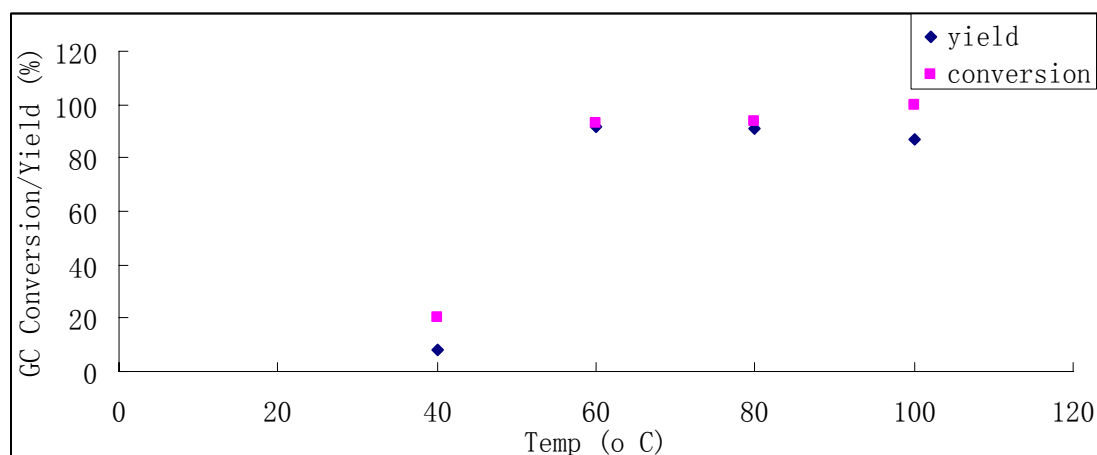


Figure S2. Effect of the temperature on the Wacker oxidation of 1-dodecene in EC
Reaction conditions: dodecene (0.5 mmol, 0.11 mL), PdCl₂ (0.01 mmol, 1.77 mg), NaOAc (10 mol %, 4.1 mg), EC (3 mL), time 12 h, P_{O₂} (10 atm).

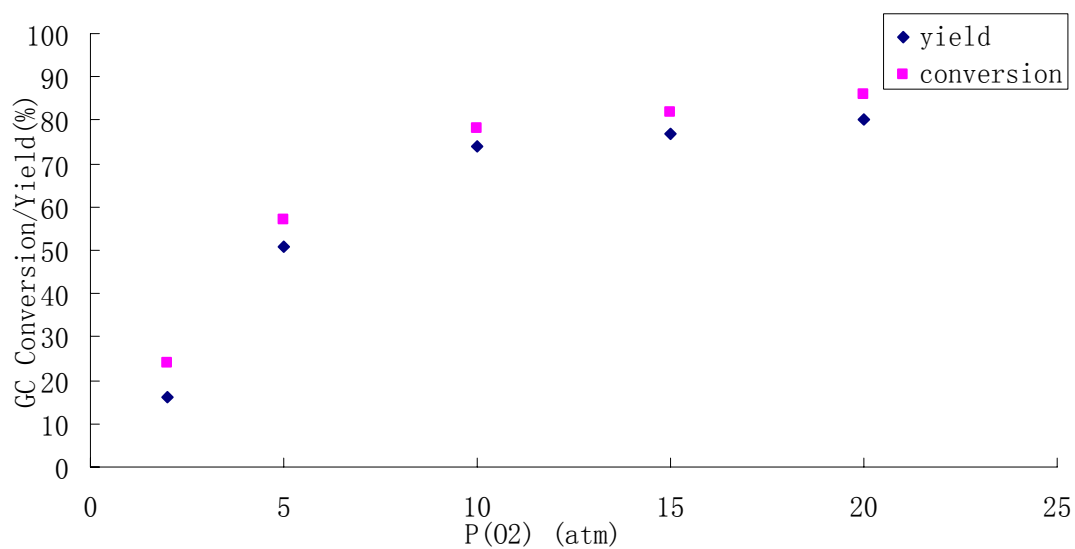


Figure S3. Effect of the pressure of O₂ on the Wacker oxidation of 1-dodecene in EC.
Reaction conditions: 1-dodecene (0.5 mmol, 0.11 mL), PdCl₂ (0.01 mmol, 1.77 mg), EC (3 mL), NaOAc (10 mol %, 4.1 mg), Temp. 60 °C, time 6 h.

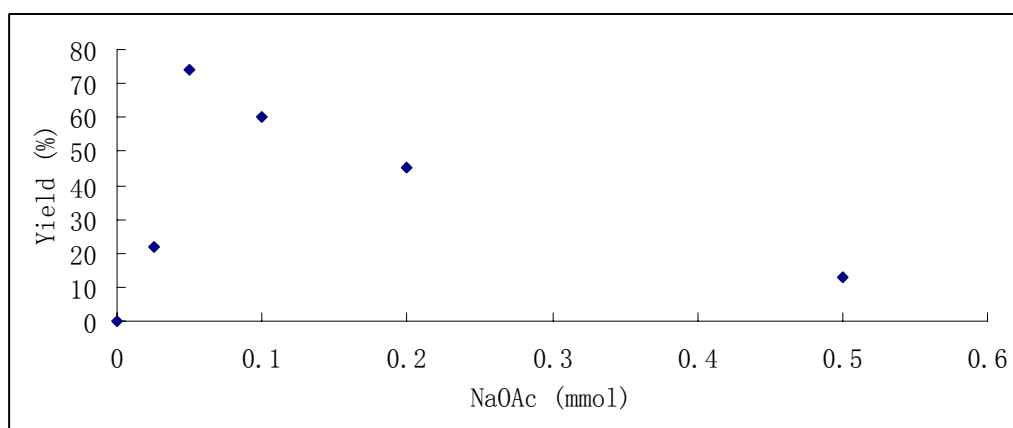


Figure S4. Effect of the amount of NaOAc on the Wacker oxidation of 1-dodecene in EC. Reaction conditions: 1-dodecene (0.5 mmol, 0.11 mL), PdCl₂ (0.01 mmol, 1.77 mg), EC (3 mL), Temp. 60 °C, time 6 h, Po₂ (10 atm).

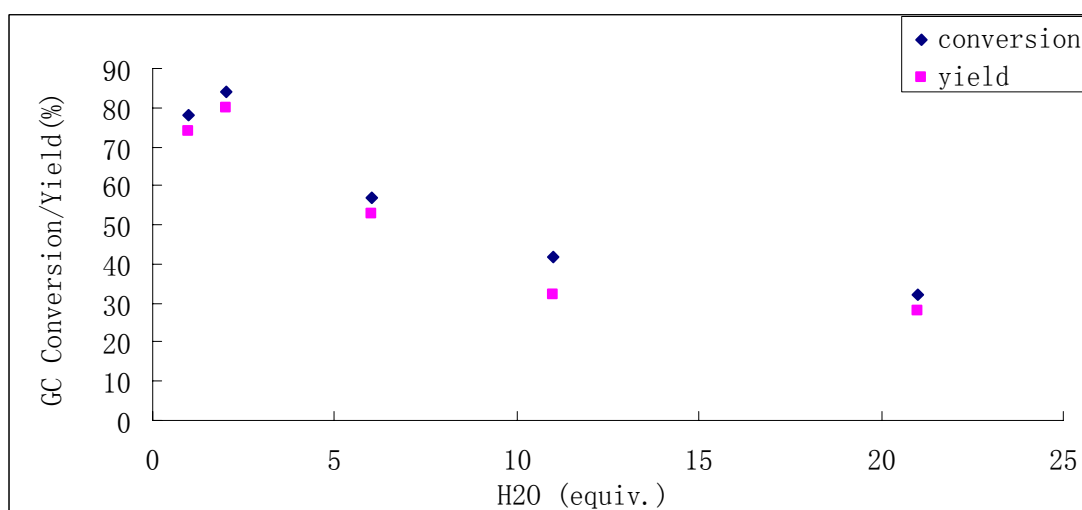


Figure S5. Effect of the amount of water on the Wacker oxidation of 1-dodecene in EC. Reaction conditions: dodecene (0.5 mmol, 0.11 mL), PdCl₂ (0.01 mmol), EC (3 mL), NaOAc (10 mol %, 4.1 mg), Temp. 60 °C, time 6 h, Po₂ (10 atm).

Table S1 Effect of additives on the Wacker oxidation of 1-dodecene in EC

Entry	Additive	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)
1	Pyridine	60	6	0	0
2	1,10-phenanthroline	60	6	3	0
3	NEt ₃	60	6	0	0
4	PPh ₃	60	6	0	0
5	acac	60	6	14	0
6	LiOAc	60	6	23	13
7	KOAc	60	6	23	2
8	KOAc	80	6	57	50
9	KOAc	100	6	80	72
10	Mg(OAc) ₂	60	6	0	0
11	K ₂ CO ₃	60	6	0	0
12	n-Bu ₄ Cl	60	6	0	0
13	n-Bu ₄ NBr	60	6	0	0

Reaction conditions: dodecene (0.5 mmol, 0.11 mL), PdCl₂ (0.01mmol, 1.77 mg), additive (10 mol %), EC (3 mL), Po₂ (10 atm).

(3) The ¹H NMR and ¹³C NMR data for products

Octan-2-one (**1a**): ¹H NMR(400MHz, CDCl₃): δ 2.38(t, *J* = 7.2MHz, 2H), 2.10(s, 3H), 1.51-1.55(m, 2H), 1.24 (m, 6H), 0.84(q, *J* = 5.1MHz, 3H); ¹³C NMR(100.4MHz, CDCl₃): δ 209.4, 43.8, 31.6, 29.9, 28.9, 23.9, 22.5, 14.0.

Decan-2-one (**1b**): ¹H NMR(300MHz, CDCl₃): δ 2.40(t, *J* = 7.4MHz, 2H), 2.11(s, 3H), 1.52-1.57(m, 2H), 1.25 (m, 10H), 0.86(q, *J* = 6.9MHz, 3H); ¹³C NMR(75MHz, CDCl₃): δ 209.2, 43.8, 31.8, 29.8, 29.3, 29.2, 29.1, 23.9, 22.6, 14.0.

Dodecan-2-one (**1c**): ¹H NMR(300MHz, CDCl₃): δ 2.40(t, *J* = 7.4MHz, 2H), 2.10(s, 3H), 1.52-1.58(m, 2H), 1.24 (m, 14H), 0.86(q, *J* = 6.9MHz, 3H); ¹³C NMR(75MHz, CDCl₃): δ 209.1, 43.8, 31.9, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 23.9, 22.6, 14.0.

Hexadecan-2-one (**1d**): ¹H NMR(400MHz, CDCl₃): δ 2.40(t, *J* = 7.4MHz, 2H), 2.12(s, 3H), 1.54-1.59(m, 2H), 1.24 (m, 22H), 0.86(q, *J* = 6.5MHz, 3H); ¹³C NMR(100.4MHz, CDCl₃): δ 209.5, 43.8, 31.9, 29.9, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 23.9, 22.7, 14.0.

Acetophenone (**1e**): ¹H NMR(300MHz, CDCl₃): δ 7.93 (m, 2H), 7.54(m, 1H), 7.45(m, 2H), 2.57(s, 3H); ¹³C NMR(75MHz, CDCl₃): δ 198.0, 137.2, 133.0, 128.5, 128.3, 26.5.

p-Methylacetophenone (**1f**): ^1H NMR(400MHz, CDCl_3): δ 7.87 (d, $J = 8.2\text{MHz}$, 2H), 7.26 (d, $J = 8.0\text{MHz}$, 2H), 2.58 (s, 3H), 2.41 (s, 3H); ^{13}C NMR(100.4MHz, CDCl_3): δ 197.8, 143.9, 134.7, 129.2, 128.4, 26.5, 21.6.

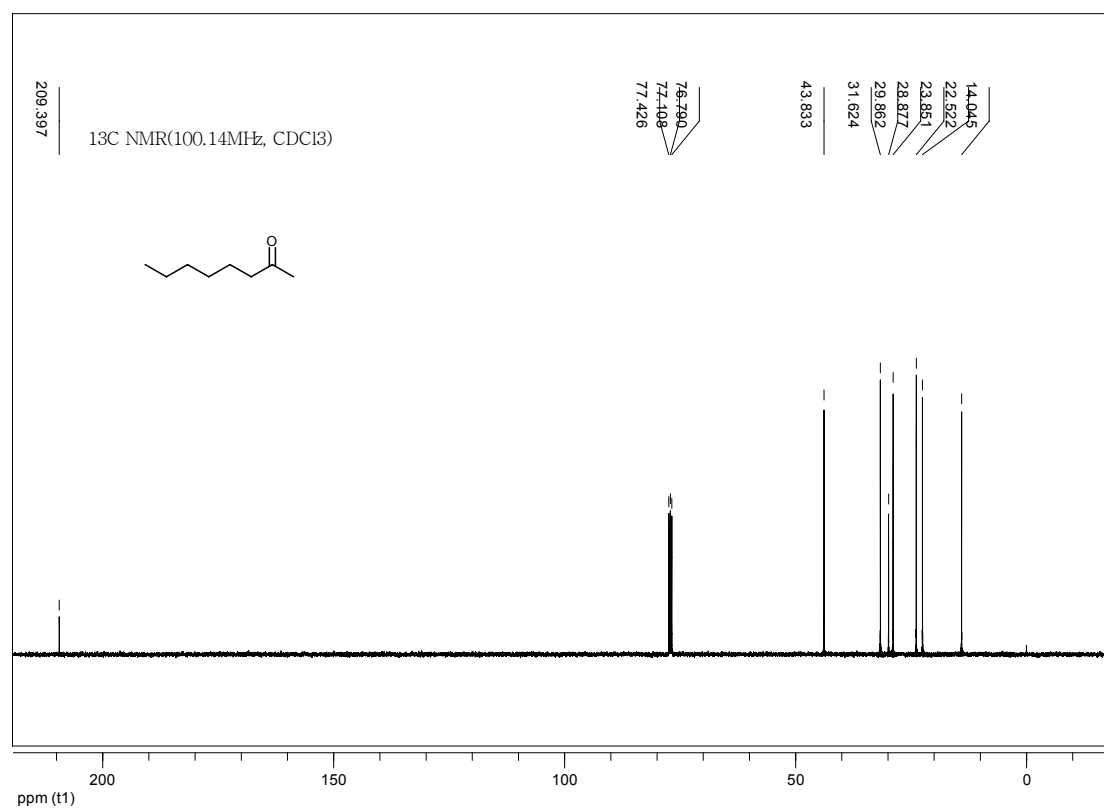
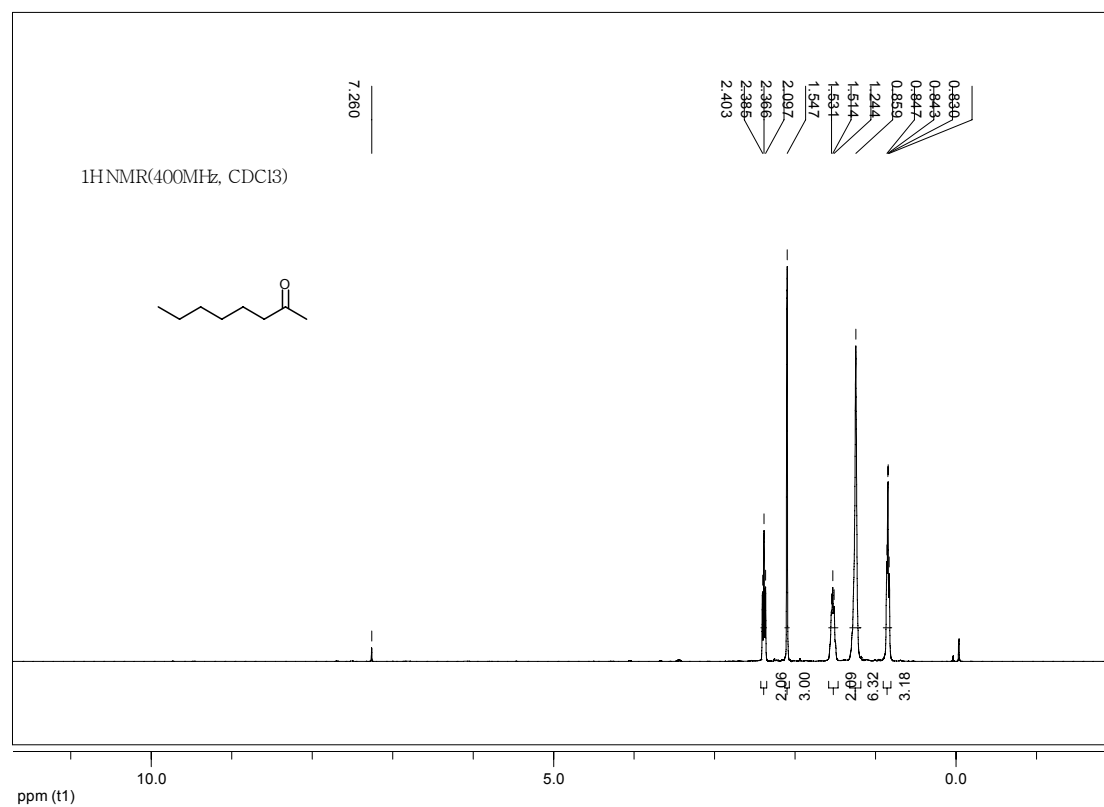
p-Methoxyacetophenone (**1g**): ^1H NMR(400MHz, CDCl_3): δ 7.94 (d, $J = 8.8\text{MHz}$, 2H), 6.93 (d, $J = 8.8\text{MHz}$, 2H), 3.87 (s, 3H), 2.56 (s, 3H); ^{13}C NMR(75MHz, CDCl_3): δ 196.7, 130.6, 113.7, 55.5, 26.3.

m-Methylacetophenone (**1h**): ^1H NMR(300MHz, CDCl_3): δ 7.68 (m, 2H), 7.28 (m, 2H), 2.52 (s, 3H), 2.30 (s, 3H); ^{13}C NMR(75MHz, CDCl_3): δ 197.4, 137.3, 136.1, 132.8, 127.8, 127.4, 124.6, 26.5, 20.3.

o-Methylacetophenone (**1i**): ^1H NMR(300MHz, CDCl_3): δ 7.46 (m, 4H), 2.58 (s, 3H), 2.540 (s, 3H); ^{13}C NMR(75MHz, CDCl_3): δ 200.7, 137.4, 136.7, 131.0, 130.5, 128.3, 124.1, 28.5, 20.5.

p-chloroacetophenone (**1j**): ^1H NMR(300MHz, CDCl_3): δ 7.88 (d, $J = 8.4\text{MHz}$, 2H), 7.42 (d, $J = 8.4\text{MHz}$, 2H), 2.58 (s, 3H); ^{13}C NMR(75MHz, CDCl_3): δ 196.8, 139.6, 135.4, 129.7, 128.8, 26.6.

(4) The ^1H NMR and ^{13}C NMR charts for products



2a

