Supporting Information

SO$_3$H and NH$_2^+$ Functional Carbon-based Solid Acid Catalyzed Transesterification and Biodiesel Production

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1. General information

a. Reagents and materials

D-glucose, p-toluenesulfonic acid monohydrate, diphenylamine, methyl phenylacetate, methyl benzoate, methyl 4-phenylbutyrate, methyl dodecanoate, methyl oleate, methyl pivalate, methyl cinnamate, methyl crotonate, octanol, hexanol, benzyl alcohol, allyl alcohol, cyclohexanol, dodecanol, triolein, toluene, heptane, methanol, isopropanol, deuterated chloroform, etc. were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai). Cyclododecanol, and (-)-Menthol were purchased from TCI (Shanghai) Development Co., Ltd.. Rice oil and Butter were obtained from Wilmar Biotechnology Research and Development Center (Shanghai). All chemicals were analytical grade and were used without further purification.

b. Techniques used

The NMR spectra were obtained using Bruker 400 or 500 MHz Fourier-transform NMR spectrometer. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. GC analysis were carried out with a Hewlett Packard HP 5890 instrument (Agilent, Wilmington, DE) equipped with a capillary inlet (on column mode) and an FID detector, the GC capillary columns used were a Agilent 19091J-433 HP-5 column (30 m × 0.25 mm × 0.25 μm). HPLC were analyzed with a Agilent1200 instrument, column was Eclipse XDB-C8 (4.6 × 150mm, 5um, Agilent), mobile phase gradient is MeOH : H₂O = 90 : 10, 0.5% acetic acid. Eluants from the column were detected by an evaporator light-scattering detector (ELSD: alltech3300).

2. Preparation of the catalyst GDTCSA¹

3.6 g glucose (20.0 mmol) and 1.9 g p-toluenesulfonic acid monohydrate (10.0 mmol) were mixed in toluene (40 mL) in 100 ml three-neck flask, then 3.41 g diphenylammonium tosylate (10.0 mmol) prepared in advance² was added in the flask. The mixture was stirred by mechanical agitation under a flow of nitrogen, the water formed during the reaction and the toluene were distilled off while heating to 180 °C slowly. After reacting for 5 hours, the product was washed with hot toluene for 5 × 25 mL (toluene and 1.3 g p-toluenesulfonic acid were recovered) to get a black powder GDTCSA (5.7 g). The nominal sample composition was determined by elemental analysis to be CH₀.₈₉O₀.₂₂N₀.₀₃S₀.₀₄, the acid amount of SO₃H groups and [Ph₂NH₂][OTs]⁻ is 2.43 mmol·g⁻¹.
3. General experimental procedure for transesterification
The reaction mixture, methyl carboxylate (2.0 mmol), alcohol (3.0 mmol) and 5 mol% of GDTCSA (2.43 mmol NH$_2^+$ and SO$_3$H-g$^{-1}$; 40 mg, 0.1 mmol) were stirred at a certain temperature with a distilling apparatus. Then separation of GDTCSA by filtration gave the crude product, which was purified by column chromatography to give the desired colorless oil carboxylic ester.

4. General experimental procedure for preparing biodiesel
a. Typical procedure for esterification of oleic acid and methanol (or isopropanol)
The reaction mixture, oleic acid (564 mg, 2.0 mmol), alcohols (1.128 g) and 2 mol% of GDTCSA (2.43 mmol NH$_2^+$ and SO$_3$H-g$^{-1}$; 16 mg, 0.04 mmol) were stirred at 80 ºC. Then separation of GDTCSA by filtration gave the crude product, which was purified by column chromatography to give the colorless oil.

b. Typical procedure for transesterification of triolein and methanol (or isopropanol)
The reaction mixture, triolein (0.89 g, 1 mmol), alcohol (0.54 g) and 15 mol% of GDTCSA (2.43 mmol NH$_2^+$ and SO$_3$H-g$^{-1}$; 60 mg, 0.15 mmol) were stirred at 100 ºC for 8 hours in the seal tube (50 mL). Then filtered, washed GDTCSA with heptane. The filtrate was separated to give glycerol (lower layer) and the solution of crude material (upper layer). And removed solvent by evaporation in vacuum to give the crude product, which was purified by column chromatography to give the colorless oil alkyl oleate.

c. Cycle usage experiments for transesterification of triolein and methanol
The reaction mixture, triolein (0.89 g, 1 mmol), methanol (0.54 g, 17 mmol), and 15 mol% of GDTCSA (2.43 mmol NH$_2^+$ and SO$_3$H-g$^{-1}$; 60 mg, 0.15 mmol) were stirred in the seal tube (50 mL) at 100 ºC for 8 hours. The mixture was centrifuged and the solution phase was decanted to separate GDTCSA, which was washed three times with heptane, dried and reused for the next reaction under the same conditions.

d. Typical procedure for preparing biodiesel with rice oil and Butter
The reaction mixture, greases (5.3 g), alcohols (3.2 g), and GDTCSA (2.43 mmol NH$_2^+$ and SO$_3$H-g$^{-1}$; 0.36 g, 0.9 mmol) were reacted in the seal tube (50 mL) under
100 °C for 8 hours. Then filtered, washed GDTCSA with heptane. The filtrate was separated to give glycerol (lower layer) and the solution of crude product (upper layer). And removed solvent by evaporation in vacuum to give the crude product, which was purified by column chromatography to give the colorless oil.

e. Cycle usage experiments for transesterification of rice oil and isopropanol
The reaction mixture, rice oil (5.3 g), isopropanol (3.2 g), and GDTCSA (2.43 mmol NH$_2^+$ and SO$_3$H·g$^{-1}$; 0.36 g, 0.9 mmol) were stirred in the seal tube (50 mL) at 100 °C for 8 hours. The mixture was centrifuged and the solution phase was decanted to separate GDTCSA, which was washed three times with heptane, dried and reused for the next reaction under the same conditions.

5. Characterization of carboxylic esters
Dodecyl 2-phenylacetate (1)$^3$:

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\]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33-7.24 (m, 5H), 4.08 (t, $J$ = 7.0 Hz, 2H), 3.61 (s, 2H), 1.62-1.57 (m, 2H), 1.25 (s, 18H), 0.88 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 171.7, 134.2, 129.2, 128.5, 127.0, 65.0, 41.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 28.6, 25.9, 22.7, 14.1 ppm.

Benzyl 2-phenylacetate (2)$^4$:

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$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34-7.25 (m, 10H), 5.13 (s, 2H), 3.67 (s, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 171.4, 135.8, 133.9, 129.3, 128.6, 128.5, 128.2, 128.1, 127.1, 66.6, 41.3 ppm.

Hexyl 4-phenylbutyrate (3)$^1$:

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$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32-7.17 (m, 5H), 4.06 (t, $J$ = 7.0 Hz, 2H), 2.65 (t, $J$ = 7.5 Hz, 2H), 2.32 (t, $J$ = 7.5 Hz, 2H), 1.98-1.92 (m, 2H), 1.64-1.58 (m, 2H), 1.36-1.30 (m, 6H), 0.89 (t, $J$ = 7.0 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.6, 141.5, 128.5, 128.4, 126.0, 64.5, 35.2, 33.7, 31.5, 28.6, 26.6, 25.6, 22.6, 14.0 ppm.

Octyl 4-phenylbutyrate (4)$^5$:

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$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30-7.12 (m, 5H), 4.06 (t, $J$ = 7.0 Hz, 2H), 2.65 (t, $J$ = 7.5 Hz, 2H), 2.32 (d, $J$ = 7.5 Hz, 2H), 1.99-1.94 (m, 2H), 1.63-1.60 (m, 2H), 1.31-1.27 (m, 10), 0.88 (t, $J$ = 7.0 Hz, 3H) ppm.
ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 173.6, 141.5, 128.5, 128.4, 126.0, 64.5, 35.2, 33.7, 31.8, 29.3, 29.2, 28.7, 26.6, 26.0, 22.7, 14.1 ppm.

Hexyl dodecanoate (5)$^6$:

$^1$H NMR (500 MHz, CDCl$_3$) δ 4.07 (t, $J = 7.0$ Hz, 2H), 2.30 (t, $J = 7.5$ Hz, 2H), 1.64-1.60 (m, 4H), 1.39–1.27 (m, 26H), 0.92-0.88 (m, 6H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): δ 174.1, 64.4, 34.4, 31.9, 31.4, 29.6, 29.5, 29.3, 29.2, 28.6, 25.6, 25.0, 22.7, 22.5, 14.1, 14.0 ppm.

Hexyl oleate (6)$^7$:

$^1$H NMR (500 MHz, CDCl$_3$) δ 4.06 (t, $J = 6.8$ Hz, 2H), 1.61-1.58 (m, 2H), 1.39-1.28 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 178.6, 64.4, 38.7, 31.4, 28.6, 27.2, 25.5, 22.5, 13.9 ppm.

Hexyl pivaloate (7)$^8$:

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.05 (t, $J = 6.8$ Hz, 2H), 1.65-1.58 (m, 2H), 1.39-1.28 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.1, 144.6, 134.5, 130.2, 128.9, 118.3, 64.8, 31.5, 28.7, 25.7, 22.6, 14.0 ppm.

Hexyl benzoate (8)$^9$:

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.06-8.04 (m, 2H), 7.57-7.42 (m, 3H), 4.32 (t, $J = 6.8$ Hz, 2H), 1.80-1.73 (m, 2H), 1.45-1.33 (m, 6H), 0.91 (t, $J = 6.8$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.7, 132.8, 130.5, 129.5, 128.3, 65.2, 31.5, 28.7, 25.7, 22.6, 14.0 ppm.

Hexyl cinnamate (9)$^{10}$:

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, $J = 16.0$ Hz, 1H), 7.54-7.52 (m, 2H), 7.39-7.37 (m, 3H), 6.45 (d, $J = 16.0$ Hz, 1H), 4.20 (t, $J = 6.8$ Hz, 2H), 1.72-1.67 (m, 2H), 1.41-1.33 (m, 6H), 0.91 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.8, 31.5, 28.7, 25.7, 22.6, 14.0 ppm.

Hexyl 2-butenoate (10)$^{11}$:

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.01-6.92 (m, 1H), 5.87-5.83 (m, 1H), 4.11 (t, $J = 6.8$ Hz, 2H), 1.88 (dd, $J = 6.8$, 1.6 Hz, 3H), 1.66-1.63 (m, 2H), 1.38-1.31 (m, 6H), 0.89 (t, $J = 6.8$ H, 3H); $^{13}$C
NMR (100 MHz, CDCl₃): δ 165.7, 143.4, 121.8, 63.3, 30.4, 27.6, 24.6, 21.5, 16.9, 13.0 ppm.

**Allyl 2-phenylacetate (11)**:  
$^1$H NMR (500 MHz, CDCl₃) δ 7.34-7.26 (m, 5H), 5.94-5.86 (m, 1H), 5.29-5.20 (m, 2H), 4.60 (d, $J = 5.5$ Hz, 2H), 3.65 (s, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl₃): δ 171.3, 133.9, 132.0, 129.3, 128.6, 127.1, 118.3, 65.5, 41.3 ppm.

**Cyclododecyl phenylacetate (12)**:  
$^1$H NMR (500 MHz, CDCl₃) δ 7.33-7.24 (m, 5H), 5.05-5.00 (m, 1H), 3.59 (s, 2H), 1.71-1.67 (m, 2H), 1.51-1.33 (m, 20H) ppm; $^{13}$C NMR (125 MHz, CDCl₃): δ 171.4, 134.5, 129.2, 128.5, 126.9, 72.8, 41.8, 29.1, 24.1, 23.9, 23.4, 23.2, 20.9 ppm.

**Cyclododecyl 4-phenylbutyrate (13)**:  
$^1$H NMR (500 MHz, CDCl₃) δ 7.28-7.16 (m, 5H), 5.05-5.00 (m, 1H), 2.64 (t, $J = 7.5$ Hz, 2H), 2.29 (t, $J = 7.5$ Hz, 2H), 1.97-1.91 (m, 2H), 1.73-1.66 (m, 2H), 1.52-1.30 (m, 20H); $^{13}$C NMR (125 MHz, CDCl₃): δ 173.1, 141.6, 128.5, 128.4, 126.0, 72.1, 35.2, 34.1, 29.2, 26.8, 24.1, 24.0, 23.5, 23.3, 21.0 ppm.

**Cyclohexyl phenylacetate (14)**:  
$^1$H NMR (500 MHz, CDCl₃) δ 7.34-7.24 (m, 5H), 4.80-4.74 (m, 1H), 3.59 (s, 2H), 1.82-1.79 (m, 2H), 1.71-1.66 (m, 2H), 1.54-1.49 (m, 1H), 1.45-1.23 (m, 5H) ppm; $^{13}$C NMR (125 MHz, CDCl₃): δ 171.1, 134.4, 129.2, 128.5, 126.9, 73.0, 41.8, 31.5, 25.4, 23.6 ppm.

**Cyclohexyl dodecanoate (15)**:  
$^1$H NMR (500 MHz, CDCl₃) δ 4.77-4.74 (m, 1H), 2.27 (t, $J = 7.5$ Hz, 2H), 1.84-1.81 (m, 2H), 1.73-1.70 (m, 2H), 1.62-1.56 (m, 4H), 1.39-1.26 (m, 20H), 0.88 (t, $J = 7.0$ Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl₃): δ 173.3, 72.2, 34.8, 31.9, 31.7, 29.6, 29.5, 29.3, 29.1, 25.4, 25.1, 23.7, 22.7, 14.1 ppm.

**L-(−)-Menthyl 4-phenylbutyrate (16)**:  
$^1$H NMR (500 MHz, CDCl₃) δ 7.32-7.20 (m, 5H), 4.74 (dt, $J = 11.0$, 4.5 Hz, 1H), 2.67 (t, $J = 8.0$ Hz, 2H), 2.33 (t, $J = 7.5$ Hz, 2H), 2.03-1.88 (m, 4H), 1.72-1.68 (m, 2H).
1.55-1.47 (m, 1H), 1.43-1.37 (m, 1H), 1.13-0.90 (m, 9H), 0.80 (d, \( J = 7.0 \) Hz, 3H); 
\(^{13}\)C NMR(125 MHz, CDCl\(_3\)): \( \delta \) 173.0, 141.5, 128.5, 128.4, 126.0, 74.0, 47.1, 41.0, 35.2, 34.3, 34.1, 31.4, 26.8, 26.3, 23.5, 22.1, 20.1, 16.3 ppm.

**Methyl oleate (17)\(^{16}\):**

\(^{1}\)H NMR (400 MHz; CDCl\(_3\)) \( \delta \) 5.36-5.33 (m, 2H), 3.67 (s, 3H), 2.30 (t, \( J = 7.6 \) Hz, 2H), 2.03-1.97 (m, 4H), 1.62-1.59 (m, 2H), 1.33-1.25 (m, 20H), 0.88 (t, \( J = 6.8 \) Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz; CDCl\(_3\)) \( \delta \) 174.3, 130.0, 129.8, 51.4, 34.1, 31.9, 29.8, 29.7, 29.5, 29.3, 29.3, 29.2, 29.1, 29.1, 27.2, 27.1, 24.9, 22.7, 14.1 ppm

**Isopropyl oleate (18)\(^{17}\):**

\(^{1}\)H NMR (400 MHz; CDCl\(_3\)) \( \delta \) 5.38-5.33 (m, 2H), 5.04-4.97 (m, 1H), 2.25 (t, \( J = 7.2 \) Hz, 2H), 2.03-1.99 (m, 4H), 1.62-1.59 (m, 2H), 1.30-1.25 (m, 20H), 1.23 (d, \( J = 6.4 \) Hz, 6H) 0.88 (t, \( J = 7.2 \) Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz; CDCl\(_3\)) \( \delta \) 173.5, 130.0, 129.8, 67.3, 34.7, 31.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.3, 29.2, 29.1, 27.2, 27.1, 25.0, 22.7, 21.9, 14.1 ppm.
6. Spectra of carboxylic esters

Fig. S1 The $^1$H NMR spectrum of dodecyl 2-phenylacetate (1).

Fig. S2 The $^{13}$C NMR spectrum of dodecyl 2-phenylacetate (1).
Fig. S3 The $^1$H NMR spectrum of benzyl 2-phenylacetate (2).

Fig. S4 The $^{13}$C NMR spectrum of benzyl 2-phenylacetate (2).
Fig. S5 The $^1$H NMR spectrum of hexyl 4-phenylbutyrate (3).

Fig. S6 The $^{13}$C NMR spectrum of hexyl 4-phenylbutyrate (3).
Fig. S7 The $^1$H NMR spectrum of octyl 4-phenylbutyrate (4).

Fig. S8 The $^{13}$C NMR spectrum of octyl 4-phenylbutyrate (4).
Fig. S9 The $^1$H NMR spectrum of hexyl dodecanoate (5).

Fig. S10 The $^{13}$C NMR spectrum of hexyl dodecanoate (5).
Fig. S11 The $^1$H NMR spectrum of hexyl oleate (6).

Fig. S12 The $^{13}$C NMR spectrum of hexyl oleate (6).
Fig. S13 The $^1$H NMR spectrum of hexyl pivaloate (7).

Fig. S14 The $^{13}$C NMR spectrum of hexyl pivaloate (7).
Fig. S15 The $^1$H NMR spectrum of hexyl benzoate (8).

Fig. S16 The $^{13}$C NMR spectrum of hexyl benzoate (8).
Fig. S17 The $^1$H NMR spectrum of hexyl cinnamate (9).

Fig. S18 The $^{13}$C NMR spectrum of hexyl cinnamate (9).
Fig. S19 The $^1$H NMR spectrum of hexyl 2-butenoate (10).

Fig. S20 The $^{13}$C NMR spectrum of hexyl 2-butenoate (10).
Fig. S21 The $^1$H NMR spectrum of allyl 2-phenylacetate (11).

Fig. S22 The $^{13}$C NMR spectrum of allyl 2-phenylacetate (11).
Fig. S23 The $^1$H NMR spectrum of cyclododecyl phenylacetate (12).

Fig. S24 The $^{13}$C NMR spectrum of cyclododecyl phenylacetate (12).
Fig. S25 The $^1$H NMR spectrum of cyclododecyl 4-phenylbutyrate (13).

Fig. S26 The $^{13}$C NMR spectrum of cyclododecyl 4-phenylbutyrate (13).
Fig. S27 The $^1$H NMR spectrum of cyclohexyl phenylacetate (14).

Fig. S28 The $^{13}$C NMR spectrum of cyclohexyl phenylacetate (14).
Fig. S29 The $^1$H NMR spectrum of cyclohexyl dodecanoate (15).

Fig. S30 The $^{13}$C NMR spectrum of cyclohexyl dodecanoate (15).
Fig. S31 The $^1$H NMR spectrum of L-(−)-menthyl 4-phenylbutyrate (16).

Fig. S32 The $^{13}$C NMR spectrum of L-(−)-menthyl 4-phenylbutyrate (16).
Fig. S33 The $^1$H NMR spectrum of methyl oleate (17).

Fig. S34 The $^{13}$C NMR spectrum of methyl oleate (17).
Fig. S35 The $^1$H NMR spectrum of isopropyl oleate (18).

Fig. S36 The $^{13}$C NMR spectrum of isopropyl oleate (18).
Fig. S37 The $^1$H NMR spectrum of rice oil.

Fig. S38 The $^1$H NMR spectrum of rice oil methyl ester.
Fig. S39 The $^1$H NMR spectrum of rice oil isopropyl ester.

Fig. S40 The $^1$H NMR spectrum of Butter.
Fig. S41 The $^1$H NMR spectrum of Butter methyl ester.

Fig. S42 The $^1$H NMR spectrum of Butter isopropyl ester.
7. References