

Glycerol carbonate as a versatile alkylating agent for the synthesis of β -aryloxy alcohols

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Supplementary information

Supplementary information contains 12 pages including 16 figures and 2 tables.

X-ray diffraction (XRD)

X-ray diffraction (XRD) characterization was carried out on catalysts powders. The diffraction patterns of the catalysts were recorded using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$, Ni-filtered) on a Philips X'Pert vertical diffractometer in Bragg-Brentano geometry, featuring a pulse height analyser and a secondary curved graphite-crystal monochromator.

Specific surface area (SSA) determination (BET)

The BET surface area of MgO was determined by N₂ physisorption at the temperature of liquid N₂ using a Sorptly 1750 Fison instrument. A sample of 0.2 g was initially outgassed at 150 °C before N₂ absorption. The value of the surface area obtained was then divided by the mass of the sample to obtain SSA.

CO₂ and NH₃ Temperature Programmed Desorption (TPD) analysis

The acidity and basicity of catalysts were measured by Temperature Programmed Desorption (TPD) of NH₃ and CO₂ respectively, using a Micromeritics AutoChem II 2920 instrument. Effluents were analysed using a Cirrus 2 quadrupole mass spectrometer recording the intensity of the following mass/charge ratio current signals: NH₃ (m/z = 17), H₂O (m/z = 18), CO₂ (m/z = 44). Typically, 0.2 g of samples were charged in a quartz tube in He flow (30 mL/min), with a heating rate of 10 °C/min up to 550 °C for Na-Mordenite and 500 °C for MgO. The final temperature was kept for 60 min to clean the adsorbed water and carbonates from the catalyst surface. After cooling, NH₃ and CO₂ chemisorption was conducted at 100 °C for 20 min of flowing 10% NH₃/He (30 mL/min) and 40 °C for 60 min of flowing 10% CO₂/He (30 mL/min), respectively. Before desorption, samples were fluxed with He (30 mL/min) for 60 min at the adsorption temperature to remove the weakly physisorbed probe molecules. Finally, temperature-programmed desorption (TPD) was conducted using the same ramp as for the sample surface cleaning.

Melting point determination (DSC)

The melting points of the two obtained products, mono-phenoxy-1,2-propanediol (MPP) and 1,3-diphenoxy-2-propanol (DPP) were determined by differential scanning calorimetry (DSC) analyses. In detail, measures were performed with a DSC Q2000 system. The samples were heated from 22 °C up to 200 °C under N₂ flow as gas purge. The maximums of the endotherms at 56.35 °C and 82.25 °C for MPP and DPP respectively, were taken as the melting temperature (T_m) for each sample.

Critical Micellar Concentrations (CMC) determination

Critical Micellar Concentration (CMC) of MPP and DPP were determined fluorometrically using Nile Red as fluorescence probe molecule. In detail, fluorescence spectra of 2.0 μM Nile Red solutions in water containing increasing concentrations of MPP ranging from 0.1 to 20 mM or DPP ranging from 0.1 to 2.0 mM have been recorded with a Varian Cary Eclipse fluorescence spectrophotometer.

The recorded intensities in correspondence of the emission peak of Nile red ($\lambda = 650 \text{ nm}$) have been plotted versus the concentration of the investigated product.

As a matter of fact, the emission intensity of Nile red rises with increasing MPP concentration, due to the short-range interactions between MPP and the probe molecule. As MPP concentration approaches CMC value, emission signal intensity reaches a plateau, due to the maximum degree of interactions between the probe and the surfactant micelle. The CMC of MPP can be derived from the intersection of two linear fitting curves. For DPP instead, it was not possible to determine the CMC value due to the limited solubility of this compound in distilled water.

MPP and phenol condensation control test

In order to exclude the contribution of the direct condensation between PhOH and MPP a dedicated control test has been set up. In particular, a 1:1 molar ratio of MPP and PhOH has been loaded inside the flask along with a 1/15 equivalent of Cs_2CO_3 and heated up to $170 \text{ }^\circ\text{C}$ for 1 h. Noteworthy, negligible conversions of both the reactants (higher for phenol, ca. 5% probably due to its salification with the basic catalyst) exclude an important contribution of the direct etherification between the two reactants, nonetheless traces ($Y < 1\%$) of DPP has been observed.

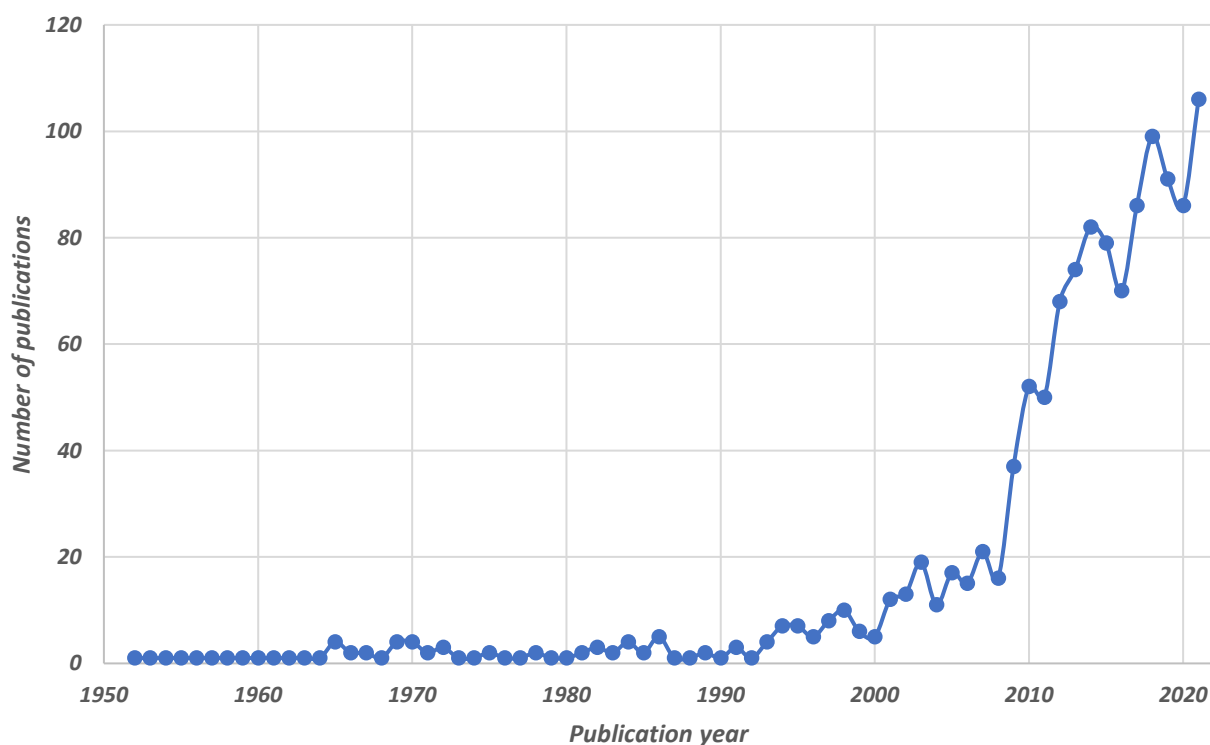


Figure S1. Publication trends about glycerol carbonate on Scopus.

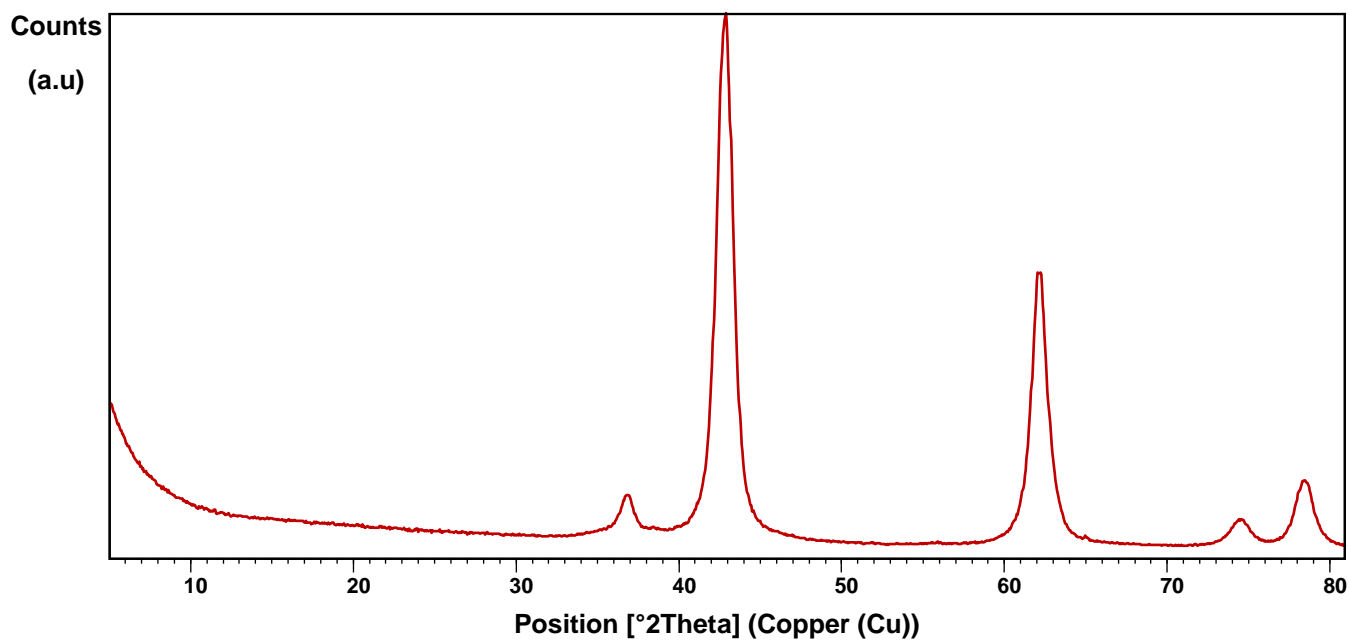


Figure S2. XRD pattern of MgO corresponding to Periclase structure, PDF reference code 01-075-0447.

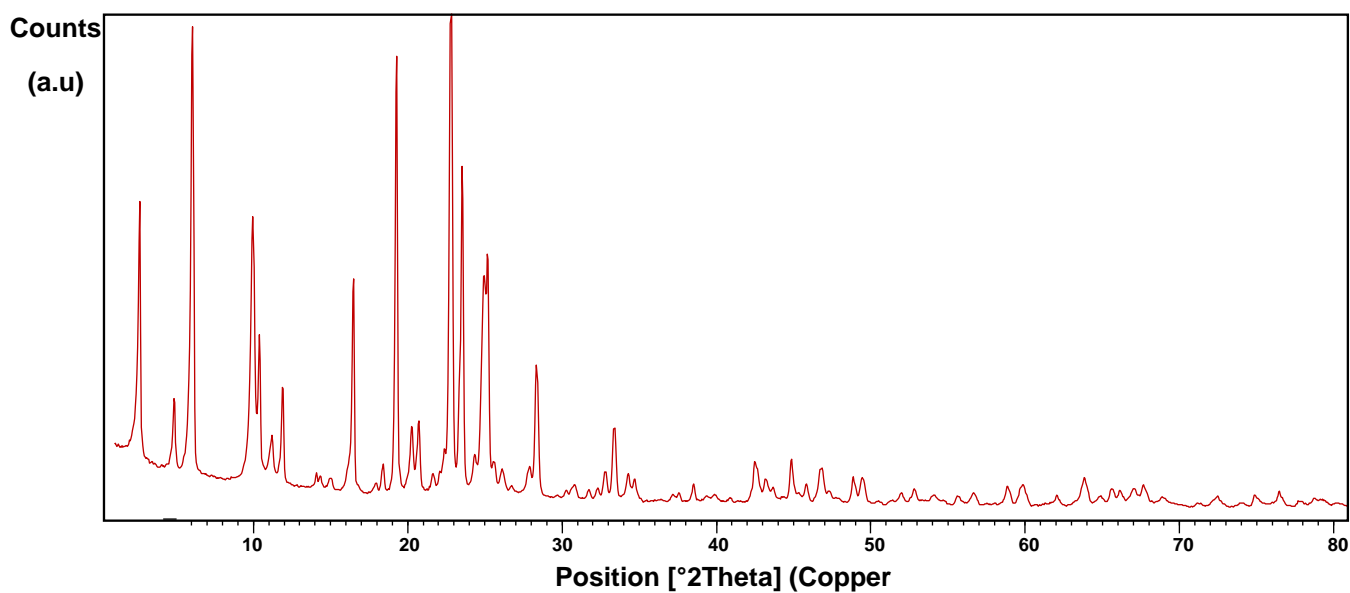


Figure S3. XRD pattern of Na-Mordenite corresponding to Mordenite, syn structure (chemical formula $\text{Na}_{0.31}(\text{Al}_{3.55}\text{Si}_{42.72}\text{O}_{96})(\text{H}_2\text{O})_{2.76}$), PDF reference code 01-080-0645.

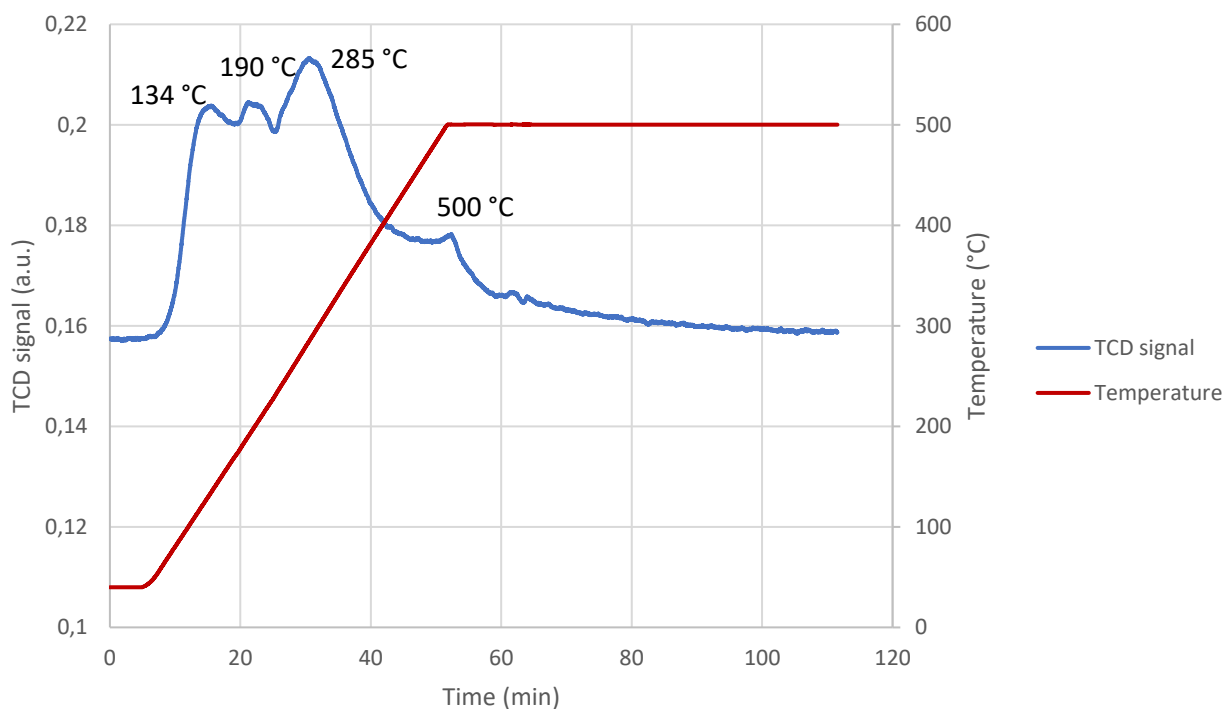


Figure S4. Temperature Programmed Desorption (TPD) of CO₂ on MgO, TCD signal and temperature profile.

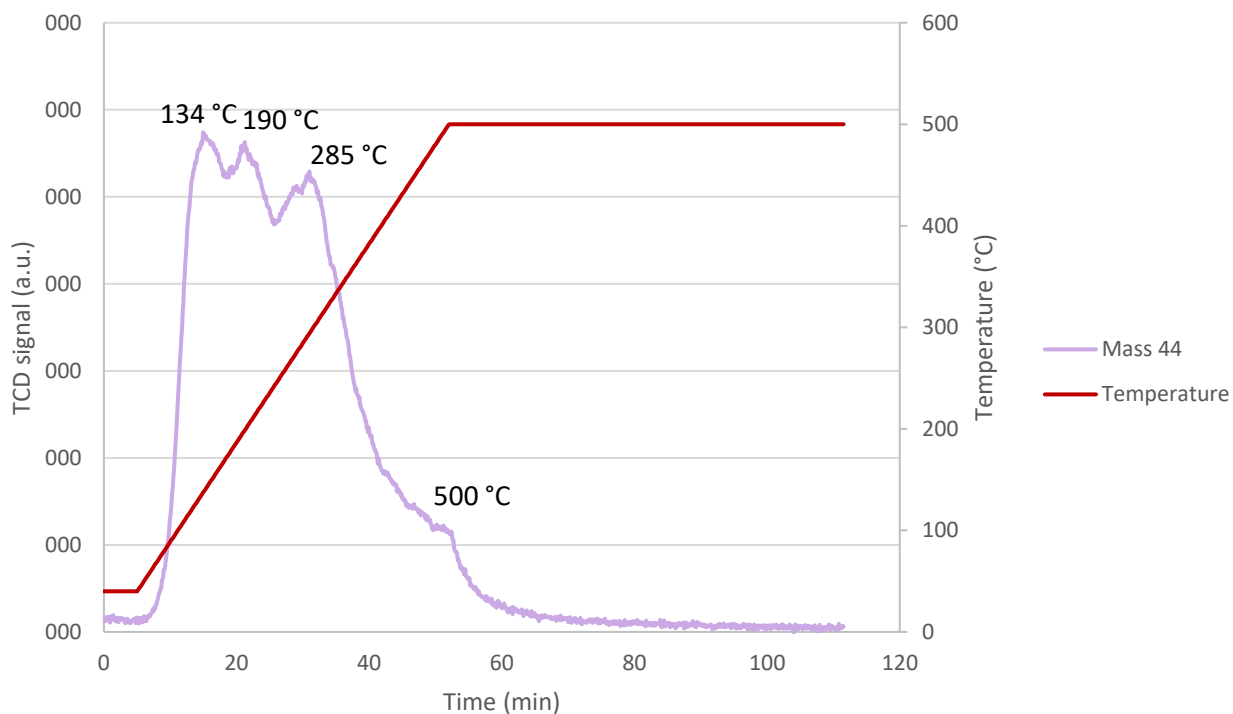


Figure S5. Temperature Programmed Desorption (TPD) of CO₂ on MgO, MS signals and temperature profile.

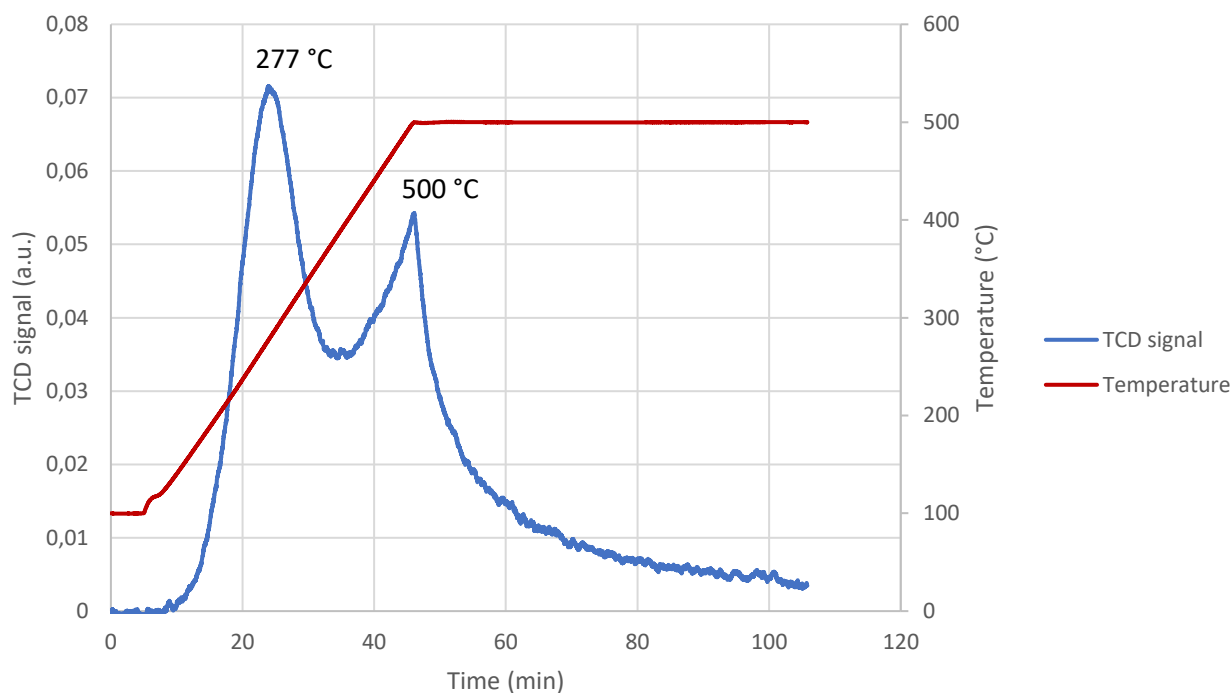


Figure S6. Temperature Programmed Desorption (TPD) of NH₃ on MgO, TCD signal and temperature profile. The observed signal was ascribable to the desorption of water as confirmed by MS profiles.

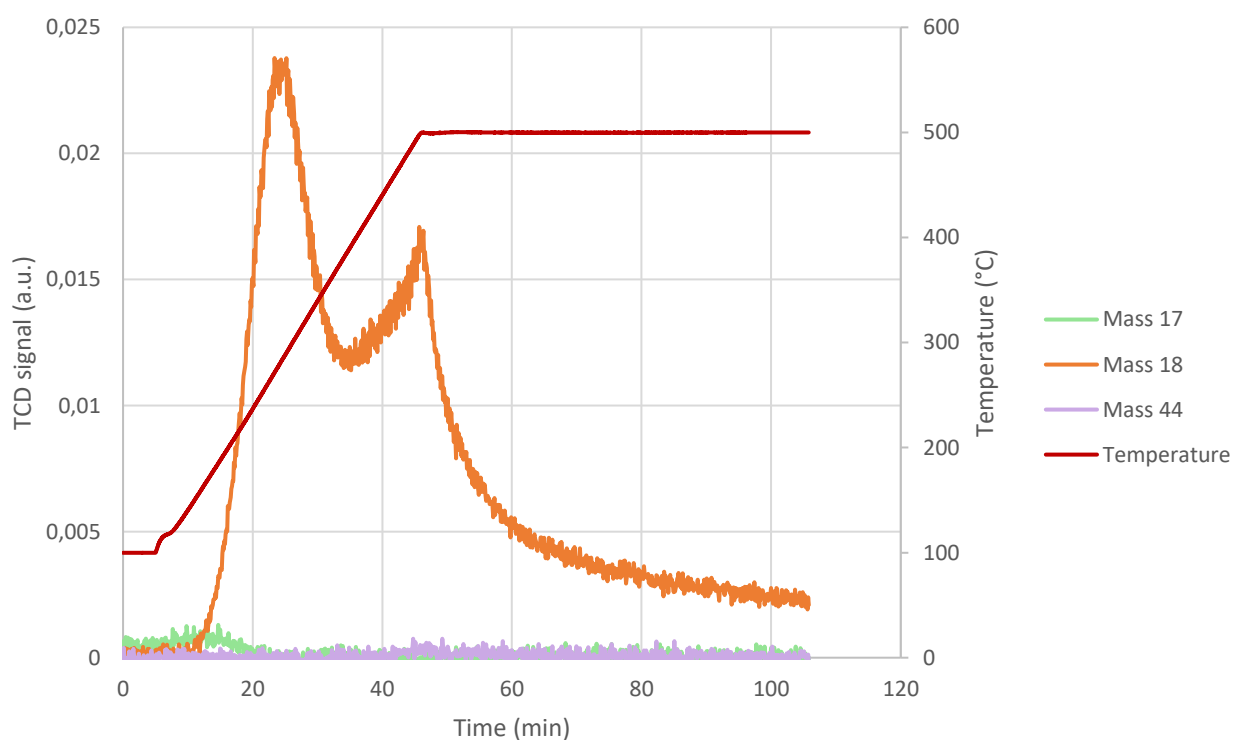


Figure S7. Temperature Programmed Desorption (TPD) of NH₃ on MgO, MS signals and temperature profile.

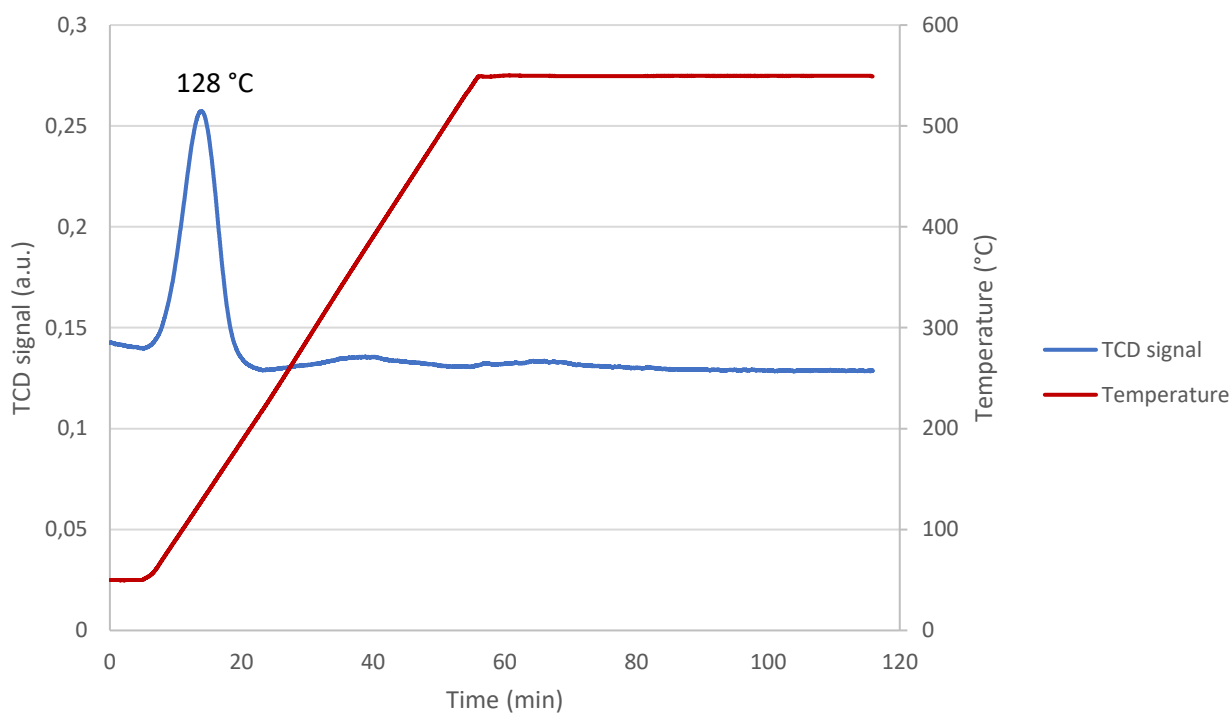


Figure S8. Temperature Programmed Desorption (TPD) of CO₂ on Na-Mordenite, TCD signal and temperature profile.

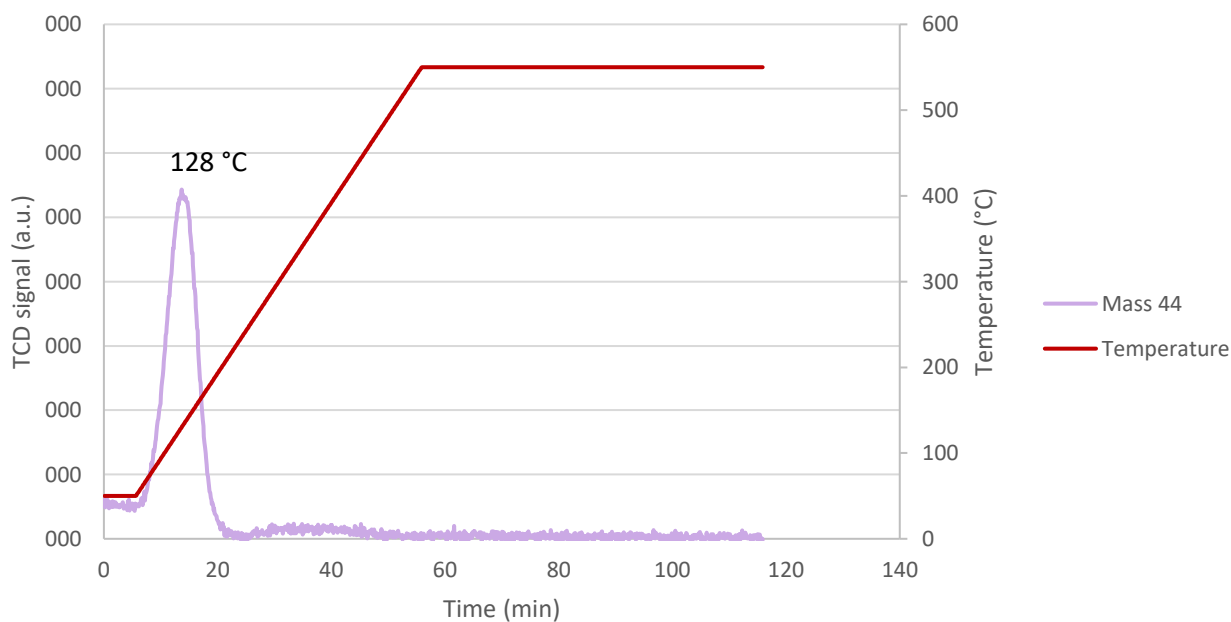


Figure S9. Temperature Programmed Desorption (TPD) of CO₂ on Na-Mordenite, MS signals and temperature profile.

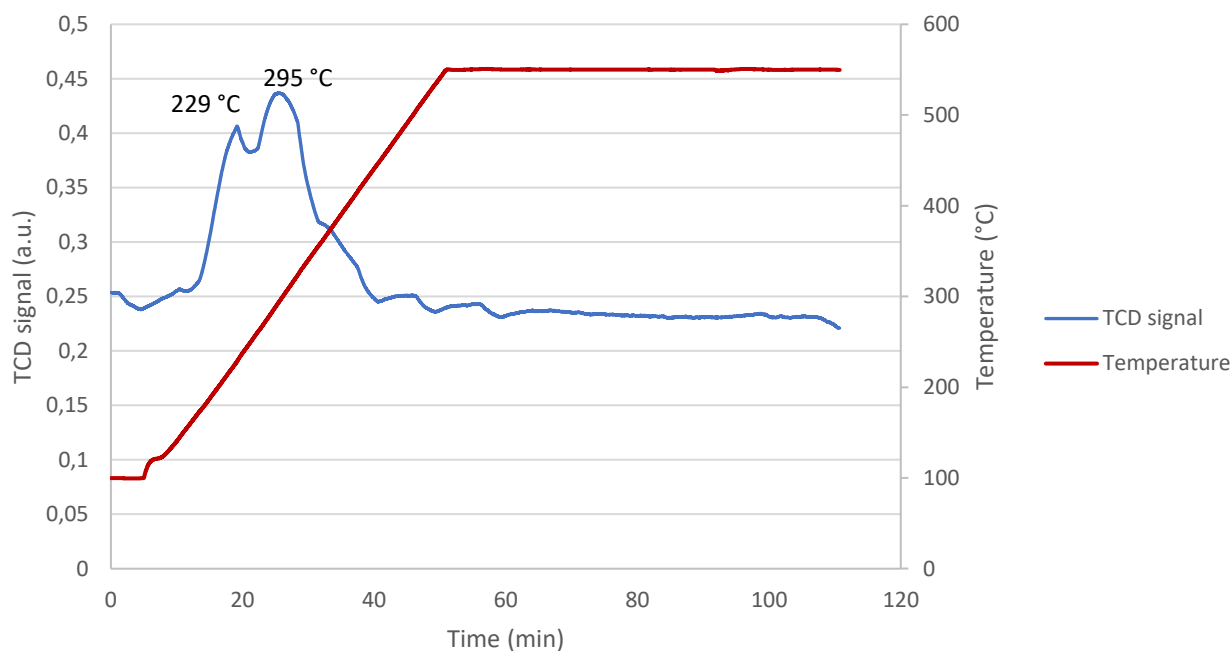


Figure S10. Temperature Programmed Desorption (TPD) of NH_3 on Na-Mordenite, TCD signal and temperature profile.

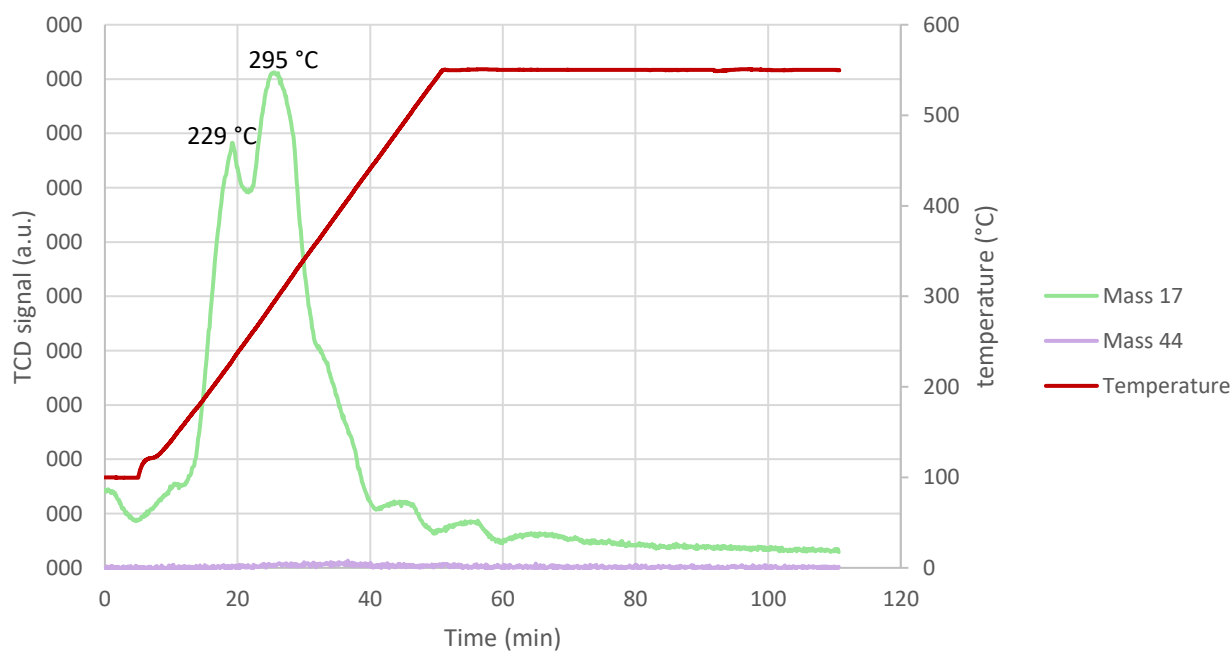


Figure S11. Temperature Programmed Desorption (TPD) of NH_3 on Na-Mordenite, MS signals and temperature profile.

Catalyst	BET SSA (m ² /g)	TPD-CO ₂		TPD-NH ₃	
		(μmol/g)	(μmol/m ²)	(μmol/g)	(μmol/m ²)
MgO	160	640	4	17	0.1
Na-Mordenite	350	1007	2.9	1500	4.3

Table S1. BET SSA of heterogeneous catalysts and quantification of both basic (CO₂-TPD) and acidic surface sites (NH₃-TPD) expressed both in μmol/g and μmol/m² (obtained by dividing the first number by the SSA).

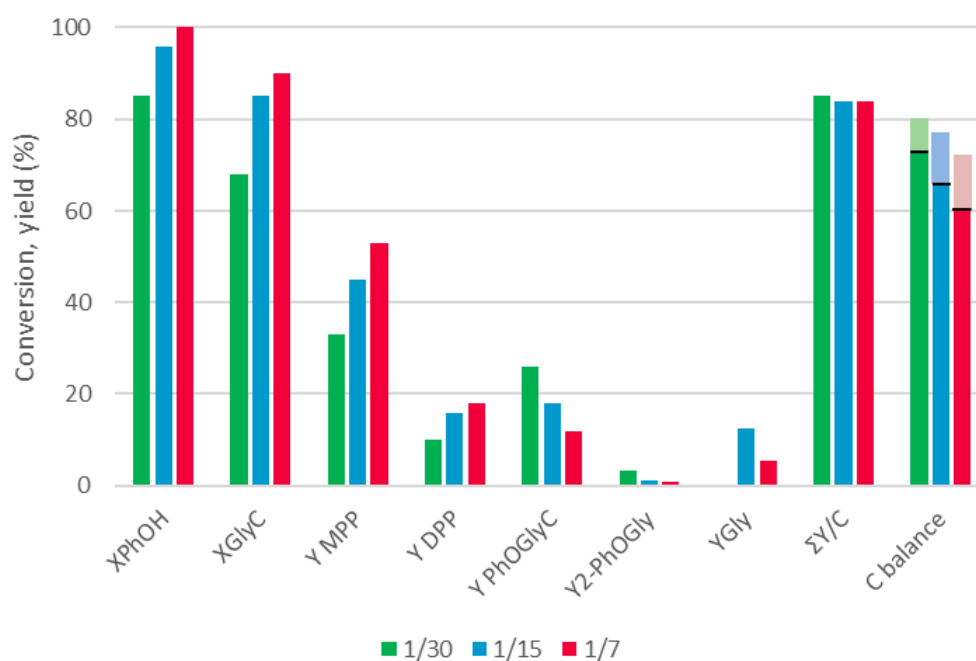


Figure S12. Effect of catalyst amount in homogeneous catalysis.

Conditions: molar ratio PhOH:GlyC = 1:2; T = 140 °C; t = 5 h; P = 1 bar.

Some preliminary optimisations regarding the amount of base have been performed taking also into account the previous experience of the group with a similar reaction (i.e. catechol alkylation with GlyC for the formation of substituted benzodioxanes; Green Chem., 2019, 21, 329). In particular, the effect of the amount of NaOCH₃ was investigated in the reaction between phenol and GlyC. Considering that we are working in neat conditions we chose the 1/15 equivalent with respect of PhOH as the best compromise to obtain a relatively fast kinetic with an acceptable amount of base.

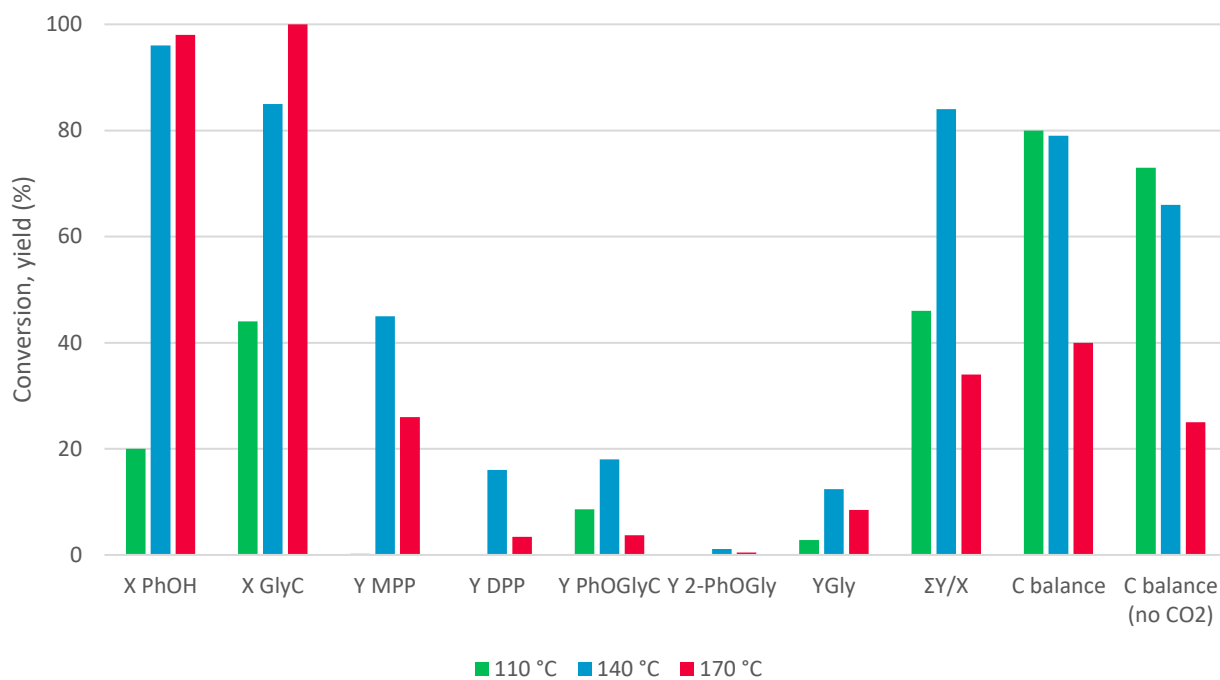


Figure S13. Effect of reaction temperature in homogeneous catalysis.

Conditions: molar ratio PhOH:GlyC:NaOCH₃ = 1:2:0.067; t = 5 h; P = 1 bar.

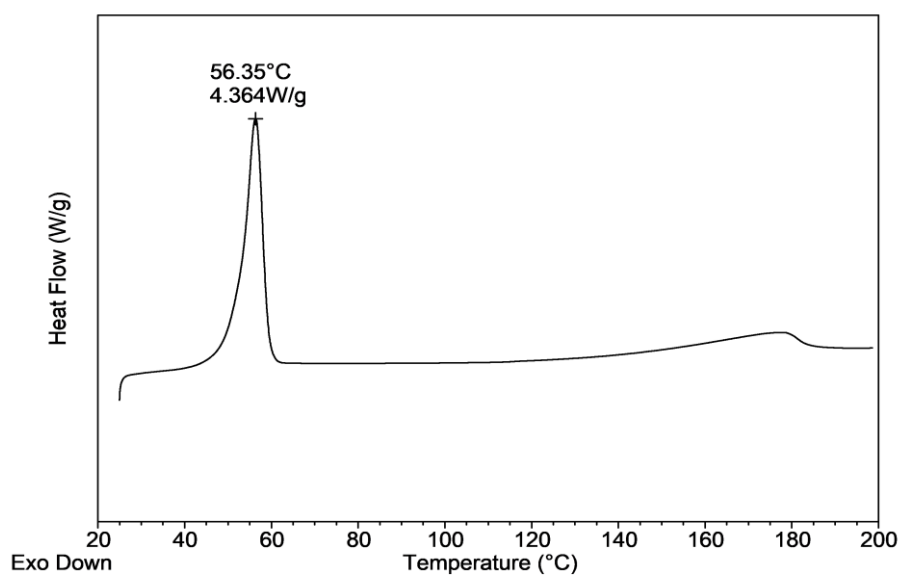


Figure S14. DSC thermogram of MPP.

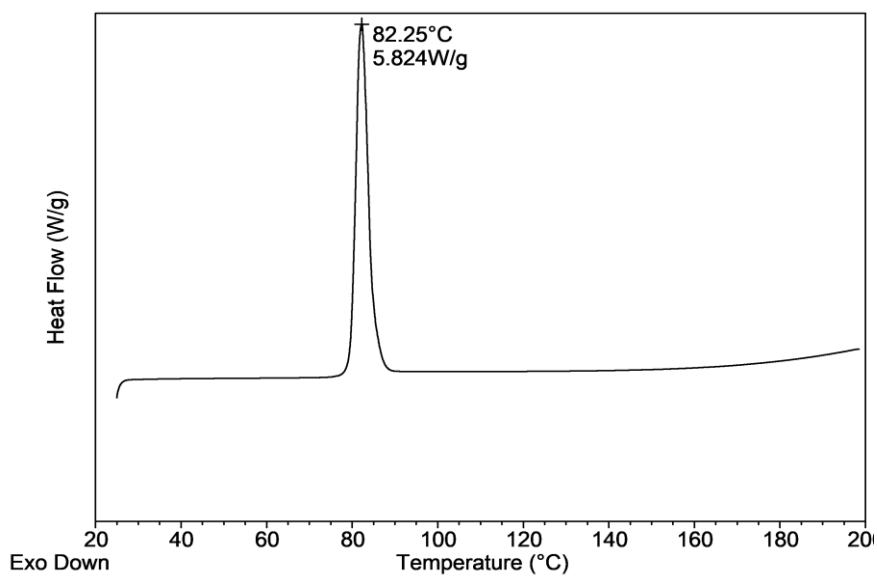


Figure S15. DSC thermogram of DPP.

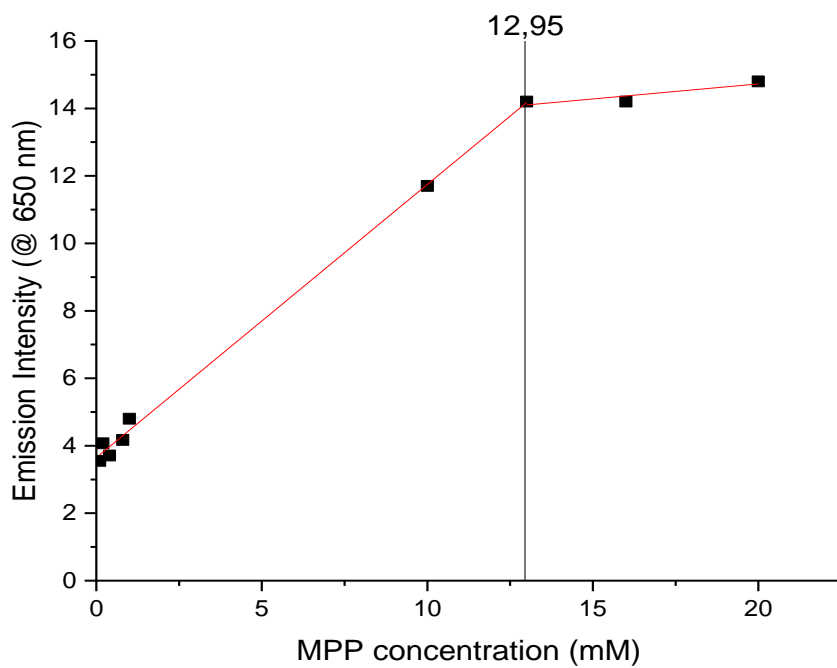


Figure S16. Emission intensity of Nile Red at 650 nm in MPP (squares) solutions.

The intersections of two linear fits (red lines) provides the CMC of MPP.

Products isolation procedure

As a tentative workup procedure after a dedicated test (1/15 equivalent of Cs_2CO_3 , 140°C , 3h, GlyC:PhOH molar ration equal to 2) the obtained mixture was cooled in an ice bath and then firstly recovered in ethyl acetate and then in distilled water, in this way allowing us to completely clean the reaction flask with no residues. Then the ethyl acetate solution has been extracted few times with distilled water, anhydried with sodium sulphate, filtered and distilled under vacuum to remove the solvent and recover the products. The final solution was then weighted and analysed by GC and GC-MS. Interestingly, this mixture is only composed by analysable products like MPP, MPP isomer, DPP and PhOGlyC as demonstrated by the good accordance between the weighted mass of the sample and the quantified moles of products observed. No PhOH, glycerol and GlyC have been observed, the latter probably being completely hydrolysed during the extraction, while the formers readily solubilised in water. Noteworthy, in this way the obtained yields are in good accordance with the one previously reported (without any extraction with water), with the only exception of MPP (see the following table), probably due to its slight solubility in water. Interestingly, unlike GlyC, no losses of PhOGlyC have been detected demonstrating a lower tendency to the hydrolysis of this compound during the extractions.

Entry	X_{PhOH}	X_{GlyC}	Y_{MPP}	Y_{DPP}	Y_{PhOGlyC}	$Y_{2\text{-PhOGly}}$	Y_{Gly}
1) Usual product recovery in acetone after reaction	94	81	52	17.4	14.3	4.3	8.4
2) $\text{H}_2\text{O}/\text{EtOAc}$ extraction	100	100	33	17	16	2.9	0

Table S2: conversion and yields, calculated by GC-FID in the case of 1) usual mixture recovery in acetone after the reaction and 2) after an extraction of the crude mixture with $\text{H}_2\text{O}/\text{EtOAc}$

By a comparison with the available literature we found that Truscello et al. (Green Chem., 2013,15, 625-628, Supporting Information) have followed a similar workup procedure, using a saturated aqueous solution of NaCl, nonetheless no comments neither on MPP repartition nor isolated yields were reported in that paper.

Therefore, we also performed a silica gel column chromatography on the oil obtained after the extraction (the one of entry 2 in the previous table) using a petroleum ether/ethyl acetate eluent mixture starting from 80:20 to 50:50. In this way the efficient separation of all the products has been achieved following this order: DPP (isolated yield of 16.8%), PhOGlyC (isolated yield 14.5%) and MPP+2-PhOGly (isolated yield 34.2%).