Supporting Information

Acid-Catalyzed Reactions of Isopropenyl Esters and Renewable Diols. A 100% Carbon Efficient Transesterification/Acetalization Tandem Sequence, from Batch to Continuous Flow

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General

Commercially available reagents and solvents were used as received unless otherwise stated. MeOH, $CHCl_3$, tetrahydrofuran (THF), petroleum ether, ethyl acetate, toluene, $CDCl_3$, H_2SO_4, Na_2CO_3, octanoic acid, octanoyl chloride, phenylbutyryl chloride, ethylene glycol, 1,2-propanediol, Silica gel for chromatography, molecular sieves (3Å), Amberlyst-15 and isopropenyl acetate (iPAc) were sourced from Sigma Aldrich (now Merck). Phenylbutyric acid and α-Al_2O_3 for chromatography were sourced from Fluka (now Merck). Cyclopentylmethyl ether (CPME) was sourced from Zeon Chemicals (Japan).

$BSMIMHSO_4$ was synthesized according to a procedure reported elsewhere.[1]

Isopropenyl phenylbutyrate **2b** and isopropenyl octanoate **2c** were prepared from isopropenyl acetate **2a** (see SI section). The synthesis is described on p. S16.

GC–MS (EI, 70 eV) analyses were performed with an HP5-MS capillary column (L=30 m, Ø=0.32 mm, film=0.25 mm), and GC analyses (CG/FID) were performed with an Elite-624 capillary column (L=30 m, Ø=0.32 mm, film=1.8 mm). ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. The chemical shifts were reported downfield from tetramethylsilane (TMS), and $CDCl_3$ was used as the solvent.

Reactivity between propan-1,2-diol (PG) and *iso*-propenyl acetate (iPAc) under batch conditions

Dilution effect

Using Amberlyst-15 as catalyst (15.8 mg, 15 wt %, $7.9 \cdot 10^{-2}$ meq H^+), equimolar amounts of PG (**1**) and iPAc (1.39 mmol) were set to react at T = 70 °C adding CPME as solvent (0.5, 1, and 2.5 mL, corresponding to 2.8, 1.4 and 0.6 M solutions), respectively. Figure 1 depicts PG conversion and products' distribution in function of time. For clarity, Figure 1 (taken for the main text) is shown top left.

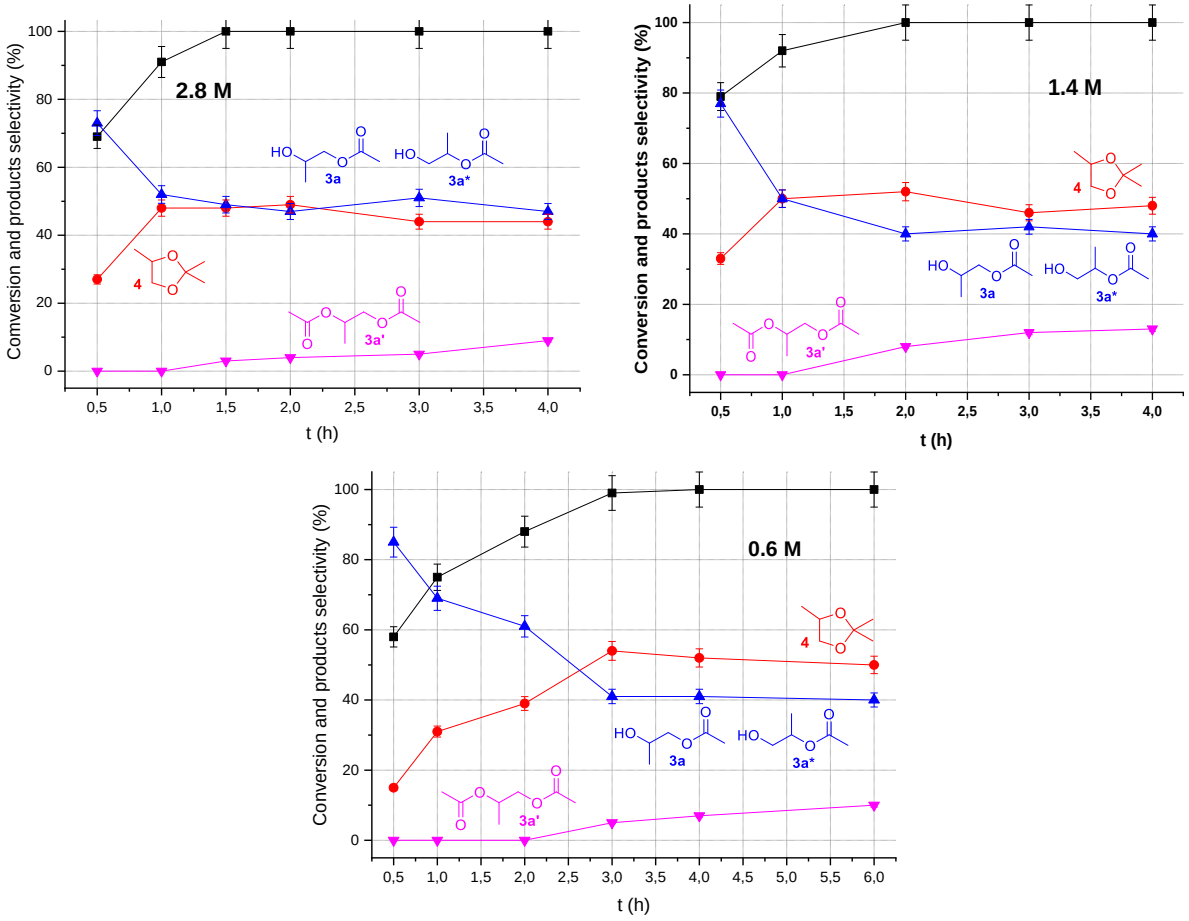
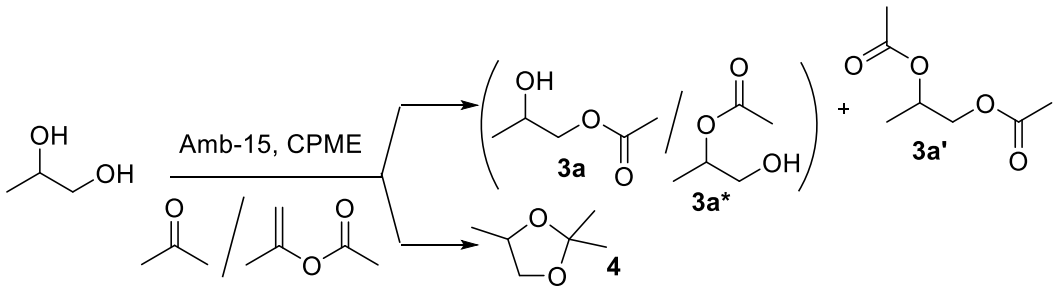


Figure S1. Observed reactivity between PG (1.39 mmol) and iPAc (1.39 mmol, 1 equiv.) using CPME as solvent. Experiments were carried out starting from 2.8 M (top left), 1.4 M (top right) and 0.6 M (bottom) solutions. (-■-) conversion of **1**; (-•-) acetal (**4**) selectivity; (-▲-) mono-acetate (**3a**) selectivity; (-▼-) di-acetate (**3a'**) selectivity.

As expected, employing more diluted reaction mixtures (Figure S1, bottom), resulted in longer reaction times. However, varying the molar concentration between 2.8 - 0.6 M did not alter the selectivity towards transesterification (both mono- and di-acetate, **3a** and **3a'**) and acetalization (**4**) products substantially.

Competitive reactions

Experiments were carried out mixing equimolar amounts of acetone, iPAc and PG (11.3 mmol each) using CPME as solvent (8 mL, 1.4 M) (Scheme S1). After three evacuation/back-fill cycles with N_2, the mixture was set to react at different temperatures (T = 50, 70 and 90 °C), in presence of Amberlyst-15 as catalyst (129 mg, 15 wt %). Figure S2 reports the conversion of PG (**1**) and products' distribution as function of time.



Scheme S1. Competitive reaction of propylene glycol with iPAc and acetone

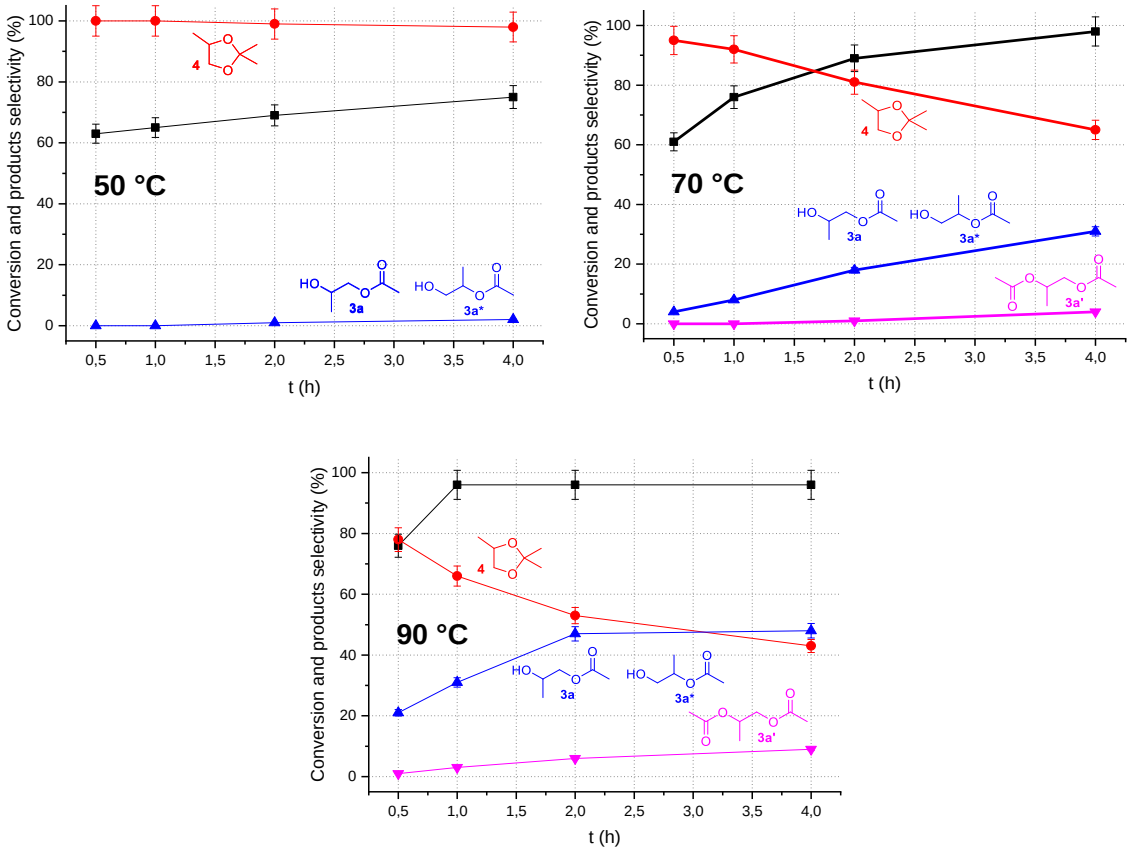
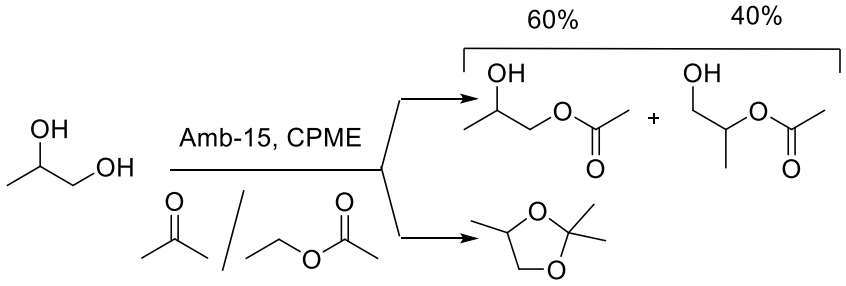


Figure S2. Observed reactivity of equimolar mixtures of acetone, iPAc and PG (11.3 mmol each) using CPME as solvent (8 mL, 1.4 M). Experiments were performed at T = 50 (top left), 70 (top right), and 90 °C (bottom). (-■-) conversion of **1**; (-●-) acetal (**4**) selectivity; (-▲-) mono-acetate (**3a**) selectivity; (-▼-) di-acetate (**3a'**) selectivity.

Additional competitive reactions were carried out under the same conditions described for Figure S2, replacing iPAc with ethyl acetate (Scheme S2). Observed conversions and selectivities are depicted in Figure S3.



Scheme S2. Competitive reaction of propylene glycol with ethyl acetate and acetone

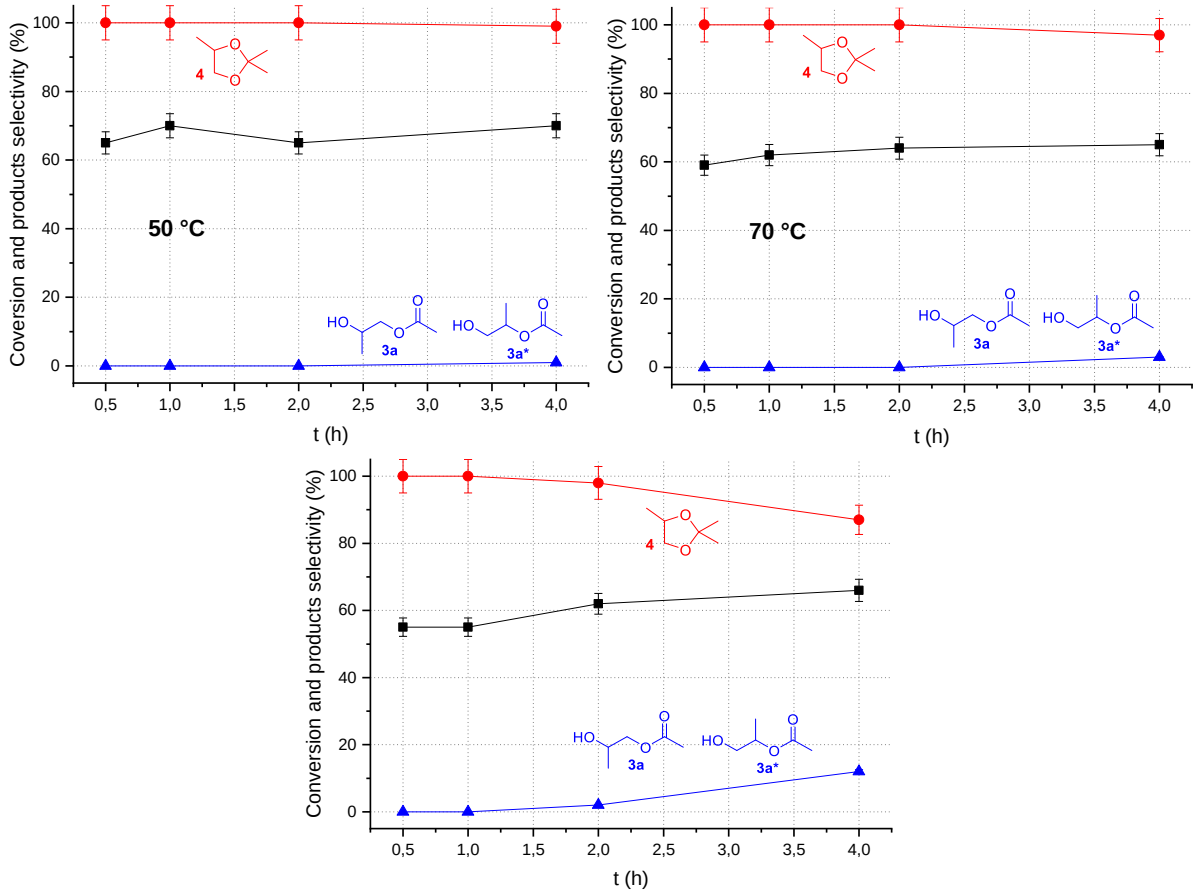


Figure S3. Competitive control experiments between acetone, ethyl acetate and PG (11.3 mmol each) using CPME as solvent (8 mL, 1.4 M). Experiments were carried out at T = 50 (top left), 70 (top right), and 90 °C (bottom), respectively. (-■-) conversion of **1**; (-•-) acetal (**4**) selectivity; (-▲-) mono-acetate (**3a**) selectivity.

Experiments not only confirmed the trend observed in Figure S2, but showed considerably larger differences in the reactivity of acetone compared to ethyl acetate. These were due to a higher reactivity of enol esters towards nucleophilic attack compared to conventional saturated ones.[2]
In analogy to the reaction of isopropenyl acetate, mono-ester isomers **3a** e **3a*** in a 1.5:1 ratio were detected also in this case.

Influence of Reaction Stoichiometry

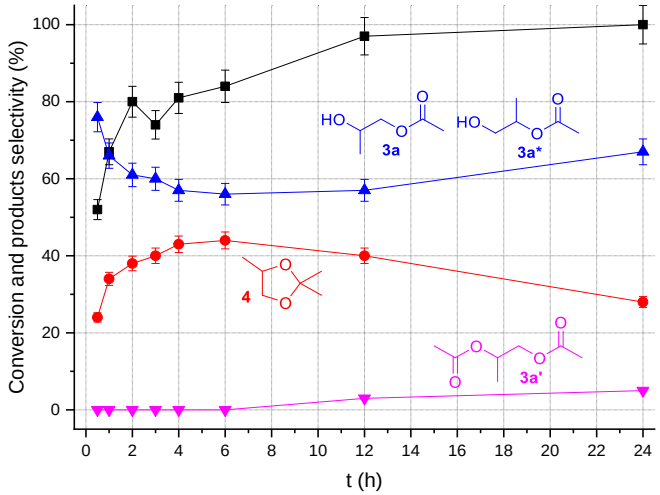


Figure S4. The reaction of PG (1.39 mmol) and iPAc (0.70 mmol) in a 2:1molar ratio, respectively (stoichiometric ratio, Scheme 1), at T = 50 °C, using CPME (1 mL) as solvent. (-■-) conversion of **1**; (-•-) acetal (**4**) selectivity; (-▲-) mono-acetate (**3a**) selectivity; (-▼-) di-acetate (**3a'**) selectivity.

Solvent and catalyst effect

Solvent.

Consistent with the polar nature of the reaction intermediates, tetrahydrofuran (THF), which is slightly more polar than CPME, was investigated as an alternative solvent.[3] Both compounds (THF and CPME) are ethereal solvents.

Transesterification reactions were carried out in THF under the conditions of Figure 1 (PG/iPAc = 1:1 mol/mol) at T = 65 °C (T_{reflux} THF). Reactants' concentration varied between 0.6 and 2.8 M: in all cases, conversion and products distribution in THF were similar to those achieved in CPME (cfr. Figure 1 right and Figure S1). Variations, on average, were within ±3 %.

Both polar aprotic media as CPME and THF improved the tandem sequence by helping the acetalization process, plausibly through solubilization and confinement of (volatile) acetone in the liquid phase of reagents. By contrast, a non-negligible drop of selectivity for the overall tandem process was observed when performing the reaction under solventless conditions: mixing equimolar amounts of **1** and **2a** in presence of Amberlyst-15 (15 wt %) as catalyst at T = 50 °C resulted in quantitative conversion of **2a** in t = 6 h, however diol transesterification prevailed over its acetalization. Products **3a**/**3a*** and **4** were obtained in 56 and 44% yield, respectively.

Common protic solvents as light alcohols were obviously ruled out due to their competitive reactivity with PG, while other commonly employed polar aprotic solvents, such as DMF and DMSO, were not tested because of their high boiling points, difficult separation and/or toxicity.

Catalyst.

The catalytic performance of heterogeneous Amberlyst-15 was compared to that of two homogeneous Brønsted acid catalysts: H_2SO_4, a commonly employed as transesterification catalyst, and an organocatalyst, the ionic liquid $BSMIMHSO_4$. The latter was prepared as above described.[1]

Control experiments were carried out under the conditions of Figure 1: at T = 50 °C: equimolar amounts of **1** and **2a** (1.39 mmol) were dissolved in CPME (1 mL; 1.4 M) and set to react in presence of the chosen acid catalyst. The amount of homogeneous catalyst employed was calculated based on acid sites available for the reaction catalyzed by Amberlyst 15 (15.8 mg, 15 wt %, $7.9 \cdot 10^{-2}$ H^+ m_{eq}). A blank test without catalyst was also performed, confirming that neither transesterification nor acetalization of **1** took place.

Results are reported in Table S1, which summarizes conversion and products' distribution after t = 4 h. For the reader's convenience, results obtained with Amberlyst-15 are also included (Entry 2, Table S1).

Table S1. Acid catalysed tandem acetalyzation/transesterification between PG and iPAc.[a]

Entry	Catalyst (amount, mg)	Conv. (%)[b]	Selectivity[b]		
			3a/3a*[c]	4	3a'
1	None	< 1			
2	Amb-15 (15.8)	78	62	38	
3	H_2SO_4 (3.63)	62	59	36	5
4	$BSMIMHSO_4$ (22.4)	71	61	35	4

[a]All reactions were carried out at T = 50°C for t = 4 h, starting from an equimolar solution of PG and iPAc (1.39 mmol) in CPME (1 mL, 1.4 M). [b]Conversion and selectivity were determined by GC with responses corrected by calibration curves.

The observed products were mono-acetate ester isomers **3a**/**3a*** , dimethyl acetal **4**, and diacetate **3a',** as depicted in Scheme 4. [c]Mixture of isomers **3a** and **3a***.

Among acid catalysts, the organic resin gave not only the highest conversion (78%), but also the best tandem selectivity (entry1, Table S1). Additionally, Amberlyst-15 was easily removed by filtration of the reaction mixture and recycled. This solid was chosen as the catalyst to continue the investigation.

Reactivity of PG with and isopropenyl phenylbutanoate 2b and isopropenyl octanoate 2c

Effect of the reaction temperature

The reaction of PG with isopropenyl phenylbutyrate (**2b**) and isopropenyl octanoate (**2c**) was explored in the range of 50-110 °C, under the same conditions of Figure 1 (main text). An equimolar mixture of PG (1.39 mmol) and **2b** (or **2c**) was dissolved in CPME as a solvent (1 mL; [**1**]=[**2b/c**]=1.4 M) and set to react in the presence of Amberlyst-15 (15.8 mg; 15% mol) as a catalyst.
Results are summarized in Figure S5A-C

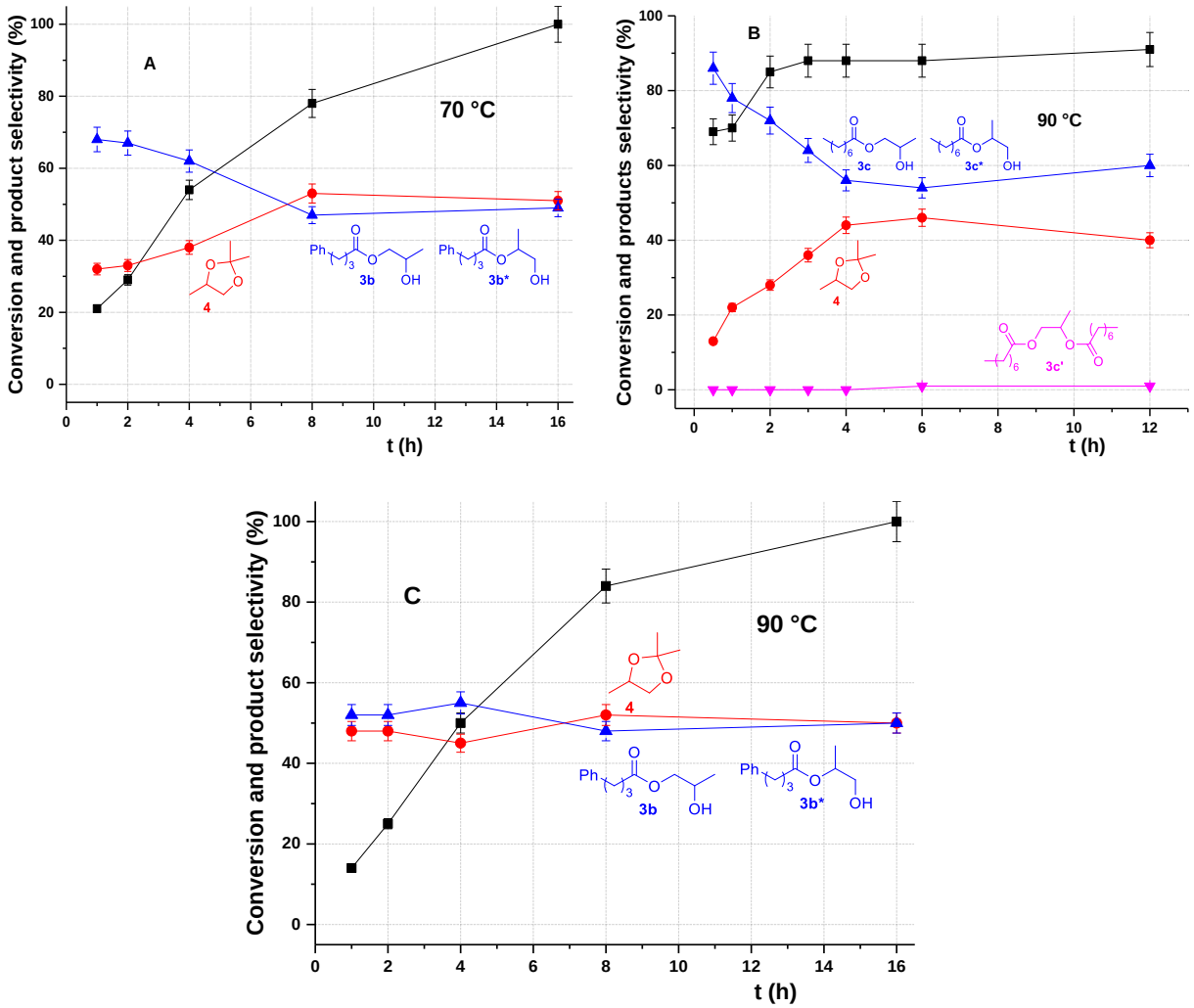


Figure S5. The reaction of an equimolar solution of propylene glycol (**1**, 1.39 mmol) with: A) *i*-propenyl phenylbutyrate (**2b**) at 70 °C; B) *i*-propenyl octanoate (**2c**) at 90 °C; C) *i*-propenyl phenylbutyrate (**2b**) at 90 °C. Other conditions: CPME solvent (1 mL) and Amberlyst-15 (15 wt%). Reactions at 90 °C were carried out in a closed vessel (autoclave). (-■-) conversion of **1a**; (-●-) acetal (**4**) selectivity; (-▲-) mono-ester isomer product (**3b**/**3b***, left; **3c**/**3c***, right) selectivity; (-▼-) di-ester product (**3c'**, right) selectivity.

Continuous-flow (CF) apparatus

A schematic chart of the experimental setup used for continuous-flow (CF) reactions is depicted in Figure S6.

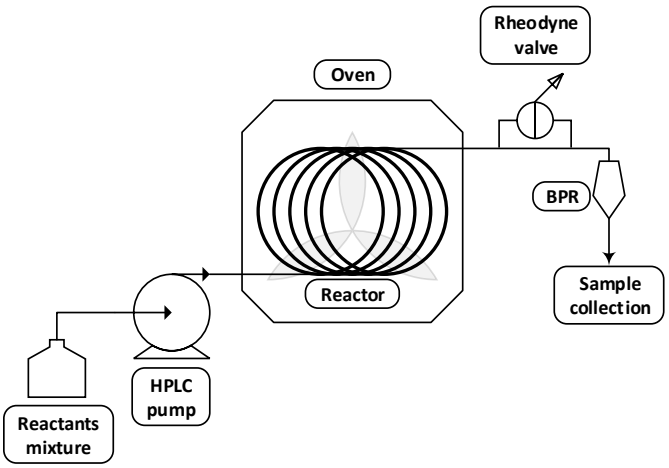


Figure S6. Experimental setup used for continuous-flow reactions.

The apparatus was assembled in-house. An HPLC pump was used to convey the reactants solution (diol, enol ester, and THF or CPME solvent) to a stainless-steel tubular reactor (l = 12 cm, i.d. = ¼", inner volume = 1.16 cm^3) filled with the heterogeneous catalyst (Amberlyst-15: 0.8 g). The reactor was placed horizontally inside a thermostated fan oven and heated at the desired operating temperature (30-70 °C). At the outlet of the reactor, a manual Swagelok KPB1N0G412 back pressure regulator (BPR), equipped with an electronic pressure sensor, was used to control the system pressure. Reactions were all carried out at a pressure of 1.3-1.5 bar slightly above ambient conditions to overcome the pressure drop within the continuous-flow system. A Rheodyne valve (7725i) with a 100 µL loop, was placed between the reactor and the BPR and used to sample the reaction mixture. In the case of reactions using THF, even when the temperature (70 °C) was slightly above the boiling point of the solvent, the process took place smoothly due to dynamic conditions in the plug-flow type reactor. Mixtures collected at the outlet of the CF-reactor were analyzed by GC and GC/MS, and the corresponding conversion of **1** and products distribution were determined as described for batch reaction.

Mass balance for reactions of Figure 2

Table S2. Mass balance for the reaction of PG (**1**) and iPAc (**2a**) under the conditions of Figure 2A-C. Conditions: THF solvent, 3h, Amberlyst-15 (0.8 g), [**1**]=[**2a**]=1.2 M.

Entry	T (°C)	Flow rate (mL min^{-1})	Mass flow (mL)		Conv. (%)[c]	Product selectivity (%)				Yield 3a/3a* (g, %)[e]
			In[a]	Out[b]		3a/3a*	4	3a'	Tandem selectivity[d]	
1	30	0.1	18	17.8	74	48	52	-	100	
2		0.3	54	53	48	52	48	-	100	1.8, 94
3		0.6	108	106	33	58	42	-	100	
4	50	0.1	18	17.2	96	34	57	9	91	
5		0.3	54	52.5	93	39	52	9	91	
6		0.6	108	105	78	42	49	9	91	
7	70	0.1	18	17.5	95	38	52	11	90	
8		0.3	54	52.3	97	28	53	19	81	
9		0.6	108	106	83	32	48	20	80	

[a] Volume of reactants solution delivered to the CF-reactor. [b] Volume of solution (unconverted reagents plus products of the esterification and acetalization reactions) collected at the outlet of the CF-reactor. [c] Conversion of 1,2-propanediol; [d] Total selectivity of the tandem reaction for the formation of monoester isomers **3a**/**3a*** and the acetal **4**.[e] Isolated yield of monoester isomers **3a**/**3a*** after vacuum distillation of the mixture (out) collected at the end of reaction of entry 2.

Fresh and used Amberlyst-15

Weight measures. Before use, Amberlyst-15 was dried under vacuum (10 mbar) at 70 °C for 24 h. The solid was allowed to rehydrate by exposure to air for 62 h. Thereafter, a carefully weighed amount (0.807 g) of the resin was used to fill the continuous-flow reactor of figure of the setup in Figure S6. After use, once the experiment of Figure 3 was complete (30 °C, 0.3 mL min^{-1}, 160 h), the catalytic bed was washed with methanol (50 mL at 5 mL min^{-1}) and acetone (50 mL at 5 mL min^{-1}). The catalyst was then removed from the reactor, and dried (70 °C, 10 mbar, 24 h) and rehydrated (air, 62 h) as described above for the fresh catalyst. The solid resin was then weighed. The ponderal difference was ca 1.2%. Results are reported in Table S3.

Table S3. Weight of Amberlyst-15 before and after use in the continuous flow apparatus.

Entry	Catalyst	Weight (g)
1	*Fresh*[a]	0.807
2	*Used*[b]	0.817

[a] Fresh catalyst loaded in the CF-reactor; [b] Catalyst after 160 h of time-on-stream, in the reaction of 1,2-propanediol and isopropenyl acetate (conditions of Figure 3).

Titration of Amberlyst-15. The acid exchange capacity of both the fresh and the used catalysts was determined by acid-base titration with standard NaOH solution according to procedure reported elsewhere.[4] In a typical experiment, a solid sample of Amberlyst-15 (0.05 g; weight determined after

drying/rehydration of the catalyst, according to the above described method) was suspended in an aqueous NaCl solution (2 M; 25 mL) and stirred at room temperature for 24 h until the resin was completely Na-exchanged and its original acidity released in solution. Thereafter, the resulting suspension was titrated with standard NaOH solution ($5x10^{-3}$ M). Bromothymol blue was used as indicator. The titration was repeated three times for each sample. Results are reported in Table S4 for the Amberlyst-15 resin as received from the supplier, and the resin after its use for 160 h as a catalyst for the continuous-flow reaction of 1,2-propanediol and isopropenyl acetate under the conditions of Figure 3.

Table S4. Acid titre of the Amberlyst-15 before and after its usage.

Sample	**Titrating solution (mL)[a]**			**Concentration of active sites (eq/Kg)[b]**			
	T_1	T_2	T_3	T_1	T_2	T_3	Average[c]
fresh Amb-15	28.5	27.8	28.2	2.7	2.7	2.7	2.7
used Amb-15	30.5	31.2	31.6	2.8	2.8	2.8	2.8

[a] Amounts (mL) of aq. NaOH solution ($5x10^{-3}$M) added for the titration of the aq. suspension of the Na-exchanged resin. [b] Equivalents of H^+ acid sites per Kg of wet resin determined in three independent titration tests (T_1, T_2, and T_3, respectively). [c] Average acid titre of the resin.

The supplier (Sigma-Aldrich) of Amberlyst-15 reports that acid sites of the product are ≤ 4.7 eq/Kg.

CF reactions between PG and iPAc

Effect of CPME as solvent

An equimolar solution of **1** and **2a** ([**1**] = [**2a**] = 1.2 M) in CPME, was fed continuously to a tubular stainless-steel reactor filled with the catalyst (Amberlyst-15, 0.8 g) (other details of the CF-apparatus are described in the experimental section and in Figure S6). Tests were carried out at atmospheric pressure by varying T and flow rate (F) between 30-50 °C and 0.1-0.6 mL·min^{-1}, respectively. Reaction mixtures were collected at the outlet of the CF-reactor and analyzed by GC and GC/MS. Conversion of **1** and products' distribution were determined as previously described for batch reactions. The results are summarized in Figure S7: a 3D-view was chosen to report composition of reaction mixtures after t = 3 h as a function of the operating temperature and flow rates.

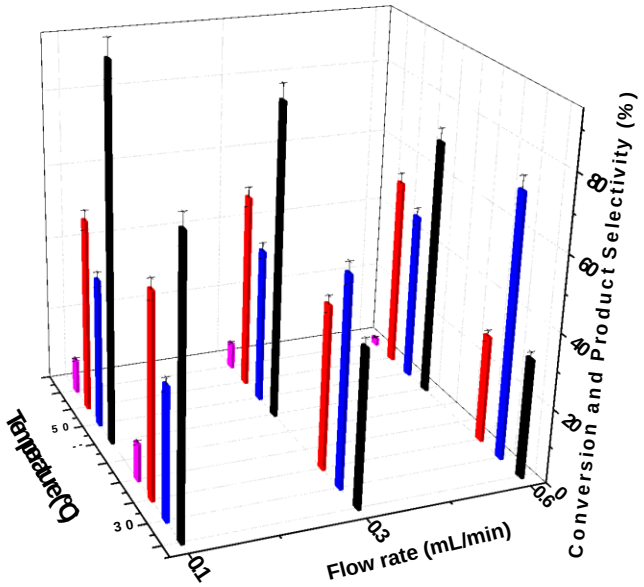


Figure S7. Tandem CF transterification/ acetalization between equimolar amounts of PG (**1**) and iPAc (**2a**) in CPME ([**1**] = [**2a**] = 1.2 M), in presence of Amberlyst-15 (0.8 g). The flow rate was set at 0.1, 0.3, and 0.6 mL·min^{-1} and the operating T was varied between 30 and 50 °C. The reaction time was t = 3 h in all cases. (-■-) conversion of **1**; (-■-) acetal (**4**) selectivity; (-■-) mono-acetate (n**3a**) selectivity; (-■-) di-acetate (**3a'**) selectivity.

Choosing CPME as solvent had minor effects on PG conversion, but generally favoured the esterification process. This was noticed when performing the tandem reaction at T = 30 °C, observing formation of the corresponding transesterification (**3a/3a***) and acetalization (**4**) products in selectivity of 56 and 44 % at F = 0.3 mL·min^{-1}, and 71 % and 29 % at F = 0.6 mL·min^{-1}, respectively. Although this behaviour is still unclear, short contact times of CF-reactions likely emphasized the differences in boiling points and dielectric constants of THF (66 °C and 7.58) and CPME (106 °C and 4.76). Other properties as η, ρ, and surface tension are indeed very similar from one solvent to another.[5]

Effect of reactants' molar ratio

A 2:1 mol/mol mixture of PG and iPAc (Scheme 4) in THF ([**1**] = 1.0 M, [**2a**] = 0.5 M), was set to react under CF-conditions. CF-reactions were performed at F = 0.3 mL·min^{-1}, varying the operating temperature between 30, 50 and 70 °C. The observed reaction outcome is depicted in Figure S8.

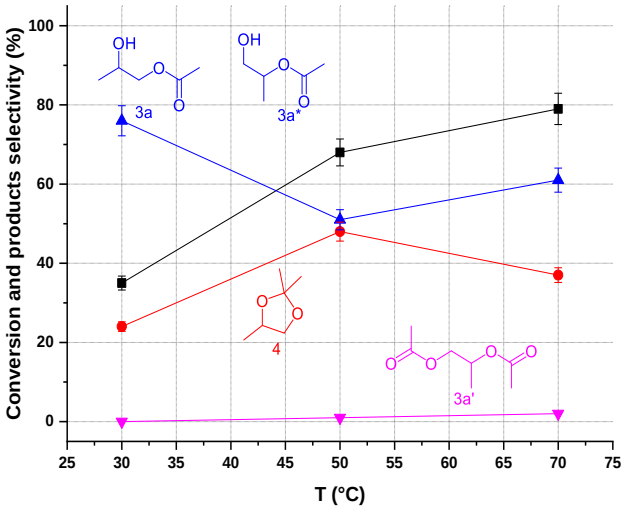


Figure S8. Reactivity profile for the tandem transesterification/acetalization between PG and iPAc, where PG/iPAc = 2:1 mol/mol. The reaction was performed in THF ([PG] = 1 M, [iPAc] = 0.5 M) and catalysed by Amberlyst-15 (0.8 g). Other conditions: F = 0.3 mL·min^{-1}; T = 30, 50, and 70 °C, t = 3 h. (-■-) conversion of **1**; (-■-) acetal (**4**) selectivity; (-■-) mono-acetate (**3a/3a***) selectivity; (-■-) di-acetate (**3a'**) selectivity.

The mixture of isomeric monoesters **3a**/**3a*** was the predominant product when performing the reaction at T = 30 °C, suggesting that the acetone concentration was not sufficient to impart an adequate acetalization rate. Increasing the temperature to T = 50 °C, instead, resulted in an increase of conversion to 68 % and improved the kinetics of the acetal formation so that the expected tandem products formed with comparable selectivities (51 % for **3a/3a***and 48 % for **4**). A further increase of the operating temperature to T = 70 °C led to an unbalanced products' distribution, favouring the formation of transesterification derivatives **3a**/**3a*** as well as undesired diesterification product **3a'**.

Different reagents in the CF-mode: enol esters 2b and 2c.

CF-reactions of 1,2-propanediol and *i*-propenyl -phenylbutyrate **2b**, or -octanoate **2c**, were explored in the CF-mode using the same catalytic bed (Amberlyst-15, 0.8 g) previously described. Under the conditions of Figure 4 (F=0.3 mL min^{-1}, [**1**]=[**2b/2c**]=1.4 M), the usage of compounds **2b** and **2c** was in the range of 4.5-5 g h^{-1}. The need for such a large amount limited the investigation since both esters since were not commercially available, and their synthesis was not easily scalable (see p. S16). Most salient results are summarised in Table S2. Reaction mixtures were collected at the reactor outlet and analysed after 4 hours, once steady conversion and products distribution were reached. Values for such variables (conversion and selectivity) differed by less than 5% in duplicated runs.

CF-experiments showed that reactions required a progressive increase of the temperature, from 30 to 50 and 70 °C, when the enol ester was changed from acetate to phenylbutyrate and octanoate, respectively (compare Figure 4 and Table S3). This trend confirmed the same reactivity order observed under batch conditions: **2a**>**2b**>**2c**. However, the limited number of tests did not allow any optimisation of the tandem selectivity.

Table S5. The reaction of 1,2-propanediol with *i*-propenyl esters **2b** and **2c** in the continuous-flow mode.

Entry	Enol ester	T (°C)	Flow rate (mL/min)	Conv (%)[a]	Product selectivity (%)[a]			
					3b/3b*	3c/3c*	3c'	4
1	**2b**	50	0.3	88	75			25
2	**2c**	70	0.3	83		68	1	31

Reactions were carried using an equimolar (1.4 M) solution of 1,2-propanediol and enol ester, **2b** or **2c**, in THF as the solvent. [a] Conversion of 1,2-propanediol, products distribution, and mass balance were validated and determined by an external standard (see experimental). Data refer to 4 h runs. Mono-ester isomers **3b-3b*** and **3c-3c*** formed in a 1.5:1 ratio.

Reaction of EG (5) with isopropenyl esters 2a, 2b, and 2c.

*Reaction of 5 with enol esters **2a**, **2b**, and **2b** under batch conditions.* An equimolar solution of **5** and **2a** (1.39 mmol) in CPME as a solvent (1 mL; [**1**]=[**2a**]=1.4 M) was set to react in the presence of Amberlyst-15 (15.8 mg, 15 wt%, $7.9 \cdot 10^{-2}$ H^+ meq) as a catalyst. Two sets of tests were run at 70 and 90 °C, for 4 hours, in all cases. In the case of 2a, additional experiments were run also at 50 °C. Glass reactors were used up to 70 °C, while stainless-steel autoclaves were dedicated for tests at 90 °C to avoid loss of volatiles by evaporation (acetone and acetal products). The structures of products, conversion and selectivity were assigned and determined as described for PG (see experimental and SI).

Figures S9A-C detail the profiles of conversion and selectivity for the reaction of each single enol ester, at 70 and 90 °C, respectively.

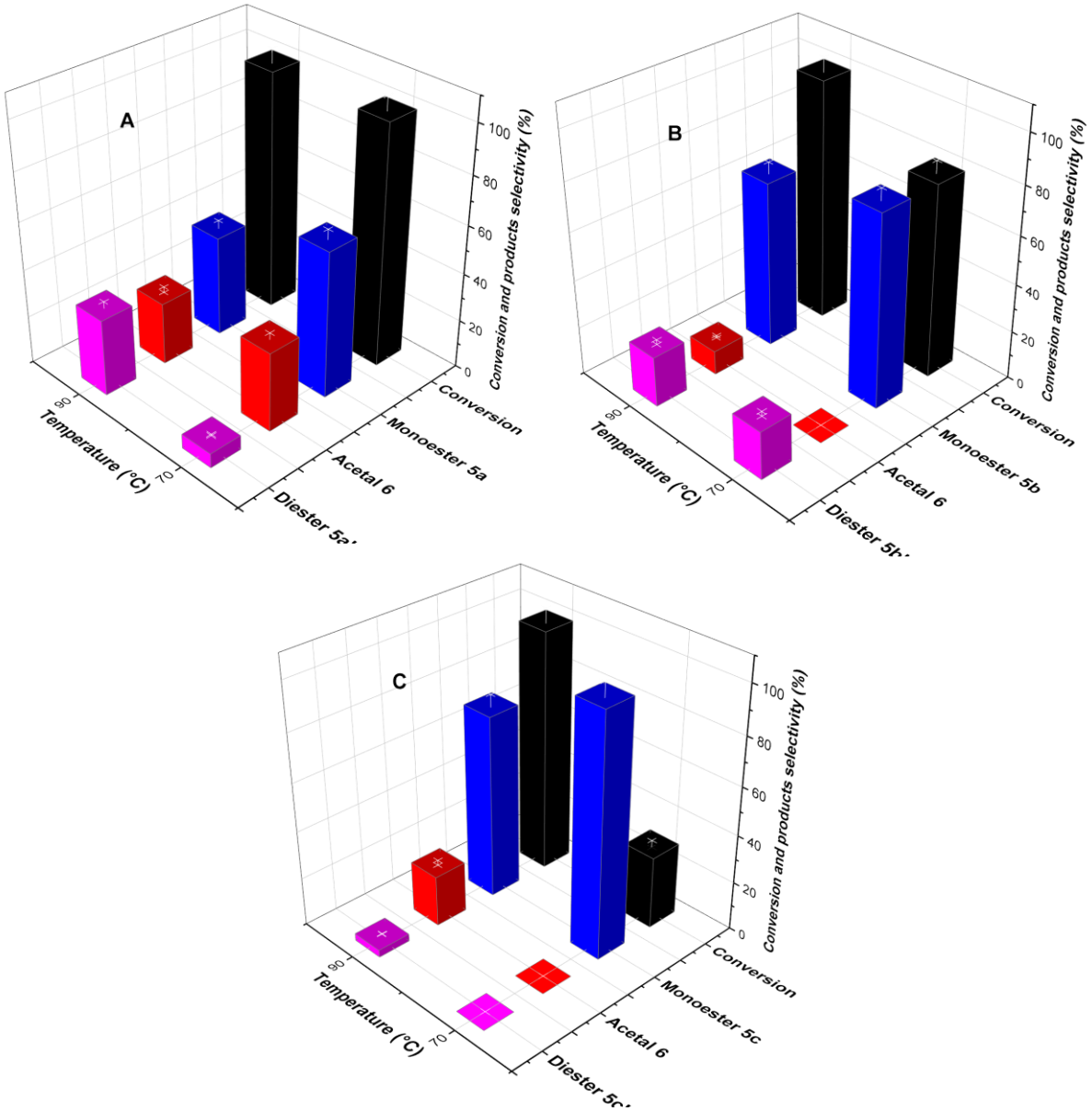


Figure S9. The reaction of an equimolar solution of ethylene glycol (**5**, 1.39 mmol) with: A) *i*-propenyl acetate (**2a**); B) *i*-propenyl phenylbutyrate (**2b**); C) *i*-propenyl octanoate (**2c**). Other conditions: CPME solvent (1 mL) and Amberlyst-15 (15 wt%). (-■-) conversion of **5**; (-■-) acetal (**5**) selectivity; (-■-) mono-ester product (**5a** or **5b** or **5c**) selectivity; (-■-) di-ester product (**5a'** or **5b'** or **5c'**) selectivity.

Additional experiments carried out in an autoclave at 70 and 90 °C under a moderate pressure of N_2 (8 bar) thought to favour condensation of acetone in the liquid phase and aid the acetalization step, proved unsuccessful.

*Reaction of **5** and **2a** in the continuous-flow mode*. A solution of **5** and **2a** in THF was continuously delivered to a tubular stainless-steel reactor filled with the catalyst (Amberlyst-15, 0.8 g) (Details of the CF-apparatus are described in the Experimental Section and in Figure S6). Tests were carried out at atmospheric pressure by varying T, flow rate (F), reactants' concentrations and relative molar ratio as shown in Table S6. Reaction mixtures were collected at the outlet of the CF-reactor and analyzed by GC and GC/MS. Conversion of **5** and products distribution were determined as previously described for batch reactions.

Table S6. Continuous-flow reaction between EA (**5**) and iPAc (**2a**).

Entry	Flow rate ($mL \cdot min^{-1}$)	T (°C)	2a:5 (mol:mol)	Conc. (M)[a]	Conv. (%)[a]	Product selectivity (%)[a]		
						5a	5a'	6
1	0.1	30	1:1	1.2	73	69		31
2	0.1	50	1:1	1.2	98	69	4	27
3	0.1	70	1:1	1.2	99	69	9	22
4	0.3	50	1:1	1.2	94	67	2	31
5	0.6	50	1:1	1.2	75	67	1	32
6	0.9	50	1:1	1.2	65	69	1	30
7	0.1	50	1:1	2.4	97	69	4	27
8	0.1	50	1:1	4.8	99	79	3	18
9	0.1	50	0.5:1	1.2	68	71		29

[a]Molar concentration of **5** in THF

Isopropenyl esters

The synthesis of isopropenyl esters (iPEs)

The preparation of iPEs was carried out by adapting already reported protocols based on both the esterification of carboxylic acids and the nucleophilic substitution of acyl chlorides.[6,7] In a typical example, a mixture of octanoic acid (0.51 g, 3.55 mmol) or octanoyl chloride (0.52 g, 3.20 mmol), isopropenyl acetate (**2a**, 3.47 g, 34.70 mmol), and H_2SO_4 (17.4 mg, 0.17 mmol) as a catalyst, was subjected to four evacuation/back-fill cycles with N_2 and set to react at 95 °C under stirring. Once the reaction was complete, the product (isopropenyl octanoate, **2c**) was purified by FCC (see below), and isolated as a colorless liquid. Yields were 31 and 90 % starting from the acid and the chloride as reactants, respectively.
Isopropenyl phenylbutyrate (**2b**) was prepared by the same methods: yields of **2b** were 42 and 85% starting from phenylbutyric acid and phenylbutyric chloride, respectively.
The synthesis of compound **2c** was also carried out starting from the reaction of isopropenyl acetate with either octanoic acid or octanoyl chloride in the presence of $BSMIMHSO_4$ (55.0 mg, 0.17 mmol) as a catalyst, in place of H_2SO_4. Product **2c** was obtained in 45 and 56% GC/MS-yields, form acid and chloride, respectively.
Products **2b** and **2c** were characterized by both ^{1}H and ^{13}C NMR and GC/MS analyses. Spectra are reported below.

General isolation procedure

Isopropenyl esters (**2b**, **2c**) were isolated by flash column chromatography (stationary phase: neutral Al_2O_3, eluent: petroleum ether/ethyl acetate 9:1 v/v).

Prop-1-en-2-yl 4-phenylbutanoate (isopropenyl phenylbutyrate, 2b)

The product was isolated in 85% yield upon reactin g4-phenylbutanoic chloride (0.5 g, 2.49 mmol) and iPAc (2.503 g, 24.9 mmol) in presence of H_2SO_4 (25.5 mg, 0.26 mmol) as catalyst.

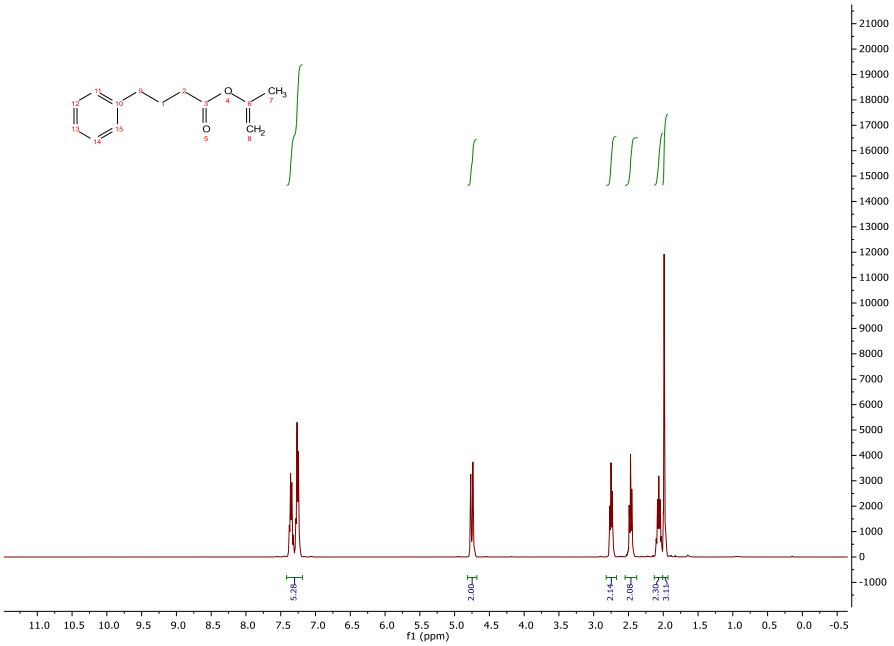


Figure S10. ^{1}H NMR spectrum of compound **2b**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 7.32-7.23 (m, 5H), 4.70 (m, 2H), 2.71 (m, 2H), 2.43 (t, *J* = 7.46 Hz, 2H), 2.10 (m, 2H), 1.95 (d, *J* = 1.10 Hz, 3H).

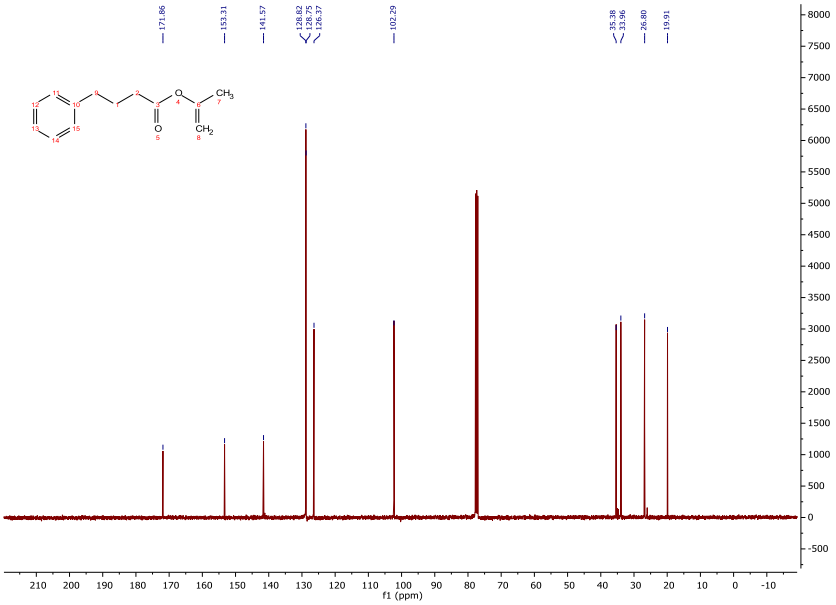


Figure S11. ^{13}C NMR spectrum of compound **2b**.

^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 171.86, 153.31, 141.57, 128.82, 128.75, 126.37, 102.29, 36.38, 33.96, 26.80, 19.91.

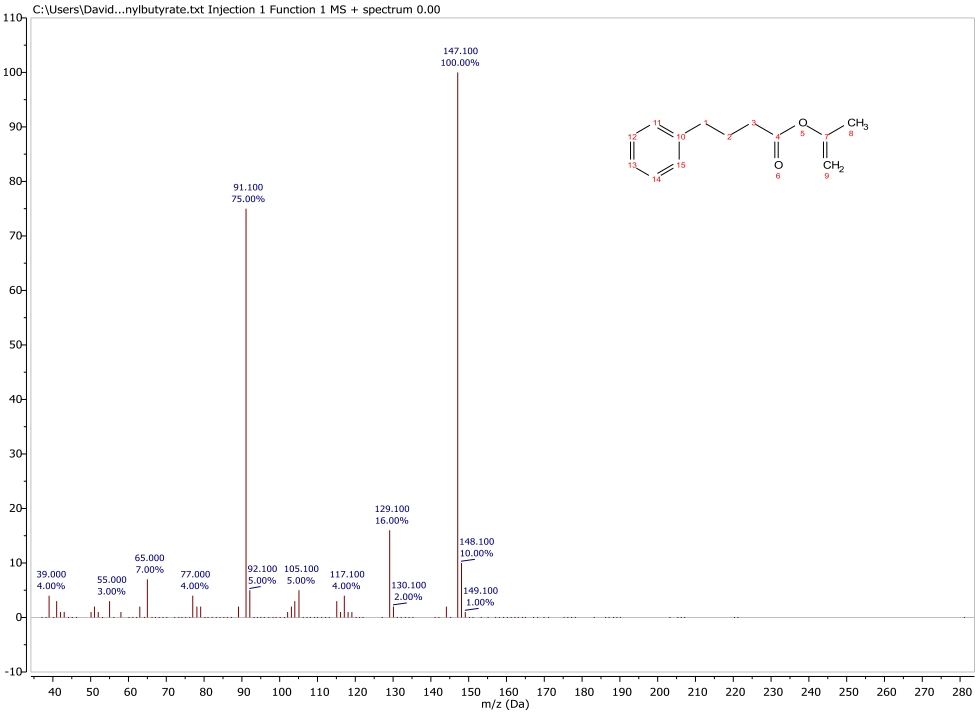


Figure S12. MS spectrum of compound **2b**.

GC/MS (EI, 70 eV) *m/z*: 148 (10), 147 (100), 129 (16), 117 (4), 105 (5), 92 (5), 91 (75), 65 (7), 39 (4).

Prop-1-en-2-yl octanoate (isopropenyl octanoate, 2c)

The product was isolated in 90% yield upon reacting octanoyl chloride (0.5 g, 3.09 mmol) and iPAc (3.1 g, 30.9 mmol) in presence of H_2SO_4 (25.1 mg, 0.25 mmol) as catalyst.

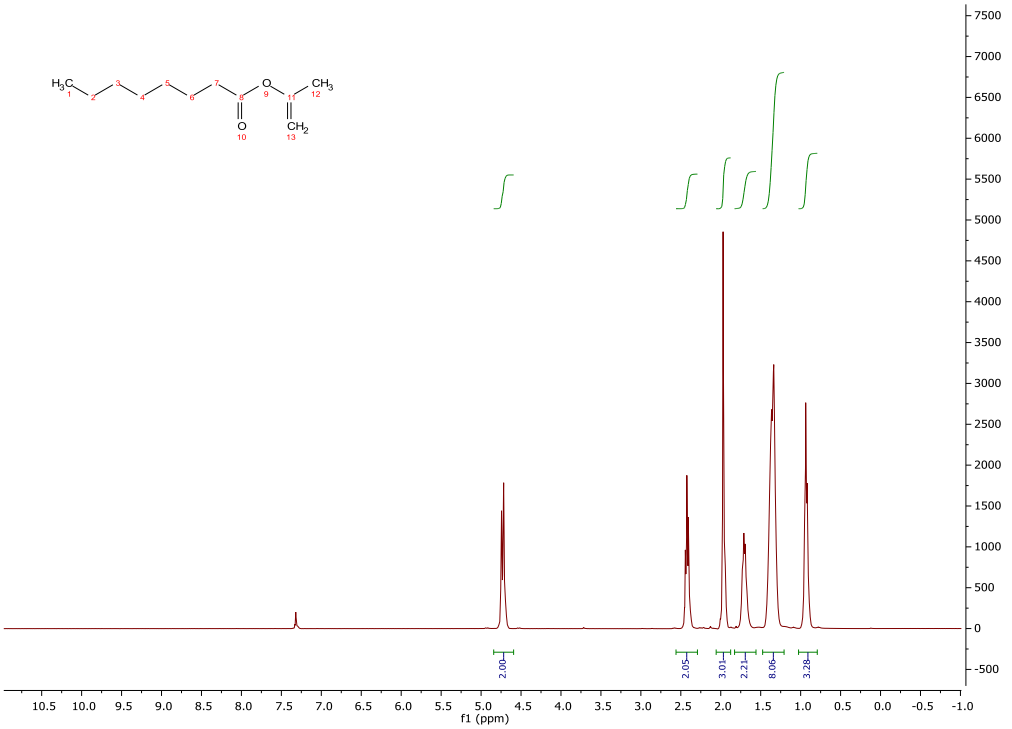


Figure S13. ^{1}H NMR spectrum of compound **2c**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 4.69 (m, 1H), 4.67 (dd, 1H), 2.38 (t, 2H), 1.92 (d, 3H), 1.58-1.72 (m, 2H), 1.20-1.40 (m, 8H), 0.89 (m, 3H).

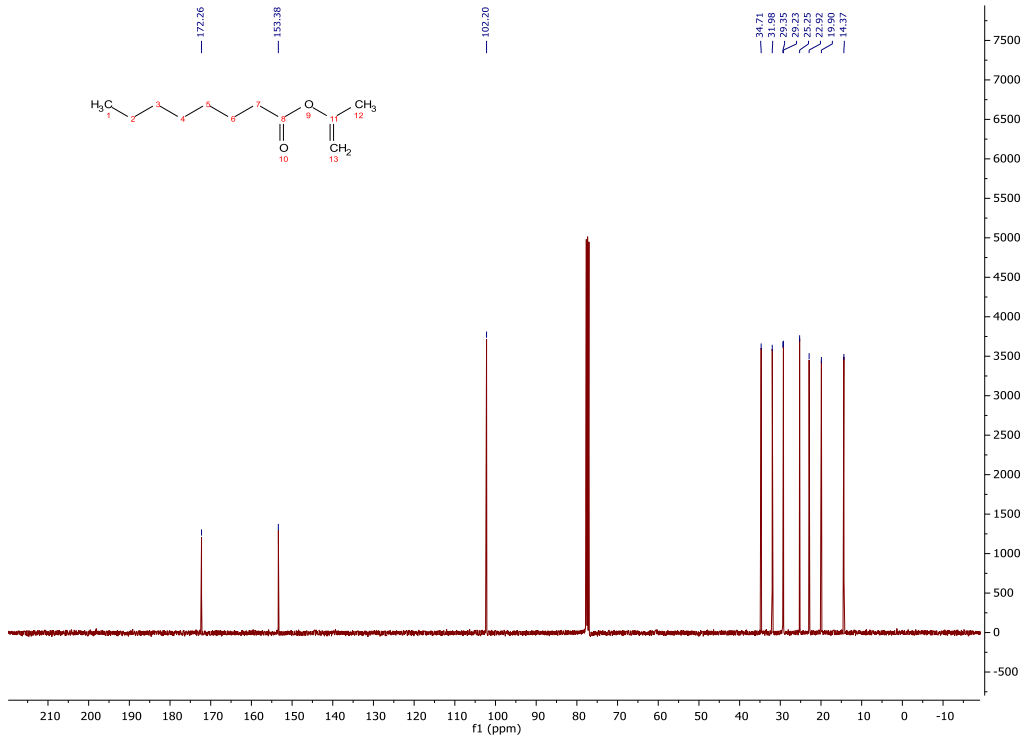


Figure S14. ^{13}C NMR spectrum of compound **2c**.

$^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 172.26, 153.38, 102.20, 34.71, 31.98, 29.35, 29.23, 25.25, 22.92, 19.90, 14.37.

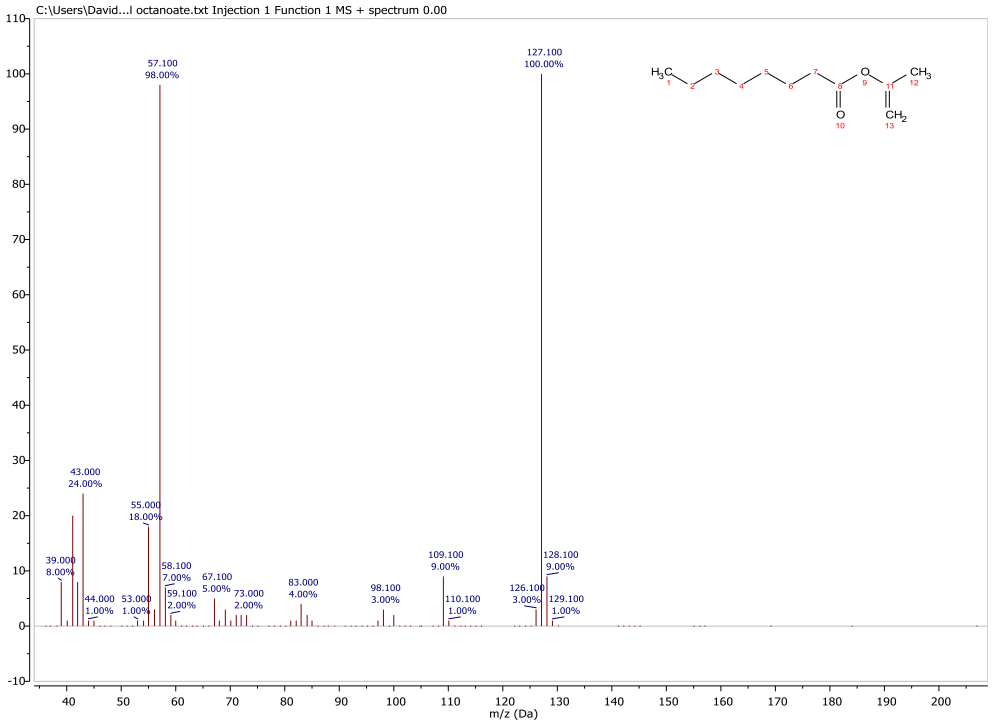


Figure S15. MS spectrum of compound **2c**.

GC/MS (EI, 70 eV) *m/z*: 128 (9), 127 (100), 109 (9), 67 (5), 57 (98), 55 (18), 43 (24), 42 (8), 41 (20), 39 (8).

Characterization of acetalization and transesterification products from tandem reactions

Starting from propylene glycol, the observed acetalization and transesterification products were propanediol acetal (2,2,4-trimethyl-1,3-dioxolane, **4**), propanediol monoacetate (2-hydroxypropyl acetate **3a** and 1-hydroxypropan-2-yl acetate **3a***), propanediol diacetate (1,2-diacethoxy propane, **3a'**), propanediol monophenylbutyrate (2-hydroxypropyl 4-phenylbutanoate **3b**, and 1-hydroxy propan-2-yl 4-phenylbutanoate **3b***), 2-(3-phenylpropoxy)propyl 4-phenylbutanoate (**3b'**), and propanediol monooctanoate (2-hydroxypropyl octanoate **3c** and 1-hydroxypropan-2-yl octanoate **3c***), propanediol dioctanoate (propylene glycol dicaprilate, **3c'**).
Starting from ehtylene glycol, the observed acetalization and transesterification products were ethylenglycol acetal (2,2-dimethyl-1,3-dioxolane, **6**), ethylene glycol monoacetate (2-hydroxyethyl acetate, **5a**), ethylene glycol diacetate (**5a'**), ethylene glycol monophenylbutyrate (2-hydroxyethyl 4-phenylbutanoate, **5b**), ethylene glycol diphenylbutyrate [2-(3-phenylpropoxy)ethyl 4-phenylbutanoate, **5b'**], and ethylene glycol monooctanoate (2-hydroxyethyl octanoate, **5c**), ethylene glycol dioctanoate (ethyleneglycol dioctanoate, **5c'**).

General isolation procedure for propanediol monoesters

Propanediol monoesters (**3a/3a***, **3b/3b***, **3c/3c***) were isolated by flash column chromatography (stationary phase: SiO_2, eluent: petroleum ether/ethyl acetate 9:1 v/v).

General isolation procedure for propanediol diesters

Propanediol diesters (**3a'**, **3b'**, **3c'**) were isolated upon washing the reaction mixture with a saturated $NaHCO_3$ solution (3x10 mL).

General isolation procedure for ethylene glycol diesters

Ethylene glycol diesters (**5a'**, **5b'**, **5c'**) were isolated upon washing the reaction mixture with a saturated $NaHCO_3$ solution (3x10 mL).

2-hydroxypropyl acetate, 1-hydroxypropan-2-yl acetate (propanediol monoacetates, 3a,3a*)

Products were isolated both in batch and continuous flow conditions:

i) batch: in 89% yield upon reacting of iPAc (1.3 g, 13.14 mmol) and PG (1.0 g, 13.19 mmol) in presence of Amberlyst-15 (150.5 mg) as catalyst.

ii) continuous flow: in 94% yield collecting the output mixture obtained upon mixing iPAc and PG using THF as solvent (iPAc/PG/THF molar ratio = 1:1:10) at T = 30 °C for t = 8h (other conditions: F = 0.3 mL·min^{-1}, [iPAc] = [PG] = 1.2 M).

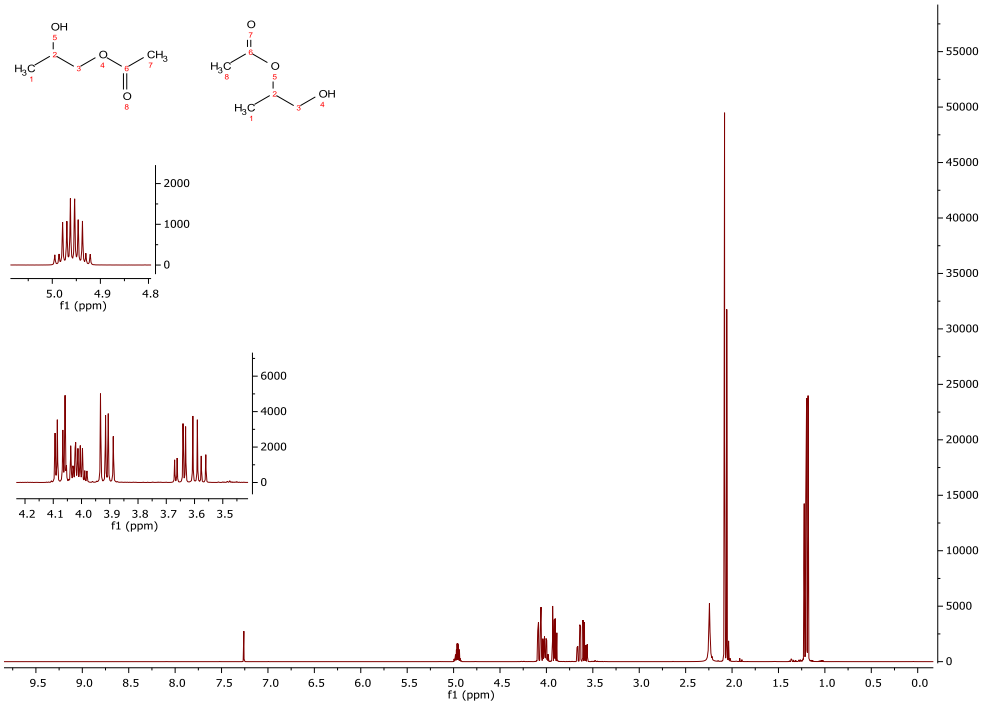


Figure S16. ^{1}H NMR spectrum of compounds **3a** and **3a***.

3a: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 4.09-3.90 (m, 2H), 4.02 (m, 1H), 2.08 (s, 3H), 1.19 (d, 3H).

3a*: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 4.95 (m, 1H), 3.60 (m, 2H), 2.09 (s, 3H), 1.21 (d, 3H).

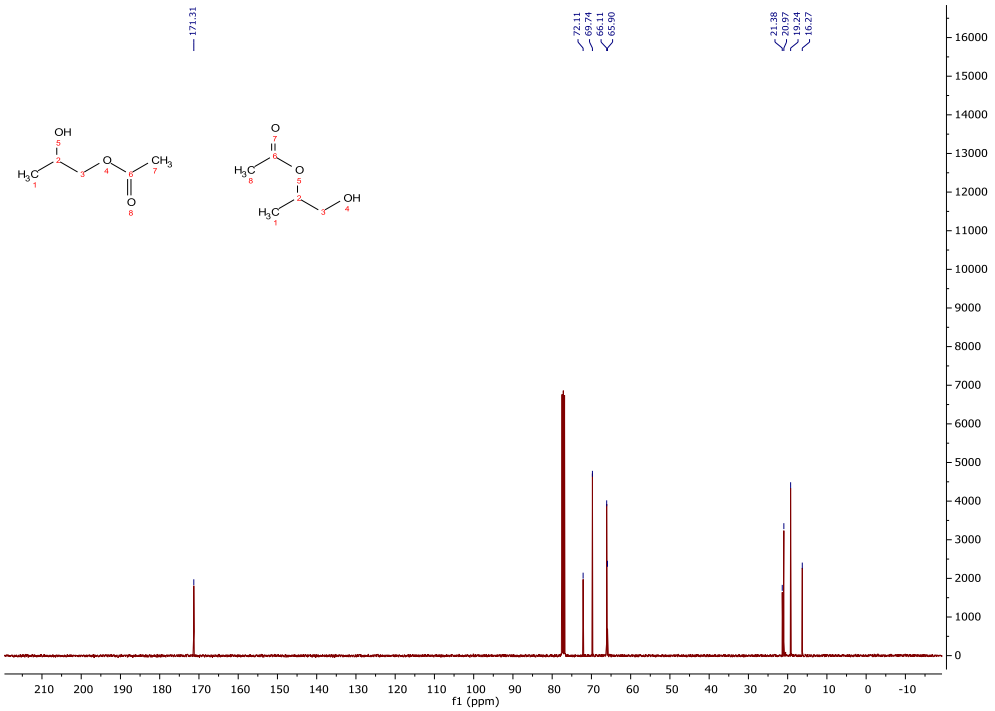


Figure S17. ^{13}C NMR spectrum of compounds **3a** and **3a***.

3a: ^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 171.31, 69.74, 66.11, 20.97, 19.24.

3a*: ^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 171.31, 72.11, 65.90, 21.38, 16.27.

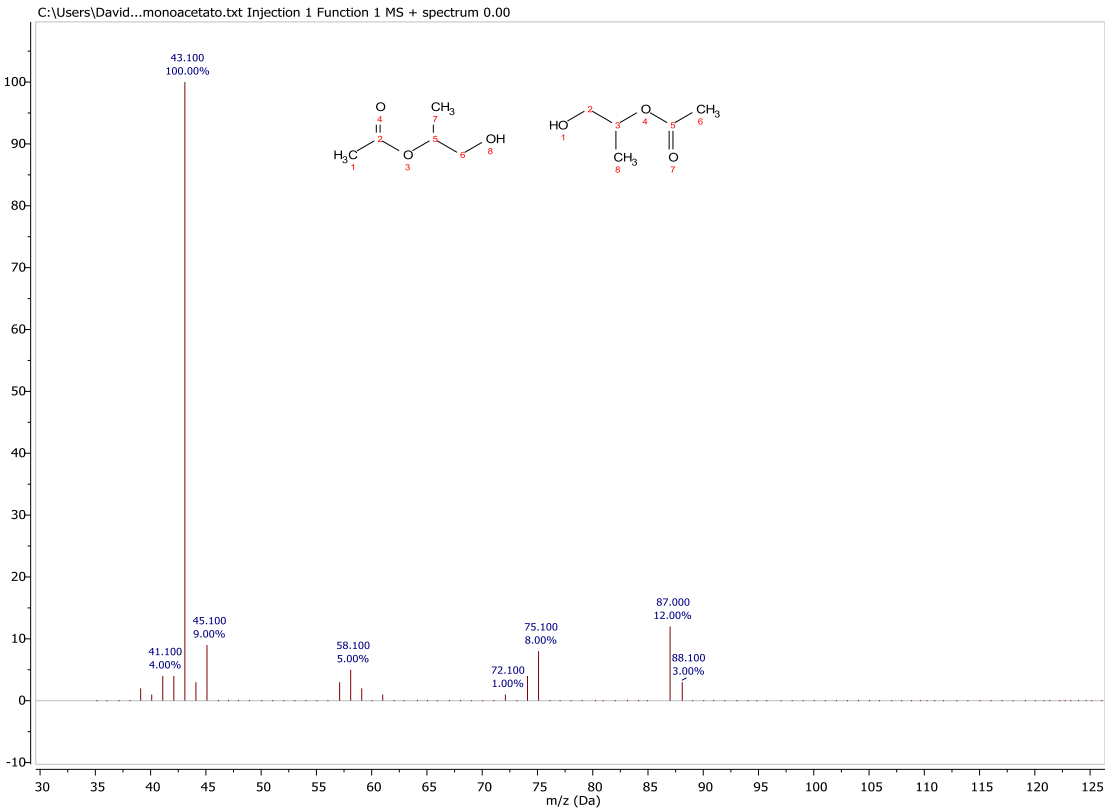


Figure S18. MS spectrum of compounds **3a** and **3a***.

GC/MS (EI, 70 eV) *m/z*: 87 (12), 75 (8), 58 (5), 45 (9), 43 (100).

2-hydroxypropyl 4-phenylbutanoate, 1-hydroxypropan-2-yl 4-phenylbutanoate (propanediol monophenylbutyrates, 3b,3b*)

Products were isolated in both batch and continuous flow conditions:

i) batch: in 92% yield upon reacting isopropenyl 4-phenylbutanoate (2.7 g, 13.29 mmol) and PG (1.0 g, 13.29 mmol) in presence of Amberlyst-15 (150.4 mg) as catalyst.

ii) continuous flow: in 87% yield collecting the output mixture obtained upon mixing isopropenyl 4-phenylbutanoate and PG in THF as solvent (iPC_4Ph/PG/THF molar ratio = 1:1:10) for t = 8 h (conditions: F = 0.3 $mL \cdot min^{-1}$, T = 50°C, [iPC_4Ph] = [PG] = 1.2 M).

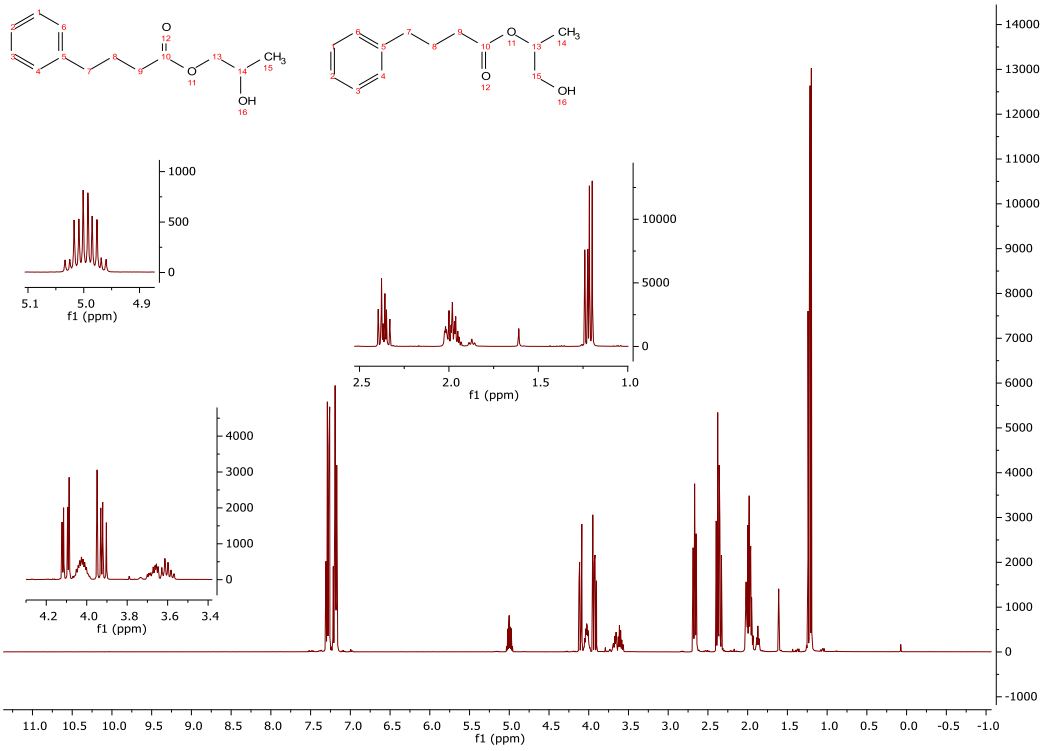


Figure S19. ^{1}H NMR spectrum of compounds **3b** and **3b***.

3b: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 7.32-7.16 (m, 5H), 4.15-3.90 (m, 2H), 4.03 (m, 1H), 2.65 (m, 2H), 2.35 (m, 2H), 1.95 (m, 2H), 1.20 (d, 3H).

3b*: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 7.32-7.16 (m, 5H), 5.00 (m, 1H), 4.15-3.90 (m, 2H), 2.65 (m, 2H), 2.35 (m, 2H), 1.95 (m, 2H), 1.22 (d, 3H).

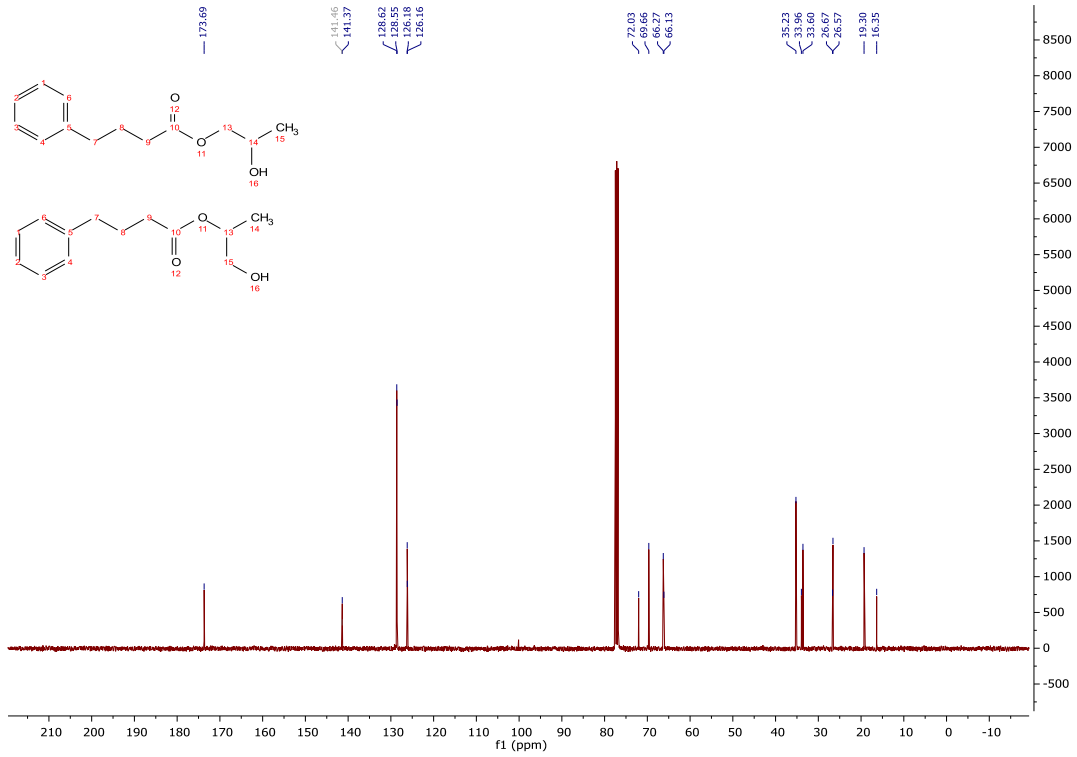


Figure S20. ^{13}C NMR spectrum of compounds **3b** and **3b***.

3b: ^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 173.69, 141.37, 128.62, 128.55, 126.18, 69.66, 66.27, 35.23, 33.60, 26.57, 19.30.

3b*: ^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 173.69, 141.46, 128.62, 128.55, 126.16, 72.03, 66.13, 35.23, 33.96, 26.67, 16.35.

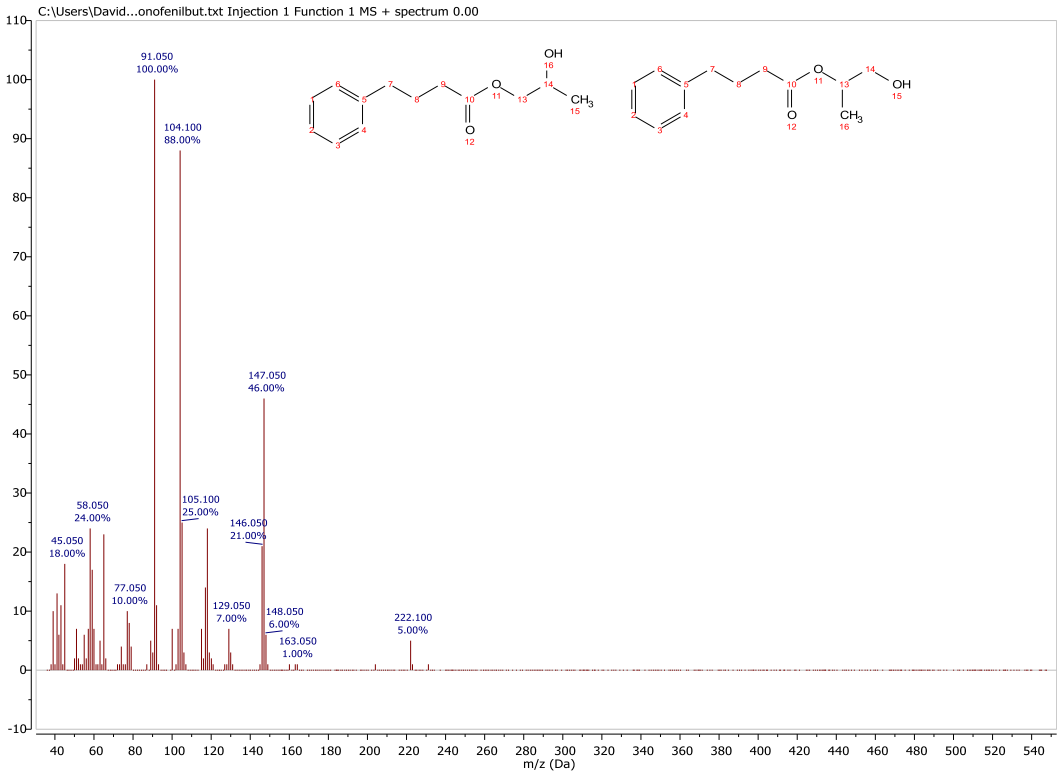


Figure S21. MS spectrum of compounds **3b, 3b***.

GC/MS (EI, 70 eV) *m/z*: 222 (M^+, 5), 147 (46), 118 (24), 105(25), 104 (88), 91 (100), 65 (23), 58 (24), 45 (18).

2-hydroxypropyl octanoate, 1-hydroxypropan-2-yl octanoate (propanediol monooctanoates, 3c,3c*)

Products were isolated in both batch and continuous flow conditions:

i) batch: in 92% yield upon reacting isopropenyl octanoate (iPC_8, 2.4 g, 13.26 mmol) and PG (1.0 g, 13.26 mmol) in presence of Amberlyst-15 (150.7 mg) as catalyst.

ii) continuous flow: in 81% yield collecting the output mixture, obtained upon mixing isopropenyl octanoate and PG in THF (iPC_8/PG/THF molar ratio = 1:1:10) for t = 8 h (conditions: F = 0.3 mL·min^{-1}, T = 70 °C, [iPC_8] = [PG] = 1.2 M).

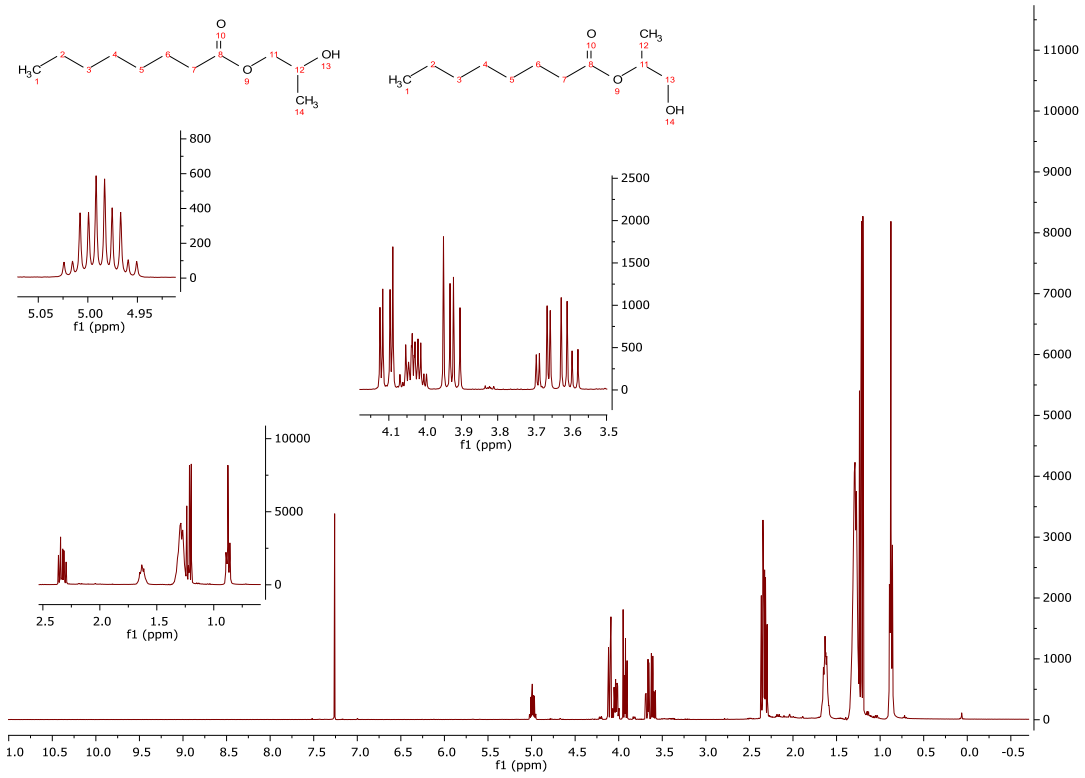


Figure S22. ^{1}H NMR spectrum of compounds **3c, 3c***.

3c: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 4.15-3.90 (m, 2H), 4.04 (m, 1H), 2.35 (m, 2H), 1.65 (m, 2H), 1.30 (m, 8H), 1.20 (d, 3H), 0.9 (t, 3H).

3c*: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 5.00 (m, 1H), 3.70-3.55 (m, 2H), 2.35 (m, 2H), 1.65 (m, 2H), 1.30 (m, 8H), 1.24 (d, 3H), 0.9 (t, 3H).

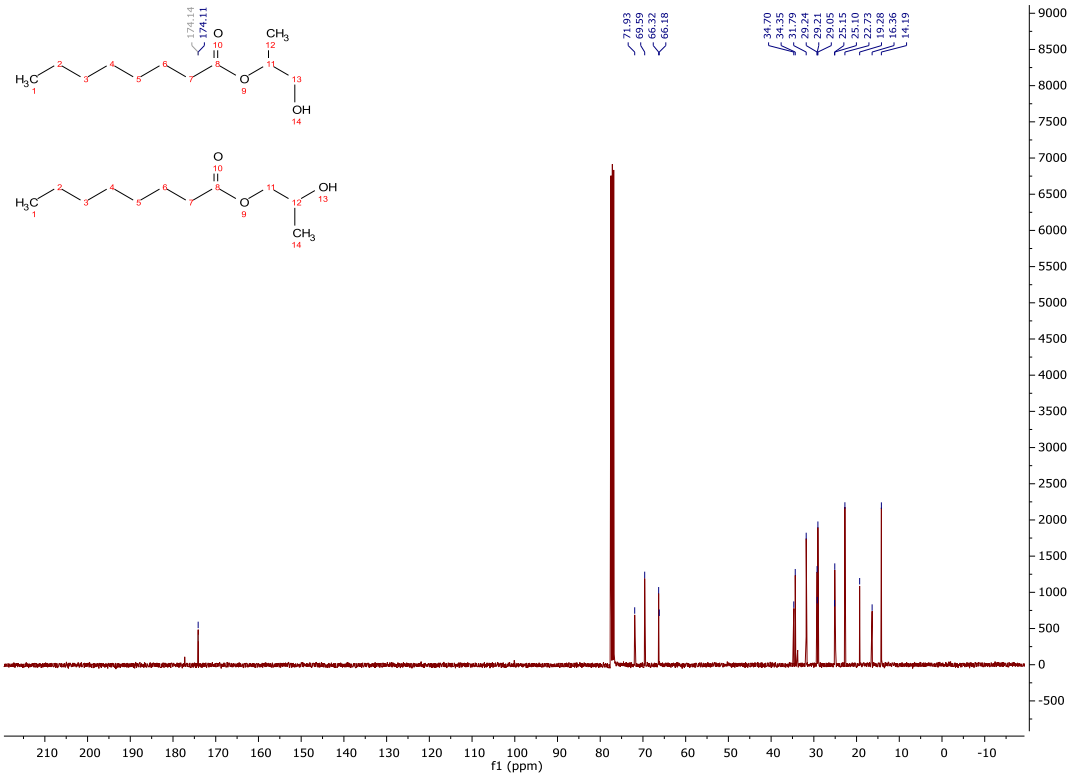


Figure S23. ^{13}C NMR spectrum of compounds **3c, 3c***.

3c: $^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 174.11, 69.59, 66.32, 34.35, 31.79, 29.05, 25.10, 22.73, 19.28, 16.36, 14.19.

3c*: $^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 174.14, 71.93, 66.18, 34.70, 29.24, 29.21, 25.15, 22.73, 19.28, 16.36, 14.19.

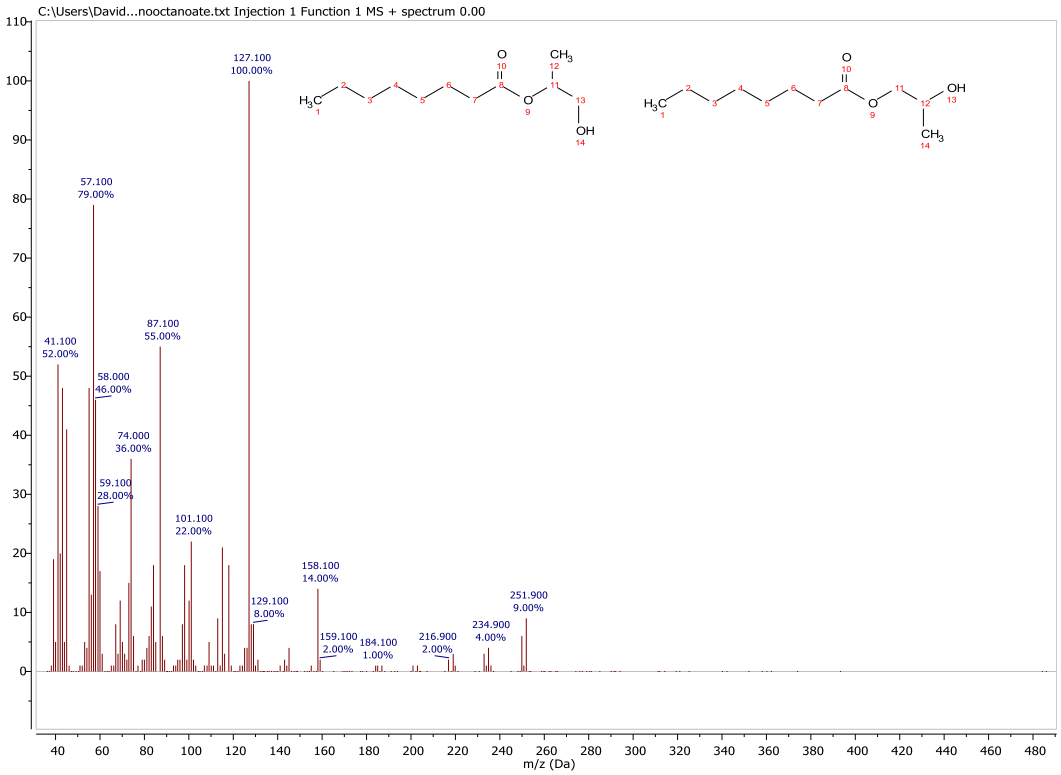


Figure S24. MS spectrum of compounds **3c** and **3c***.

GC/MS (EI, 70 eV) *m/z*: 158 (14), 128 (8), 127 (100), 118 (18), 115 (21), 101 (22), 100 (12), 98 (18), 87 (55), 84 (18), 74 (36), 59 (28), 58 (46), 57 (79), 55 (48), 45 (41), 43 (48), 41 (52).

Propane-1,2-diol diacetate (propanediol diacetate, 3a')

The product was isolated in 72% yield upon reacting iPAc (6.7 g, 66.75 mmol) and PG (1.0 g, 13.35 mmol) in presence of H_2SO_4 (50.8 mg, 0.51 mmol) as catalyst.

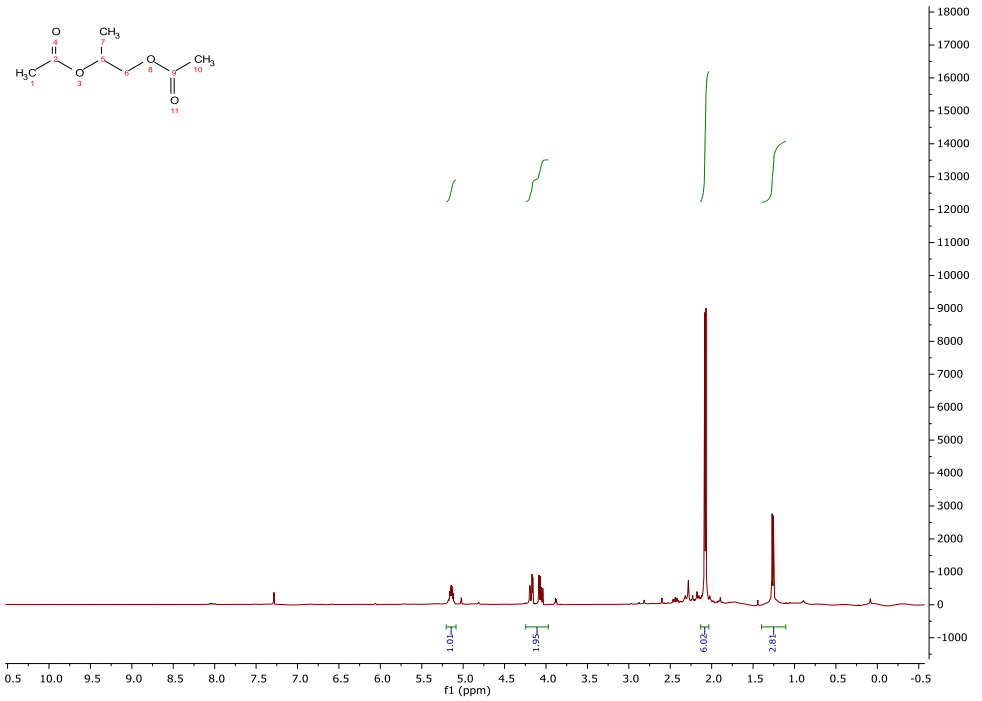


Figure S25. ^{1}H NMR spectrum of compound **3a'**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 5.15 (m, 1H), 4.20-4.00 (m, 2H), 2.08 (d, 6H), 1.25 (d, 3H).

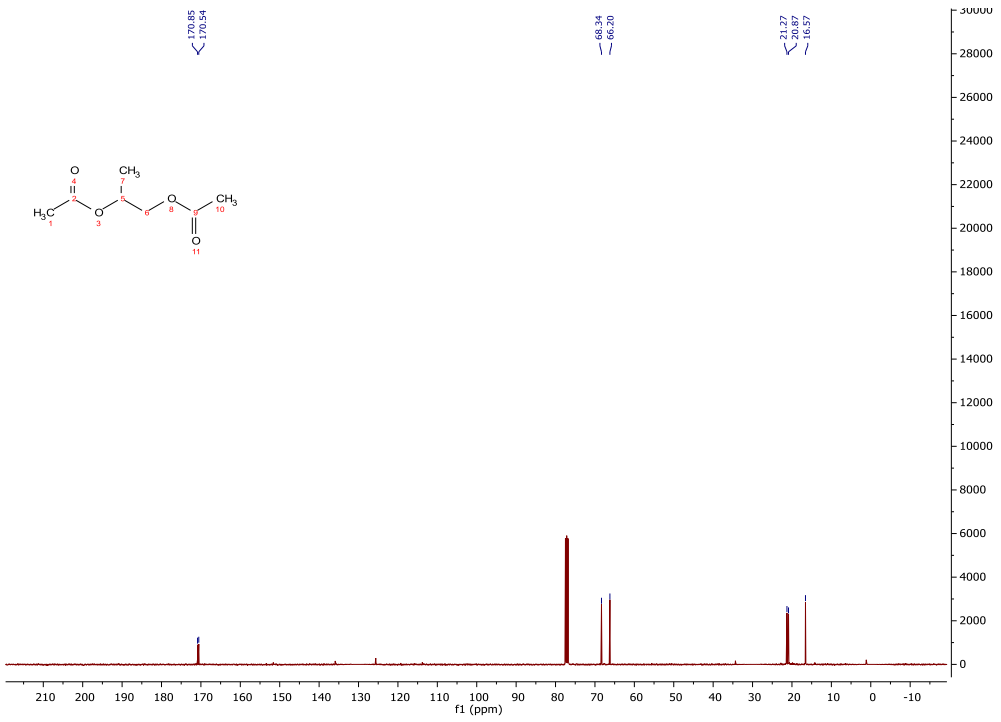


Figure S26. ^{13}C NMR spectrum of compounds **3a'**.

$^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 170.85, 170.54, 68.34, 66.20, 21.27, 20.87, 16.57.

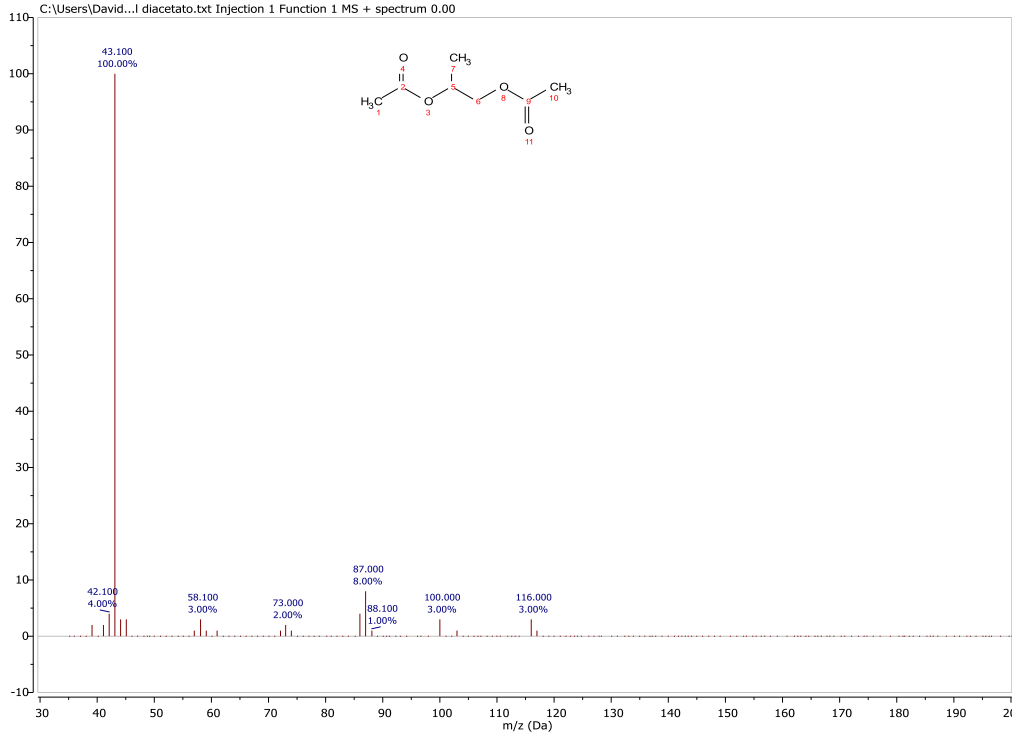


Figure S27. MS spectrum of compound **3a'**.

GC/MS (EI, 70 eV) *m/z*: 116 (3), 100 (3), 87 (8), 58 (3), 43 (100).

1-(3-phenylpropoxy)propan-2-yl 4-phenylbutanoate (propanediol diphenylbutyrate, 3b')

The product was isolated in 95% yield upon reacting 4-phenylbutanoic acid (10.8 g, 65.77 mmol) and PG (1.0 g, 13.15 mmol) in presence of H_2SO_4 (50.0 mg) as catalyst.

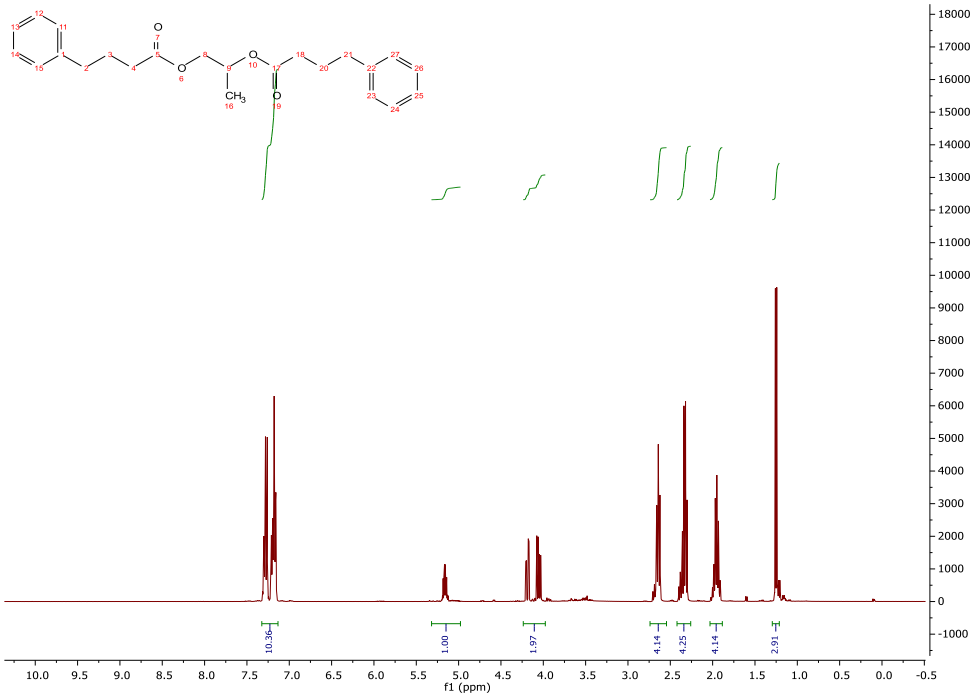


Figure S28. ^{1}H NMR spectrum of compounds **3b'**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 7.32-7.16 (m, 10H), 5.15 (m, 1H), 4.20-4.00 (m, 2H), 2.65 (m, 4H), 2.35 (m, 4H), 1.95 (m, 4H), 1.25 (d, 3H).

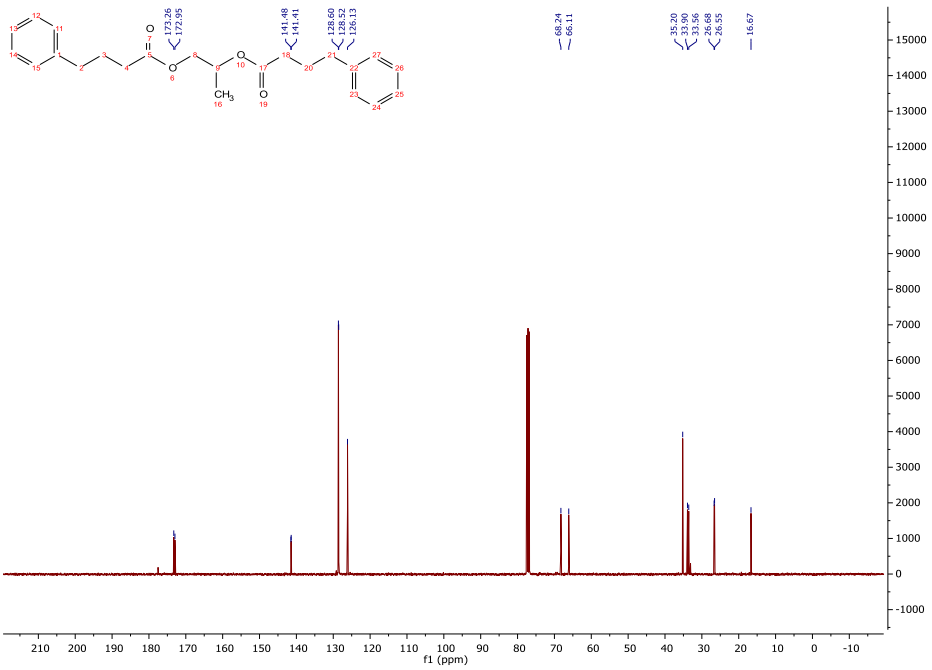


Figure S29. ^{13}C NMR spectrum of compounds **3b'**.

$^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 173.26, 172.95, 141.48, 141.41, 128.60, 128.52, 126.13, 68.24, 66.11, 35.20, 33.90, 33.56, 26.68, 26.55, 16.67.

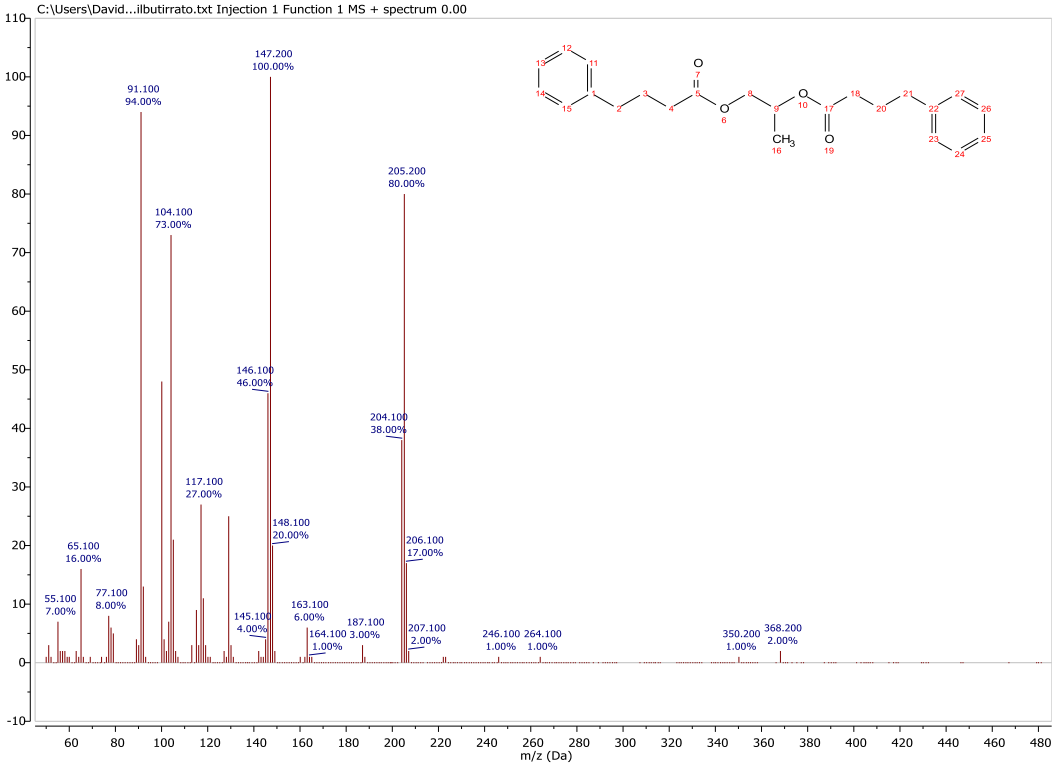


Figure S30. MS spectrum of compound **3b'**.

GC/MS (EI, 70 eV) *m/z*: 368 (M^+, 2), 206 (80), 147 (100), 117 (27), 104 (73), 91 (94), 65 (16).

Propane-1,2-diyl dioctanoate (propanediol dioctanoate, 3c')

The product was isolated in 87% yield upon reacting octanoic acid (10.0 g, 69.25 mmol) and PG (1.0 g, 13.85 mmol) in presence of Amberlyst-15 (49.9 mg) as catalyst.

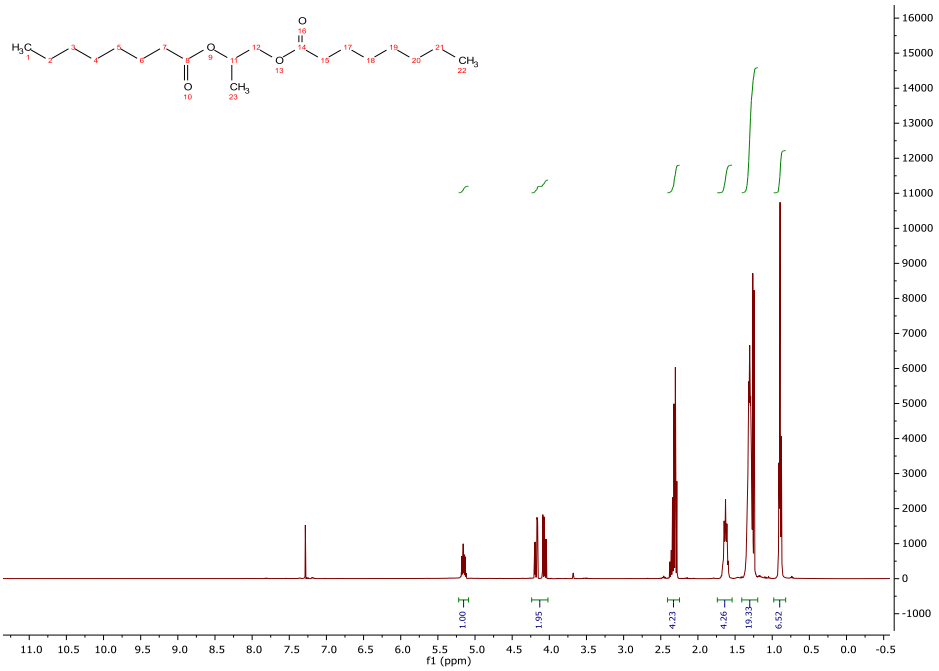


Figure S31. ^{1}H NMR spectrum of compounds **3c'**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 5.15 (m, 1H), 4.20-4.00 (m, 2H), 2.30 (m, 4H), 1.63 (m, 4H), 1.30 (m, 19H), 0.90 (t, 6H).

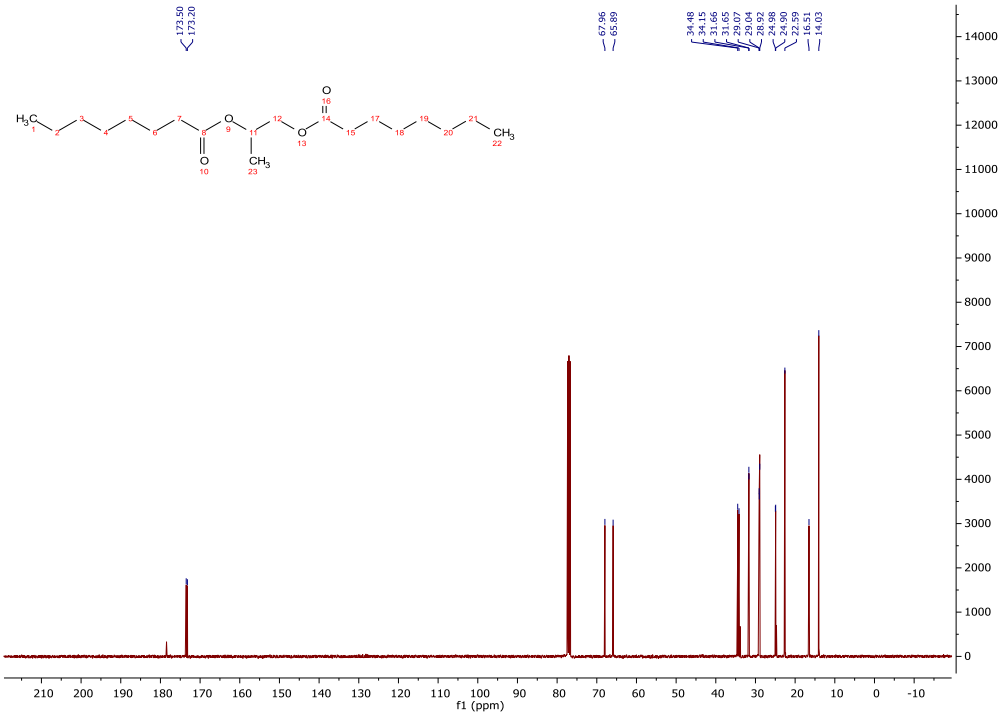


Figure S32. ^{13}C NMR spectrum of compounds **3c'**.

$^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 173.50, 173.20, 67.96, 65.89, 34.48, 34.15, 31.66, 31.65, 29.07, 29.04, 28.92, 24.98, 24.90, 22.59, 16.51, 14.03.

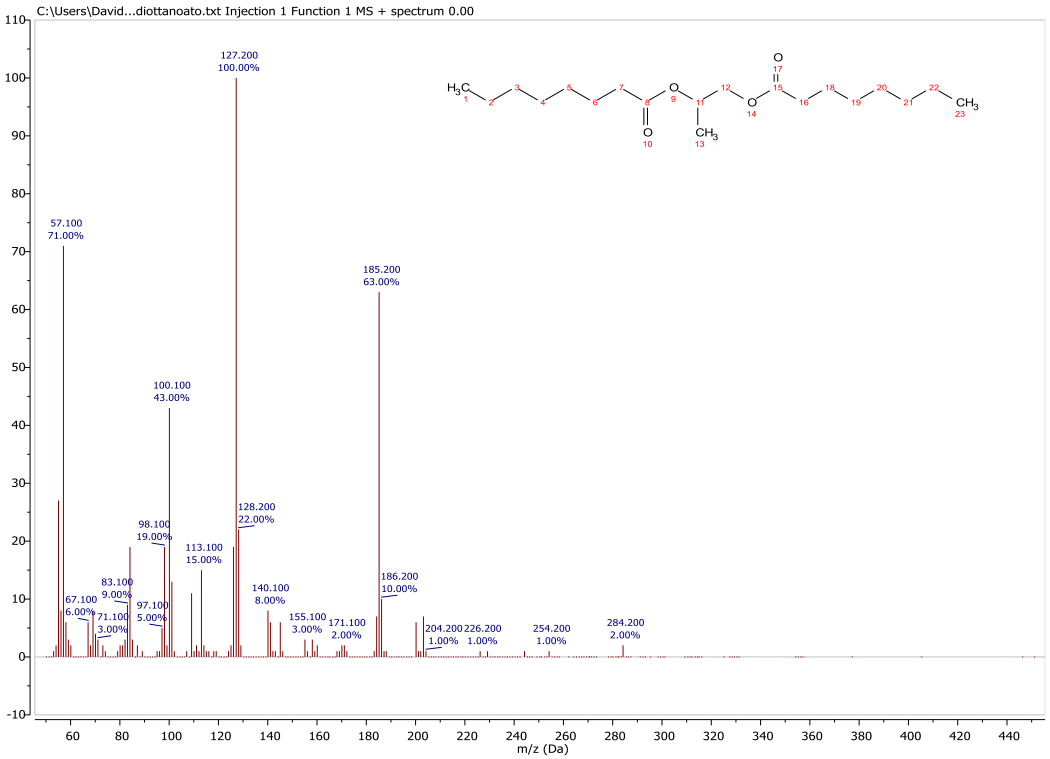


Figure S33. MS spectrum of compound **3c'**.

GC/MS (EI, 70 eV) *m/z*: 281 (2), 185 (63), 127 (100), 100 (43), 57 (71).

2,2,4-trimethyl-1,3-dioxolane (propanediol acetal) (4)

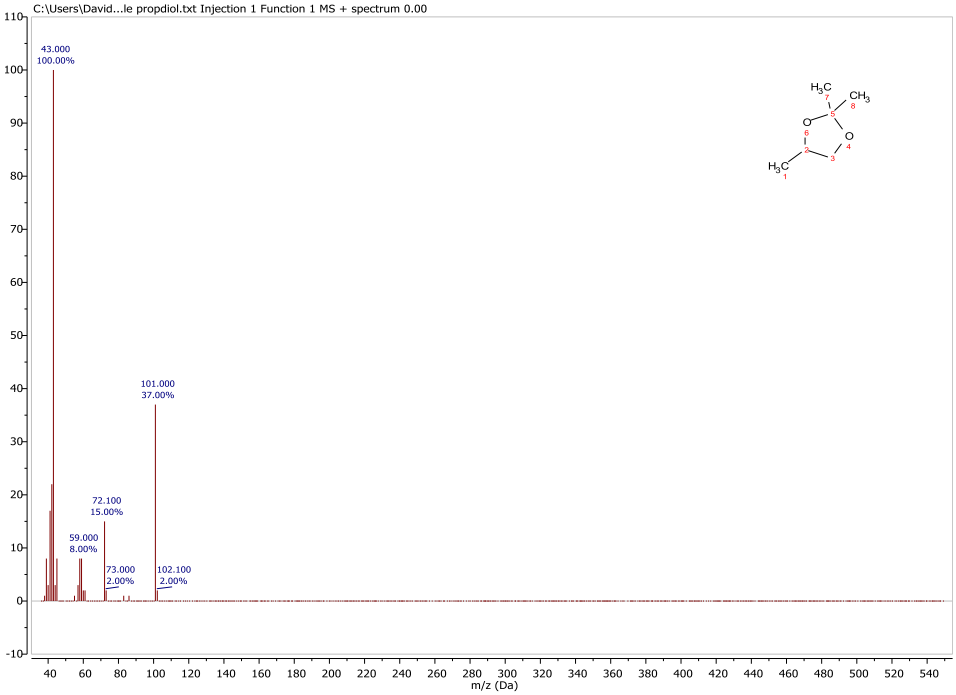


Figure S34. MS spectrum of compound **4**.

GC/MS (EI, 70 eV) *m/z*: 101 (37), 72 (15), 59 (8), 58 (8), 43 (100), 42 (22), 41 (17).

2-hydroxyethyl acetate (ethylene glycol monoacetate) (5a)

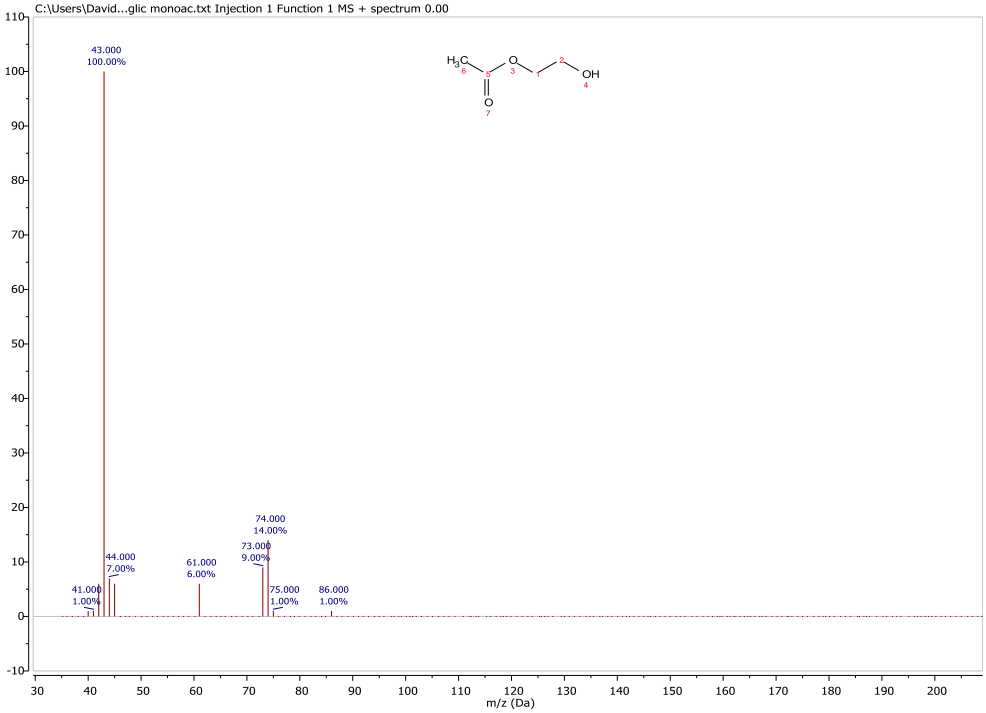


Figure S35. MS spectrum of compound **5a**.

GC/MS (EI, 70 eV) *m/z*: 74 (14), 61 (6), 44 (7), 43 (100).

2-hydroxyethyl 4-phenylbutanoate (ethylene glycol monophenylbutyrate) (5b)

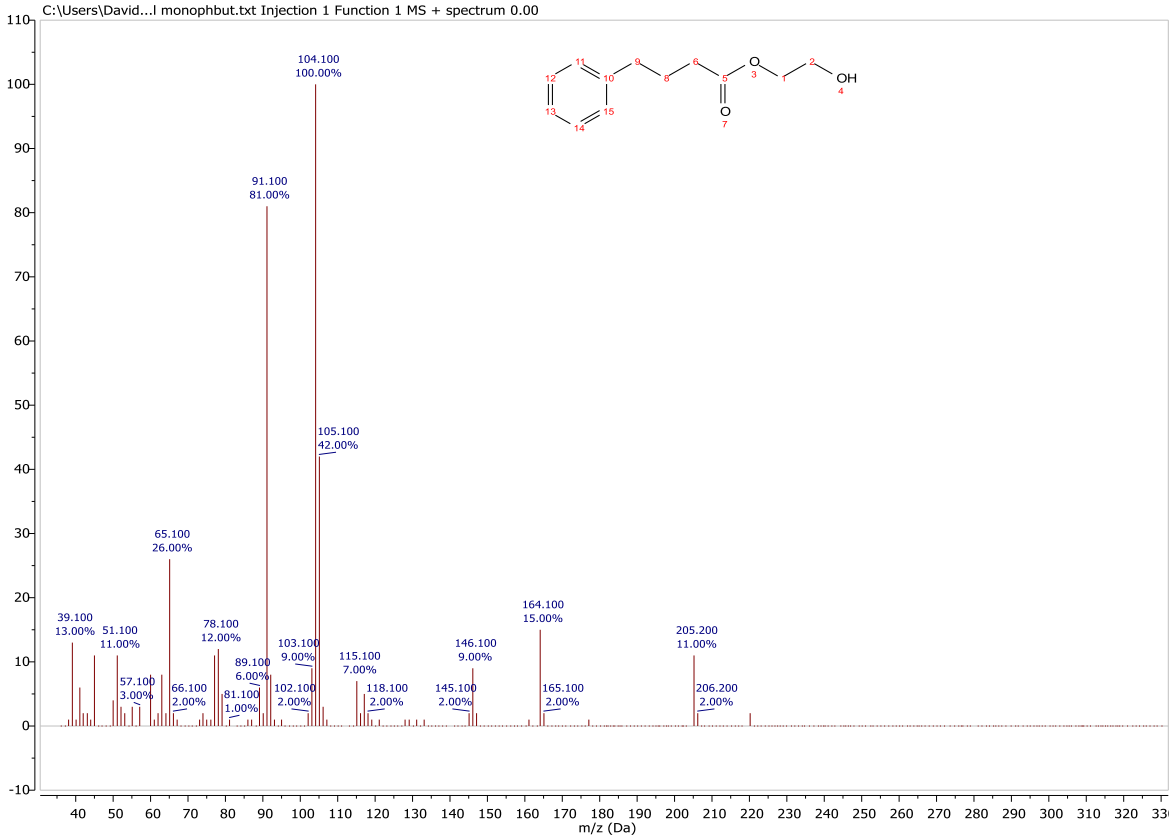


Figure S36. MS spectrum of compound **5b**.

GC/MS (EI, 70 eV) *m/z*: 205 (11), 164 (15), 146 (9), 105 (42), 104 (100), 91 (81), 78 (12), 65 (26), 45 (11).

2-hydroxyethyl octanoate (ethylene glycol monooctanoate) (5c)

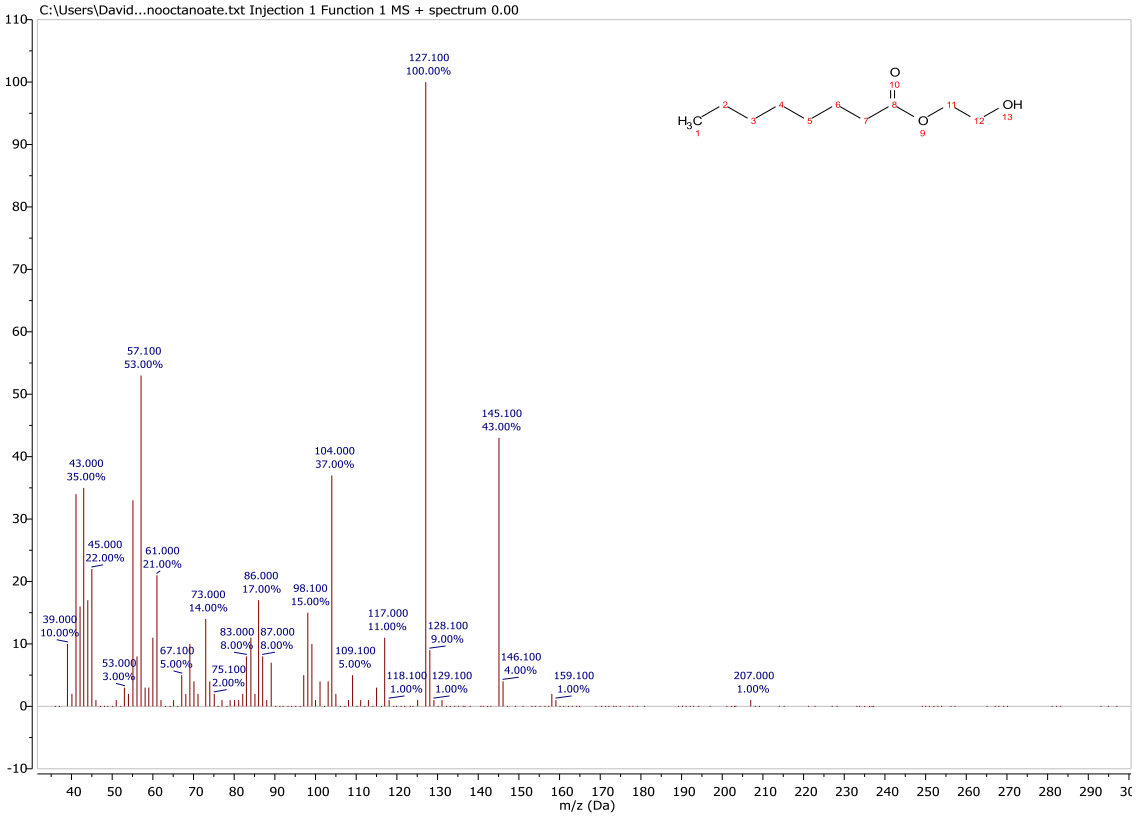


Figure S37. MS spectrum of compound **5c**.

GC/MS (EI, 70 eV) *m/z*: 159 (1), 145 (43), 127 (100), 117 (11), 104 (37), 98 (15), 86 (17), 61 (21), 57 (53), 43 (35).

Ethane-1,2-diol diacetate (ethylene glycol diacetate, 5a')

The product was isolated in 75% yield upon reacting iPAc (8.3 g, 82.5 mmol) and EG (1.0 g, 16.5 mmol) in presence of H_2SO_4 (49.7 mg) as catalyst.

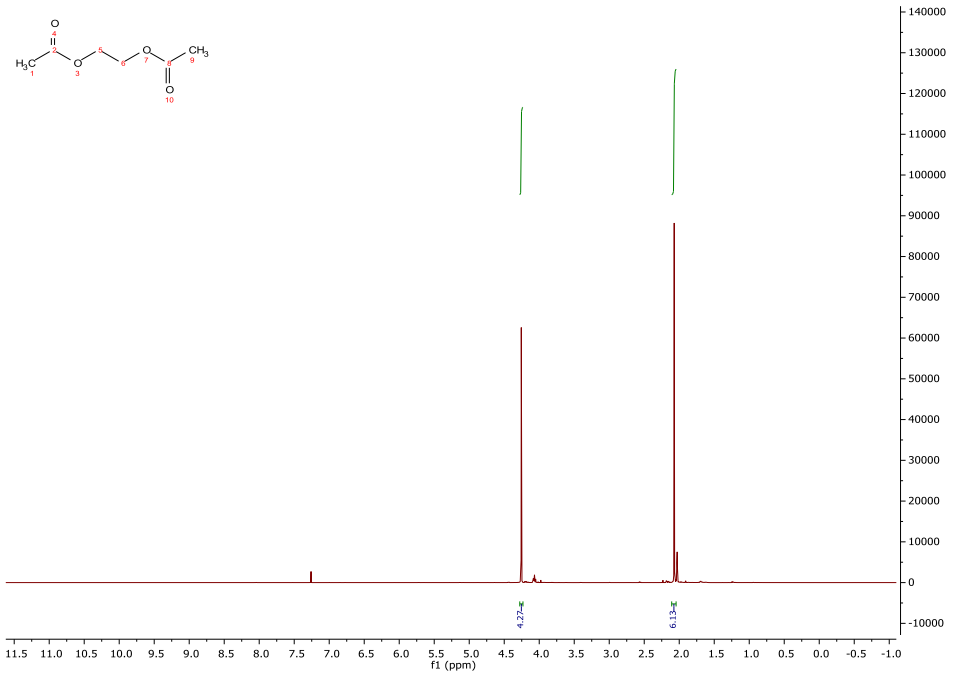


Figure S38. ^{1}H NMR spectrum of compound **5a'**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 4.26 (s, 4H), 2.75 (s, 6H).

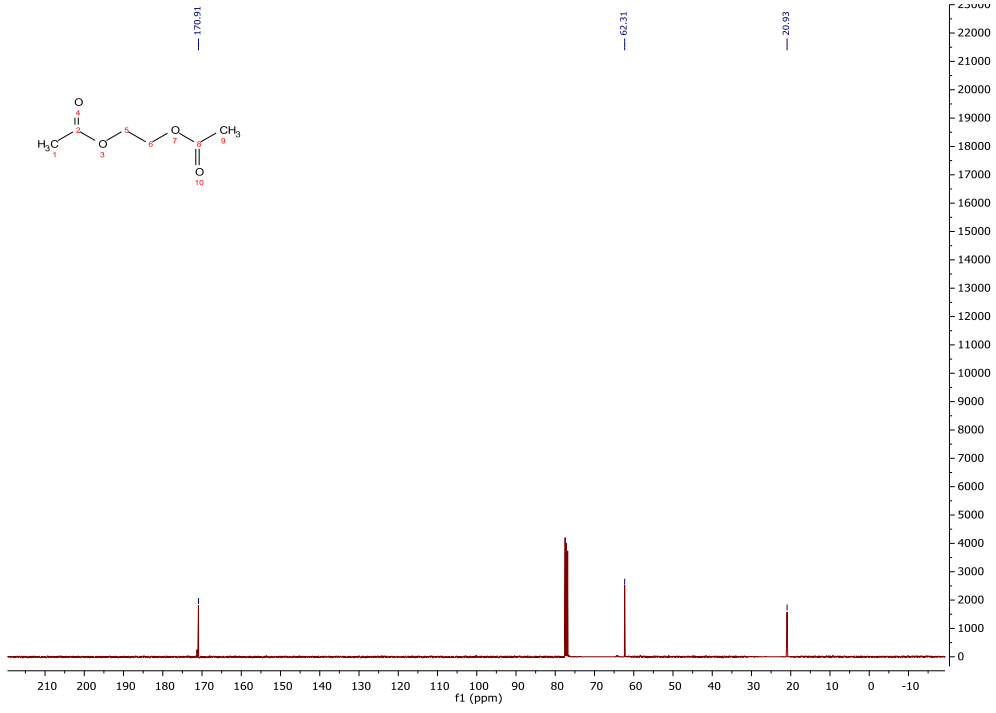


Figure S39. ^{13}C NMR spectrum of compound **5a'**.

^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 170.91, 62.31, 20.93.

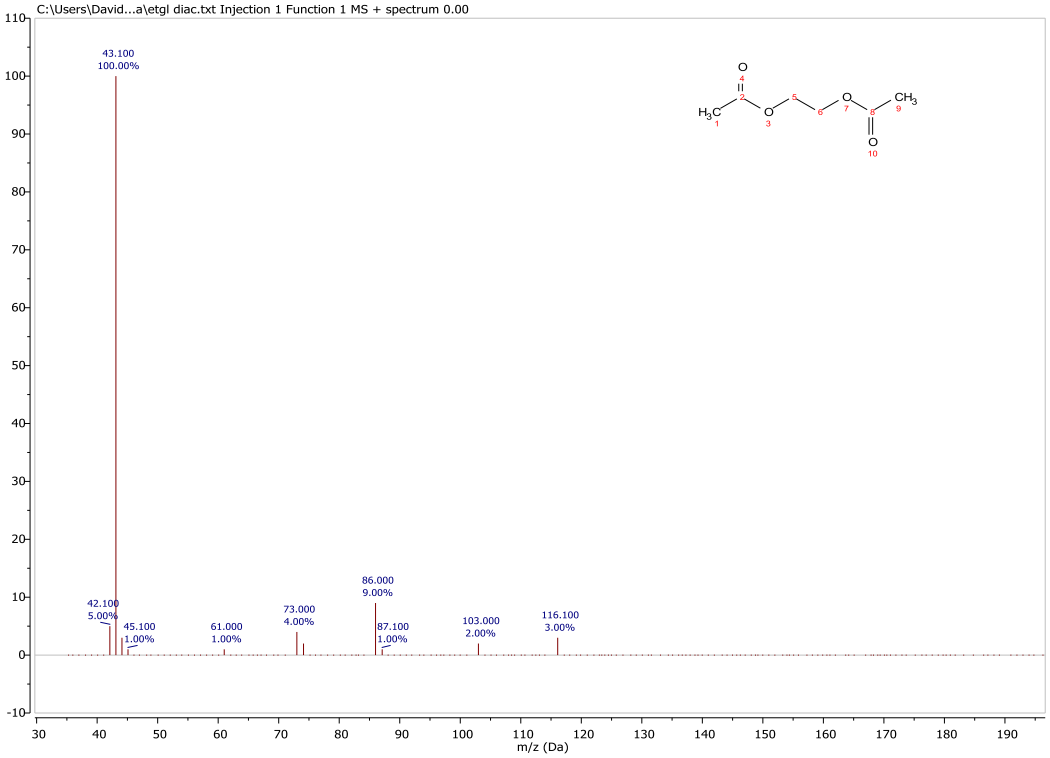


Figure S40. MS spectrum of compound **5a'**.

GC/MS (EI, 70 eV) *m/z*: 116 (3), 103 (2), 86 (9), 73 (4), 44 (3), 43 (100).

Ethane-1,2-diyl bis(4-phenylbutanoate) (ethylene glycol diphenylbutyrate, 5b')

The product was isolated in 81% yield upon reacting 4-phenylbutanoic acid (13.4 g, 81.8 mmol) and EG (1.0 g, 16.3 mmol) in presence of H_2SO_4 (51.1 mg) as catalyst.

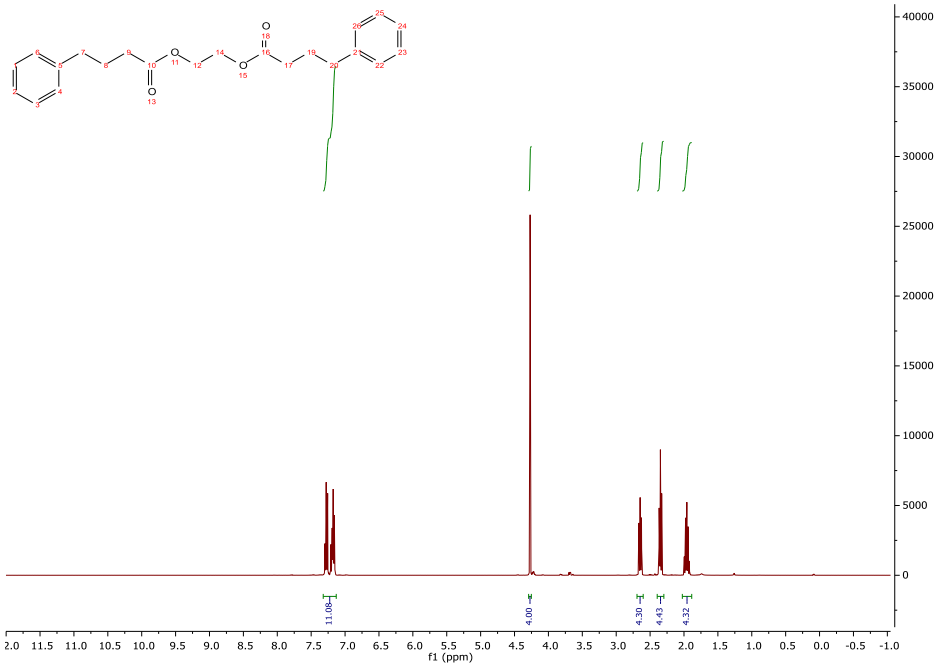


Figure S41. ^{1}H NMR spectrum of compound **5b'**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 7.30-7.15 (m, 10H), 4.27 (s, 4H), 2.65 (t, 4H), 2.35 (t, 4H), 1.95 (m, 4H).

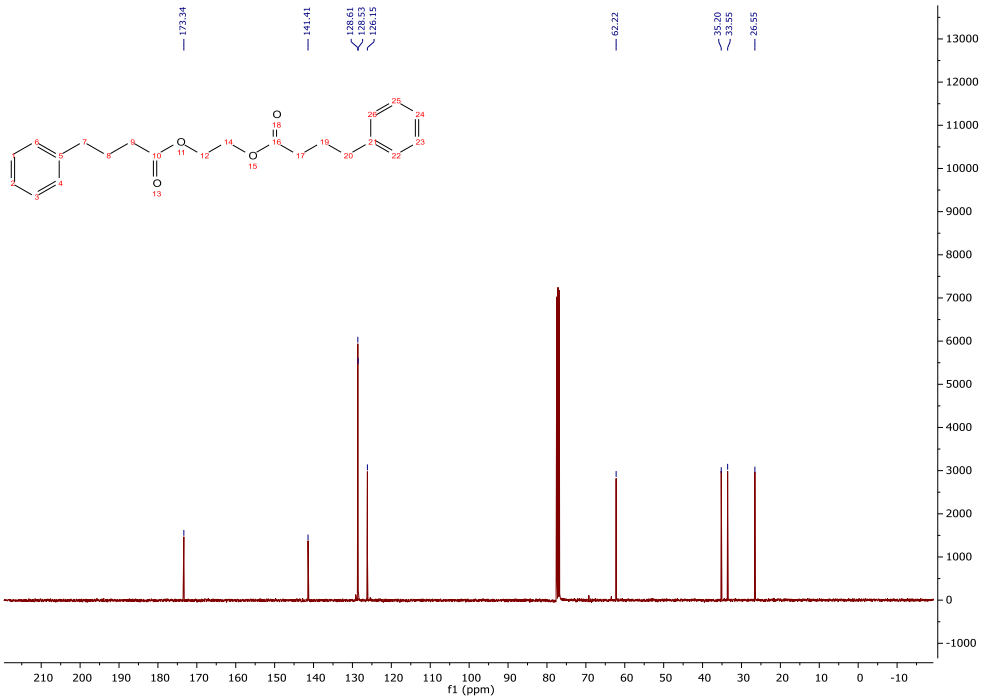


Figure S42. ^{13}C NMR spectrum of compound **5b'**.

$^{13}C\{H\}$ NMR (101 MHz, 298 K, $CDCl_3$) δ: 173.34, 141.41, 128.61, 128.53, 126.15, 62.22, 35.20, 33.55, 26.55.

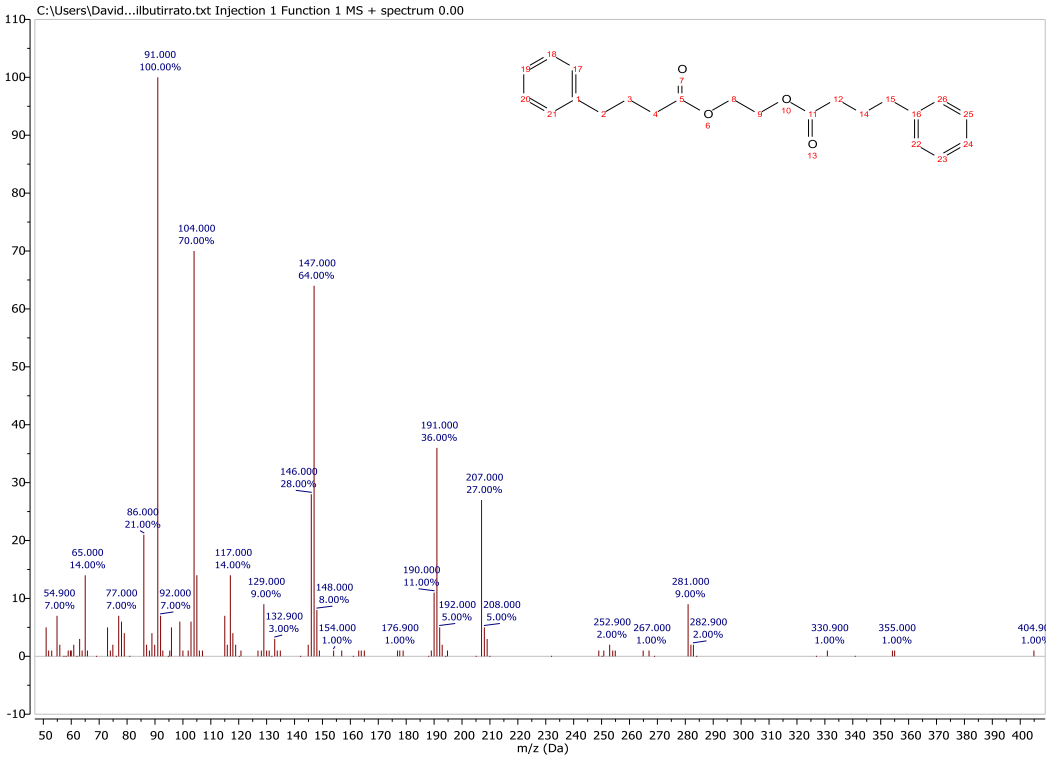


Figure S43. MS spectrum of compound **5b'**.

GC/MS (EI, 70 eV) *m/z*: 355 ($[M+1]^+$, (1), 281 (9), 207 (27), 191 (36), 147 (61), 101 (70), 91 (100), 86 (21), 65 (14).

Ethane-1,2-diyl dioctanoate (ethylene glycol dioctanoate, 5c')

The product was isolated in 88% yield upon reacting octanoic acid (11.6 g, 80.8 mmol) and EG (1.0 g, 16.2 mmol) in presence of H_2SO_4 (50.1 mg) as catalyst.

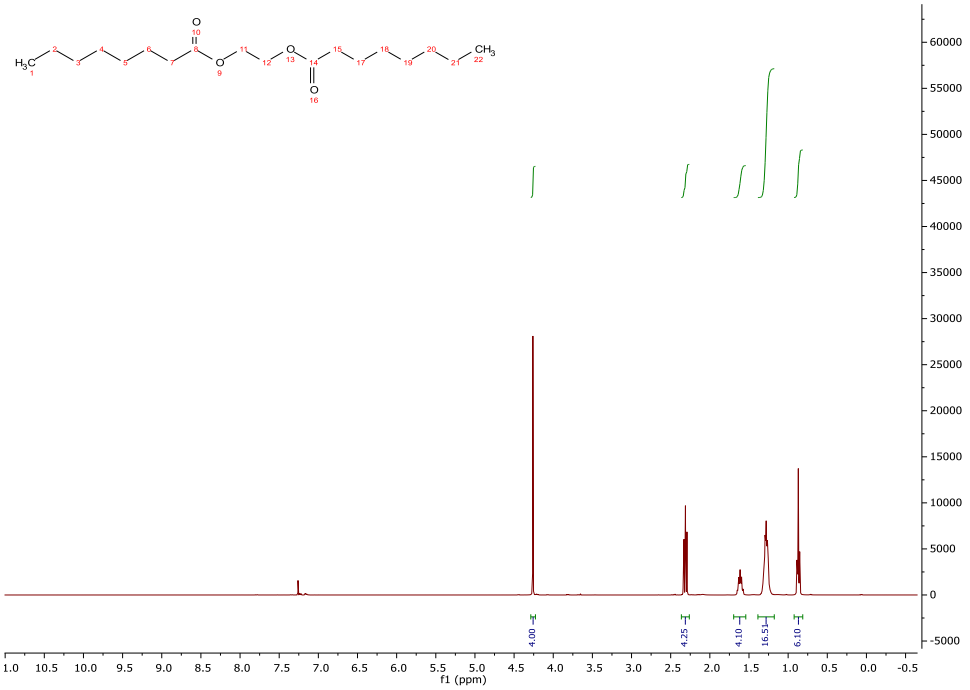


Figure S44. ^{1}H NMR spectrum of compound **5c'**.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ: 4.26 (s, 4H), 2.31 (t, 4H), 1.61 (m, 4H), 1.28 (m, 16H), 0.87 (t, 6H).

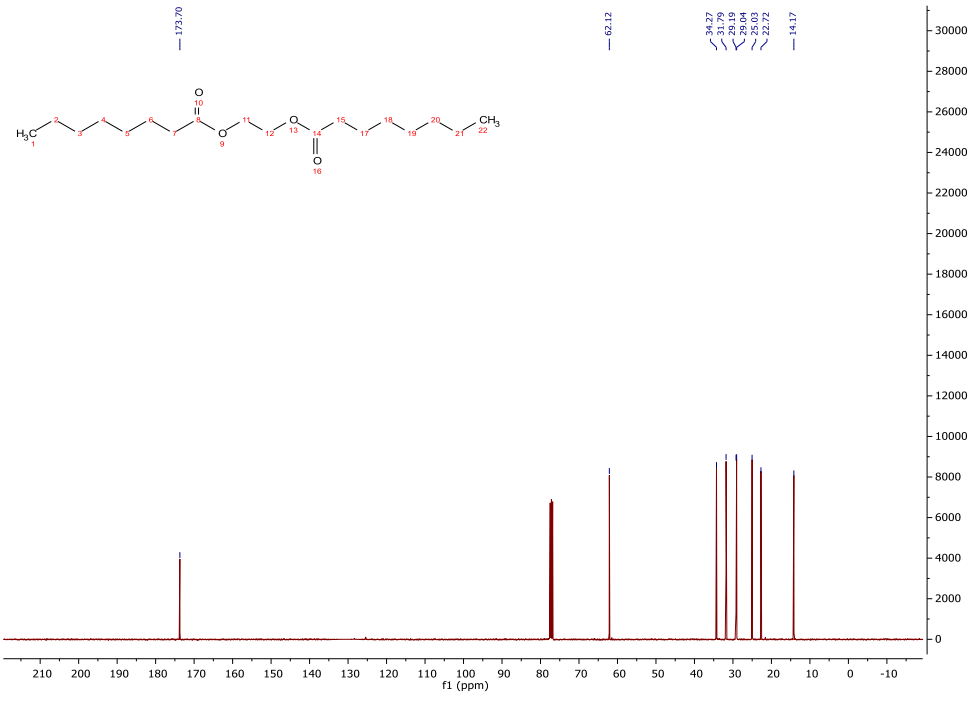


Figure S45. ^{13}C NMR spectrum of compound **5c'**.

^{13}C{H} NMR (101 MHz, 298 K, $CDCl_3$) δ: 173.70, 62.12, 34.27, 31.79, 29.19, 29.04, 25.03, 22.72, 14.17.

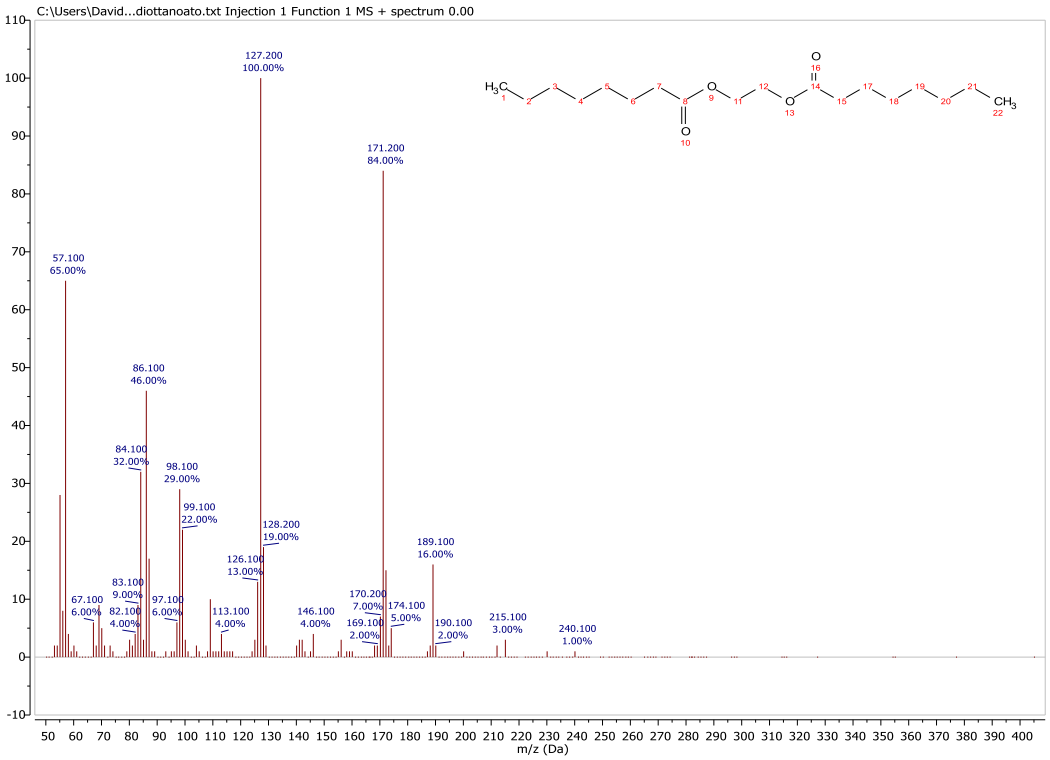


Figure S46. MS spectrum of compound **5c'**.

GC/MS (EI, 70 eV) *m/z*: 240 (1), 189 (16), 171 (84), 127 (100), 98 (29), 86 (46), 57 (65).

2,2-dimethyl-1,2-dioxolane (ethylene glycol acetal) (6)

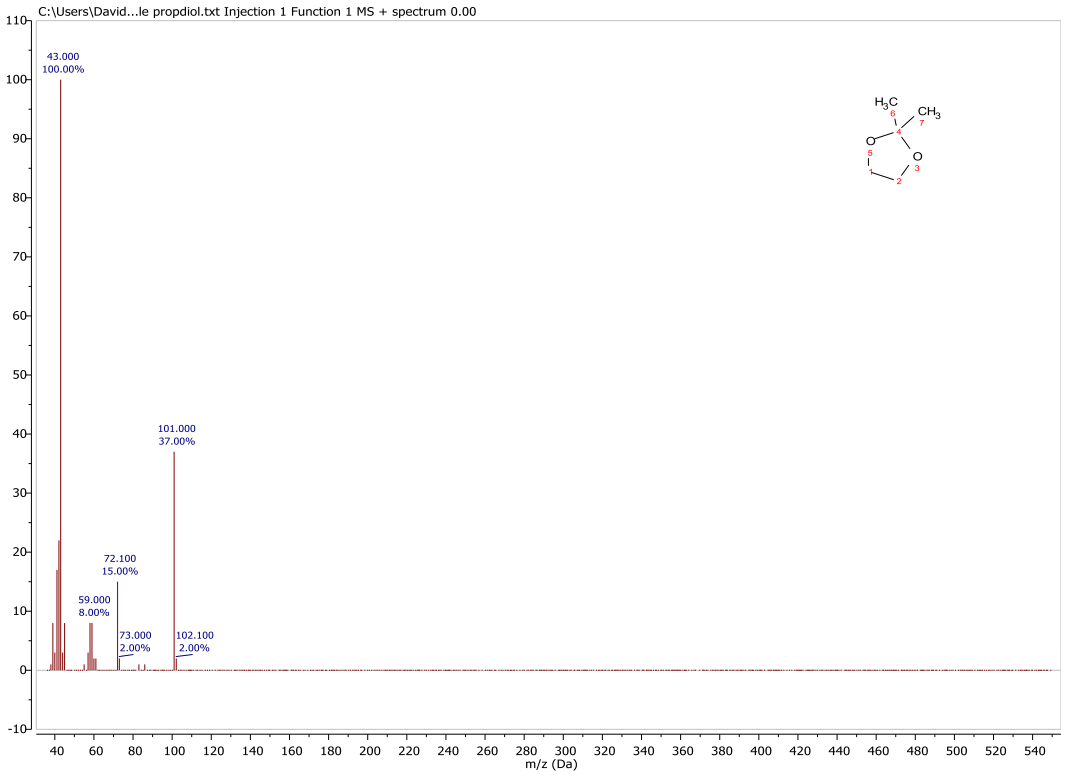


Figure S47. MS spectrum of compound **6**.

GC/MS (EI, 70 eV) *m/z*: 101 (37), 72 (100), 59 (5), 43 (100).

Quantitative evaluation of conversion and products' selectivity

Calibration curves were used to determine both vicinal diols conversion and selectivity towards mono-, di-esterification and acetalization products. In a typical example, a tandem acetalization/transesterification reaction was performed with equimolar amounts of PG (**1**) and iPAc (**2a**) at T = 50 °C in CPME ([PG] = [iPAc] = 1.4 M, V_{CPME} = 1 mL), in presence of Amberlyst-15 (15 wt. %) as catalyst. After the desired reaction time (t = 1 - 12 h), the reaction mixture was diluted with 5 mL of THF. Then, an aliquot (V = 0.5 mL) of the mixture was withdrawn and diluted with a solution of mesitylene at known concentration (100 ppm, 24.5 mL) used as external standard.

The GC response factor for reagent **1** was evaluated starting from four solutions at known concentration of the diol of choice (100, 300, 600 and 1000 ppm, respectively) prepared using THF as solvent. Each standard solution of diol contained the same concentration of mesitylene (100 ppm). The corresponding calibration curve for PG is shown in Figure S47.

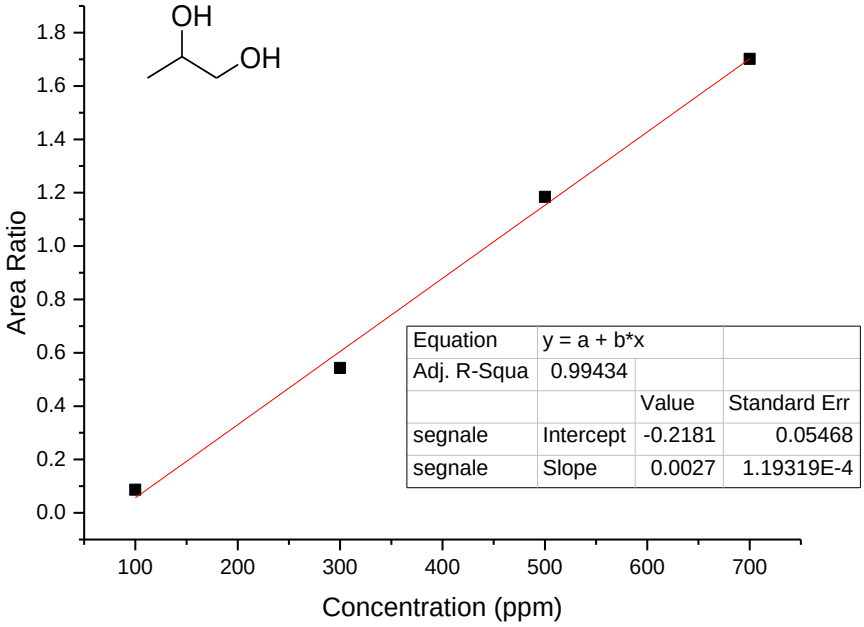


Figure S48. Calibration curve for reagent **1a** using mesitylene as external standard.

Calibration curves for EG (**5**) and esterification products (**3a'**, **3b'**, **3c'**, **5a'**, **5b'**, **5c'**) were constructed applying the same methodology.

Calibration curves for acetals 2,2,4-trimethyl-1,3-dioxolane (**4**), 2,2-dimethyl-1,3-dioxolane (**6**), were constructed upon synthesis of the above-mentioned compounds in high purity. The synthesis was carried out by mixing acetone (12.8 g, 219.6 mmol, 10 mL) and PG (1.0 g, 13.3 mmol) or EG (1.0 g, 16.2 mmol) at T = 50 °C, in presence of Amberlyst-15 (50 mg, 5 wt %) as catalyst. Although both **4** and **6** were obtained as the main reaction products, attempts in isolating them in a high purity (> 99 %) were unsuccessful: this was ascribed to the presence of residual acetone or unreacted diol. Therefore, in place of **4** and **6**, commercially available compounds as 4-(methoxymethyl)-2,2-dimethyl-1,3-dioxolane (solketal methyl ether, **7**) and 1,2-diethoxyethane (ethylene glycol diethyl ether, **8**) were used. From comparative GC and GC/MS analyses, it was demonstrated that compounds **7** and **8** had response factors very similar to compounds **4** and **6**, respectively. Preparation of the corresponding calibration curves was carried out according to the above described procedure.

References

[1] Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z..; Sun, Z. Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification, *Catal. Commun.* **2004**, *5*, 473–477

[2] Calmanti, R.; Galvan, M.; Amadio, E.; Perosa, A.; Selva, M. High-Temperature Batch and Continuous-Flow Transesterification of Alkyl and Enol Esters with Glycerol and Its Acetal Derivatives *ACS Sustainable Chem Eng*., **2018**, *6*, 3964-3973.

[3] Watanabe, K.; Yamagiwa N.; Torisawa, Y. Cyclopentyl Methyl Ether as a New and Alternative Process Solvent *Org. Proc. Res. Develop*., **2007**, *11*, 251-258.

[4] Zhang, X.; Zhao, Y.; Xu, S.; Yang, Y.; Liu, J.; Wei, Y.; Yang, Q. Polystyrene sulphonic acid resins with enhanced acid strength via macromolecular self-assembly within confined nanospace, *Nat Commun*, **2014**, *5*:3170. doi: 10.1038/ncomms4170.

[5] (a) Randová, A.; Vopička, O.; Bartovská, L.; Friess, K. Cyclopentyl methyl ether, *tert*-amyl methyl ether and *tert*-butyl methyl ether: density, dynamic viscosity, surface tension and refractive index, *Chem. Pap.* 2018, *72*, 947-954; (b) http://www.zeon.co.jp/business_e/enterprise/spechemi/spechemi5-13.html, last access April 23, 2019.

[6] Rothman, E. S.; Moore, G. C. Enol esters. XII. C-acylations with enol esters, *J. Org. Chem*., **1970**, *35*, 2351-2353

[7] Young, F. G.; Frostick, Jr., F. C.; Sanderson, J. J.; Hauser, C. R. Conversion of Ketone Enol Esters to ß-Diketones by Intramolecular Thermal Rearrangement and by Intermolecular Acylations using Boron Fluoride *J. Am. Chem. Soc.,* **1950**, *72*, 3635-3642