Supporting Information
An efficient electrochemical method for the paired synthesis of carbonyl compounds and homoallylic alcohols in a simple home-made cell
Li Zhang, Zhenggen Zha*, Zhiyong Wang*

Hefei National Laboratory for Physical Science at Microscale, Joint- Lab of Green Synthetic Chemistry and Department of Chemistry University of Science and Technology of China Hefei, 230026 (P. R. China)
Fax: (+86) 551-360-3185
E-mail: zwang3@ustc.edu.cn

Contents:

Experimental Section S2-S3
Characterization data of all products S3-S9
NMR Spectra of all products S9-S31

General Remarks: $^1$H NMR and $^{13}$C NMR were recorded on a Bruker AC-300 FT ($^1$H: 300 MHz, $^{13}$C: 75 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer.
1. **Experimental Section.**

Apparatus and reagents.

**Preparation of the cell:** To 100 mL of saturated KNO₃ solution, 3 g of agaragar was added. The mixture was heated to 100 °C. We applied latex nipple to seal one side of glass apparatus prepared beforehand. Then the melting agaragar gel was added dropwise from another side of the apparatus until the part of U tube was full and cooled to the room temperature for solidation. (Figure S1)

**Reaction equipment** is All the substrates were reagent-grade materials and purified prior to use. All solutions were prepared from double distilled water. Electrochemical experiments were carried out on dual display potentiostat (CJS-292) and the instrument for measuring CV is CHI660D workstation (CHI, USA).

Anode reaction:

\[
\text{CH}_2\text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}
\]

Cathode reaction:

\[
\text{CHO} + \text{Br} \rightarrow \text{OH}
\]

Representative procedure for 1-phenylbut-3-en-1-ol and benzaldehyde: A divided cell with salt bridge of KNO₃ was equipped with a graphite electrode (dia.3.0 mm) as an anode and another graphite electrode (dia.3.0 mm vs SCE) as a cathode (Figure S1 in supporting information). To a solution of 0.4 M KNO₃ (5 mL) in the anodic compartment, benzyl alcohol (5 mmol) was added.
In the cathodic compartment, a solution of allyl bromide (7.5 mmol) and SnCl$_2$ (1 mmol) was added into 0.4 M KNO$_3$ solution (5 mL). The reaction mixture was stirred and electrolyzed at constant potential of 0.6 V until the alcohols were converted into the corresponding aldehydes. Then the produced aldehydes were transferred to the cathodic chamber by simple phase separation. Meanwhile, the alcohol (5 mmol) mentioned above were supplemented in the anodic chamber. The electrolytes were stirred and electrolyzed at constant potential of 0.6 V for 4–5 hours. Then the allylation product in the cathodic compartment was extracted with ether (3×10 mL), washed with water and dried over anhydrous Na$_2$SO$_4$, respectively. Then the solvents were removed under reduced pressure and the residues were purified by flash column chromatography. The produced aldehyde in the anodic compartment was separated by a phase separation and was added to the cathodic compartment for the next cycle.

2. Characterization data of all products.

General Remarks: $^1$H NMR and $^{13}$C NMR were recorded on a Bruker AC-300 FT ($^1$H: 300 MHz, $^{13}$C: 75 MHz) using TMS as internal reference. The chemical shifts ($\delta$) and coupling constants ($J$) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

1-phenylbut-3-en-1-ol (1b)

![1-phenylbut-3-en-1-ol](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 7.39-7.21$ (m, 5 H), 5.90-5.69 (m, 1 H), 5.21-5.10 (q, 2 H), 4.78-4.60 (q, 1 H), 2.42-2.62 (m, 2 H), 2.00 (s, 1 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 144.0$, 134.6, 128.5, 127.6, 125.9, 118.4, 73.4, 43.9; IR (liquid film, cm$^{-1}$): $\nu = 3401, 3077, 3030, 2979, 2908, 1641, 1493, 1453, 1307, 1048, 1001, 916, 758, 700, 644, 609$.

Benzaldehyde (1a)

![Benzaldehyde](image)

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 10.02$ (s, 1 H), 7.88 (d, $J = 6.9$ Hz, 2 H), 7.72-7.61 (m, 1 H), 7.61-7.45 (m, 2 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 192.3$, 136.5, 134.4, 129.7, 128.9; IR (liquid film, cm$^{-1}$): $\nu = 3387, 3064, 2819, 2737, 1702, 1655, 1584, 1203, 827, 745, 688, 649$.

1-(4-chlorophenyl)but-3-en-1-ol (2b)

![1-(4-chlorophenyl)but-3-en-1-ol](image)
4-chlorobenzaldehyde (2a)

\[
\begin{align*}
\text{H-NMR (CDCl}_3, 300 MHz, ppm): \delta &= 7.42-7.20 (m, 4 H), 5.92-5.65 (m, 1 H), 5.24-5.08 (m, 2 H), 4.82-4.65 (m, 1 H), 2.61-2.46 (m, 2 H), 2.01 (s, 1 H); \\
\text{^13C-NMR (CDCl}_3, 75 MHz, ppm): \delta &= 142.4, 134.1, 133.2, 128.6, 127.3, 118.8, 72.7, 43.9; \\
\text{IR (liquid film, cm}^{-1}): v &= 3378, 3078, 2907, 1641, 1493, 1411, 1091, 1050, 1013, 919, 829.
\end{align*}
\]

1-(4-bromophenyl)but-3-en-1-ol (3b)

\[
\begin{align*}
\text{H-NMR (CDCl}_3, 300 MHz, ppm): \delta &= 7.62-7.40 (m, 2 H), 7.35-7.10 (m, 2 H) 5.93-5.65 (m, 1 H), 5.28-5.02 (m, 2 H), 4.85-4.62 (m, 1 H), 2.61-2.36 (m, 2 H), 2.04 (s, 1 H); \\
\text{^13C-NMR (CDCl}_3, 75 MHz, ppm): \delta &= 142.9, 134.0, 131.5, 127.6, 121.2, 118.7, 72.7, 43.7; \\
\text{IR (liquid film, cm}^{-1}): v &= 3395, 3077, 2932, 1641, 1489, 1404, 1070, 1010, 919, 822.
\end{align*}
\]

4-bromobenzaldehyde (3a)

\[
\begin{align*}
\text{H-NMR (CDCl}_3, 300 MHz, ppm): \delta &= 9.97 (s, 1 H), 7.91-7.65 (m, 4 H); \\
\text{^13C-NMR (CDCl}_3, 75 MHz, ppm): \delta &= 190.9, 135.1, 132.4, 130.9, 129.7; \\
\text{IR (liquid film, cm}^{-1}): v &= 3351, 3086, 2859, 1697, 1589, 1573, 1383, 1205, 1066, 811.
\end{align*}
\]

1-(2-bromophenyl)but-3-en-1-ol (4b)

\[
\begin{align*}
\text{H-NMR (CDCl}_3, 300 MHz, ppm): \delta &= 9.97 (s, 1 H), 7.91-7.65 (m, 4 H); \\
\text{^13C-NMR (CDCl}_3, 75 MHz, ppm): \delta &= 190.9, 135.1, 132.4, 130.9, 129.7; \\
\text{IR (liquid film, cm}^{-1}): v &= 3351, 3086, 2859, 1697, 1589, 1573, 1383, 1205, 1066, 811.
\end{align*}
\]
OH
       Br

1H-NMR (CDCl₃, 300 MHz, ppm): δ = 7.71-7.45 (m, 2 H), 7.43-7.28 (m, 1 H), 7.26-7.07 (m, 1 H), 5.95-5.81 (m, 1 H), 5.31-5.15 (m, 2 H), 5.20-5.05 (m, 1 H), 2.75-2.54(m, 1 H), 2.52-2.30(m, 1 H), 2.18(s, 1 H); ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ = 142.8, 134.3, 132.7, 128.8, 127.7, 127.4, 121.8, 118.6, 71.9, 42.1; IR (liquid film, cm⁻¹): ν = 3389, 3073, 2912, 1468, 1439, 1045, 1023, 917, 754.

2-bromobenzaldehyde (4a)

CHO
       Br

1H-NMR (CDCl₃, 300 MHz, ppm): δ = 10.37 (s, 1 H), 8.01-7.82 (m, 1 H), 7.81-7.53 (m , 1 H), 7.52-7.35 (m, 2 H); ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ = 191.4, 135.2, 133.8, 133.4, 129.7, 127.8, 126.9; IR (liquid film, cm⁻¹): ν = 3067, 2924, 1700, 1590, 1570, 1471, 1440, 1057, 1025, 751.

1-(4-nitrophenyl)but-3-en-1-ol (5b)

OH
       O₂N

1H-NMR (CDCl₃, 300 MHz, ppm): δ = 8.20 (d, J = 8.7 Hz, 2 H), 7.53 (d, J = 8.7 Hz, 2H), 6.92-6.70 (m, 1 H), 5.34-5.08 (m, 2 H), 4.95-4.70 (m, 1 H), 2.61-2.42 (m, 2 H), 2.45 (s, 1 H); ¹³C-NMR (CDCl₃, 75 MHz, ppm): δ = 151.3, 147.4, 133.3, 126.7, 123.8, 119.7, 72.3, 44.0; IR (liquid film, cm⁻¹): ν = 3423, 3079, 2914, 1604, 1519, 1347, 1056, 1013, 921, 855, 700.

4-nitrobenzaldehyde (5a)

CHO
       O₂N

1H-NMR (CDCl₃, 300 MHz, ppm): δ = 10.16 (s, 1 H), 8.40 (d, J = 8.7 Hz, 2 H), 8.08 (d, J = 8.7
1-p-tolylbut-3-en-1-ol (6b)

\[
\begin{align*}
\text{1H-NMR (CDCl}_3, 300 MHz, ppm): & \quad \delta = 7.23 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2H), 6.93-6.72 (m, 1 H), 5.24-5.01 (m, 2 H), 4.75-4.50 (m, 1 H), 2.63-2.40 (m, 2 H), 2.34 (s, 3 H), 2.03 (s, 1 H); \\
\text{13C-NMR (CDCl}_3, 75 MHz, ppm): & \quad \delta = 141.1, 137.1, 134.7, 129.1, 125.9, 117.9, 73.3, 43.7, 21.1; \\
\text{IR (liquid film, cm}^{-1}): & \quad v = 3385, 2979, 2923, 1641, 1514, 1432, 1045, 915, 816, 538.
\end{align*}
\]

4-methylbenzaldehyde (6a)

\[
\begin{align*}
\text{1H-NMR (CDCl}_3, 300 MHz, ppm): & \quad \delta = 9.96 (s, 1 H), 7.77 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 2.47 (s, 3 H); \\
\text{13C-NMR (CDCl}_3, 75 MHz, ppm): & \quad \delta = 191.8, 145.5, 134.3, 129.8, 129.7, 21.8; \\
\text{IR (liquid film, cm}^{-1}): & \quad v = 2924, 1703, 1605, 1209, 1169, 847, 808, 758, 481.
\end{align*}
\]

1-(naphthalene-1-yl)but-3-en-1-ol (7b)

\[
\begin{align*}
\text{1H-NMR (CDCl}_3, 300 MHz, ppm): & \quad \delta = 8.10-7.92 (m, 1 H), 7.90-7.81 (m, 1 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.62 (d, J = 6.9 Hz, 1 H), 7.55-7.31 (m, 3 H), 6.00-5.81 (m, 1 H), 5.52-5.40 (m, 1 H), 5.28-5.07 (m, 2 H), 2.80-2.65 (m, 1 H), 2.65-2.50 (m, 1 H), 2.26 (s, 1 H); \\
\text{13C-NMR (CDCl}_3, 75 MHz, ppm): & \quad \delta = 139.6, 134.9, 133.9, 130.4, 129.0, 128.0, 126.1, 125.6, 125.5, 123.1, 122.9, 118.2, 70.2, 42.9; \\
\text{IR (liquid film, cm}^{-1}): & \quad v = 3393, 3070, 1639, 1509, 1055, 916, 800, 778.
\end{align*}
\]
1-naphthaldehyde (7a)

\[
\begin{align*}
\text{CHO} & \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta$ = 10.36 (s, 1 H), 9.23 (d, $J$ = 8.7 Hz, 1 H), 8.05 (d, $J$ = 8.1 Hz, 1 H), 8.00-7.81 (m, 2 H), 7.72-7.60 (m, 1 H), 7.60-7.45 (m, 2 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta$ = 193.4, 136.5, 135.2, 133.8, 131.5, 130.6, 129.1, 128.5, 126.9, 124.9; IR (liquid film, cm$^{-1}$): $v$ = 3051, 2726, 1688, 1573, 1509, 1217, 1169, 1055, 886, 802, 772.

1-phenylpent-4-en-2-ol (8b)

\[
\begin{align*}
\text{OH} & \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta$ = 7.42-7.18 (m, 5 H), 5.92-5.72 (m, 1 H), 5.25-5.11 (m, 2 H), 3.95-3.80 (m, 1 H), 2.92-2.65 (m, 2 H), 2.41-2.15 (m, 2 H), 1.72 (s, 1 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta$ = 138.6, 134.8, 129.5, 128.6, 126.6, 118.1, 71.8, 43.4, 41.3; IR (liquid film, cm$^{-1}$): $v$ = 3422, 2925, 1495, 454, 1078, 1032, 997, 915, 744, 700.

2-phenylacetaldehyde (8a)

\[
\begin{align*}
\text{CHO} & \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta$ = 9.80-9.71 (m, 1 H), 7.41-7.18 (m, 5 H), 3.67 (d, $J$ = 2.1 Hz, 2 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta$ = 199.2, 131.9, 129.5, 128.9, 128.4, 128.2, 127.3, 50.4; IR (liquid film, cm$^{-1}$): $v$ = 3429, 3029, 1723, 1496, 1454, 1079, 1031, 749, 700.

Dec-1-en-4-ol (9b)

\[
\begin{align*}
\text{OH} & \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta$ = 5.91-5.71 (m, 1 H), 5.21-5.11 (m, 2 H), 3.65 (d, $J$ = 4.5 Hz, 1 H), 2.41-2.25 (m, 1 H), 2.21-2.11 (m, 1 H), 1.60 (s, 1 H), 1.46 (s, 3 H), 1.30-1.21 (m, 7 H), 0.87 (d, $J$ = 6.6 Hz, 3 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta$ = 135.5, 118.4, 71.3, 42.5, 37.4, 32.4, 29.9, 26.2, 23.2, 14.6; IR (liquid film, cm$^{-1}$): $v$ = 3368, 2957, 2928, 2857, 1462, 912.
Heptanal (9a)

\[
\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CO}\\
\]

\(^1\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \(\delta = 9.76\) (s, 1 H), 2.51-2.35 (m, 2 H), 1.71-1.53 (m, 2 H), 1.30 (s, 6 H), 0.93-0.82 (m, 3 H); \(^13\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \(\delta = 202.3, 43.7, 31.4, 28.7, 22.3, 21.9, 13.8\); IR (liquid film, cm\(^{-1}\)): \(\nu = 3434, 2929, 2859, 2714, 1727, 1462, 1112\).

Benzophenone (10a)

\[
\text{C}_6\text{H}_5\text{C}=\text{C}\\
\]

\(^1\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \(\delta = 7.85-7.71\) (m, 4 H), 7.67-7.52 (m, 2 H), 7.51-7.42 (m, 4 H); \(^13\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \(\delta = 196.7, 137.8, 132.5, 130.1, 128.4\); IR (liquid film, cm\(^{-1}\)): \(\nu = 3448, 3055, 1652, 1594, 1575, 1447, 1321, 1278, 705, 694, 637\).

2-phenylpent-4-en-2-ol (11b)

\[
\text{C}_6\text{H}_5\text{CH}=	ext{CH}\text{CH}_{2}\text{CH}=\text{CH}\\
\]

\(^1\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \(\delta = 7.58-7.41\) (m, 2 H), 7.40-7.29 (m, 2 H), 7.27-7.20 (m, 1 H), 5.71-5.51 (m, 1 H), 5.18-5.10 (m, 2 H), 2.76-2.62 (m, 1 H), 2.54-2.42 (m, 1 H), 2.04 (s, 1 H), 1.55 (s, 3 H); \(^13\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \(\delta = 147.8, 133.8, 128.3, 126.7, 124.9, 119.5, 73.8, 48.6, 30.0\); IR (liquid film, cm\(^{-1}\)): \(\nu = 3429, 2976, 2928, 1445, 1069, 914, 765, 700\).

Acetophenone (11a)

\[
\text{C}_6\text{H}_5\text{CO}\\
\]

\(^1\)H-NMR (CDCl\(_3\), 300 MHz, ppm): \(\delta = 8.01-7.90\) (m, 2 H), 7.62-7.51 (m, 1 H), 7.49-7.41 (m, 2 H) 2.61 (s, 3 H); \(^13\)C-NMR (CDCl\(_3\), 75 MHz, ppm): \(\delta = 198.1, 137.3, 133.2, 128.7, 128.4, 26.6\); IR (liquid film, cm\(^{-1}\)): \(\nu = 3651, 3063, 2926, 1685, 1599, 1449, 1359, 1266, 955, 760, 690, 589\).
1-allylcyclohexanol (12b)

\[
\text{OH} \quad \text{=C=CH} \quad \text{OH}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 5.95-5.80$ (m, 1 H), 5.17-5.02 (m, 2 H), 2.22 (d, $J = 7.5$ Hz, 2 H), 1.71-1.39 (m, 10 H), 1.27 (s, 1 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 133.9, 118.7, 71.1, 46.9, 37.6, 32.1, 29.8, 25.9, 22.4$; IR (liquid film, cm$^{-1}$): $\nu = 3425, 2925, 2854, 1736, 1462, 1379, 1285, 1049$.

Cyclohexanone (12a)

\[
\text{O}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz, ppm): $\delta = 2.40-2.31$ (m, 4 H), 1.92-1.81 (m, 4 H), 1.80-1.69 (m, 2 H); $^{13}$C-NMR (CDCl$_3$, 75 MHz, ppm): $\delta = 211.9, 41.9, 26.9, 24.9$; IR (liquid film, cm$^{-1}$): $\nu = 2940, 2865, 1707, 1450, 1420, 124, 908, 750$.

3. NMR Spectra of all products.

1b
5a
7b
8a