Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2015

Electronic Supplementary Information

Preparation of functionalized castor oil derivatives with tunable physical properties using heterogeneous acid and base catalysts

Sivashunmugam Sankaranarayanan[a][b] and Kannan Srinivasan*[a][b]

[a]Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA.

[b]Academy of Scientific and Innovative Research, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA.

Manuscript Correspondence:

Prof. Dr. Kannan Srinivasan

Inorganic Materials and Catalysis Division

Central Salt and Marine Chemicals Research Institute

Council of Scientific and Industrial Research

Bhavnagar - 364 002

India

Tel: +91-278-2567760

FAX: +91-278-2567562

E-mail: skannan@csmcri.org ; kanhem1@yahoo.com (S. Kannan)

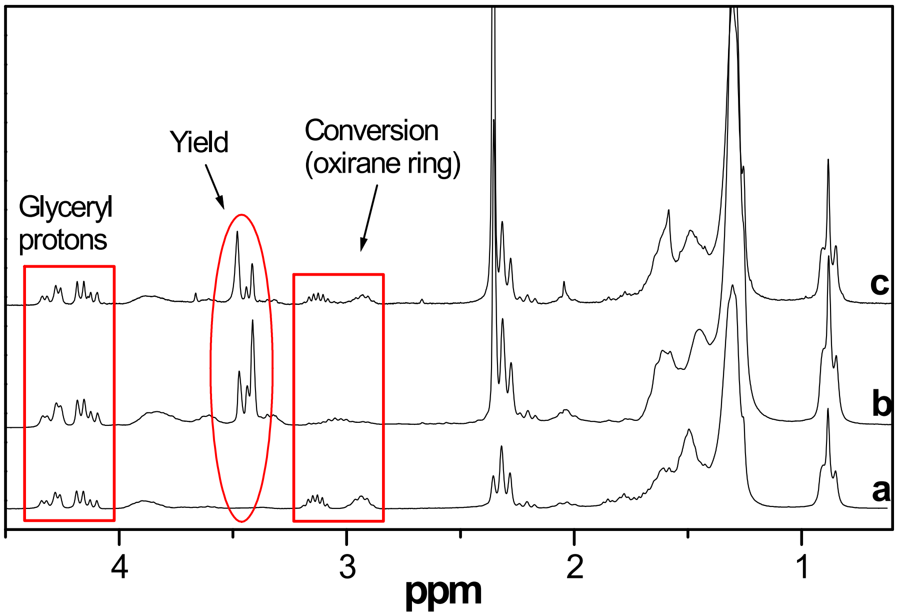
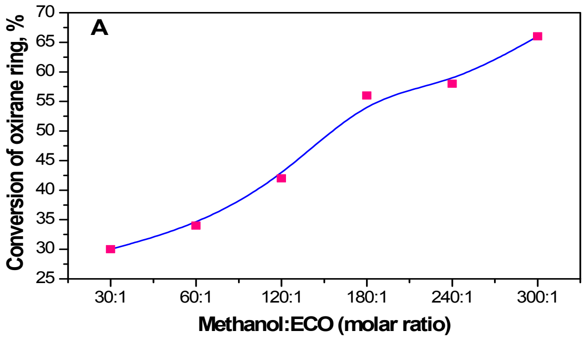
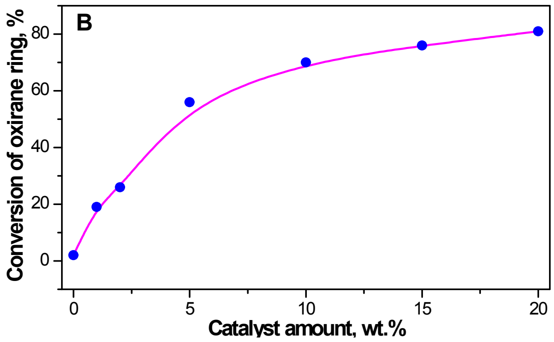


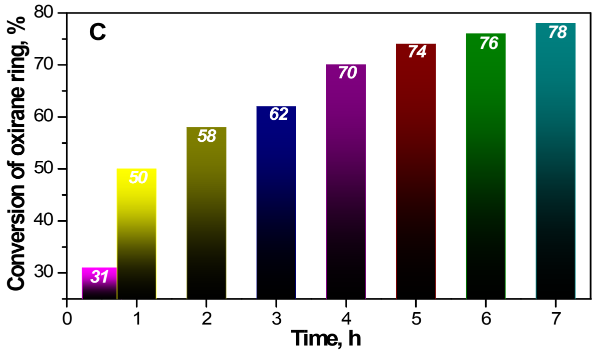
Fig. S1. ^{1}H NMR spectra of (a) Epoxidized castor oil, (b) Methoxylated castor polyol-1 (Zn triflate catalyst), (c) Methoxylated castor polyol-2 (Amberlyst 15 catalyst) (Reaction conditions as given in Table 1).



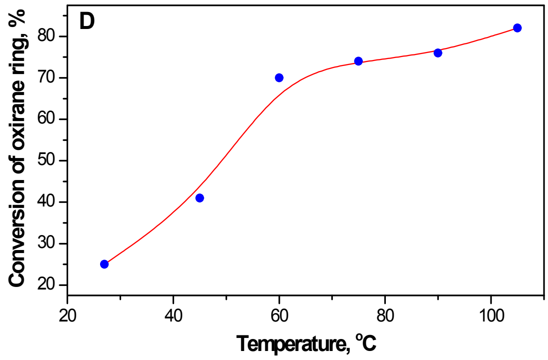
Methanol amount variation studies: ECO = 0.5 g, Toluene = 3 ml, Catalyst (Amberlyst 15) = 5 wt.% w.r.t. ECO, Temp. = 60 °C, Time = 4 h.



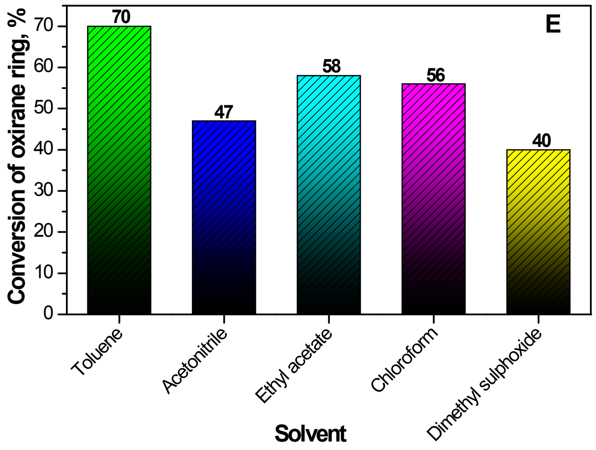
Catalyst (Amberlyst 15) amount variation studies: ECO = 0.5 g, Methanol:ECO molar ratio = ~180:1, Toluene = 3 ml, Temp. = 60 °C, Time = 4 h.



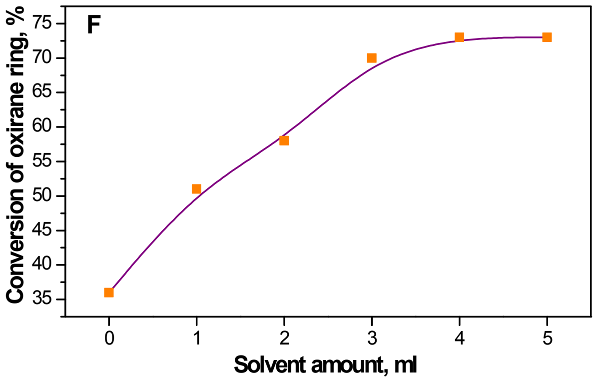
Time variation studies: ECO = 0.5 g, Methanol:ECO molar ratio = ~180:1, Toluene = 3 ml, Catalyst (Amberlyst 15) = 10 wt.% w.r.t. ECO, Temp. = 60 °C.



Temperature variation studies: ECO = 0.5 g, Methanol:ECO molar ratio = ~180:1, Toluene = 3 ml, Catalyst (Amberlyst 15) = 10 wt.% w.r.t. ECO, Time = 4 h.



Solvent variation studies: ECO = 0.5 g, Methanol:ECO molar ratio = ~180:1, Solvent = 3ml, Catalyst (Amberlyst 15) = 10 wt.% w.r.t. ECO, Temp. = 60 °C, Time = 4 h.



Toluene amount variation studies: ECO = 0.5 g, Methanol:ECO molar ratio = ~180:1, Catalyst (Amberlyst 15) = 10 wt.% w.r.t. ECO), Temp. = 60 °C, Time = 4 h.

Fig. S2. Parametric variation studies (A-F)

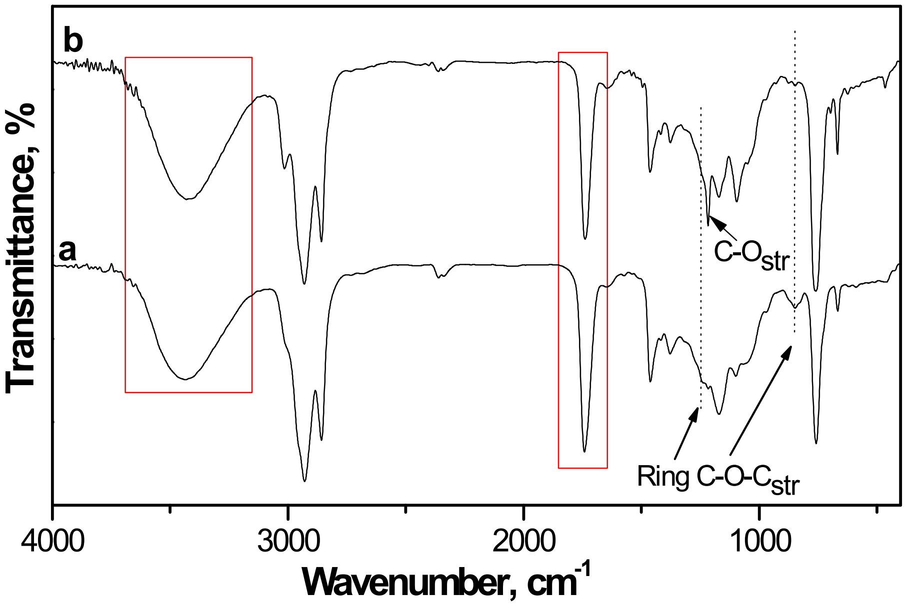


Fig. S3. FT-IR spectra of (a) Epoxidized castor oil (ECO), (b) Methoxylated castor polyol (MCP).

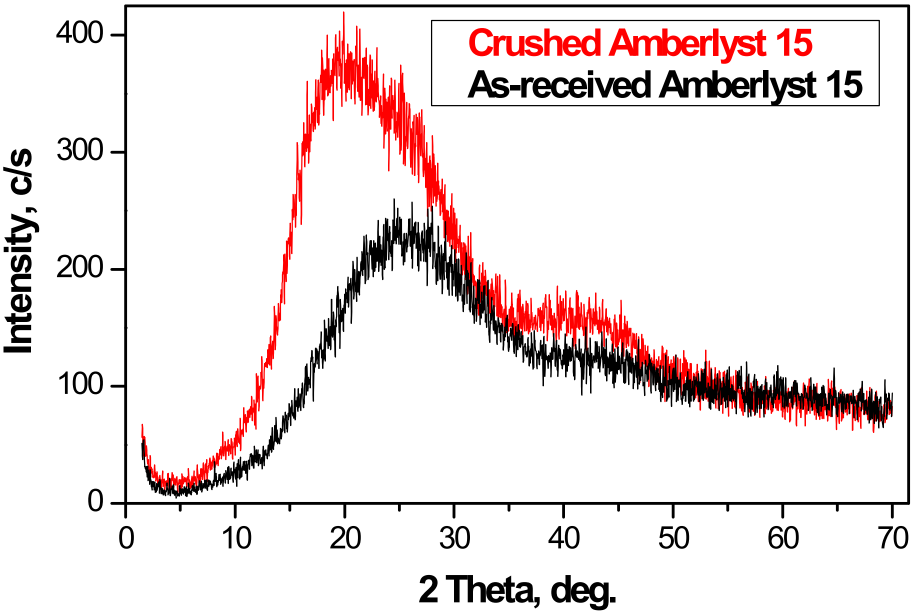


Fig. S4. PXRD patterns of as-received (bead form) and crushed Amberlyst 15.

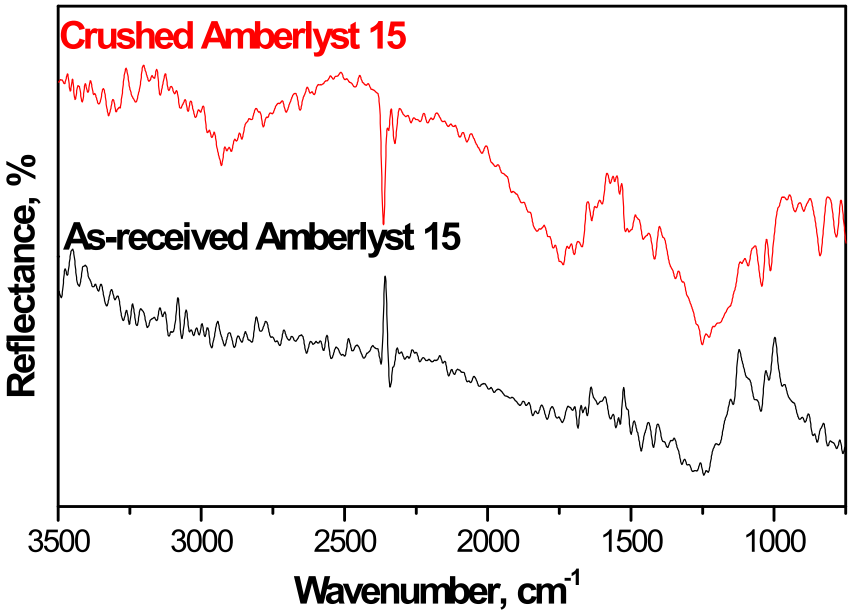


Fig. S5. DRIFT spectra of as-received (bead form) and crushed Amberlyst 15.

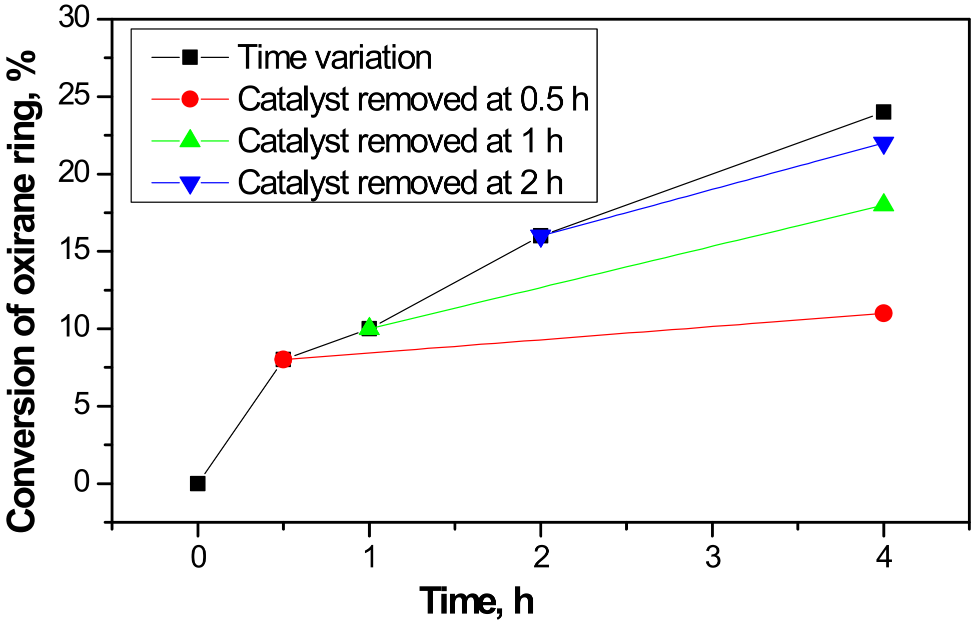


Fig. S6. Hot- filtration leaching studies. ECO = 500 mg, Methanol = 2 g, water = 1 g, Toluene = 3 ml, Amberlyst 15 = 10 wt.% w.r.t. ECO, Temp. = 60 °C, Time = 4 h.

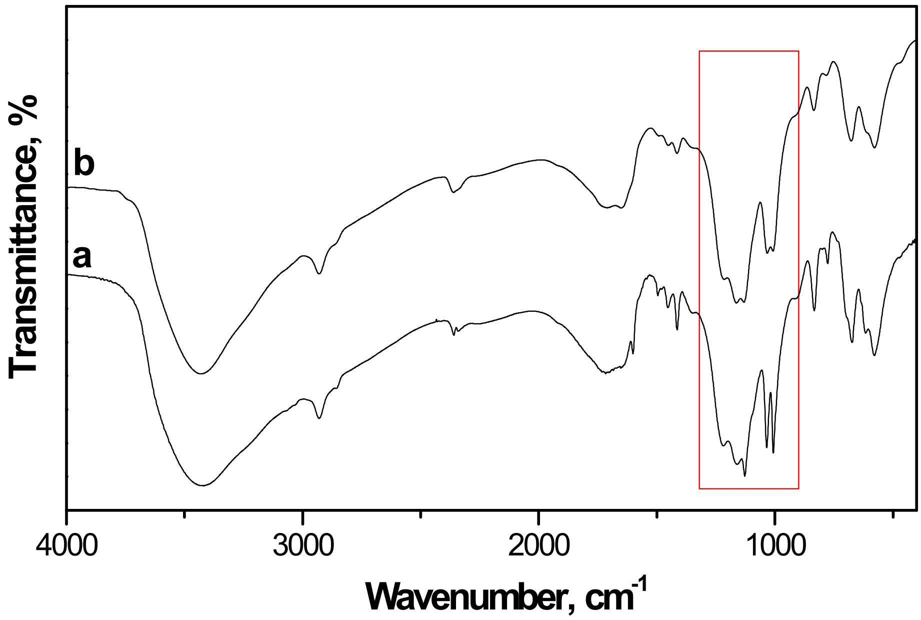


Fig. S7. FT-IR spectra of (a) Amberlyst 15, (b) Water treated Amberlyst 15.

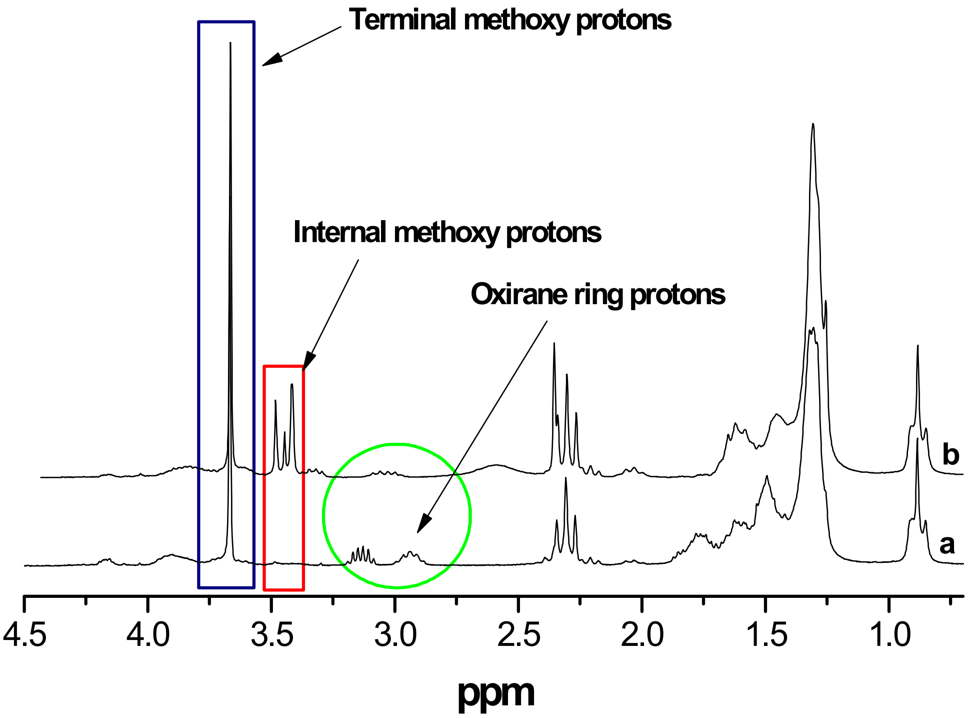


Fig. S8. ^{1}H NMR spectra of (a) Epoxy methyl ricinoleate (EMR), (b) Methoxylated methyl ricinoleate (MMR).

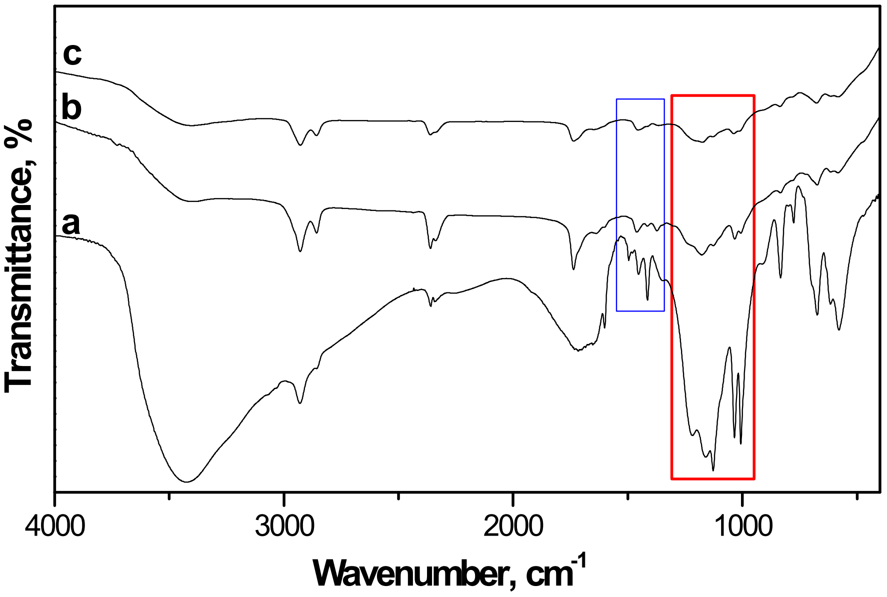


Fig. S9. FT-IR spectra of (a) Amberlyst 15, (b) Amberlyst 15 treated with epoxy ethyl linoleate, (c) Amberlyst 15 treated with epoxy methyl ricinoleate.

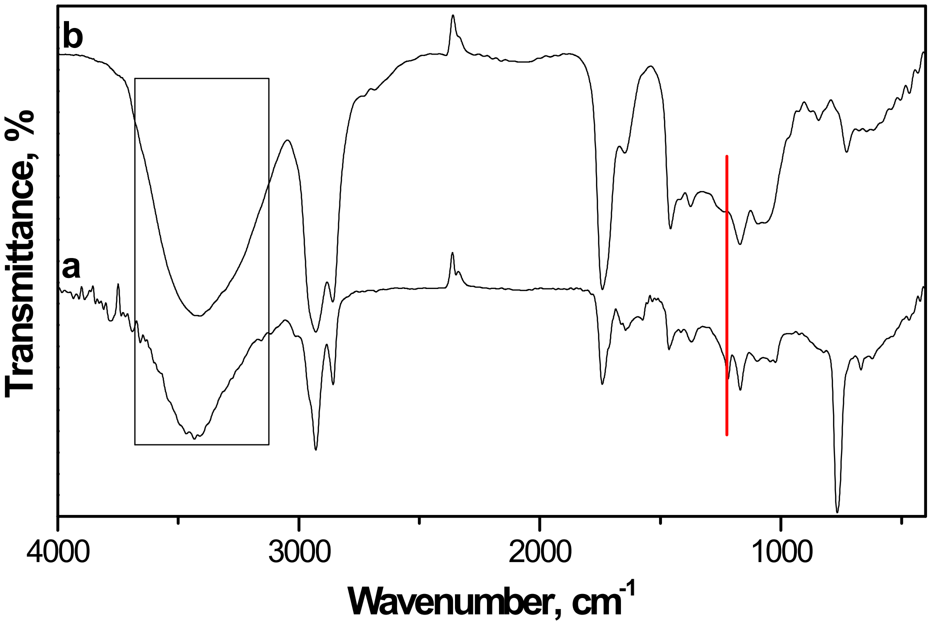


Fig. S10. FT-IR spectra of (a) Epoxidized castor oil (ECO), (b) Hydroxylated castor polyol (HCP).

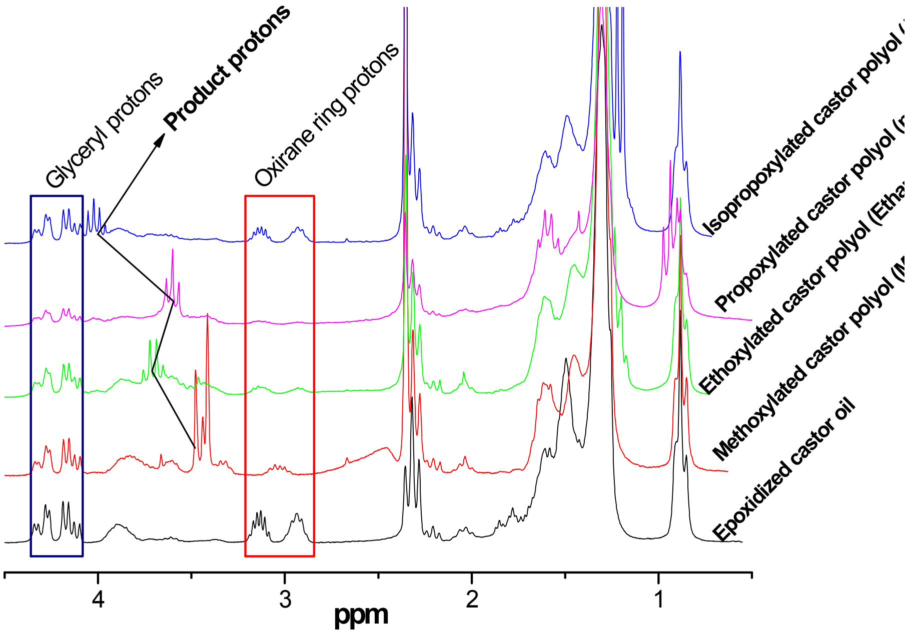


Fig. S11. Comparison of ^{1}H NMR spectra of epoxidized castor oil (ECO) along with ring opened products formed by reacting with different alcohols as nucleophiles (Names of the alcohols are given in brackets).

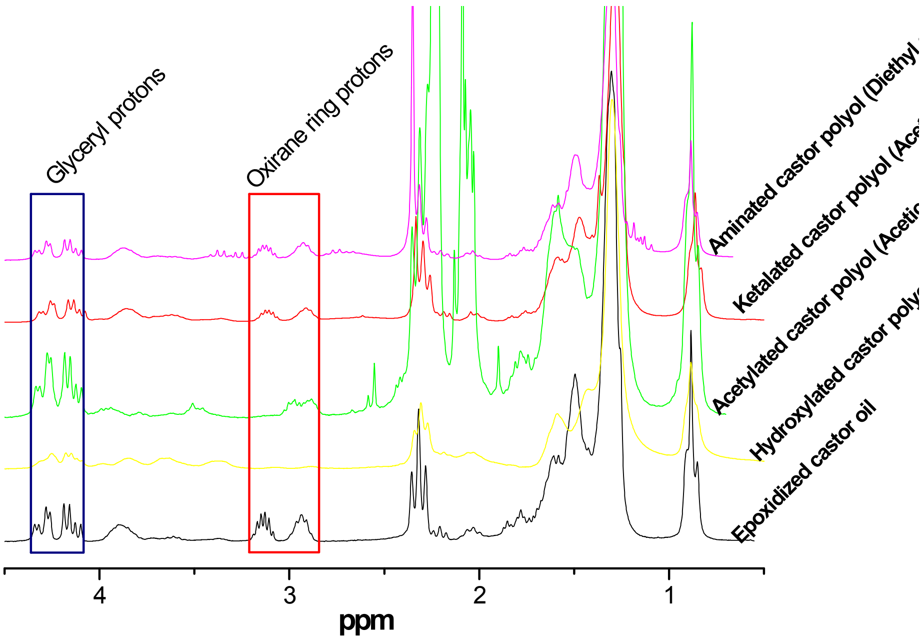


Fig. S12. Comparison of ^{1}H NMR spectra of epoxidized castor oil (ECO) along with ring opened products formed by reacting with different nucleophiles (Nucleophiles used are given in brackets).

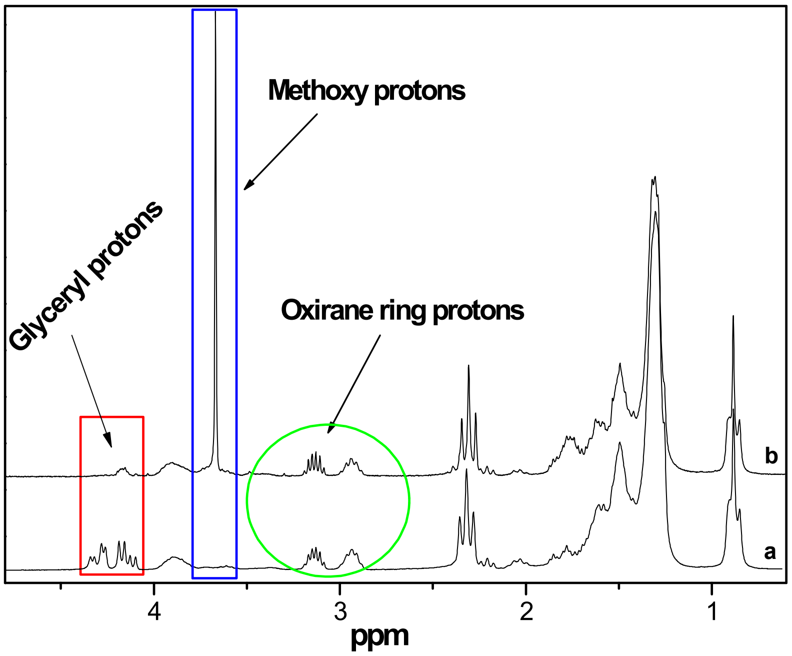


Fig. S13. ^{1}H NMR spectra of (a) Epoxidized castor oil (ECO), (b) Epoxy methyl ricinoleate (EMR).

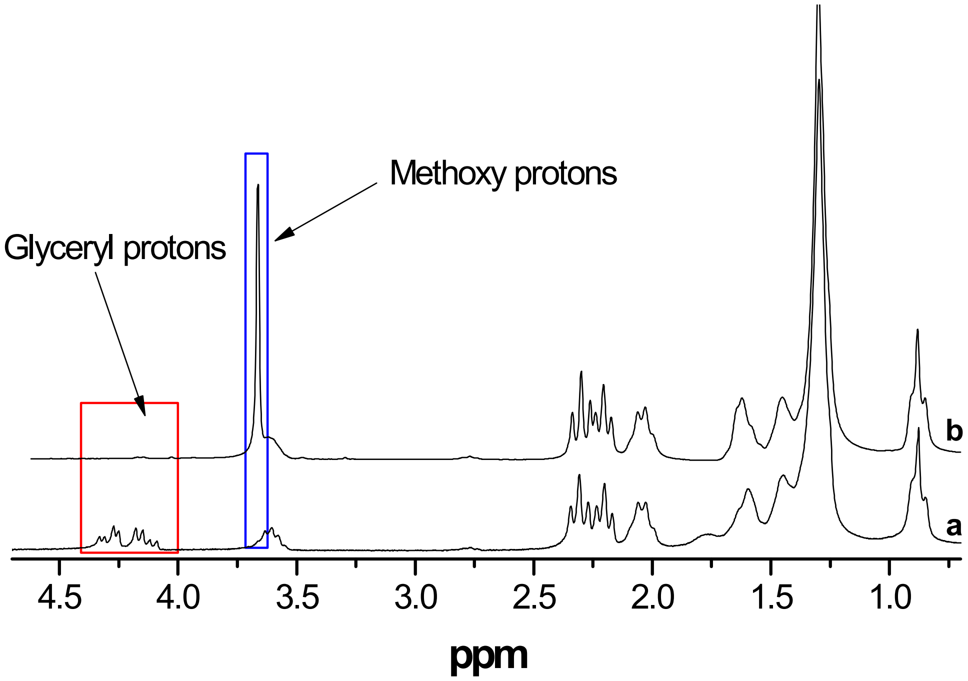


Fig. S14. ^{1}H NMR spectra of (a) Castor oil (CO), (b) Methyl ricinoleate (MR).

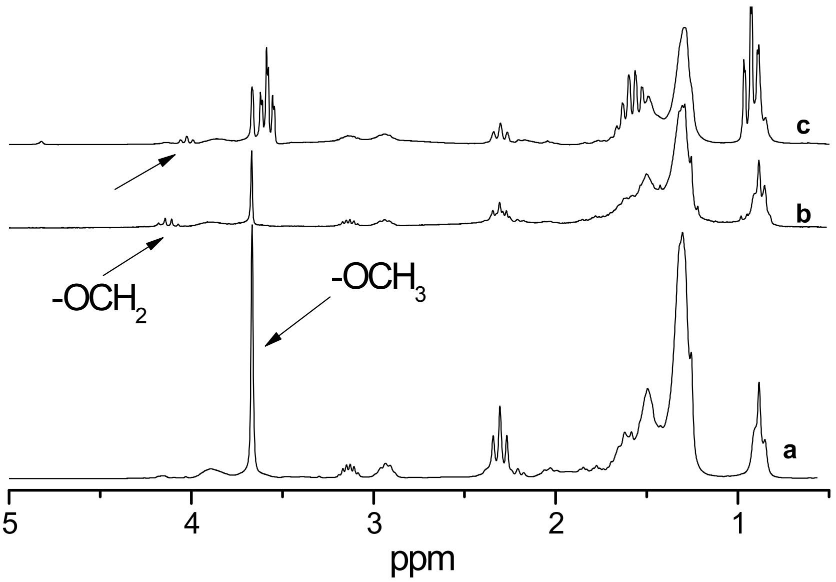


Fig. S15. ^{1}H NMR of spectra of (a) Epoxy methyl ricinoleate (EMR), (b) Epoxy ethyl ricinoleate (EER), (c) Epoxy propyl ricinoleate (EPR).

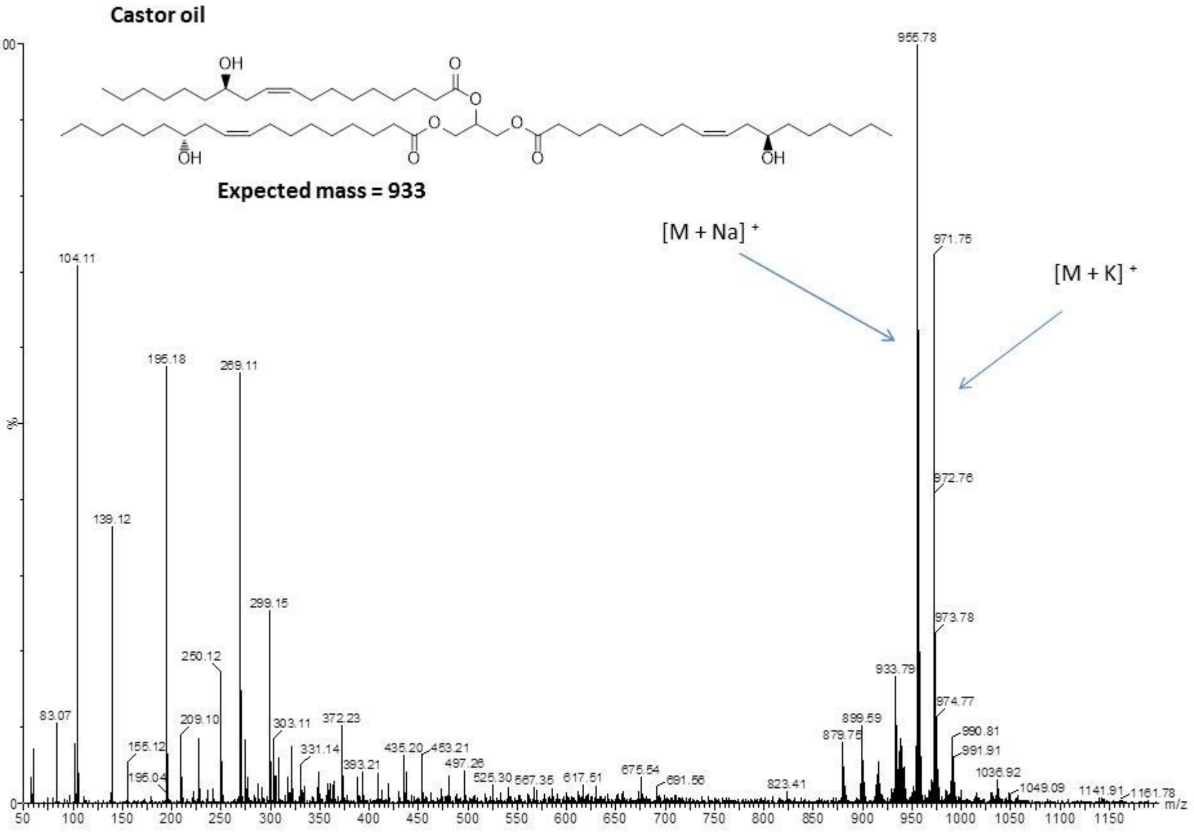


Fig. S16. ESI-MS analysis of castor oil (CO).

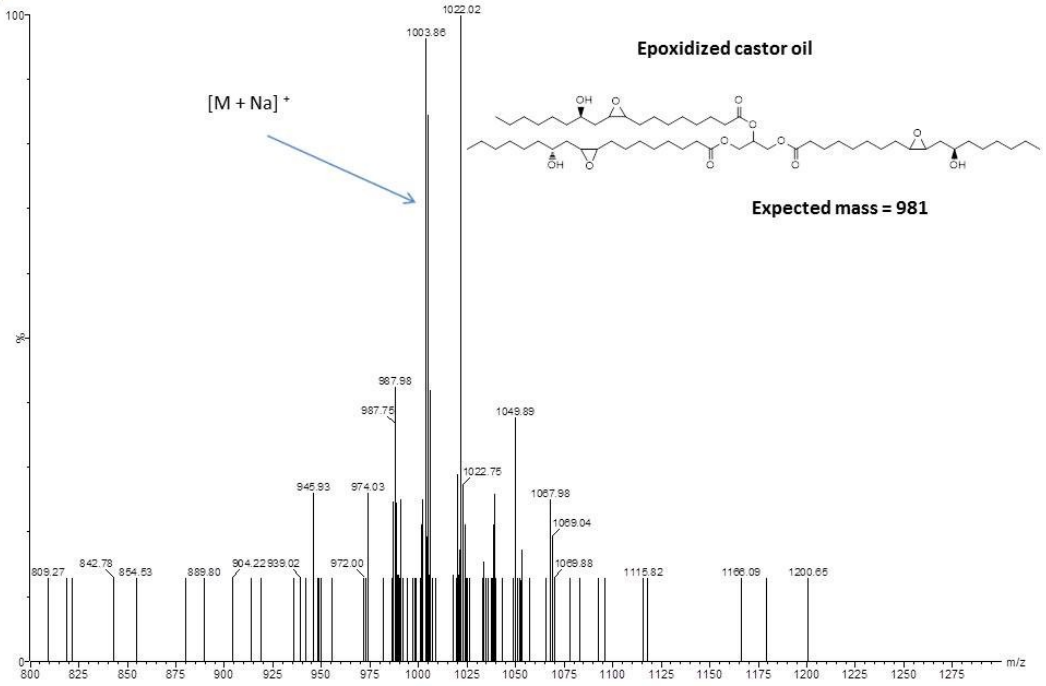


Fig. S17. ESI-MS analysis of epoxidized castor oil (ECO).

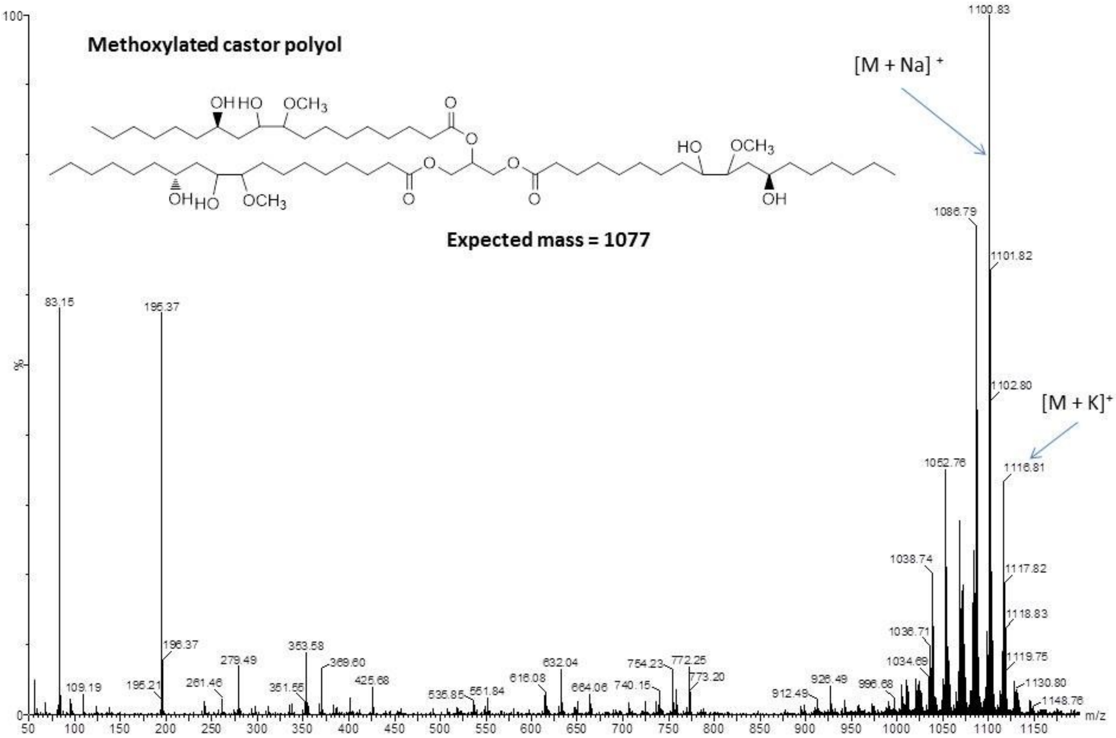


Fig. S18. ESI-MS analysis of methoxylated castor polyol (MCP).

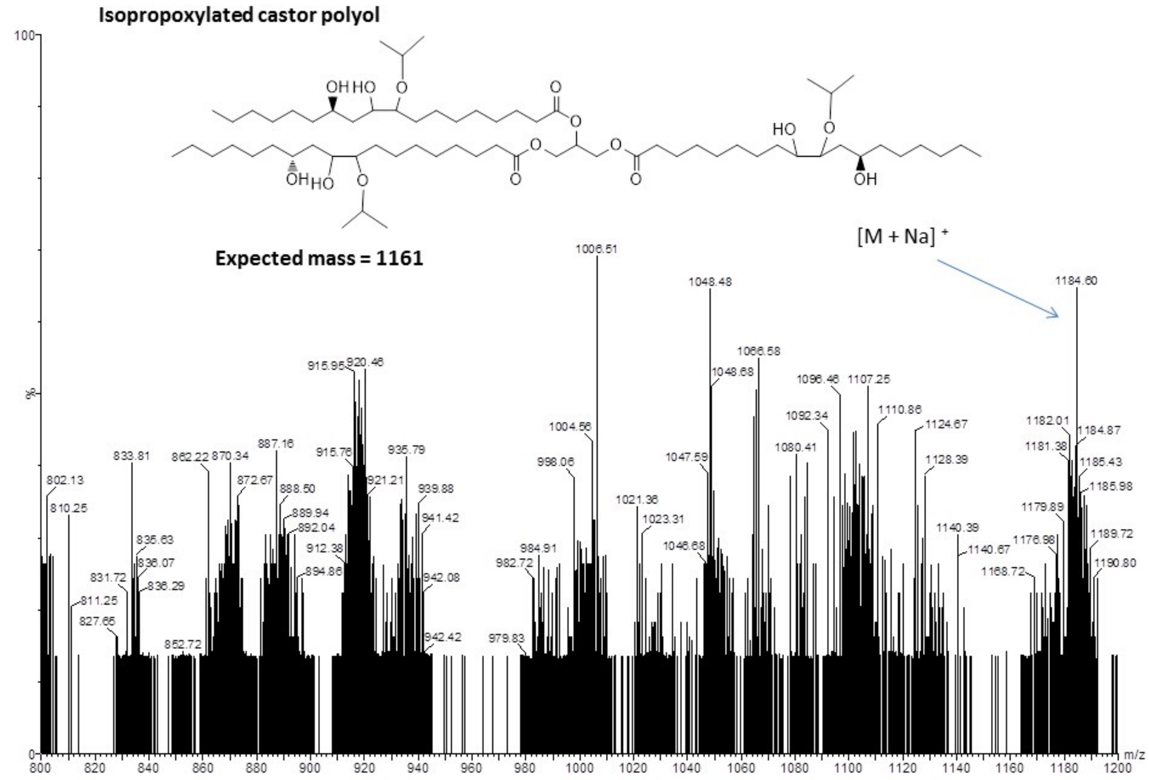


Fig. S19. ESI-MS analysis of isopropoxylated castor polyol (IPCP).

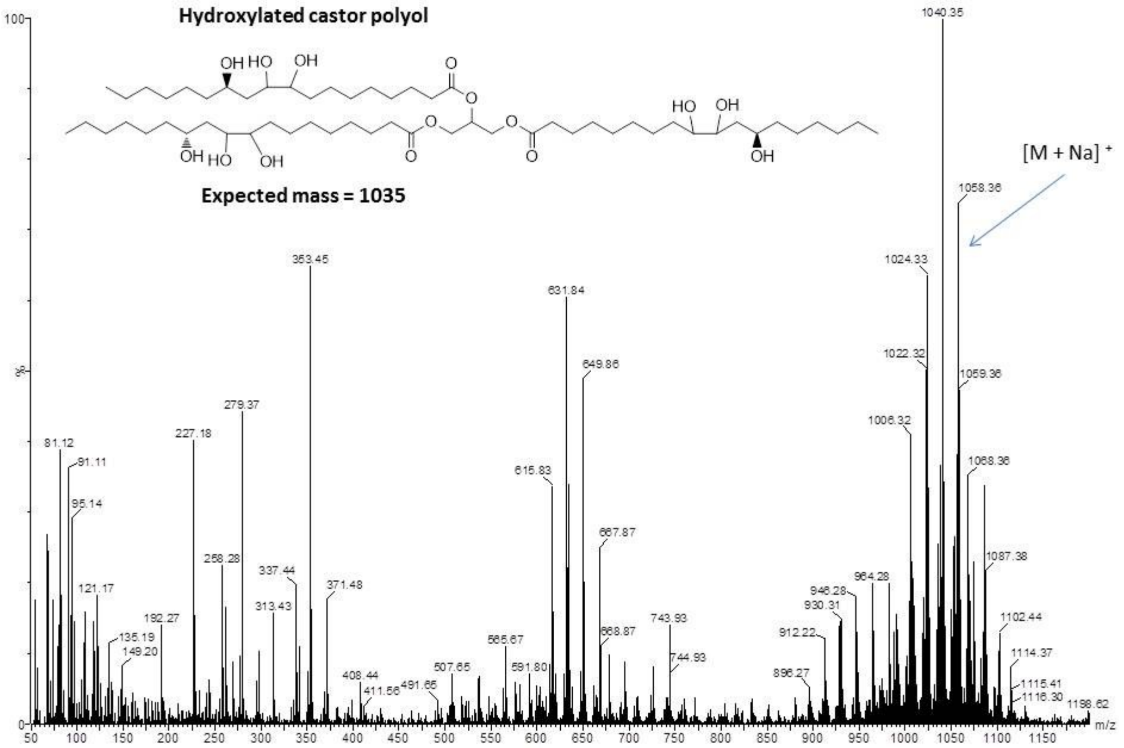


Fig. S20. ESI-MS analysis of hydroxylated castor polyol (HCP).

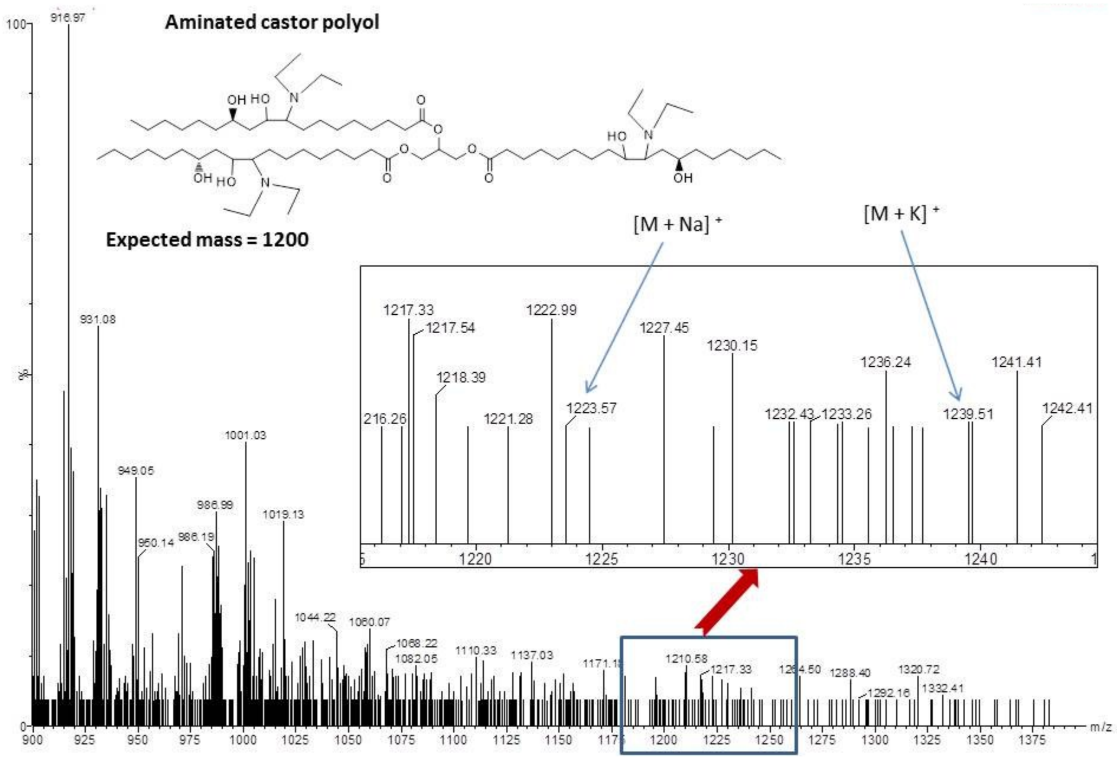


Fig. S21. ESI-MS analysis of aminated castor polyol (ACP) (Inset: Expanded region from 1215-1250).

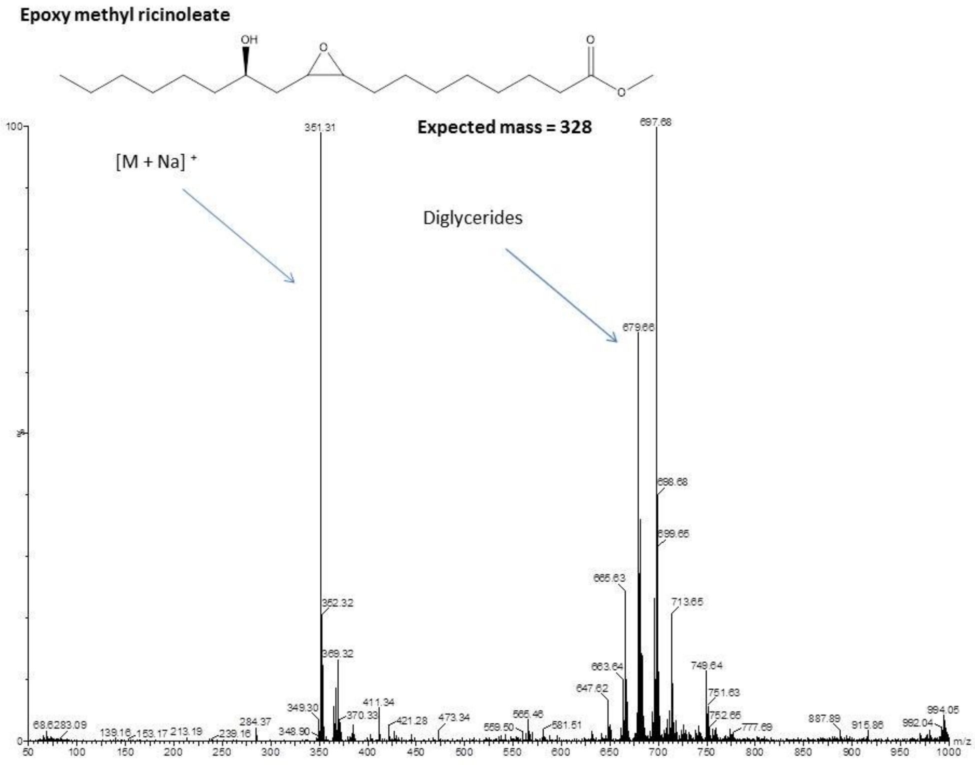


Fig. S22. ESI-MS analysis of epoxy methyl ricinoleate (EMR).

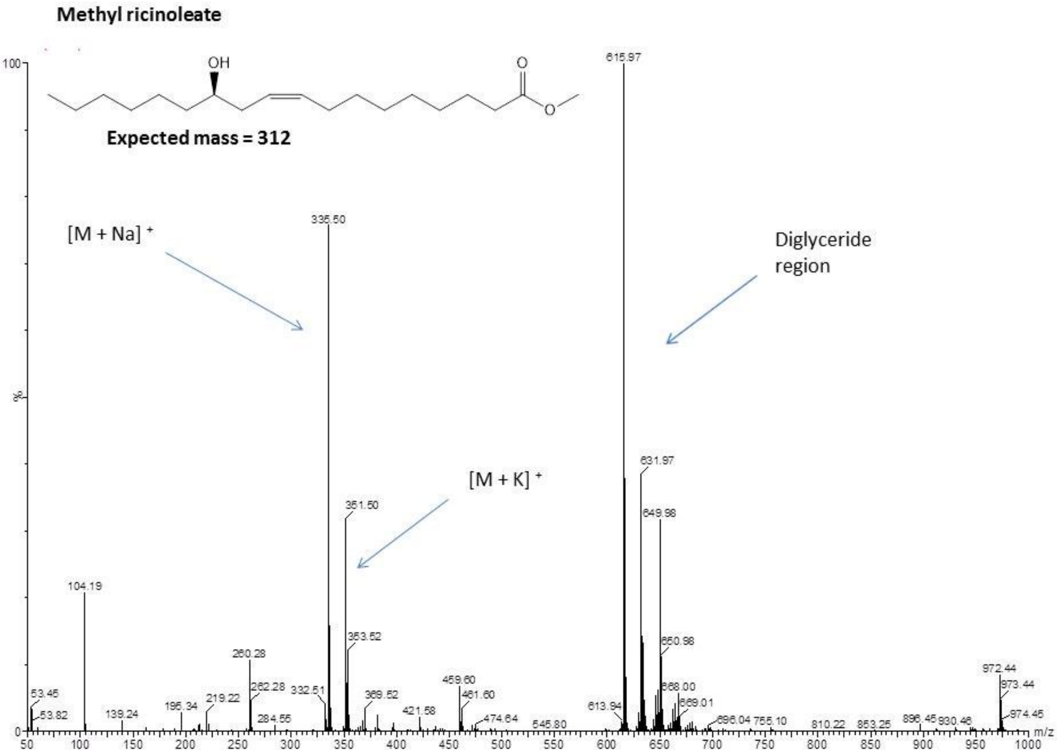


Fig. S23. ESI-MS analysis of methyl ricinoleate (MR).

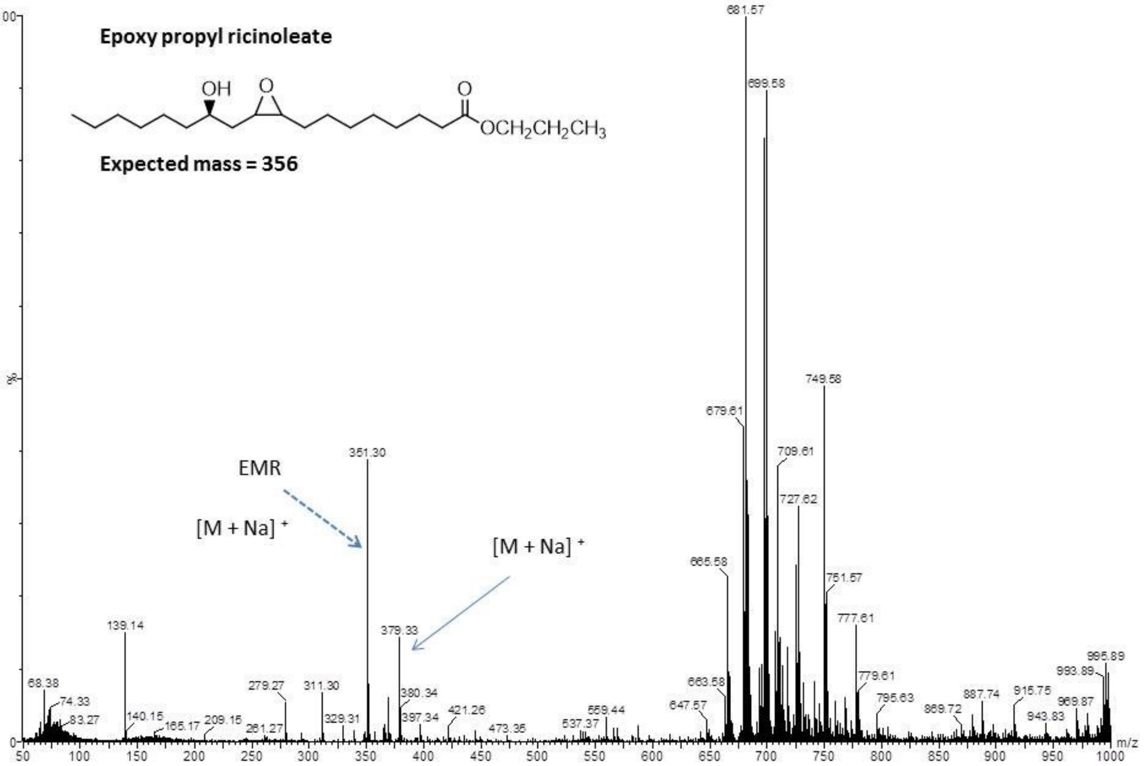


Fig. S24. ESI-MS analysis of epoxy propyl ricinoleate (EPR).

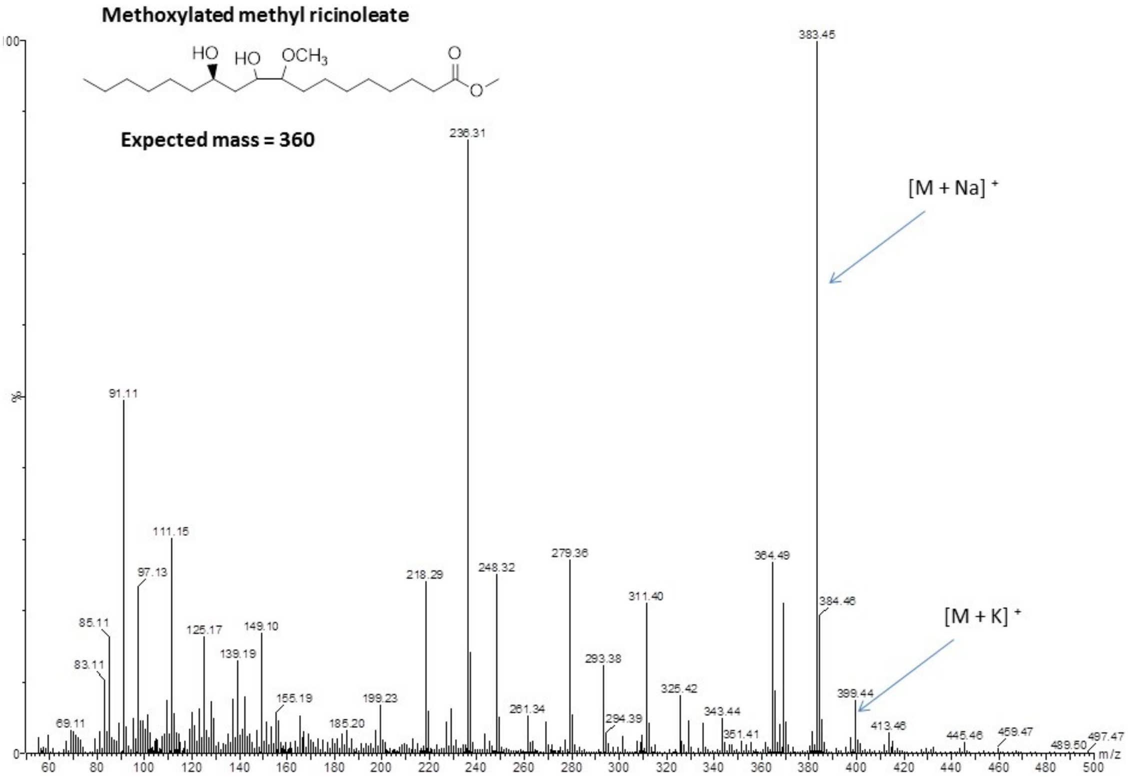


Fig. S25. ESI-MS analysis of methoxylated methyl ricinoleate (MMR).

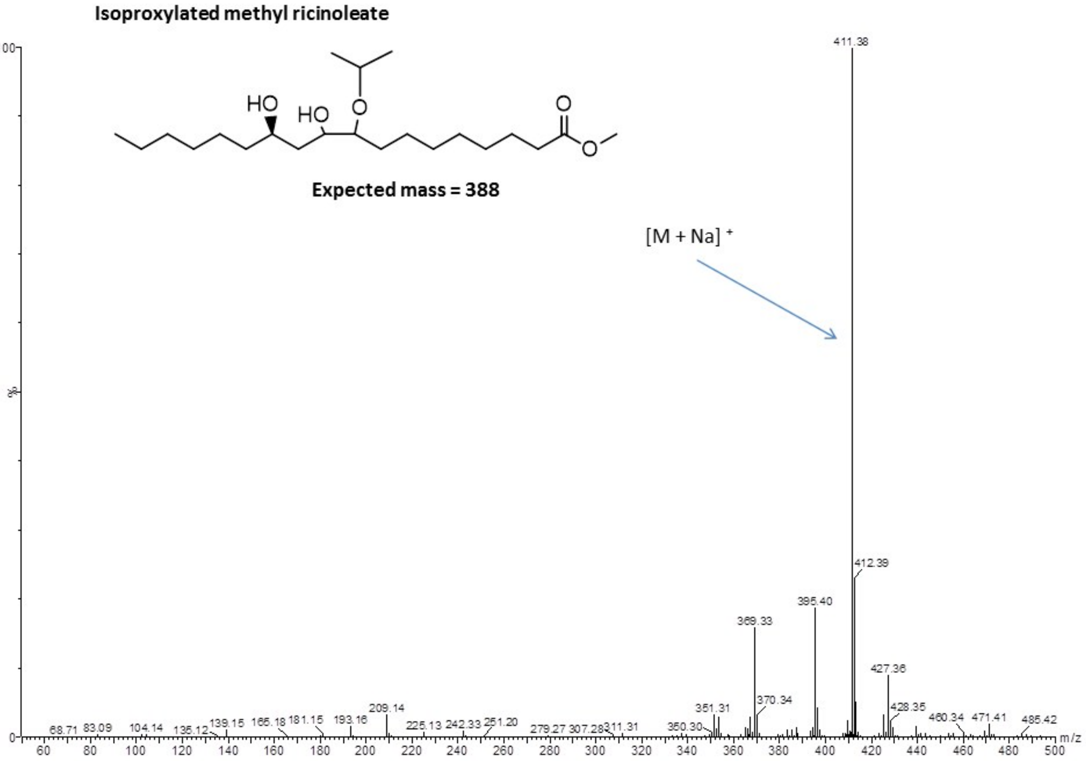


Fig. S26. ESI-MS analysis of isopropoxylated methyl ricinoleate (IPMR).

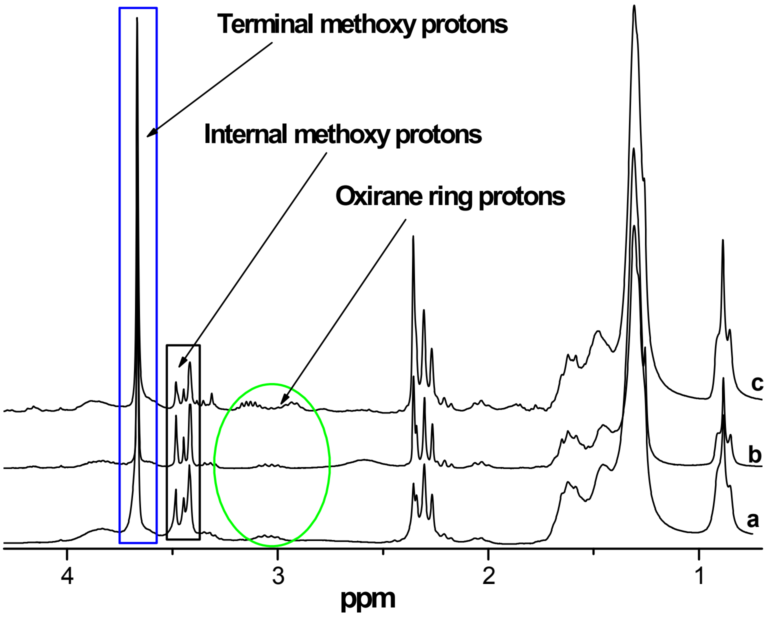


Fig. S27. Comparison of ^{1}H NMR spectra of one-pot and two-pot reactions product mixtures. (a) Two-pot reaction (as per Table 3; Entry No. 1); (b) Two-pot reaction (as per Table 3; Entry No. 2); (c) One-pot reaction (as per Table S2; Entry No. 1).

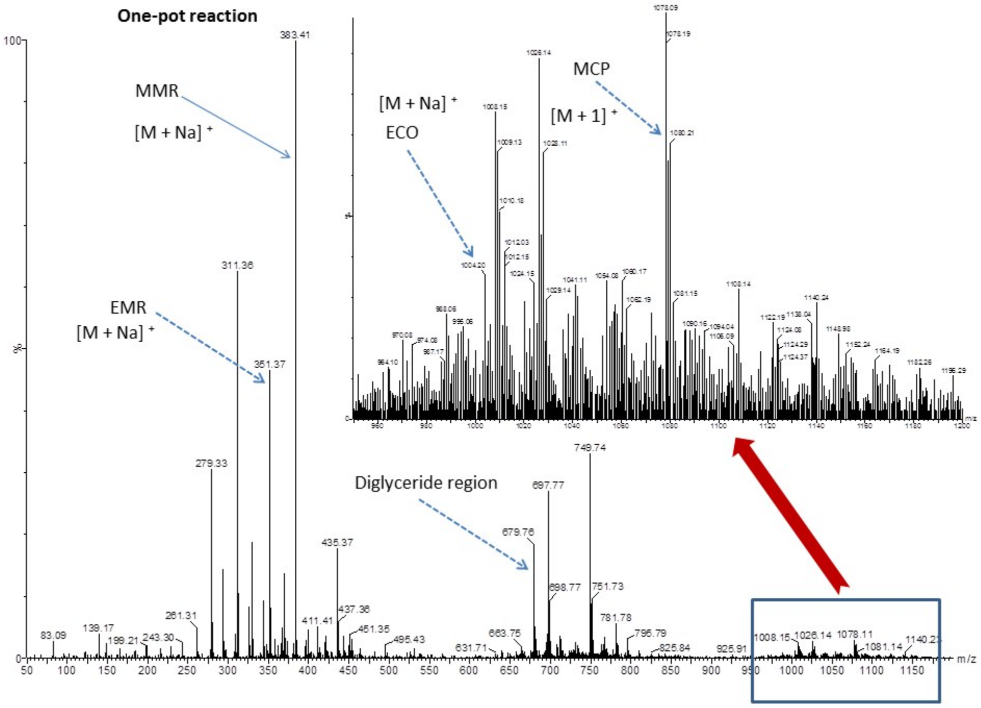
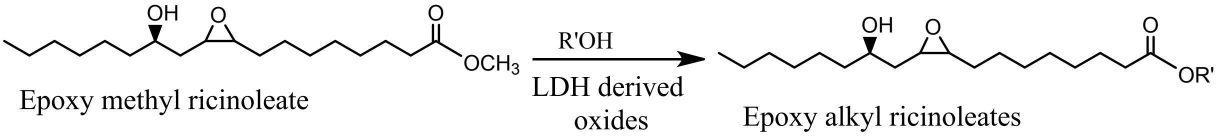


Fig. S28. ESI-MS analysis of product mixture of one-pot reaction (Expanded region from 950-1250).

Table S1. Transesterification of epoxy methyl ricinoleate with different alcohols



R' = C_2 (or) C_3

Name of the alcohol[a]	Yield[b]	Code of the product
Ethanol[c]	49	EER
n-propanol	35	EPR
Iso-propanol	23	EiPR

[a] Alcohol:EMR = 6:1, catalyst = 5 wt.% w.r.t. EMR, Temp. = reflux, Time = 5h; [b] Calculation based on comparison of decrease in the peak area of $-OCH_3$ protons in EMR and products by keeping 2.3 ppm protons as internal standard; [c] Product mixture became white wax like material.

Table S2. One-pot reaction for the preparation of ring-opened alkyl ricinoleates using heterogeneous acid and base catalysts together

Entry No.	**Time (h)**	**Conversion of oxirane ring (%)**	**Yield of transesterified product (%)**
1.	5	61	59
2.	8	57	69
3.	48	57	67

ECO = 2 g, Methanol = 12 g (Methanol:oil = ~ 180:1 molar ratio), Toluene = 10 ml, Catalyst = Amberlyst 15 (10 wt.% w.r.t. ECO) & CaAl2-$CLDH_{700}$ (5 wt.% w.r.t. ECO), Temp. = 105 °C.