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# Driving Effect of Substituent Size Changes on Reaction: A Novel Reaction for Direct Production of Triacetylglycerol from Oils and Fats

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**Table S1** Catalytic esterification of glycerol and acetic acid to TAG in literature

**Table S2** Effect of reaction conditions on the yield of TAG

**Fig.S1** $^{13}$C-NMR analysis of products catalyzed by $AlCl_3$

**Fig.S2** Stability of TAG in the $AlCl_3/CH_3COOH$ catalytic system detected by $^{13}$C-NMR analysis

**Fig.S3** $^{13}$C-NMR analysis of products catalyzed by p-DBSA

**Fig.S4** Stability of TAG in the p-DBSA/$CH_3COOH$ catalytic system detected by $^{13}$C-NMR analysis

**Fig.S5** Recycled stearic acid after the separation process

**Scheme S1** The separation process of products and recycling p-DBSA

## Materials

Phosphotungstic acid ($H_3O_{40}PW_{12}.xH_2O$, AR), methyl valerate (99% purity), glycerol monostearate (99% purity), glycerol tristearate (80% purity), anhydrous aluminum chloride ($AlCl_3$ 99% purity), methyl benzoate (98% purity) p-dodecyl benzene sulfonic acid (p-DBSA 90% purity) and deuterated chloroform ($CDCl_3$ 99.8% purity) were purchased from Shanghai Aladdin BioChem Technology Co., Ltd. p-toluene sulfonic acid (p-TSA purity > 99.5%), glacial acetic acid (purity > 99.5%), concentrated sulfuric acid ($H_2SO_4$ 95% - 98% purity), concentrated hydrochloric acid (HCl 36% - 38% purity), phosphoric acid ($H_3PO_4$ purity > 85%), chloroform ($CHCl_3$ purity > 99.0%), acetic anhydride (purity ⩾ 98.5%) and zinc chloride ($ZnCl_2$ purity > 98%) were purchased from Sinopharm Chemicals Reagent Co., Ltd. Potassium hydrogen sulfate ($KHSO_4$, 99.5% purity), sodium carbonate anhydrous (purity ⩾ 99.5%) and Amberlite 732 (AR) were purchased from Macklin Biochemical Co., Ltd. Ethyl acetate (purity ⩾ 98.5%) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Petroleum ether (60 °C-90 °C, AR) was purchased from Tianjin Damao Chemical Reagent Factory. HZSM-5 (Si/Al=3) was kindly provided by the research group of 603 in the institute of coal chemistry. The water in all the experiments was distilled water.

### Experimental

The acyl exchange reaction with glycerol tristearate as the substrate was performed in a 10 ml Teflon-lined autoclave. Typically, 0.8915 g of (0.8 mmol) glycerol tristearate, 3.6 g of (60 mmol) acetic acid and a certain amount of catalyst with 0.3 mmol dissociable $H^+$ ions were added into the 10 ml Teflon-lined autoclave. It was putted in an Oven and heated at 180 °C for 4 h. After the reaction, the reaction mixture was cooled down to room temperature, and then dissolved in 8 g of $CHCl_3$. The yield of TAG was determined by GC with methyl benzoate as the internal standard (Shimadzu GC 2010-Plus AFAPC) equipped with a flame ionization detector

(FID) and a capillary column (Rtx®-1 PONA 100 m×0.25mm). For the product analysis, the detector and inlet temperatures were all set at 300 °C. The product was analyzed by the following oven-heat procedure: the temperature was ramped from 100 to 200 °C with a rate of 10 °C/min and held at 200 °C for 15 min.

In the separation experiments, the acyl exchange reaction was performed in a 100 ml Teflon-lined autoclave at the same condition with those performed in the 10 ml Teflon-lined autoclave, in order to reduce the experimental errors caused by the separation process. After the reaction, 70 g of cold distilled water was added into the reaction mixture under vigorous stirring to separate stearic acid. Meanwhile, to prevent the hydrolysis of TAG, 0.159 g of sodium carbonate anhydrous (1.5 mmol) was added into the aqueous liquid to neutralize p-DBSA. Then, the solid and the liquid in the mixture was separated by filtering. After that, the obtained solid sample (stearic acid) was washed by 50 g of cold distilled water, and dried at 40 °C. The obtained liquid was transferred into a 500 ml of separating funnel, and then 200 ml of mixture of ethyl acetate and petroleum ether was slowly added into the funnel. This operation was repeated by five times. After that, the resulting aqueous phase and the organic phase was separated. The organic phase contains most of TAG and a small amount of acetic acid. The TAG can be obtained after removing ethyl acetate, petroleum ether, and acetic acid by rotary evaporation at 40 °C and 60 °C, respectively. The neutralized catalyst (p-sodium dodecyl benzene sulfonate (p-SDBS), formed from the neutralization of p-DBSA with sodium carbonate) and majority of acetic acid were in the aqueous phase. An excess amount of concentrated HCl solution was added into the aqueous phase to change p-SDBS into p-DBSA. Then, the aqueous phase was extracted by 200 ml of ethyl acetate. And this operation was repeated by three times. p-DBSA and most of acetic acid were extracted from aqueous phase by ethyl acetate. Ethyl acetate and acetic acid in the resulting organic phase were removed by rotary evaporation at 40 °C and 60 °C, respectively. And the p-DBSA left in flask can be recycled.

The $^{13}$C-NMR spectra of the reaction products were carried out in Deuterated chloroform ($CDCl_3$) on a Bruker AV-Ⅲ 400MHZ NMR spectrometer.

**Table S1** Catalytic esterification of glycerol and acetic acid to TAG in literature

| Entry | Catalyst | Selectivity (%) | | | Ref. |
|---|---|---|---|---|---|
| | | MAG | DAG | TAG | |
| 1 | HSiW/$ZrO_2$ | 6.4 | 61.3 | 32.3 | [1] |
| 2 | [$(HSO_3$-p$)_2$im][$HSO_4$] | 34.3 | 53.1 | 12.6 | [2] |
| 3 | Y/SBA-3 | 11 | 34 | 55 | [3] |
| 4 | $SnCl_2$ | 55 | 45 | trace | [4] |
| 5 | Heteropolyacid-in-silica | 36 | 59 | 4 | [5] |
| 6 | Amberlyst-15 | 8.65 | 46.56 | 47.79 | [6] |
| 7 | $PMo_3$_NaUSY | 59 | 37 | 2 | [7] |

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**Table S2** Effect of reaction conditions on the yield of TAG

| Entry | Catalyst mmol | Acetic acid mmol | Temp. °C | Time h | TAG yield % |
|---|---|---|---|---|---|
| 1 | 0.3 | 60 | 180 | 2 | 29.3 |
| 2 | 0.3 | 60 | 180 | 3 | 61.6 |
| 3 | 0.3 | 60 | 180 | 4 | 85.6 |
| 4 | 0.3 | 60 | 180 | 5 | 90.3 |
| 5 | 0.3 | 60 | 180 | 6 | 93.5 |
| 6 | 0.3 | 60 | 190 | 2 | 46.0 |
| 7 | 0.3 | 60 | 190 | 3 | 76.5 |
| 8 | 0.3 | 60 | 190 | 4 | 91.9 |
| 9 | 0.3 | 60 | 190 | 5 | 93.1 |
| 10 | 0.3 | 60 | 190 | 6 | 93.5 |
| 11 | 0.3 | 60 | 200 | 2 | 63.5 |
| 12 | 0.3 | 60 | 200 | 3 | 82.8 |
| 13 | 0.3 | 60 | 200 | 4 | 94.9 |
| 14 | 0.3 | 60 | 200 | 5 | 93.6 |
| 15 | 0.3 | 60 | 200 | 6 | 93.5 |
| 16 | 0.3 | 40 | 190 | 4 | 84.9 |
| 17 | 0.3 | 50 | 190 | 4 | 92.4 |
| 18 | 0.3 | 70 | 190 | 4 | 87.8 |
| 19 | 0.1 | 50 | 190 | 4 | 64.1 |
| 20 | 0.2 | 50 | 190 | 4 | 87.6 |
| 21 | 0.4 | 50 | 190 | 4 | 89.8 |
| 22 | 0.5 | 50 | 190 | 4 | 88.3 |

Reaction conditions: 0.8 mmol of Glycerol tristearate, p-DBSA catalyst.

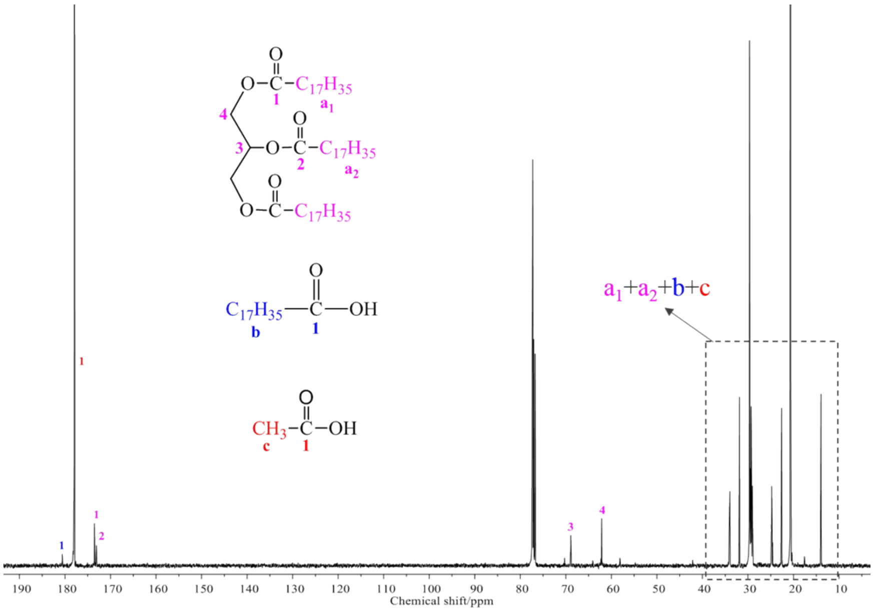


**Fig. S1** $^{13}$C-NMR analysis of products catalyzed by $AlCl_3$. Reaction conditions: 0.8 mmol of glycerol tristearate, 0.1 mmol of $AlCl_3$, 50 mmol of acetic acid, T=190 °C, and reaction time=4 h.

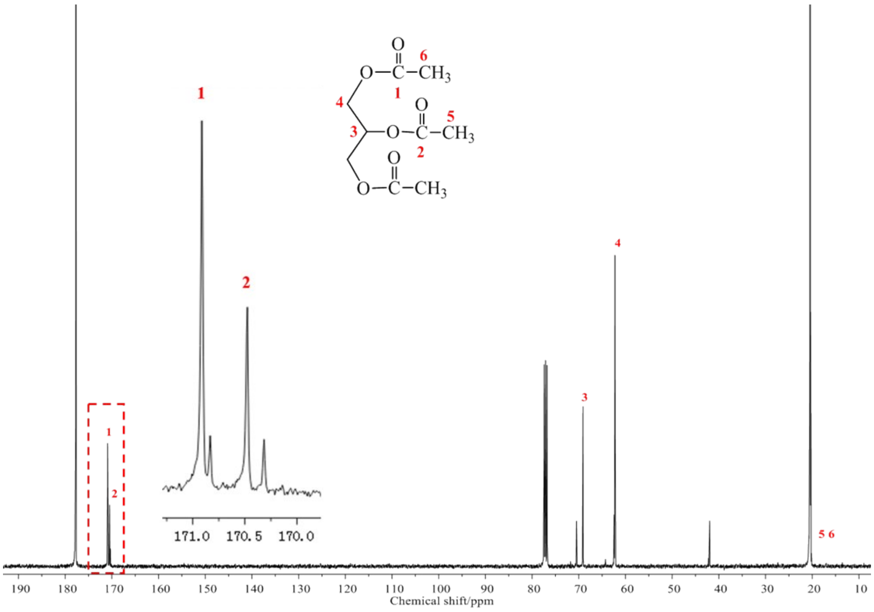


**Fig. S2** Stability of TAG in the $AlCl_3/CH_3COOH$ catalytic system detected by $^{13}C$-NMR analysis. Reaction conditions: 0.15 g of TAG, 0.1 mmol of $AlCl_3$, 50 mmol of acetic acid, T=190 °C, and reaction time=1 h.

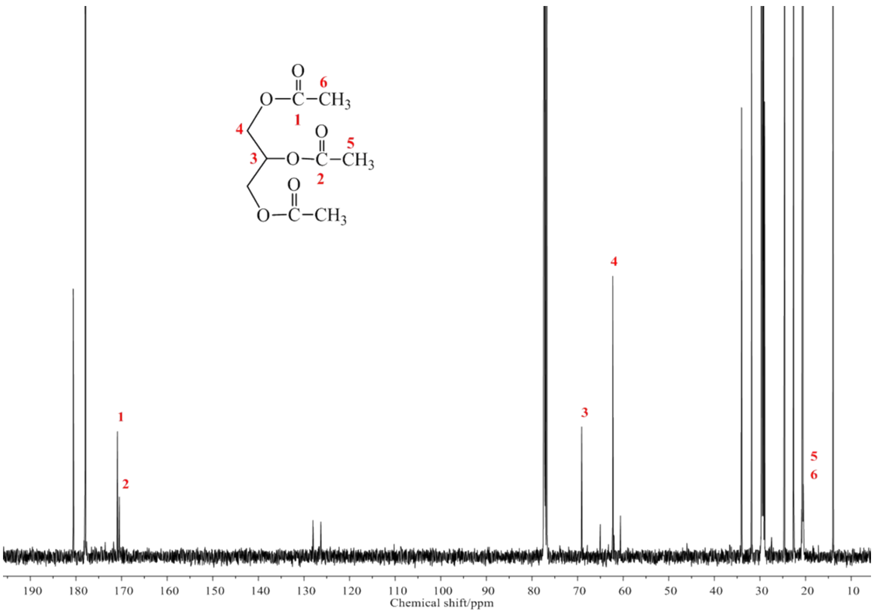


**Fig. S3** $^{13}$C-NMR analysis of products catalyzed by p-DBSA. Reaction conditions: 0.8 mmol of glycerol tristearate, 0.3 mmol of p-DBSA, 50 mmol of acetic acid, T=190 °C, and reaction time=4 h.

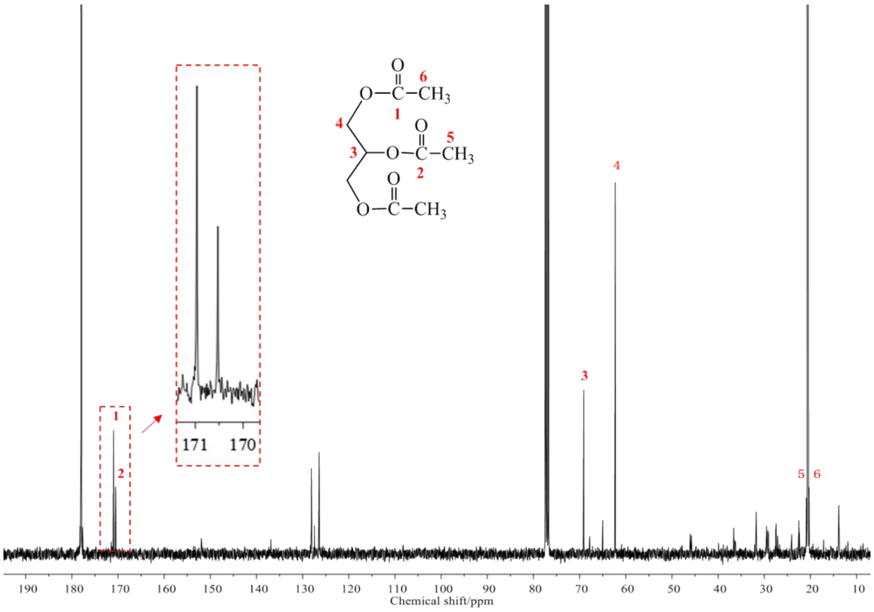


**Fig. S4** Stability of TAG in the p-DBSA/$CH_3COOH$ catalytic system detected by $^{13}C$-NMR analysis. Reaction conditions: 0.15 g of TAG, 0.1 mmol of p-DBSA, 50 mmol of acetic acid, T=190 °C, and reaction time=4 h.

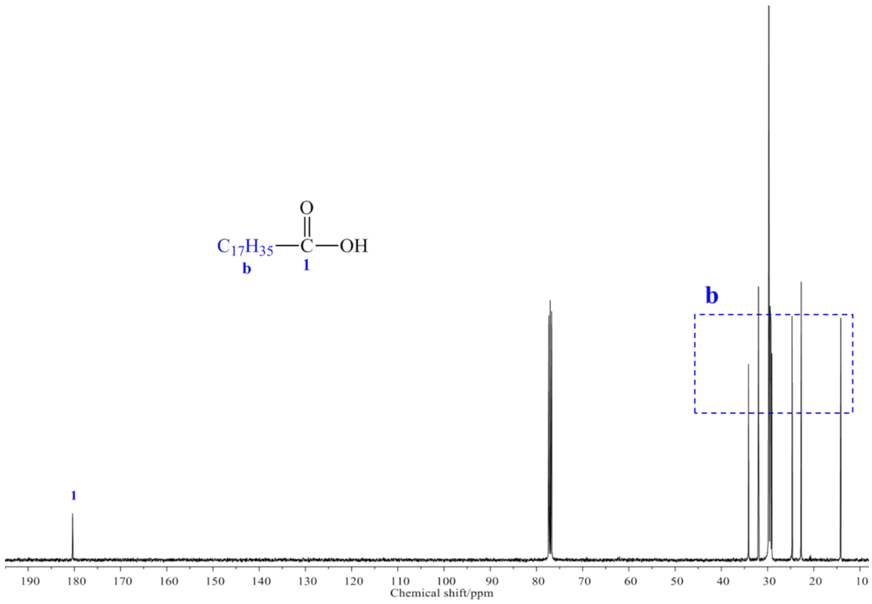
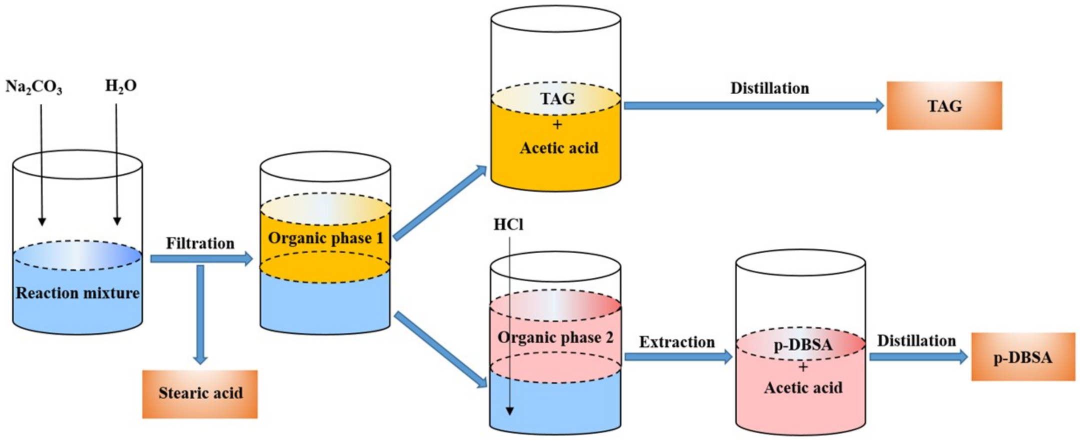


**Fig. S5** Recycled stearic acid after the separation process.



**Organic phase 1: the ethyl acetate-to-petroleum ether molar ratio of 45:55**

**Organic phase 2: ethyl acetate**

**Scheme S1** The separation process of products and recycling p-DBSA