Supporting Information

Sustainable Production of Pyromellitic Acid with Pinacol and Diethyl Maleate

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1. General information

Pinacol was purchased from Aladdin Industrial Inc. Diethyl maleate and ethyl acrylate were obtained from Tokyo Chemical Industry. Choline chloride and formic acid were supplied by Acros Organics. Other carboxylic acids were provided by Aladdin Industrial Inc. All chemicals were of analytical grade and were used without further purification.

Various deep eutectic solvents (DESs) were prepared according to literature by stirring choline chloride and the other component at 100 °C until a homogeneous liquid was formed (ca. 40 min).

Amberlyst-15 resin was purchased from Sigma-Aldrich company. The Raney Ni, Ni/C, Pd/C, Pt/C, Ru/C and Rh/C catalysts were purchased from Aladdin Industrial Inc. To facilitate the comparison, the metal contents in these catalysts were chosen as 5% by weight.

NMR spectra were recorded at room temperature in CDCl₃ on 400 MHz spectrometers. The chemical shifts for ¹H NMR were recorded in ppm downfield using the peak of CDCl₃ (7.26 ppm) or d⁶-DMSO (2.50 ppm) as the internal standard. The chemical shifts for ¹³C NMR were recorded in ppm downfield using the central peak of CDCl₃ (77.16 ppm) or d⁶-DMSO (39.52 ppm) as the internal standard. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

2. Pinacol dehydration to 2,3-dimethylbutadiene

2.1 Pinacol dehydration using Amberlyst-15 resin as catalyst

Pinacol (8.5 mmol, 1.0 g), Amberlyst-15 resin (100 mg), and solvent (4.0 g or 0 g for the solvent-free test) were added to a sealed tube (35 mL) in sequence. The
mixture was stirred at 120 °C for 12 h. Upon completion, the product was diluted with pentane and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a flame ionization detector (FID) using tridecane as the internal standard. Examples see Fig. S1 (no solvent, compound 3 in 88% carbon yield) and Fig. S2 (DMSO as solvent, compound 2 in 31% carbon yield, compound 3 in 15% carbon yield; NMP as solvent, compound 2 in 39% carbon yield, compound 3 in 21% carbon yield).

2.2 Pinacol dehydration in acidic deep eutectic solvents (DESs)

Pinacol (8.5 mmol, 1.0 g) and acidic DES (4-10 g) were added to a sealed tube (35 mL) in sequence. The reaction mixture was stirred at 100-150 °C for 12 h. Upon completion, the product was diluted with pentane and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a FID using tridecane as the internal standard. Example see Fig. S3 (8.0 g ChCl/HCOOH, 140 °C, compound 2 in 83% yield, compound 3 in 13% yield) and Fig. S4 (8.0 g ChCl/HCOOH, 150 °C, compound 2 in 71% yield, compound 3 in 16% yield).

The influence of ChCl/HCOOH dosage on the dehydration of pinacol was studied. According to Fig. S5, the carbon yield of compound 2 increased with the increment of ChCl/HCOOH dosage, reached the maximum (78%) when 8.0 g ChCl/HCOOH was used, then stabilized with further increasing the dosage. In contrast, it is noticed that the dosage of DES had no evident effect on the the carbon yield of compound 3.

We also investigated the effect of reaction temperature on the carbon yields of compounds 2 and 3. Taking into consideration that the thermal decomposition of formic acid is 160 °C, we set the maximum reaction temperature as 150 °C. As shown in Fig. S6, with the increasing of reaction temperature, the carbon yield of compound 2 slightly increased, reached the maximum (83%) when the pinacol dehydration was
performed at 140 °C, then decreased with further increment of the temperature. This can be rationalized because too high temperature led to the self D-A reaction of compound 2 (Fig. S4), which decreased its carbon yield or selectivity.

2.3 Recycling performance of ChCl/HCOOH in pinacol dehydration

Pinacol (8.5 mmol, 1.0 g) and ChCl/HCOOH (molar ratio 2:1, 8.0 g) were added to a sealed tube (35 mL) in sequence. The reaction mixture was stirred at 140 °C for 12 h. Upon completion, the upper layer was removed by decantation, diluted with pentane and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a FID using tridecane as the internal standard. The lower layer ChCl/HCOOH was dried at room temperature under vacuum for 10 h prior to use in next cycle. The water content in the desiccated ChCl/HCOOH was determined as < 2% by a Mettler Toledo DL39 Karl Fischer Titrator. Examples see Fig. S7 (the photographs of the system during the reaction) and Fig. S8 (the carbon yield of compound 2 as a function of recycle time). To check the thermal stability of formic acid under the investigated conditions, we conducted a blank experiment. From the chromatograms which were illustrated in Fig. S9, we can see that the areas of formic acid were almost the same (15703.5 vs. 15322.9). This result indicates that the formic acid was stable under the investigated conditions. No decomposition of formic acid was noticed during the reaction.

NMR and HRMS data of compounds 2 and 3

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.98 (s, 2H), 4.89 (s, 2H), 1.84 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.5, 113.1, 20.6. HRMS (ESI) calcd. for C$_6$H$_{11}$ [M + H]$^+$ 83.0855, found 83.0852.

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.07 (s, 3H), 1.07 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 214.4, 44.4, 26.5, 24.8. HRMS (ESI) calcd. for C$_6$H$_{13}$O [M + H]$^+$ 101.0961, found 101.0960.
3. D-A reaction, dehydrogenation, and hydrolysis

3.1 D-A reactions of 2,3-dimethylbutadiene with maleic anhydride, diethyl maleate, and diethyl fumarate

\[
\text{2} + \text{4} \rightarrow \text{5} \quad 60^\circ C
\]

Compound 2 (10 mmol, 1.1 mL) and maleic anhydride (10 mmol, 0.98 g) were added to a 35 mL sealed tube. The mixture was stirred at 60 °C for 1.5 h, then cooled down to room temperature and the white solid was formed. According to the NMR data (Fig. S24 and S25), D-A product (i.e. compound 5) was obtained in a nearly quantitative yield.

\[
\text{2} + \text{7} \rightarrow \text{8} \quad 120^\circ C
\]

Compound 2 (10 mmol, 1.1 mL) and diethyl maleate (10 mmol, 1.6 mL) were added to a 35 mL sealed tube. The mixture was stirred at 120 °C for 6 h, then cooled down to room temperature and analyzed by the Agilent GC 7890A equipped with an HP-5 column and a FID (Fig. S10a, nearly quantitative yield). It is noteworthy that the temperature exerted a significant effect on the D-A reaction. For example, the reaction did not occur at 60 °C and the starting materials still remained unchanged. Diethyl maleate cannot be completely consumed when the D-A reaction was performed at 100 °C for 12 h (Fig. S10b).

\[
\text{2} + \text{10} \rightarrow \text{10} \quad 120^\circ C
\]

For comparison, we also prepared compound 10 by the D-A reaction of compound 2 and diethyl fumarate. To do this, compound 2 (10 mmol, 1.1 mL) and diethyl fumarate (10 mmol, 1.6 mL) were added to a 35 mL sealed tube. The mixture was stirred at 120 °C for 6 h, then cooled down to room temperature and analyzed by the Agilent GC 7890A equipped with an HP-5 column and a FID. As shown in Fig. S11, compound 2 and diethyl fumarate were totally converted to compound 10 (nearly quantitative yield).
NMR and HRMS data of D-A adducts

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.38 – 3.28 (m, 2H), 2.43 (d, $J = 15.1$ Hz, 2H), 2.25 (d, $J = 13.9$ Hz, 2H), 1.68 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.6, 127.4, 40.5, 30.5, 19.4. HRMS (ESI) calcd. for C$_{10}$H$_{13}$O$_3$ [M + H]$^+$ 181.0859, found 181.0855.

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.12 (qd, $J = 7.1$, 1.6 Hz, 4H), 3.08 – 2.88 (m, 2H), 2.53 – 2.32 (m, 2H), 2.30 – 2.15 (m, 2H), 1.61 (s, 6H), 1.22 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.5, 124.0, 60.5, 40.6, 32.0, 19.0, 14.2. HRMS (ESI) calcd. for C$_{14}$H$_{23}$O$_4$ [M + H]$^+$ 255.1591, found 255.1594.

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.24 – 4.00 (m, 4H), 2.87 – 2.70 (m, 2H), 2.31 – 2.18 (m, 2H), 2.18 – 2.04 (m, 2H), 1.60 (s, 6H), 1.23 (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.0, 124.0, 60.6, 42.2, 34.3, 18.7, 14.3. HRMS (ESI) calcd. for C$_{14}$H$_{23}$O$_4$ [M + H]$^+$ 255.1591, found 255.1599.

3.2 Dehydrogenation of the D-A adducts under solvent-free condition

The compounds 8 or 10 (10 mmol, 2.5 g) and Pd/C (250 mg) were added to a 100 mL stainless steel batch reactor. The reaction was conducted under argon atmosphere (1 atm) at 220 °C for 24 h. The product was analyzed by the Agilent GC 7890A equipped with an HP-5 column and a FID using p-xylene as the internal standard. Examples see Fig. S12 (dehydrogenation of compound 8, 100% conversion of compound 8, 80% carbon yield of compound 9, and 11% carbon yield of compound 10) and Fig. S13 (dehydrogenation of compound 10, 87% conversion of compound 10 and 66% carbon yield of compound 9). Because the dehydrogenation of compound 8 was faster than that of 10, the side product (i.e. compound 10) was still
observed when compound 8 was completely consumed (24 h). Gratifyingly, after prolonging the reaction time to 48 h, the carbon yield of compound 9 increased to 84% (Fig. S14). It is noteworthy that the effects of the temperature on the dehydrogenation process were also investigated (Fig. S15). The reaction at higher temperature (260 °C) led to a decreased yield of compound 9, due to the formation of other unknown impurities.

The pathway for the formation of side product (i.e. compound 10) in the course of dehydrogenation of compound 8:

The isomerization of diethyl maleate under standard conditions: Diethyl maleate (10 mmol, 1.6 mL) and Pd/C (0.25 g) were added to a 100 mL stainless steel batch reactor. The mixture was stirred at 220 °C for 24 h, then cooled down to room temperature and analyzed by the Agilent GC 7890A equipped with an HP-5 column and a FID. From the result shown in Fig. S16, some diethyl maleate was isomerized to diethyl fumarate.

NMR and HRMS data of compound 9

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.38 (s, 2H), 4.25 (q, J = 7.1 Hz, 4H), 2.20 (s, 6H), 1.26 (t, J = 7.2 Hz, 6H); } ^{13}C \text{ NMR (100 MHz, CDCl}_3 \delta 167.8, 140.0, 129.9, 129.7, 61.3, 19.6, 14.1. HRMS (ESI) calcd. for C}_{14}H_{19}O_{4} [M + H]^+ 251.1278, found 251.1274. \]
3.3 One-step pinacol dehydration and D-A reaction in ChCl/HCOOH

\[
\begin{align*}
\text{HO-CH(OEt)}_2 & \xrightarrow{\text{ChCl/HCOOH, 140 }^\circ\text{C}} \text{CO}_2\text{Et} \\
1 & \quad 4 \\
& \quad \text{One-step} \\
& \quad \text{8 + 10 (7:1 : 1)} \\
& \quad \text{89% yield}
\end{align*}
\]

Pinacol (10 mmol, 1.2 g), ChCl/HCOOH (molar ratio 2:1, 9.6 g) and diethyl maleate (10 mmol, 1.6 mL) were added to a sealed tube (35 mL) in sequence. The reaction mixture was stirred at 140 °C for 12 h. Upon completion, the upper layer D-A adduct was isolated by decantation and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a FID using tridecane and p-xylene as the internal standards. Examples see Fig. S17 (89% carbon yield of D-A adduct, the ratio of compounds 8 and 10 is 7.1:1, and trace amount of pinacolone).

3.4 One-pot dehydrogenation/hydrolysis

\[
\begin{align*}
\text{CO}_2\text{Et} & \xrightarrow{1) \text{Pd/C, 220 }^\circ\text{C, 24 h}} \text{CO}_2\text{H} \\
\text{CO}_2\text{Et} & \xrightarrow{2) \text{NaOH/H}_2\text{O, 55 }^\circ\text{C}} \text{CO}_2\text{H} \\
& \quad \text{One-pot} \\
1 & \quad 11 \\
& \quad 73\% \text{ yield}
\end{align*}
\]

The resulting D-A products (10 mmol, 2.5 g) and Pd/C (250 mg) were added to a 100 mL stainless steel batch reactor. The reaction was conducted under argon atmosphere (1 atm) at 220 °C for 24 h. After that, a mixture of water (80 mL) and NaOH (25 mmol, 1.0 g) was directly added into the system, and stirred at 55 °C for 5 h. Then, Pd/C was filtered and the aqueous phase was acidified by diluted HCl solution until pH = 1. Subsequently, the aqueous solution was extracted with ethyl acetate (20 mL) for three times. The combined organic phase was dried with anhydrous MgSO\(_4\) and concentrated via rotary evaporation. Direct crystallization in ethanol afforded compound 11 as a white solid (1.42 g, 73% yield, m.p. 207–208 °C).

**NMR and HRMS data of compound 11**

\[
\begin{align*}
\text{H NMR (400 MHz, DMSO-}d_6\text{)} & \delta 12.88 (\text{s, 2H}), 7.43 (\text{s, 2H}), 2.27 (\text{s, 6H}); \\
\text{C NMR (100 MHz, DMSO-}d_6\text{)} & \delta 168.8, 139.4, 130.4, 129.4, 19.2. \text{HRMS (ESI) calcd. for C}_{10}\text{H}_{11}\text{O}_4 [M + H]^+ 195.0652, found 195.0644.}
\end{align*}
\]
4. Catalytic aerobic oxidation

\[
\text{\begin{align*}
\text{ Compound 11 (1.0 mmol, 0.19 g), } & N\text{-hydroxyphthalimide (NHPI, 20 mol\%, 32.6 mg), } Co(OAc)_2 (4 \text{ mol\%, 7.0 mg), } Mn(OAc)_2 \cdot 4H_2O (4 \text{ mol\%, 10 mg) and acetic acid} \\
& (3 \text{ mL}) \text{ were added to a 30 mL stainless steel reactor in sequence. The reaction was} \\
& \text{conducted under oxygen atmosphere (1 atm) at 120 }^\circ\text{C for 14 h. Upon completion,} \\
& \text{acetic acid was removed via rotary evaporation. The crude residue was crystallized} \\
& \text{with ethanol/acetone to afford pyromellitic acid (PMA, compound 12) as a white solid} \\
& (224.4 mg, 88\% \text{ yield, m.p. 247‒248 }^\circ\text{C).}
\end{align*}}
\]

\text{NMR and HRMS data of compound 12} 

\[
\begin{align*}
^1H \text{ NMR (400 MHz, DMSO-}d_6\text{) } & \delta 13.52 \text{ (s, 4H), 7.92 (s, 2H);} \\
^13C \text{ NMR (100 MHz, DMSO-}d_6\text{) } & \delta 167.3, 134.6, 128.5. \text{ HRMS (ESI)} \\
& \text{calcd. for } C_{10}H_6O_8Na \text{ [M + Na]}^+ 276.9955, \text{ found 276.9953.}
\end{align*}
\]
5. Production of trimellitic acid using ethyl acrylate as the feedstock

One-step pinacol dehydration and D-A reaction with acrylate: Pinacol (10 mmol, 1.2 g), ChCl/HCOOH (molar ratio 2:1, 9.6 g) and ethyl acrylate (10 mmol, 1.0 mL) were added to a sealed tube (35 mL) in sequence. The reaction mixture was stirred at 140 °C for 12 h. Upon completion, the upper layer D-A adduct was isolated by decantation and analyzed by an Agilent GC 7890A equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a FID using tridecane and toluene as the internal standards. Examples see Fig. S18 (83% carbon yield of D-A adduct 13).

One-pot dehydrogenation/hydrolysis: The resulting D-A adduct 13 (10 mmol, 1.8 g) and Pd/C (180 mg) were added to a 100 mL stainless steel batch reactor. The reaction was conducted under argon atmosphere (1 atm) at 220 °C for 24 h (the GC chromatogram of the dehydrogenation product was illustrated in Fig. S19). After that, a mixture of water (80 mL) and NaOH (12 mmol, 0.48 g) was directly added into the system, and stirred at 55 °C for 5 h. Then, Pd/C was filtered and the aqueous phase was acidified by diluted HCl solution until pH = 1. Subsequently, the aqueous solution was extracted with ethyl acetate (20 mL) for three times. The combined organic phases were dried with anhydrous MgSO₄ and concentrated via rotary evaporation. Direct crystallization in ethanol afforded 3,4-dimethylbenzoic acid 15 as a white solid (1.17 g, 78% yield, m.p. 118–119 °C).

Catalytic aerobic oxidation: To a 30 mL stainless steel reactor were added 3,4-dimethylbenzoic acid 15 (1.0 mmol, 0.15 g), N-hydroxyphthalimide (NHPI, 20 mol%, 32.6 mg), Co(OAc)₂ (4 mol%, 7.0 mg), Mn(OAc)₂•4H₂O (4 mol%, 10 mg) and acetic acid (3 mL) in sequence. The reaction was conducted under oxygen atmosphere (1 atm) at 120 °C for 14 h. Upon completion, acetic acid was removed via rotary
evaporation. The crude residue was crystallized with ethanol/acetone to afford trimellitic acid (TMA) as a white solid (189.0 mg, 90% yield, m.p. 225–226 °C).

**NMR and HRMS data of the products**

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 4.12 (q, J = 7.1 \text{ Hz, 2H}), 2.55 – 2.42 (m, 1H), 2.27 – 1.85 (m, 6H), 1.60 (d, J = 5.5 \text{ Hz, 6H}), 1.25 (t, J = 7.1 \text{ Hz, 3H}); \text{^13C NMR (100 MHz, CDCl}_3\text{)} \delta 176.2, 125.4, 124.1, 60.3, 40.4, 33.9, 31.2, 26.0, 19.1, 19.0, 14.4. HRMS (ESI) calcd. for C_{11}H_{19}O_2 [M + H]^+ 183.1380, found 183.1373.\]

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.81 (s, 1H), 7.77 (dd, J = 7.9, 1.9 \text{ Hz, 1H}), 7.18 (d, J = 7.9 \text{ Hz, 1H}), 4.36 (q, J = 7.1 \text{ Hz, 2H}), 2.31 (s, 6H), 1.39 (t, J = 7.2 \text{ Hz, 3H}); \text{^13C NMR (100 MHz, CDCl}_3\text{)} \delta 167.0, 142.2, 136.7, 130.7, 129.7, 128.2, 127.2, 60.8, 20.1, 19.8, 14.5. HRMS (ESI) calcd. for C_{11}H_{15}O_2 [M + H]^+ 179.1067, found 179.1068.\]

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{)} \delta 12.71 (s, 1H), 7.71 (s, 1H), 7.66 (d, J = 7.8 \text{ Hz, 1H}), 7.24 (d, J = 7.8 \text{ Hz, 1H}), 2.27 (s, 3H), 2.26 (s, 3H); \text{^13C NMR (100 MHz, DMSO-d}_6\text{)} \delta 167.5, 141.8, 136.5, 130.3, 129.6, 128.5, 126.9, 19.6, 19.3. HRMS (ESI) calcd. for C_{9}H_{9}O_2 [M – H]^+ 149.0597, found 149.0617.\]

\[ \text{H NMR (400 MHz, DMSO-d}_6\text{)} \delta 13.50 (s, 3H), 8.23 (s, 1H), 8.11 (d, J = 7.5 \text{ Hz, 1H}), 7.76 (d, J = 7.6 \text{ Hz, 1H}); \text{^13C NMR (100 MHz, DMSO-d}_6\text{)} \delta 168.4, 167.5, 166.0, 137.4, 134.3, 132.4, 131.7, 129.4, 128.7. HRMS (ESI) calcd. for C_{9}H_{5}O_6 [M – H]^+ 209.0081, found 209.0102.\]

6. **References**

7. Copies of GC chromatograms and NMR spectroscopy

![Image of GC chromatogram and NMR spectroscopy](image)

Fig. S1. GC chromatogram of the dehydration product of pinacol over Amberlyst-15 resin under solvent-free condition. Reaction conditions: pinacol (8.5 mmol, 1.0 g), Amberlyst-15 (100 mg), 120 °C, 12 h.
Fig. S2. GC chromatograms of the dehydration product of pinacol over Amberlyst-15 resin using DMSO or NMP as solvent. Reaction conditions: pinacol (8.5 mmol, 1.0 g), Amberlyst-15 (100 mg), DMSO or NMP (4.0 g), 120 °C, 12 h.
Fig. S3. GC chromatogram of the dehydration product of pinacol in DES ChCl/HCOOH (2:1). Reaction conditions: pinacol (8.5 mmol, 1.0 g), ChCl/HCOOH (molar ratio 2:1, 8.0 g), 140 °C, 12 h.
Fig. S4. GC chromatogram of the dehydration product of pinacol in DES ChCl/HCOOH (2:1). Reaction conditions: pinacol (8.5 mmol, 1.0 g), ChCl/HCOOH (molar ratio 2:1, 8.0 g), 150 °C, 12 h.
Fig. S5. Carbon yields of compounds 2 and 3 as a function of DES ChCl/HCOOH (2:1) dosage. Reaction conditions: pinacol (1.0 g), 120 °C, 12 h.
Fig. S6. Carbon yields of compounds 2 and 3 as a function of reaction temperature. Reaction conditions: pinacol (1.0 g), ChCl/HCOOH (2:1) 8.0 g, 12 h.
Fig. S7. Photographs of the mixture during the reaction. (a) A homogeneous liquid between pinacol (8.5 mmol, 1.0 g) and ChCl/HCOOH (molar ratio 2:1, 8.0 g) at 140 °C before reaction; (b) A biphasic system was obtained upon completion of the reaction; (c) After being cooled down to 0 °C, the lower layer became solid.
**Fig. S8.** Carbon yields of compounds 2 and 3 as a function of recycle time. Reaction conditions: pinacol (8.5 mmol, 1.0 g), ChCl/HCOOH (molar ratio 2:1) 8.0 g, 140 °C, 12 h. After each usage, the ChCl/HCOOH was dried at room temperature under vacuum for 10 h.
Fig. S9. HPLC chromatograms of (a) the solution prepared by the dilution of ChCl/HCOOH (molar ratio 2:1, 8.0 g) with 30 mL H$_2$O and (b) the solution prepared by diluting the mixture of pinacol (1.0 g), ChCl/HCOOH (molar ratio 2:1, 8.0 g) which has been heated at 140 °C for 12 h with 30 mL H$_2$O. Column: Rezex ROA-Organic Acid H$^+$, eluent: 5 mmol/L sulfuric acid, flow rate: 0.5 mL/min, detection wavelength: 210 nm, column temperature: 45 °C. The area of formic acid was comparable, indicating that HCOOH did not decompose in the course of the reaction.
Fig. S10. GC chromatograms of the D-A reaction product of compound 2 and diethyl maleate. Reaction conditions: a) compound 2 (10.0 mmol, 1.1 mL), diethyl maleate (10.0 mmol, 1.6 mL), 120 °C, 6 h; b) compound 2 (10.0 mmol, 1.1 mL), diethyl maleate (10.0 mmol, 1.6 mL), 100 °C, 12 h.
Fig. S11. GC chromatogram of the D-A reaction product of compound 2 and diethyl fumarate. Reaction conditions: compound 2 (10.0 mmol, 1.1 mL), diethyl fumarate (10.0 mmol, 1.6 mL), 120 °C, 6 h.
Fig. S12. GC chromatogram of the dehydrogenation of compound 8 at 220 °C under solvent-free condition. Reaction conditions: compound 8 (10.0 mmol, 2.5 g), Pd/C (250 mg), 220 °C for 24 h.
Fig. S13. GC chromatogram of the dehydrogenation of compound 10 at 220 °C under solvent-free condition. Reaction conditions: compound 10 (10.0 mmol, 2.5 g), Pd/C (250 mg), 220 °C for 24 h.
Fig. S14. GC chromatogram of the dehydrogenation of compound 8 at 220 °C under solvent-free condition. Reaction conditions: compound 8 (10.0 mmol, 2.5 g), Pd/C (250 mg), 220 °C for 48 h.
**Fig. S15.** Effect of dehydrogenation temperature on the conversion of compound 8 and carbon yields of compounds 9 and 10 from the solvent-free dehydrogenation. Reaction conditions: compound 8 (10.0 mmol, 2.5 g), Pd/C (250 mg), 24 h.
Fig. S16. GC chromatogram of the isomerization of diethyl maleate. Reaction conditions: diethyl maleate (10.0 mmol, 1.6 mL), Pd/C (250 mg), 220 °C, 24 h.
Fig. S17. GC chromatogram of the one-step reaction of pinacol and diethyl maleate. Reaction conditions: pinacol (10.0 mmol, 1.2 g), \( \text{CHCl/HCOOH} \) (2:1, 9.6 g), diethyl maleate (10.0 mmol, 1.6 mL), \( 140^\circ \text{C}, 12 \text{ h} \).
Fig. S18. GC chromatogram of the one-step reaction of pinacol and ethyl acrylate. Reaction conditions: pinacol (10.0 mmol, 1.2 g), ChCl/HCOOH (2:1, 9.6 g), ethyl acrylate (10.0 mmol, 1.0 mL), 140 °C, 12 h.
Fig. S19. GC chromatogram of the dehydrogenation of the D-A adduct. Reaction conditions: the D-A adduct 13 (10.0 mmol, 1.8 g), Pd/C (180 mg), 220 °C for 24 h.
Fig. S20. $^1$H NMR of compound 2

Fig. S21. $^{13}$C NMR of compound 2.
Fig. S22. $^1$H NMR of compound 3.

Fig. S23. $^{13}$C NMR of compound 3.
Fig. S24. $^1$H NMR of compound 5.

Fig. S25. $^{13}$C NMR of compound 5.
Fig. S26. $^1$H NMR of compound 8.

Fig. S27. $^{13}$C NMR of compound 8.
Fig. S28. $^1$H NMR of compound 9.

Fig. S29. $^{13}$C NMR of compound 9.
Fig. S30. $^1$H NMR of compound 10.

Fig. S31. $^{13}$C NMR of compound 10.
Fig. S32. $^1$H NMR of compound 11.

Fig. S33. $^{13}$C NMR of compound 11.
Fig. S34. $^1$H NMR of compound 12.

Fig. S35. $^{13}$C NMR of compound 12.
Fig. S36. $^1$H NMR of compound 13.

Fig. S37. $^{13}$C NMR of compound 13.
Fig. S38. $^1$H NMR of compound 14.

Fig. S39. $^{13}$C NMR of compound 14.
Fig. S40. $^1$H NMR of compound 15.

Fig. S41. $^{13}$C NMR of compound 15.
Fig. S42. $^1$H NMR of compound 16.

Fig. S43. $^{13}$C NMR of compound 16.