

## Supporting Information for

### Catalytic synthesis of biodiesel from high free fatty acid-containing feedstocks

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#### 1. Materials

Oleic acid (90%), methanol, diphenylamine, aniline, and triflic acid were purchased from Aldrich Chemical (Milwaukee, WI). Sodium methylate solution was from Degussa Corporation (Parsippany, NJ). All other reagents used were of the highest purity available as obtainable from commercial suppliers. Greases with high FFA were from Arlington International Inc. (Irving, TX).

#### 2. Instrumentation

GC analysis of FAME was 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 HP DB-1HT column (15 m x 0.25 mm x 0.25  $\mu$ m) and a HP DB-5HT column (15 m x 0.25 mm x 0.25  $\mu$ m) with He carrier gas set at a linear velocity of 22 cm/sec at 100°C. The oven temperature profile was: initial temperature 50°C, hold 1 min; ramp at 15°C/min to 180°C; ramp at 7°C/min to 230°C. Dodecane was used as an external standard.

Lipid mixtures were analyzed by HPLC with a Hewlett Packard HP 1050 instrument (Agilent, Wilmington DE). The lipid classes were analyzed with a Spherisorb

CN (Chrompack, Palo Alto, CA), column (100 × 3.0mm, 3μ) using a normal phase gradient of hexane/0.4% acetic acid and methyl t-butyl ester/0.4% acetic acid at a constant flow of 0.43 mL/min. Eluants from the column were detected by an evaporator light-scattering detector (ELSD ILA; All-tech, Deerfield, IL). The ELSD nebulizer temperature was set at 40°C and a nitrogen flow of 35 mL/min. All peaks were quantitated from standard curves obtained for standard compounds.<sup>1</sup>

NMR spectra were recorded on Bruker NMR 400 DRX and Varian Gemini 200-MHz spectrometer. Both <sup>13</sup>C and <sup>1</sup>H-NMR spectra were referenced to the proton resonance resulting from incomplete deuteration of the deuterated chloroform (δ 7.26) and deuterated acetone (δ 2.09). Microwave reactions were performed in a CEM Discover–LabMate microwave reactor. Nitrogen adsorption experiments were performed on a Quantachrome-1C surface area analyzer at liquid nitrogen temperature. All the surface areas and pore volumes were calculated based on the Barrett, Joyner, and Halenda (BJH) method.

### 3. Synthesis and characterization of diarylammonium compounds

General procedure: The sulfonic acid (10 mmol) was added to a solution of the diphenylamine (10 mmol) in toluene (~20 mL) at room temperature (r.t.) under a nitrogen flow. The reaction mixture was stirred for 15 min. and the precipitated solid filtered and washed with hexane (~125 mL) in >90% yield of diphenylammonium sulfonate.

Diphenylammonium triflate: mp 169 - 170 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 7.45 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 136.6 (s), 130.6 (s), 130.2 (s), 123.2 (s). These spectroscopic data are consistent with the literature values.<sup>2</sup>

Diphenylammonium tosylate: mp 128 – 130 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 200 MHz): δ 7.74 (m, 4H), 7.29 (m, 8H), 6.86 (m, 2H), 2.39 (s, -PhCH<sub>3</sub>, 3H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 50 MHz): δ 143.5 (s), 142.5 (s), 141.3 (s), 131.6 (s), 130.3 (s), 129.9 (s), 127.3 (s), 125.6 (s), 122.9 (s), 119.4 (s), 21.4 (s, PhCH<sub>3</sub>).

Diphenylammonium camphorsulphonate: mp 111 – 117 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 200 MHz): δ 7.21 (m, 8H), 6.86 (m, 2H), 3.3 (dd, J<sub>para</sub> = 60.8 Hz & 20 Hz, 2H), 2.45 (m, 2H), 2.0 (m, 3H), 1.45 (m, 2H), 1.12 (s, -CH<sub>3</sub>, 3H), 0.90 (s, -CH<sub>3</sub>, 3H). <sup>13</sup>C NMR

((CD<sub>3</sub>)<sub>2</sub>CO, 50 MHz):  $\delta$  213.9 (s, C=O), 143.9 (s), 131.6 (s), 130.1 (s), 125.7 (s), 122.1 (s), 118.8 (s), 59 (s), 48.7 (m), 43.2 (m), 27.4 (s), 25.9 (s), 20.1 (m, -(CH<sub>3</sub>)<sub>2</sub>).

#### 4. Synthesis of heterogeneous catalysts immobilized on porous organic polymers

*N-phenyl-4-vinylaniline*. In a glove box a 10 mL thick-walled pressure vial equipped with a silicone seal cap was charged with NaO<sup>t</sup>Bu (694 mg, 7.00 mmol), Pd(OAc)<sub>2</sub> (22.5 mg, 0.10 mmol), and *rac*BINAP (124.5 mg, 0.20 mmol). Aniline (0.46 mL, 5.0 mmol), 4-bromostyrene (0.65 mL, 5.0 mL), and distilled toluene (5 mL) were added via a syringe, and the mixture sonicated for 30 minutes. The reaction vessel was then subjected to microwave irradiation under the following conditions: power, 300 W; pressure, 100 psi; temperature, 140°C; reaction time, 25 minutes. The color of the reaction mixture changed from red to dark brown. The mixture was diluted with ethyl acetate and filtered. The filtrate was concentrated in vacuo, and the residue purified by flash column chromatography on silica using hexane and 50:1 hexane:EtOAc to give the desired product as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.31(d, 2H), 7.24 (d, 2H), 7.03 (d, 2H), 7.00 (d, 2H), 6.90 (t, 1H), 6.64 (q, 1H), 5.74 (s, 1H), 5.60 (d, 1H), 5.10 (d, 1H). MS *m/z* = 195.1 ([M<sup>+</sup>]).

*Tert-butyl phenyl(4-vinylphenyl)carbamate*. A 25 mL round bottom 2-neck flask equipped with a magnetic stir bar and a reflux condenser was flame-dried and charged with *N*-phenyl-4-vinylaniline (218.3 mg, 1.12 mmol), di-*tert*-butyl dicarbonate Boc<sub>2</sub>O (378.0 mg, 1.68 mmol), and 4-(dimethylamino)pyridine (13.6 mg, 0.11 mmol). Anhydrous acetonitrile (1 mL) was added and the mixture stirred at reflux for 24 h. After the reaction mixture cooled to r.t. water was added (25 mL). The product was extracted with EtOAc (3×20 mL) and the combined organic layers were washed with water (3×25 mL) and then dried over MgSO<sub>4</sub>, filtered and solvent removed in vacuo. The residue was purified by flash column chromatography on silica using hexane and 50:1 hexane:EtOAc to give the desired product as a pale yellow solid (186.2 mg, 56.3 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.4 - 7.1(m, 8H), 6.90 (t, 1H), 6.65 (q, 1H), 5.68 (d, 1H), 5.20 (d, 1H), 1.42 (s, 9H). MS *m/z* = 295.2 ([M<sup>+</sup>]).

*<sup>t</sup>Boc-protected porous 1,4-divinylbenzene/Phenyl(vinylaniline) (Poly-DVB/DVA-<sup>t</sup>Boc) copolymer*. A 20 mL scintillation vial equipped with magnetic stir bar and septum

was charged with 2,2'-azobis(2-methylpropionitrile) (AIBN, 11.3 mg, 0.069 mmol), 1,4-divinylbenzene (DVB, 0.66 mL, 0.60 g, 4.61 mmol) and *tert-butyl phenyl(4-vinylphenyl)carbamate* (0.15 g, 0.508 mmol), and toluene (0.7 mL, 1:1 total monomer volume). The mixture was degassed and purged three times with argon gas, the septum replaced with a screw cap, and the vial immersed in an oil bath at 80°C for 12h. At the end of the reaction, the solidified reaction mixture was dried in vacuo for 6h. The solid polymer was ground and purified by Soxhlet extraction with methanol for 24h. The residue was dried in vacuo to give a white solid of *Poly-DVB/DVA-<sup>t</sup>Boc* (0.74 g, 0.68 mmol/g). IR (cm<sup>-1</sup>): 2910.6 (b), 1627.9 (vs), 1583.6 (w), 1508.3 (w), 1491.0 (w), 1440.8 (w), 1367.5 (w), 1332.8 (b), 1161.5 (vs), 1053.1 (s), 1016.5 (s), 987.6 (s), 900.8 (s), 825.5 (s), 794.7 (vs), 758.0 (vs), 729.1 (vs), 707.9 (w), 694.4 (s), 680.9 (vs).

*Porous 1,4-divinylbenzene (DVB)/Phenyl(vinylanilinium) triflate (Poly-DVB/PVA-OTf) copolymer.* *Poly-DVB/DVA-<sup>t</sup>Boc* (0.70 g, 0.48 mmol) was treated with 20 mL of 0.125 M triflic acid in 10% 1,4-dioxane in dichloromethane (5 equiv.) for the simultaneous deprotection and activation. The mixture was allowed to stir at room temperature for 6h and then centrifuged. The solid was rinsed and centrifuged with EtOAc (5X15 mL) and dried in vacuo to afford activated product *Poly-DVB/PVA-OTf* as a dark brown solid (0.73 g, 0.68 mmol/g). IR (cm<sup>-1</sup>): 2912.5 (b), 1734.0 (s), 1597.1 (s), 1508.3 (s), 1485.2 (w), 1444.7 (w), 1435.0 (w), 1371.4 (w), 1298.1 (s), 1232.5 (vs), 1170.8 (s), 1045.4 (w), 1026.1 (s), 889.2 (w), 825.5 (s), 790.8 (vs), 706.0 (vs), 692.4 (s), 638.4 (vs), 601.8 (vs).

## 5. Catalytic reactions

*Esterification of Oleic Acid.* A mixture of oleic acid (90%, 100 mg, 0.35 mmol), methanol (230 mg, 7.1 mmol), and diphenylammonium triflate (1.1 mg, 3.5 μmol) was mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2h. The reaction mixture went from colorless to a dark red color. The mixture was allowed to cool to r.t. and ~5 mL of hexane added to transfer the mixture into a 25 mL one neck round bottom flask. The solvents were evaporated under reduced pressure and the crude product analyzed by GC and HPLC. For the time dependent conversion studies,

a small aliquot of reaction mixture was removed from the reaction vessel after a set period of time and analyzed by GC to determine the percent conversion.

*Esterification of Free Fatty Acid (FFA) in Greases using Homogeneous Catalyst.* A mixture of grease (12 wt% FFA, 1g, 0.43 mmol relative to the FFA content), methanol (180 mg, 5.6 mmol), and diphenylammonium triflate (1.8 mg, 5.8  $\mu$ mol) was mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 95 °C for 2h. The reaction went from light yellow to a dark brown color. The mixture was allowed to cool to r.t. and transferred with hexane (~5 mL) into a 25 mL one neck round bottom flask. The solvents were evaporated under reduced pressure. 10 $\mu$ L of crude product was pipetted into a 2 mL vial and ~1.5 mL of hexane was added. The mixture was passed through a syringe filter and analyzed by HPLC.

*Esterification of FFA in Greases with Heterogeneous Catalysts.* A mixture of grease (12 wt% FFA, 5g, 2.1 mmol relative to the FFA content), methanol (1.4 g, 0.043 mol), and *Poly-DVB/PVA-OTf* (0.68mmol/g, 78 mg, 0.053mmol) was mixed in a 25mL 3-neck round bottom flask equipped with a thermometer and a reflux condenser. The reaction mixture was placed into a mineral oil bath set at 95 °C for 2h. The reaction went from light yellow to a dark brown color. The mixture was cooled to r.t. and a small amount (~10 $\mu$ L) of the product was pipetted out for HPLC analysis.

The esterification reaction of FFA in greases was carried out as above in a 50g scale with a 600 mL high pressure stainless steel vessel (Parr Instrument, Moline IL) equipped with a mechanical stirrer and an electric heating mantle equipped with a temperature controller. The vessel was sealed and purged with 40 psi N<sub>2</sub> (3  $\times$  for 15 min each). The N<sub>2</sub> gas in the reactor was removed and the mixture was heated to 95 °C for ~2 h. The mixture was cooled to r.t. and a small amount (~10 $\mu$ L) of the product was pipetted out for HPLC analysis.

*Transesterification of Pretreated Greases.* The oil phase (<1wt.% FFA, 0.25g), methanol (180 mg, 5.6 mmol), and a 5.55 N sodium methylate in methanol solution (2.5  $\mu$ L, 0.3wt.%, relative to the equivalent moles of FFA in the pretreated grease) were mixed in a 4 mL vial with a Teflon cap. The vial was capped tightly and heated at 50 °C for ~2h. The reaction mixture went from brown to light yellow color. The mixture was allowed to cool to r.t. and two phases were observed. The mixture was transferred with

hexane into a 60 mL separator funnel and ~5mL of 1N HCl was added to the mixture to neutralize the base. The hexane layer was washed with water (~30 mL, 2x), dried with MgSO<sub>4</sub>, and solvent removed under reduced pressure. The light yellow liquid product was analyzed by HPLC.

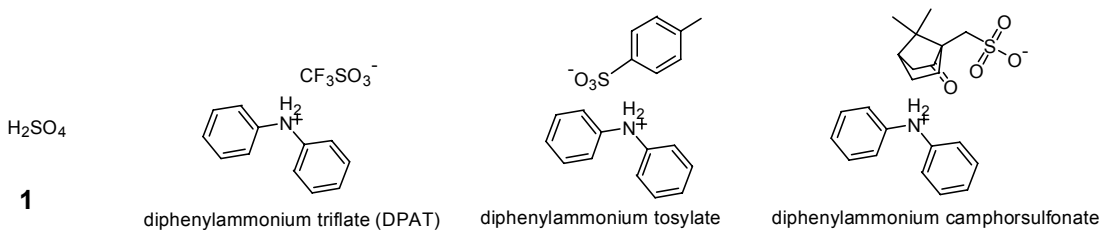


Figure S1. Chemical structures of the homogeneous catalysts used in this work.

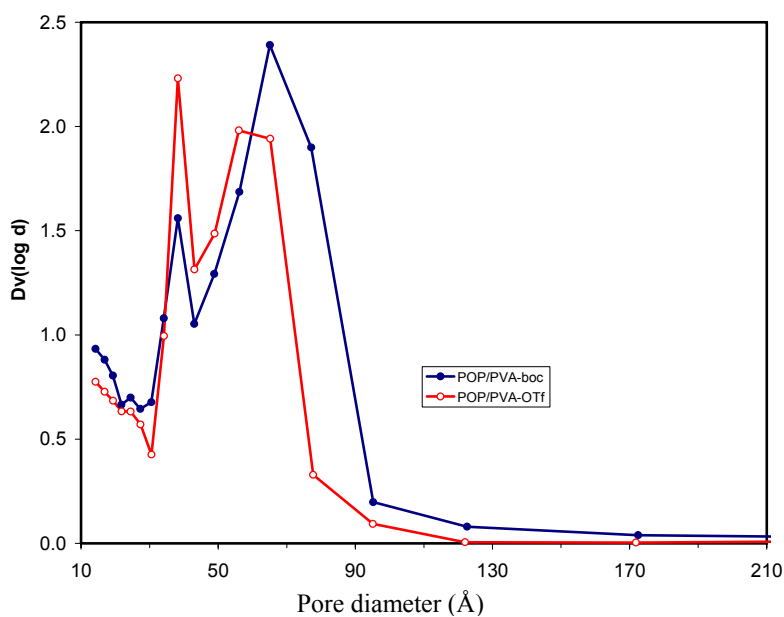


Figure S2. Pore size distributions for Poly-DVB/PVA-<sup>t</sup>Boc and Poly-DVB/PVA-OTf (**2**).

Table S1. Recycle and re-use of the *Poly-DVB/PVA-OTf* catalyst for esterifying FFA in greases

Catalysts	MeOH (eq.)	HPLC wt. %					% conv. of FFA
		FAME	FFA	TG	DG	MG	
no catalyst	---	0	12	66.0	20.4	1.6	---
1 <sup>st</sup> use	20	22.4	1.4	54.9	17.3	4.0	88
2nd use	20	13.4	1.0	64.6	19.7	1.3	92
3rd use	20	12.6	1.6	63.2	20.5	2.1	87

#### REFERENCES

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