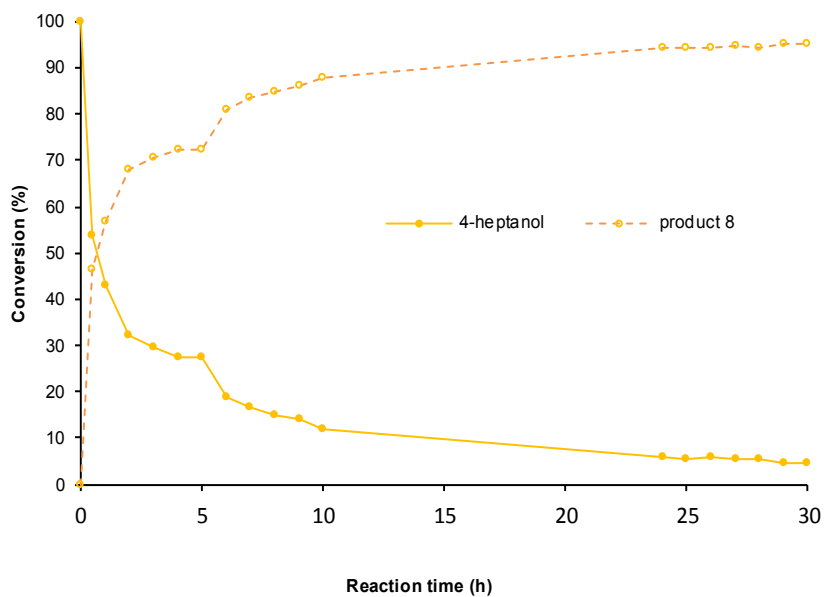


## **Electronic Supplementary Information**

### **Free-solvent Michael addition of glycerol to acrylic compounds**

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Experimental conditions: 10 mmol 4-heptanol, 10 mmol AN, 0.4 mmol NaOH (4 mol%), 25 °C, addition of 1equiv.AN at 5h, 9h, 25h, 29h

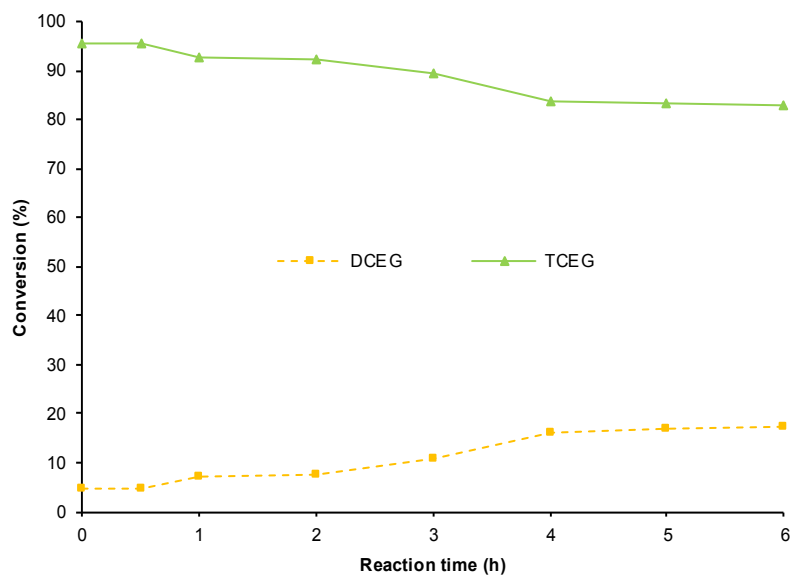
**Figure SI1†** Kinetic monitoring of the addition of 4-heptanol to AN with 4 mol% NaOH

**Table S11#** Effect of the amount of catalysts and the temperature on the reaction

Entry	Catalyst	Catalyst (mol%)	Temperature	Time (hours)	Ratio <sup>a</sup> TCEG :DCEG	Yield of TCEG
1	NaOH	10 %	25°C	6	95:5	71 %
2	KOH	10 %	25°C	6	89:11	63 %
3	NaOH	10 %	50°C	6	12 :88	68%
4	Na <sub>2</sub> CO <sub>3</sub>	10 %	25°C	6	-	0 %
5	K <sub>2</sub> CO <sub>3</sub>	10 %	25°C	6	-	0 %
6	CS <sub>2</sub> CO <sub>3</sub>	10 %	25°C	6	-	0 %
7	CS <sub>2</sub> CO <sub>3</sub>	10 %	25°C	168	93:7	63 %
8	DBU	30 %	25°C	72	88:12	73 %
9	PPh <sub>3</sub>	30 %	50°C	24	-	0 %
10	CuCl <sub>2</sub> 30 %, MeONa in MeOH	30 %	reflux	18	-	0 %

Experimental conditions: 12.5 mmol glycerol (1 equiv.), 37.5 mmol AN (3 equiv.)

<sup>a</sup> Ratio TCEG:DCEG of isolated products determined by <sup>1</sup>H NMR or GC analysis



Experimental conditions: 12.5 mmol compounds (1 equiv.), 0.5 mmol NaOH (0.04 equiv.), 25°C, 6H. Traces of MCEG <1%

**Figure S12†** Kinetic monitoring of the degradation of TCEG with 4 mol% NaOH

## Identification of Product

**Methyl 3-(heptyloxy)propanoate (1)**  $R^1 = C_7H_{15}$ ,  $R^2 = Me$ . GC/MS (EI, 70eV):  $t_R = 12.93$  min: m/z (%): 117(20), 105(20), 103(60), 88(100), 87(65), 71(30), 57(70), 45(60)

**t-butyl(3-heptyloxy)propanoate (1)**  $R^1 = C_7H_{15}$ ,  $R^2 = t-Bu$ . GC/MS (EI, 70eV):  $t_R = 14.80$  min: m/z (%): 115(5), 97(20), 89(20), 73(35), 57(100), 41(35)

**t-butyl(3-(1-propylbutyl))propanoate (1)**  $R^1 = CH(C_6H_{14})$ ,  $R^2 = t-Bu$ . GC-MS (EI, 70eV):  $t_R = 13.63$  min : m/z (%): 145(100), 73(95), 57(70), 55(35), 41(35)

**heptyl acrylate (2)**  $R^1 = C_7H_{15}$ . GC-MS (EI, 70eV):  $t_R = 10.20$  min: m/z (%): 98(20), 73(30), 70(35), 56(40), 55(100), 41(35). Data in agreement with store of correspond product.

**1-propylbutyl acrylate (2)**  $R^2 = Me$ . GC-MS (EI, 70eV):  $t_R = 15.43$  min, m/z (%): 162(25), 145(20), 127(30), 116(25), 73(40), 57(100), 41(60)

**Methyl 3-methoxypropanoate (3)**. GC-MS (EI, 70eV):  $t_R = 4.31$  min: m/z (%): 103(30), 87(30), 71(20), 58(20), 45(100), 43(20). Data in agreement with store of correspond product.

**Heptyl 3-methoxypropanoate (4)**. GC-MS (EI, 70eV):  $t_R = 13.12$  min, m/z (%): 105(25), 89(20), 87(100), 74(20), 57(60), 45(100); 41(50)

**Heptyl 3-(heptyloxy)propanoate (5)**. GC-MS (EI, 70eV):  $t_R = 19.21$  min, m/z (%): 103(20), 89(40), 73(35), 57(100), 55(40); 41(40)

**1,2,3-tri-(t-butoxycarbonyl)ethylglycerol (6)**. Colorless oil (m = 1.14g; Yield = 12%). TLC (hexane/ethyl acetate 3/1):  $R_f = 0.60$ ; IR (Neat)  $\nu$ : 2978, 1727, 1366, 1155, 1111  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta = 1.48$  (27H, s), 2.50 (6H, t), 3.58 (4H, m), 3.62 (1H, m), 3.70 (4H, t), 3.83 (2H, t);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta = 28.0, 36.3, 36.6, 66.2, 67.1, 71.0, 78.0, 80.4, 170.8, 170.9$ ; HRMS (ESI) for  $C_{24}H_{44}O_9$  (M + Na) $^+$ : calculated 499.2878; Found 499.2877

**3-(Heptyloxy)propanenitrile (7)**. IR (neat)  $\nu$ : 2927, 2858, 2251, 1112  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta = 0.90$  (3H, t), 1.33 (8H, m), 1.59 (2H, q), 2.60 (2H, t), 3.48 (2H, t), 3.65 (2H, t);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta = 14.0, 19.0, 22.5, 26.0, 29.0, 29.5, 32.0, 65.2, 71.5, 118.0$ ; GC-MS (EI, 70eV):  $t_R = 12.58$  min, m/z (%): 168(2), 154(3), 140(5), 126(7), 112(7), 98(12), 84(25), 70(100), 57(65), 54(75), 41(63)

**3-(1-propylbutyloxy)propanenitrile (8)**. IR (neat)  $\nu$ : 2933, 2872, 2558, 2252, 1100  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta = 0.93$  (6H, t), 1.3-1.55 (8H, m), 2.57 (2H, t), 3.33 (1H, q), 3.66 (2H, t);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta = 14.1, 18.5, 19.3, 36.0, 63.5, 80.2, 118.0$ ; GC-MS (EI, 70eV)  $t_R = 11.38$  min, m/z (%): 169(2), 126(100), 84(60), 72(30), 57(25), 55(80), 54(70), 43(30), 41(40)

**3-t-Butoxypropanenitrile (9)**.  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta = 1.20$  (9H, s), 2.64 (2H, t), 3.60 (2H, t);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta = 19.0, 27.2, 56.7, 73.0, 119.4$ ; GC-MS (EI, 70eV):  $t_R = 6.57$  min, m/z (%): 112(80), 84(15), 59(100), 57(70), 54(15), 43(20), 41(50)

**2-Cyanoethyl ether (10)**. Yellow liquid; IR (neat)  $\nu$ : 2251, 1113  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta = 2.65$  (2H, t), 3.75 (2H, t);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta = 18.8, 65.9, 117.6$ ; GC-MS (EI, 70eV):  $t_R = 11.41$  min, m/z (%): 97(5), 84(40), 54(100), 41(5), 31(18). Data in agreement with store of correspond product.