# Electronic Supplementary Information

## Hydroaminomethylation/hydrohydroxymethylation sequence for the one pot synthesis of aminohydroxytriglycerides

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## Materials and methods

All chemicals were purchased from Acros, Strem or Aldrich Chemicals in their highest purity. Olive oil was purchased from Aldrich while Very High Oleic Sunflower Oil (VHOSO) was provided by Oleon (France). NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for $^{1}H$ nuclei and 75 MHz for $^{13}C$ nuclei. $CDCl_3$ (99.50% isotopic purity) were purchased from Eurisotop. The NMR peak assignment was obtained by comparison with previous works[1] and from data from the literature.[2]

Triolein (European Pharmacopoeia Reference Standard Triolein from Sigma-Aldrich, http://www.sigmaaldrich.com/catalog/product/sial/y0001113) was used as model triglyceride. Compared to technical grade triglycerides, its purity and symmetrical structure derived from glycerol and oleic acid has the significant advantage of facilitating the analysis of the reaction products.

GC-MS analysis were performed using a Shimadzu GC-17A gas chromatograph using a Varian capillary column (length 30 m, internal diameter 0.025 µm) and a Shimadzu GCMS-QP500 mass spectrometer. The products were analyzed using a temperature gradient from 250 °C to 300 °C at 1.5 °C/min.

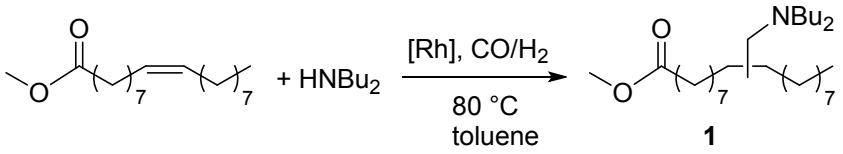
Mass spectra were recorded on a MALDI-TOF/TOF Ultraflex II Bruker Daltonics spectrometer in positive reflectron or linear mode with 2,5-dihydroxybenzoic acid (2,5-DHB) as matrix. The products quantification with MALDI-TOF gives reproducible results with a variability of less than 5% between duplicates.

All the hydroformylation experiments were carried out in laboratory reactors from Parr Instrument Company (USA). To prevent oxidation of the catalyst precursors, the reaction mixture was transferred into the reactor using the standard Schlenk technique.

Size-exclusion chromatography (SEC) was performed at the French Institute of Fats and Oils (ITERG – Pessac, France). Mobile phase: tetrahydrofuran (THF). Flow rate: 1 mL/min. Column: PLgel 5µm MIXED-D (Agilent). Oven temperature: 40 °C. Detector: Refractometer. Reference: Polystyrene (580, 970, 1280, 2170, 2940, 4910, 6940, 13030, 21720, 74800, 126500 and 281700).

[1] T. Vanbésien, E. Monflier and F. Hapiot, *Green Chem.*, 2016, **18**, 6687–6694.
[2] A. Biswas, A. Adhvaryu, S. H. Gordon, S. W. Erhan and J. L. Willett, *J. Agric. Food Chem.,* 2005**, 53**, 9485–9490.

## Catalytic experiments




**Scheme S1.** Synthesis of tertiary amine (**1**) derived from methyl oleate by HAM.

Conditions: methyl oleate (1.01 mL, 3 mmol), $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol), $HNBu_2$ (2.52 mL, 15 mmol), $CO/H_2$ (1:1) (80 bar), toluene (5 mL), 80 °C, 24 h. 5 equiv. amines were used to limit the formation of alcohols. The produced aldehydes and excess amines were separated by column chromatography using a AcOEt/heptane mixture (9:1) as eluant. The expected product **1** was obtained as a colourless liquid. Yield: 83%. See Figures S1 and S2 for NMR characterization.

## Calculation of conversion and selectivities

As the four glycerol protons B (Figure S1a) are not involved in the hydroformylation reaction, they are chosen as the reference to determine the normalization integration factor (*NF*), which specifies the integration value of one proton (*NF = B/4*). For neat **T**, the numbers of initial and final C=C double bonds ($DB_i$ and $DB_f$, respectively) are:

$$DB_i = \frac{Ai - NF}{2} = 3 \qquad DB_f = \frac{Af - NF}{2}$$

with *Ai* and *Af* the peak integrations of olefinic protons plus the internal proton of glycerol (Figures S1a and S1b, signal A) before and after reaction, respectively. Once the reaction is complete, the conversion is given by:

$$Conv.(\%) = \frac{3 - DB_f}{3} \times 100 = \frac{Ai - Af}{Ai - NF} \times 100$$

The alcohol percentage is given by:

$$Alc.\ (\%) = \frac{H/_{6NF}}{3 - DB_f} \times 100$$

where *H* is the integration value of the signal attributed to the hydroxymethyl group (H, Figure 1b).

The amine percentage is given by:

$$Amine\ (\%) = \frac{I/_{6NF}}{3 - DB_f} \times 100$$

where *I* is the integration value of the signal attributed to the aminomethyl group (I, Figure 1b).

The aldehyde percentage is given by:

$$Ald.\ (\%) = \frac{J/_{3NF}}{3 - DB_f} \times 100$$

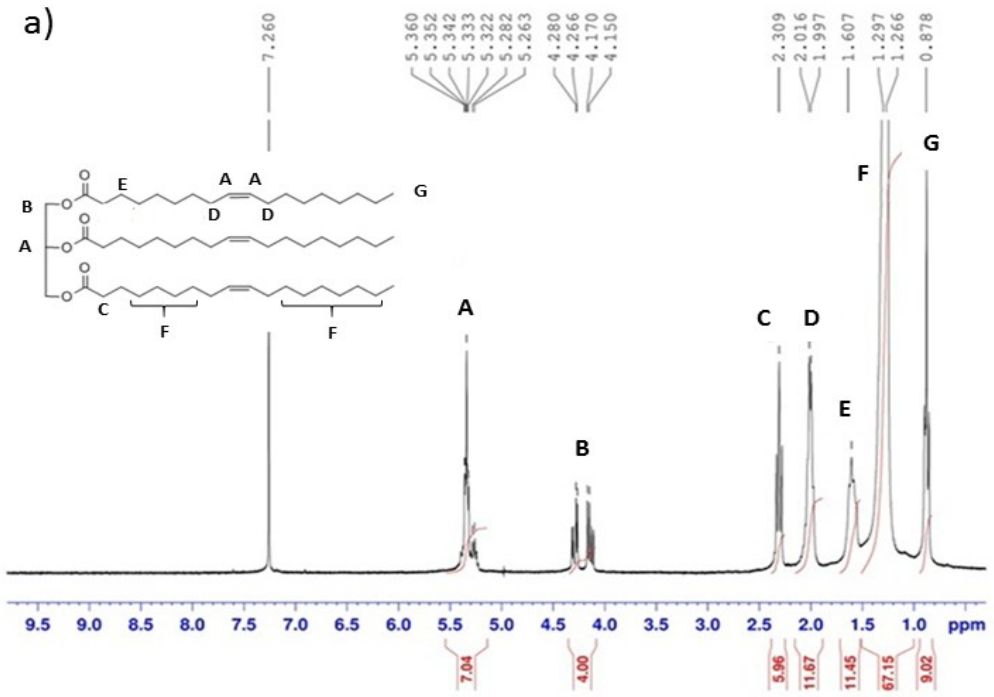
where *J* is the integration of the residual aldehyde signal (δ = 9.54 ppm in $CDCl_3$).

The percentage of hydrogenated products is given by:

$$hydrog.prod.\,(\%) = 100 - (Ald.Selec.\,(\%) + Alc.Selec.\,(\%) + Amine.Selec.\,(\%))$$

## NMR sepctra

**Figure S1.** $^{1}$H NMR spectra of a) triolein (T) in $CDCl_3$ at 25 °C and b) *N,N*-dibutylaminomethylated hydroxymethylated T in $CDCl_3$ at 25 °C. The displayed product is given as an example of possible structures.



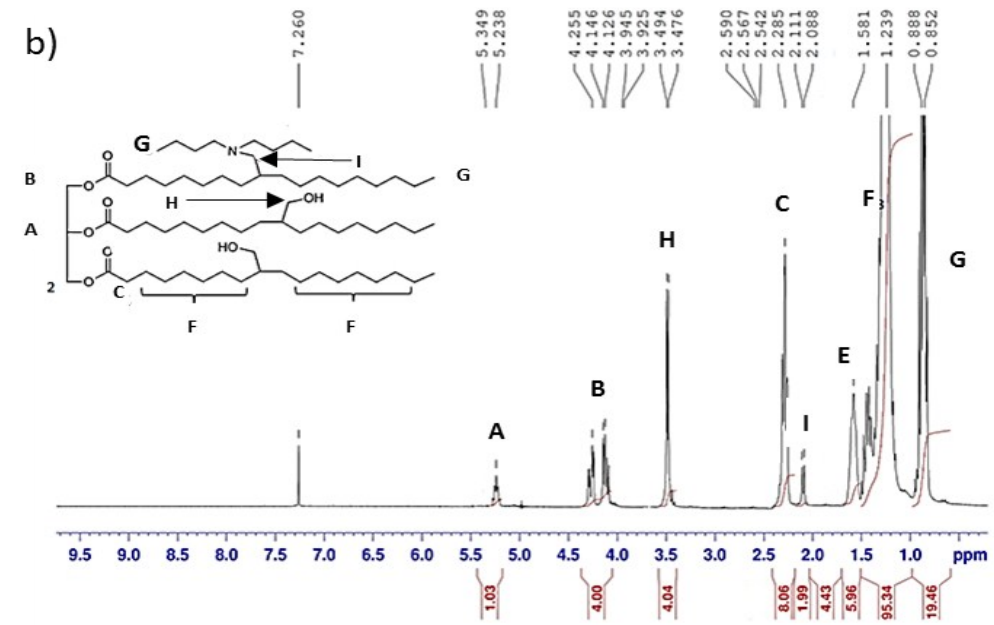



**Figure S2.** $^{1}$H NMR spectrum of methyl oleate functionalized by a *N,N*-dibutylaminomethyl group.

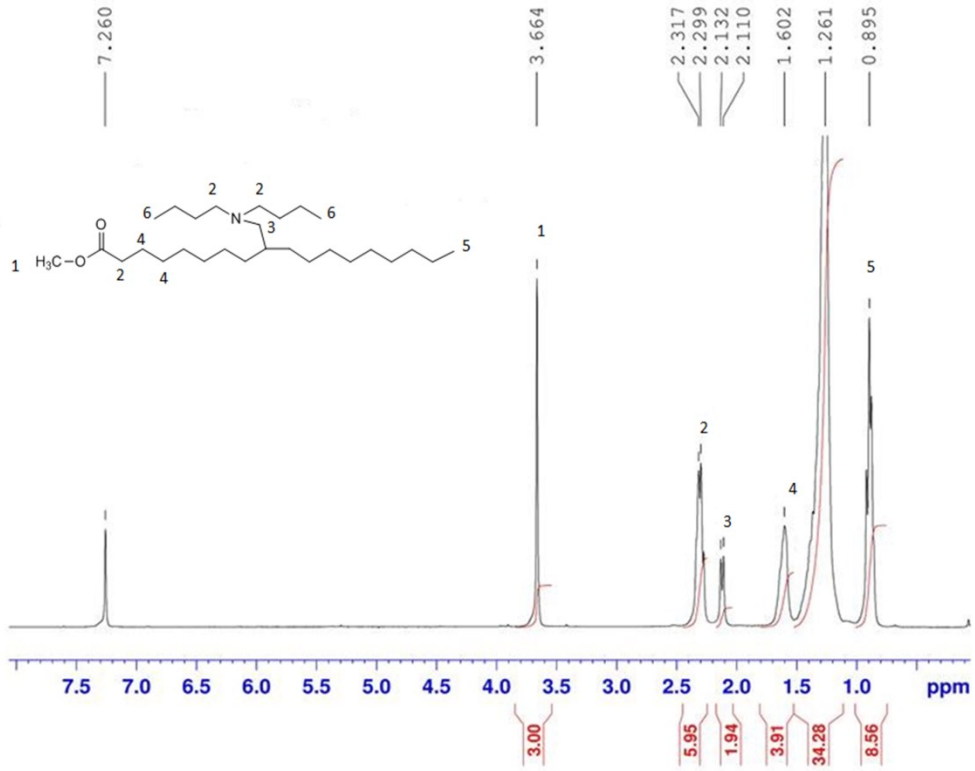
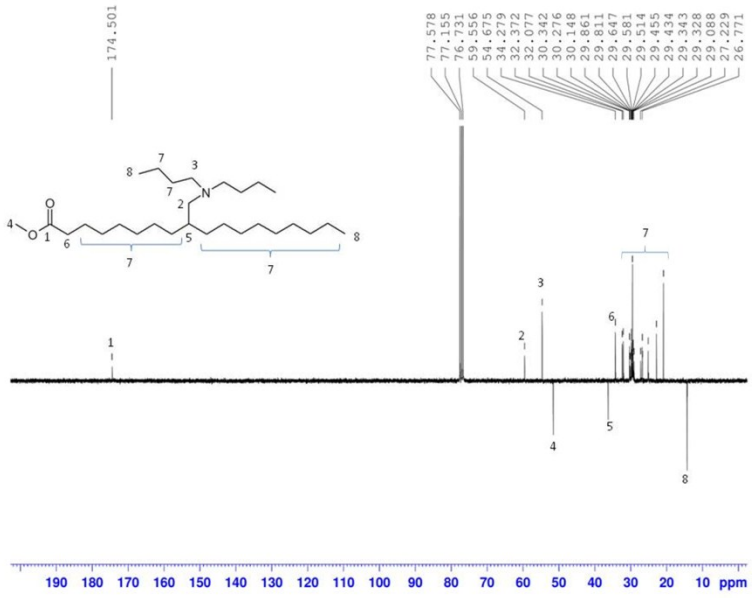
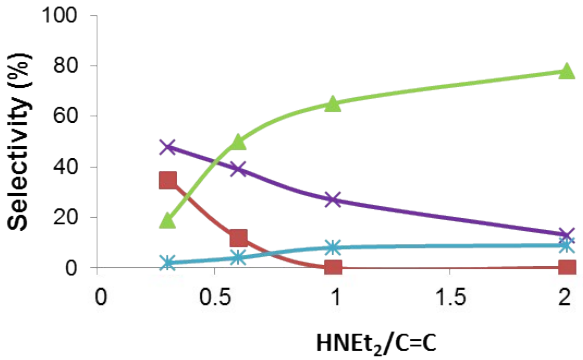



**Figure S3.** $^{13}$C NMR spectrum of methyl oleate functionalized by a *N,N*-dibutylaminomethyl group.



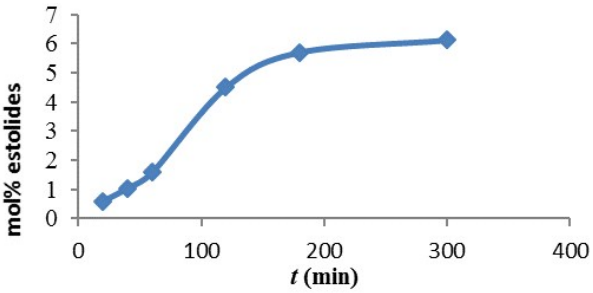
## Selectivity in Rh-catalyzed HAM of T

**Figure S4.** Evolution of the selectivity in the Rh-catalyzed HAM of **T** using $HNEt_2$ at 80 °C under 80 bar $CO/H_2$ in toluene after 18 h. Aldehyde (red), amine (green), alcohol (purple), hydrogenation products (blue).



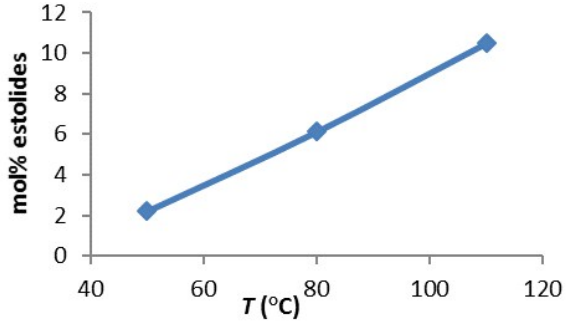

## Estolides

**Figure S5.** Percentage of estolides as a function of the reaction time.




Conditions: **T** (1 mL, 1 mmol), $HNBu_2$ (3 mmol), $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol), toluene (5 mL), 80 bar $CO/H_2$ (1:1), 80 °C.

**Figure S6.** Percentage of estolides as a function of the reaction temperature.




Conditions: **T** (1 mL, 1 mmol), $HNBu_2$ (3 mmol), $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol), toluene (5 mL), 80 bar $CO/H_2$ (1:1), 80 °C, 18 h.

## Distribution of reaction products

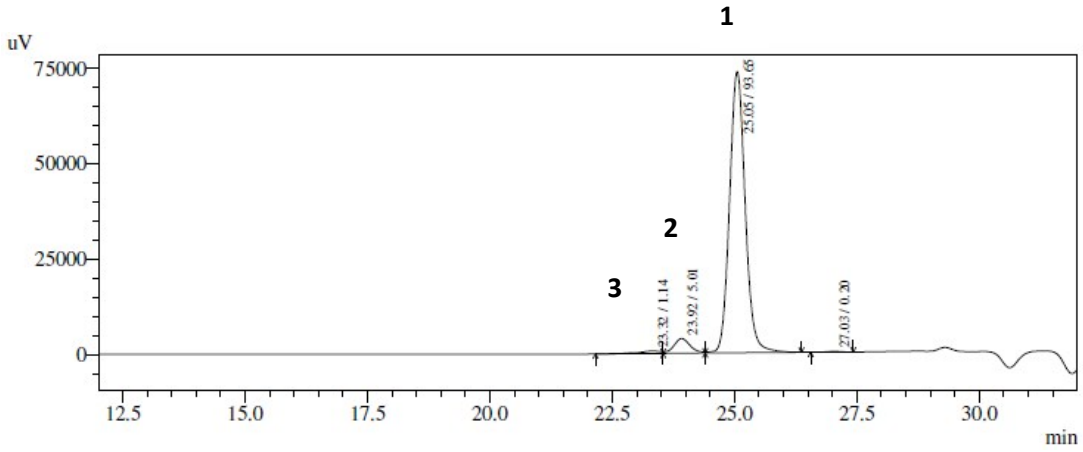
**Table S1.** Products distribution with time. Conditions: **T** (1 mL, 1 mmol), $HNBu_2$ (3 mmol), $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol), toluene (5 mL), 80 bar $CO/H_2$ (1:1), 80 °C, 18 h.

| *t* (min) | **TN1** (%) | **TN1O1** (%) | **TN1O2** (%) | **TN2** (%) | **TN2O1** (%) | **TN3** (%) |
|---|---|---|---|---|---|---|
| 20 | 47.7 | 8.52 | 0 | 28.9 | 1.97 | 3.66 |
| 40 | 31.4 | 11.6 | 1.45 | 29 | 9.98 | 11.9 |
| 60 | 21.8 | 13.4 | 2.18 | 28.6 | 12.9 | 17.4 |
| 120 | 13 | 12.4 | 5.08 | 21.9 | 16.7 | 21.1 |
| 180 | 5.23 | 8.6 | 6.26 | 19.6 | 20.8 | 28.3 |
| 300 | 1.27 | 4.28 | 6.28 | 12.4 | 17.7 | 37.8 |
| 1080 | 0 | 0 | 10 | 0 | 32 | 42 |

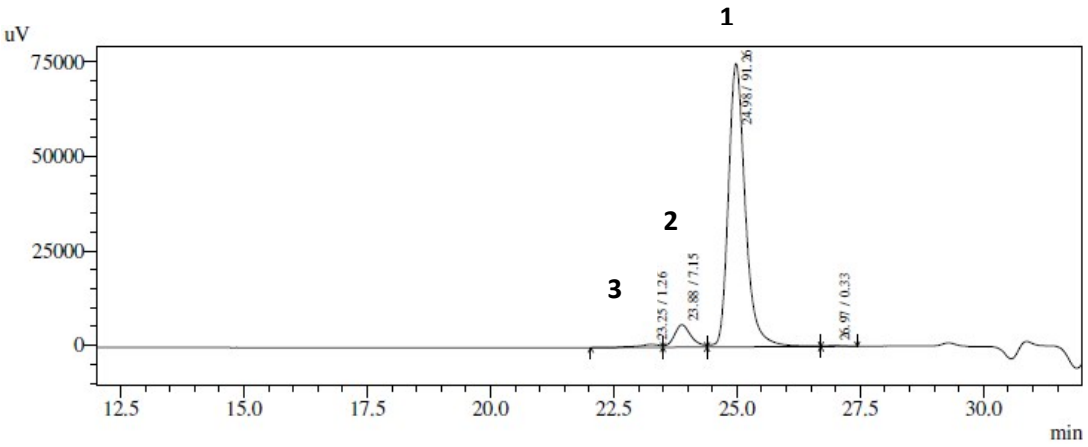
**Table S2.** Distribution of the reaction products with the reaction temperature. Conditions: **T** (1 mL, 1 mmol), $HNBu_2$ (3 mmol), $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol), toluene (5 mL), 80 bar $CO/H_2$ (1:1), 80 °C, 18 h.

| T (°C) | **TN1** (%) | **TN1O1** (%) | **TN1O2** (%) | **TN2** (%) | **TN2O1** (%) | **TN3** (%) |
|---|---|---|---|---|---|---|
| 50 °C | 8.05 | 21.89 | 17.84 | 15.2 | 22.9 | 9.77 |
| 80 °C | 1.27 | 4.28 | 6.29 | 12.4 | 27.7 | 37.8 |
| 110 °C | 0 | 3.32 | 8.79 | 1.68 | 30.3 | 40.3 |

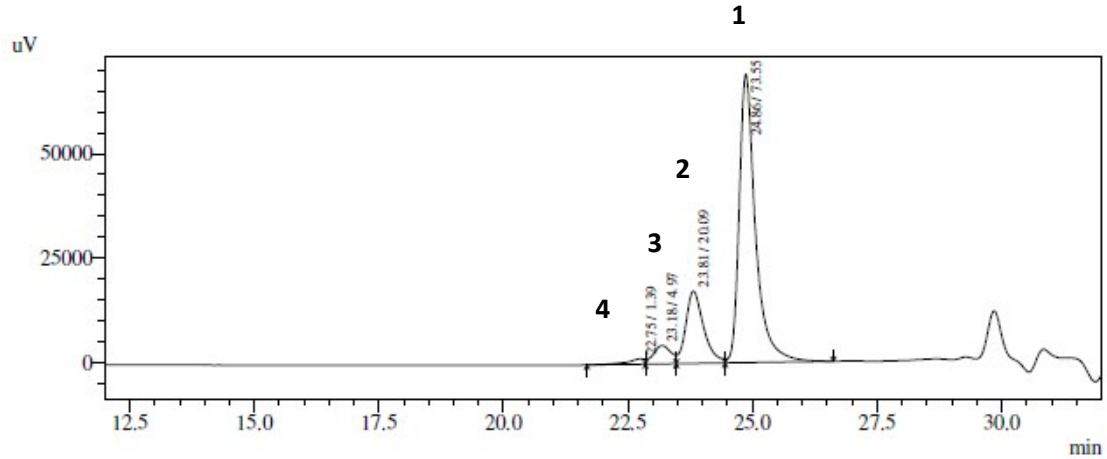
## Size exclusion chromatography (SEC)




*after 1 h reaction time*




*after 3 h reaction time*




*after 6 h reaction time*

| Peak | Retention time (min) | HAM 1h | | HAM 3h | | HAM 6h | |
|---|---|---|---|---|---|---|---|
| | | % | Mn | % | Mn | **%** | Mn |
| **1** | 25.0 | **93.7** | 1469 | **91.3** | 1501 | **73.6** | 1579 |
| **2** | 23.9 | **5.0** | 2936 | **7.2** | 2970 | **20.1** | 3062 |
| **3** | 23.3 | **1.1** | 4577 | **1.3** | 4725 | **5.0** | 4660 |
| **4** | 22.8 | **0** | - | **0** | - | **1.4** | 6577 |

| **Echantillon** | **HAM 1h** | **HAM 3h** | **HAM 6h** |
|---|---|---|---|
| $M_n$ | 1512 | 1558 | 1837 |
| $M_w$ | 1594 | 1671 | 2130 |
| $Đ_M$ ($M_w/M_n$) | 1.05 | 1.07 | 1.16 |