Supporting information

LOW-IMPACT SYNTHESIS OF MESOSTRUCTURED ACIDIC CATALYSTS: TOWARD THE EFFICIENT CONVERSION OF CRUDE GLYCEROL

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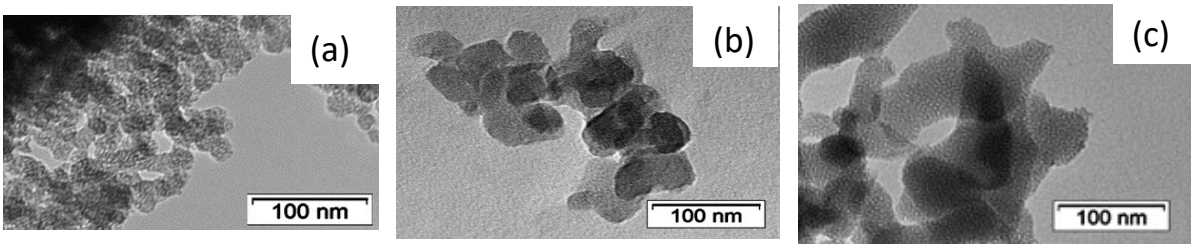

Figure S1. TEM images of Ga-NS synthetized with (a) 1g NH_3 (b) 5g NH_3 (c) 5g of NH_3 followed by hydrothermal treatment

Table 1. Specific surface area assessed by N_2 physisorption of three nanospheres synthetized with different amount of NH_3 and with or without hydrothermal treatment

Synthesis	S_{BET} (m^2/g)
1g NH_3	1166
5g NH_3	1156
5g NH_3 + Hydrothermal treatment	862

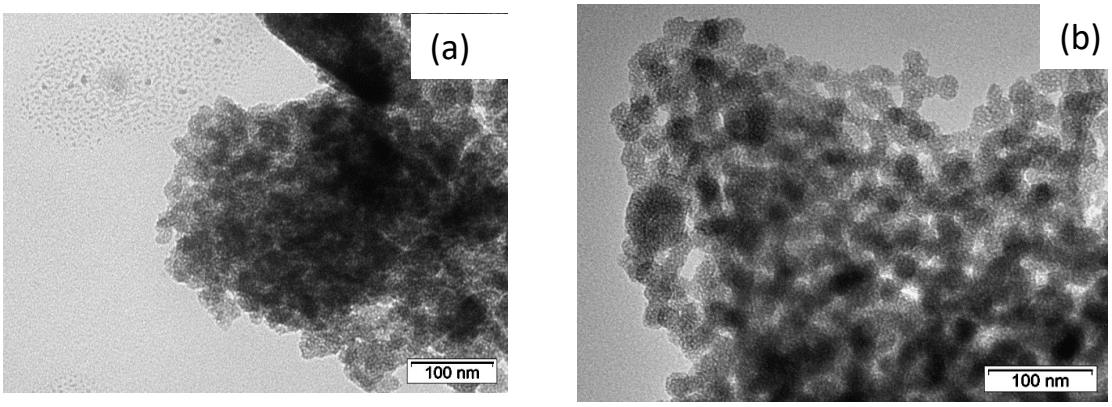

Figure S2. TEM images of Ga nanospheres with different Si/Ga ratio. (a) Ga-NS-42, (b) Ga-NS-137

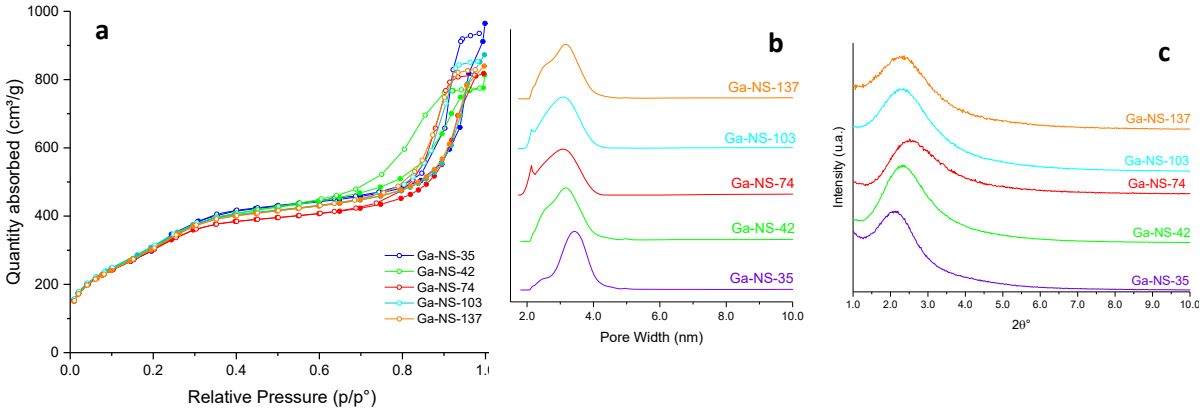

Figure S3. N_2 physisorption of Ga nanospheres (a), DFT pore size distribution (b) and XRD pattern (c)

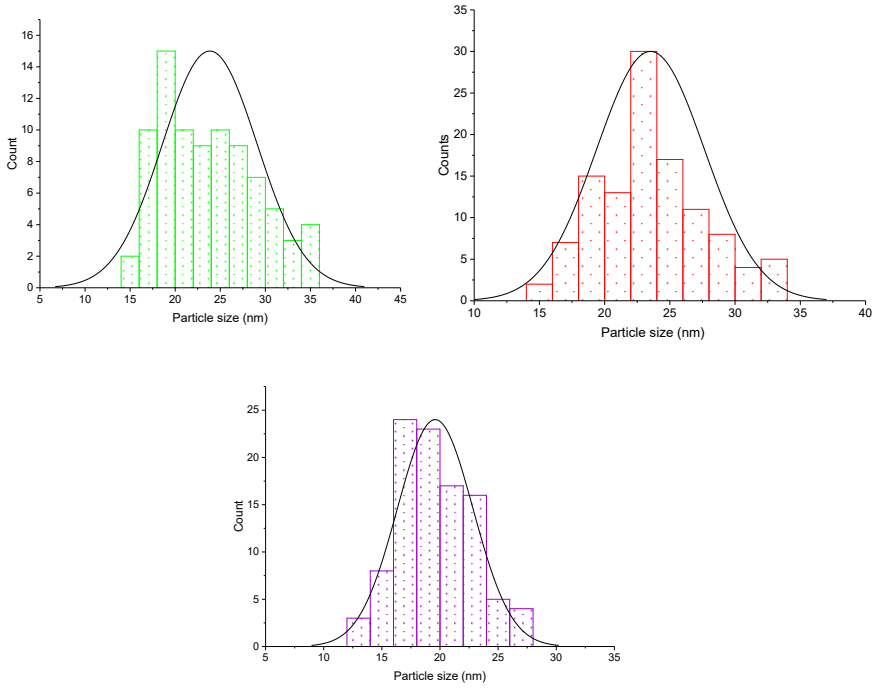

Figure S4. Particle size distribution over 100 particles of Ga-NS-37 (in green), Ga-NS-74 (in red) and Ga-NS-37 (in purple).

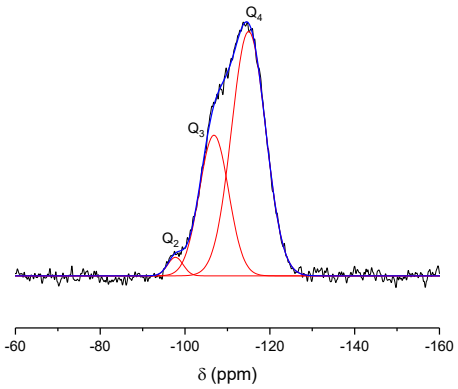

Figure S5. ^{29}Si solid state MAS NMR spectrum, Direct Excitation experiment (DE), of Ga-NS-74. The precise assignment of the Q^n chemical shifts was based on Cross Polarization (CP) experiments presented below.

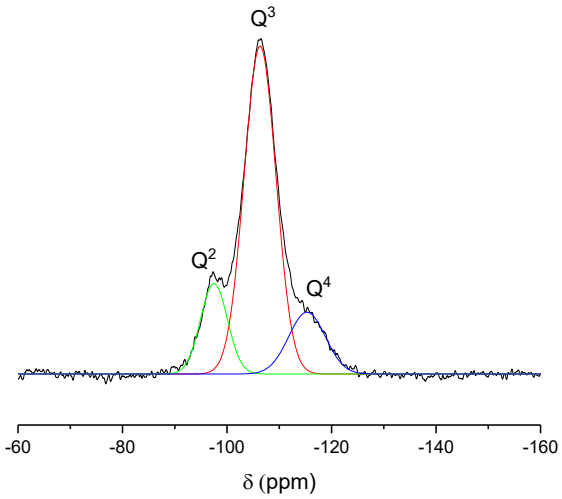

Figure S6. ^{29}Si solid state MAS NMR spectrum, Cross Polarization experiment, of Ga-NS-74

XPS WAGNER PLOT ANALYSIS

The two Auger parameters, A and α', are respectively indicators of initial-states and final-states effect which are related to the chemical environment of the Ga species.[1] In order to visualize these two parameters, the results are plotted in a three-axis Wagner Plot: on the X axis, the binding energy of the X-ray photoelectrons, on the left side, the kinetic energy of the

Auger electrons and on the right side, the Auger parameters (Figure S7). The Auger parameter is the intercept of the linear relationship presented in the following equation:

$$E_K = \alpha' - E_B$$

where E_K is the kinetic energy of the Auger electron, α' the modified Auger parameter and E_B is the binding energy of $Ga3d_{5/2}$.

In a Wagner Plot representation, the relation between E_K and E_B can be expressed according to the hereby equation:

$$E_K = [const + 2(V_M + kQ)] - 3E_B$$

The value [const + 2(VM + kQ)] is related to the initial state of the ionized atom, where V_M is the local Madelung potential, Q is the ground-state valence charge and k is the change in core potential resulting from the removal of a valence electron [36].

The latter equation highlights the fact that compounds with similar initial state effects will appear in a on a slope 3 straight line . Initial state effects can be seen as shifts in the orbital energies of an atom before it is subjected to X-ray irradiation.

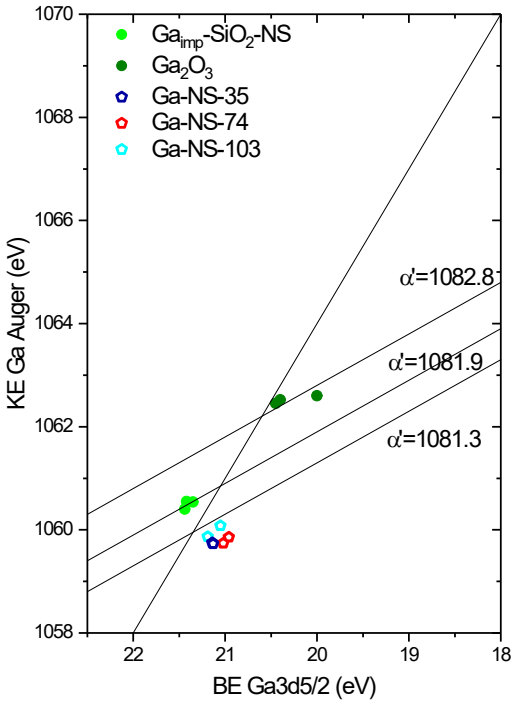

Figure S7. Wagner plot (Ga LMM Auger vs. XPS Ga3d5/2) of Ga-NS-35, Ga-NS-74 and Ga-NS-103, gallium impregnated and gallium oxide.

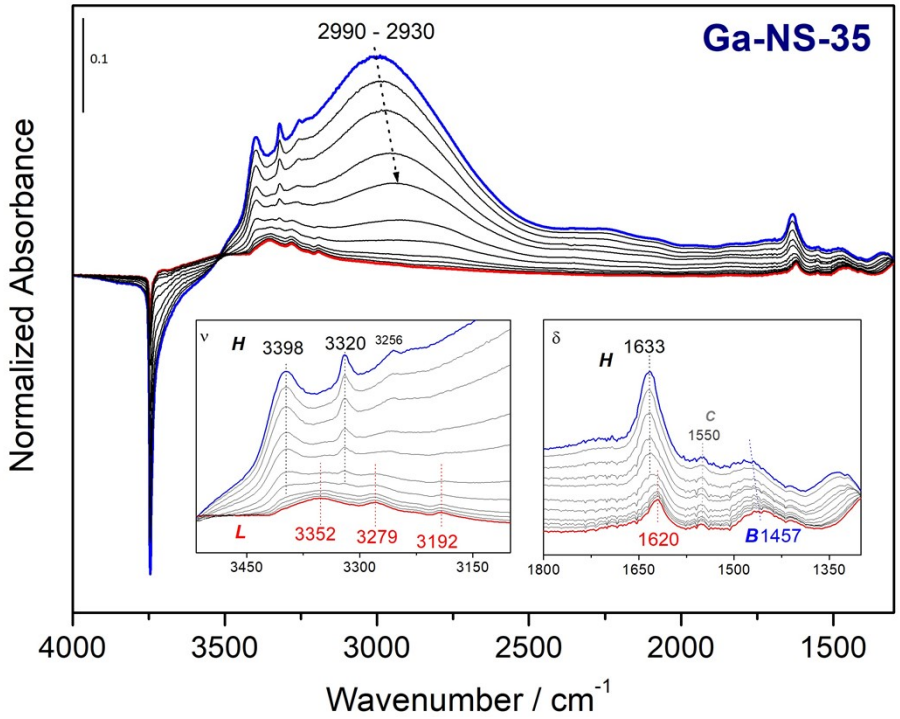

Figure S8. Difference spectra of ammonia dosages on Ga-NS-35 (insets are related to a magnification of the high and low frequency regions)

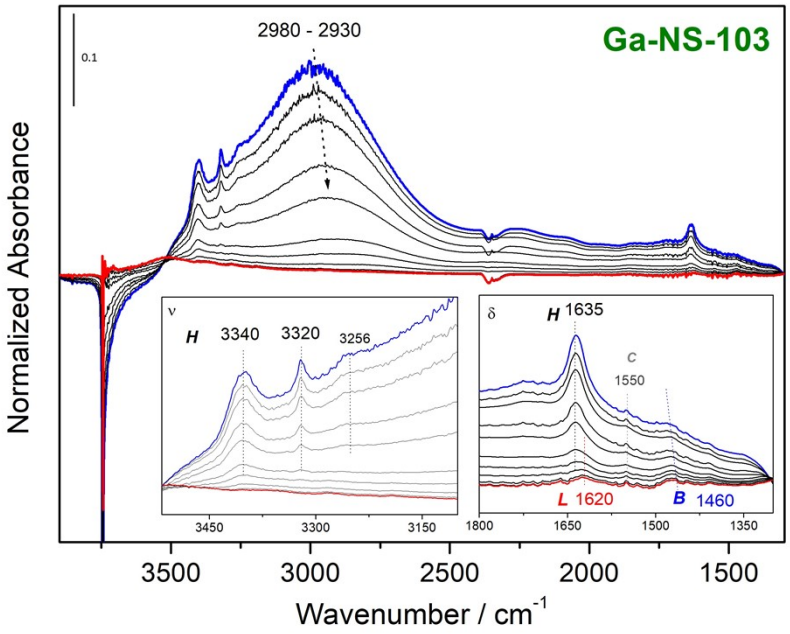

Figure S9. Difference spectra of ammonia dosages on Ga-NS-103 (insets are related to a magnification of the high and low frequency regions)

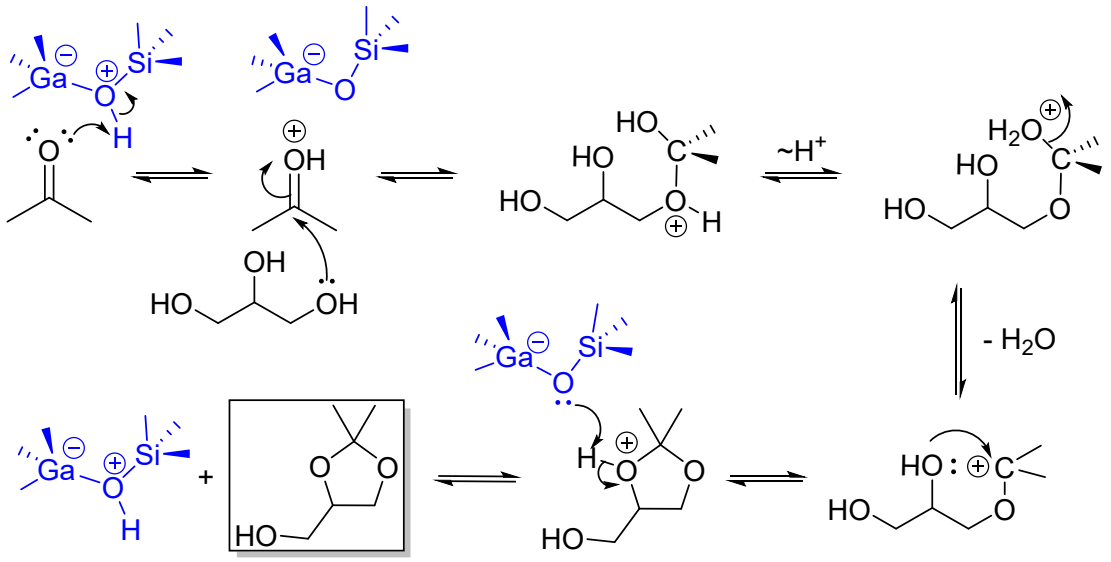

Figure S10. Proposed mechanism of the formation of solketal involving the Brønsted acidity caused by the isomorphic substitution of Si by Ga. In blue, a schematic gallosilicate structure of the solid material.

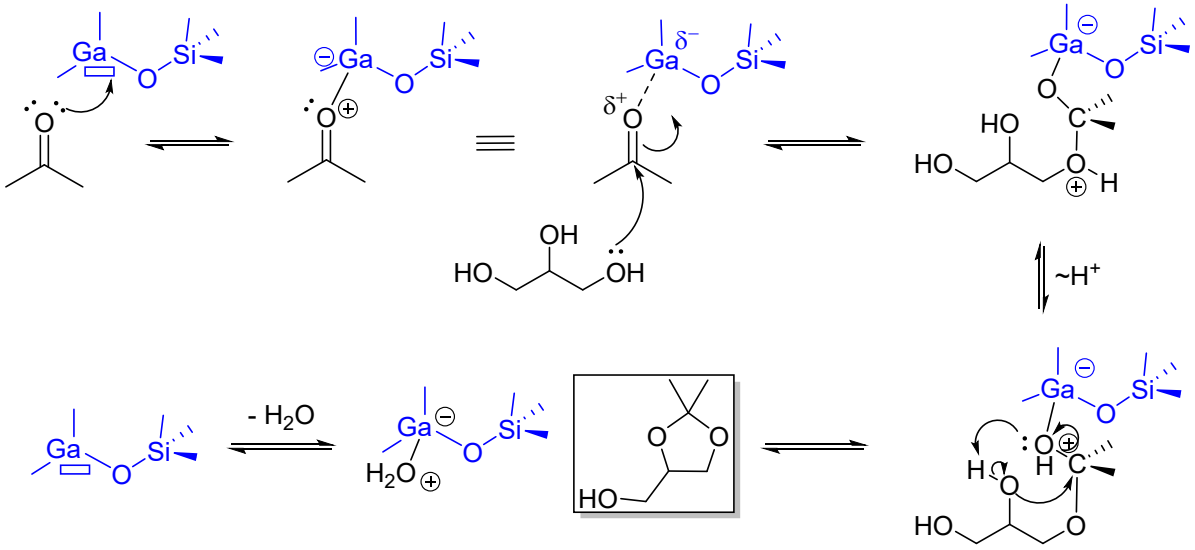

Figure S11. Mechanism of the formation of solketal involving the Lewis acidity of trivalent Ga atom inserted in the structure. In blue, a schematic representation of an active site of the solid material. Mechanism proposed by Li et al.[2]

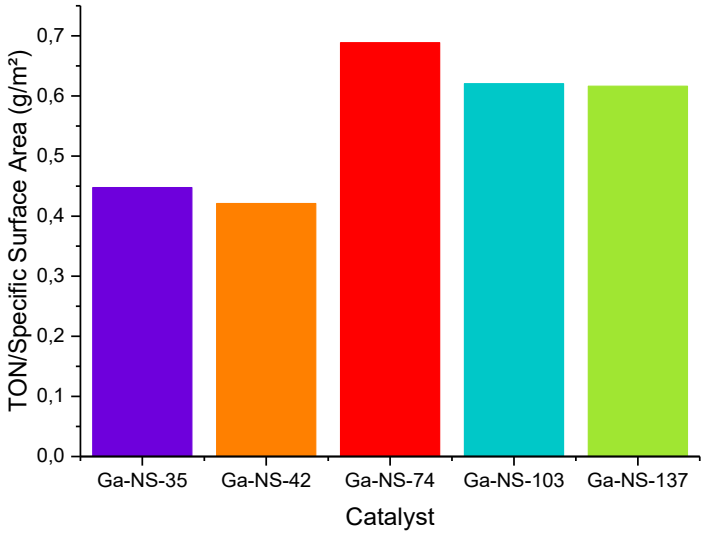

Figure S12. Normalization of the catalytic activity with the specific surface area assessed by N_2 physisorption

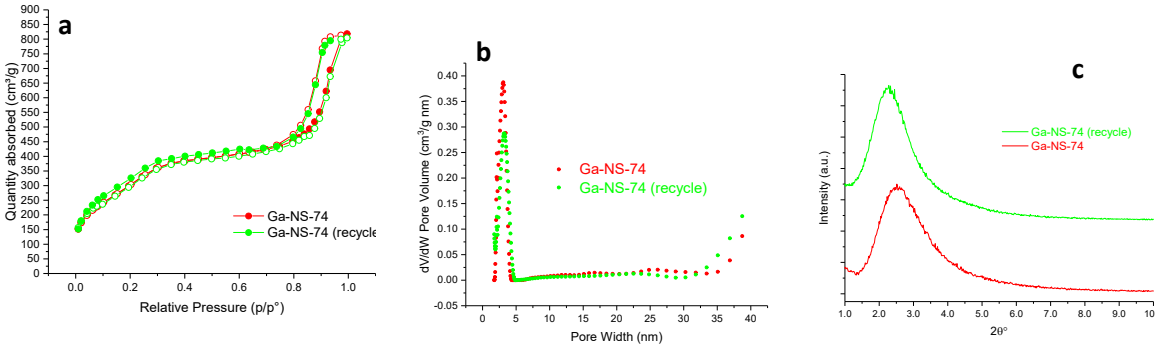

Figure S13. N_2 physisorption isotherm (a), Pore size distribution (b) and XRD pattern (c) of Ga-NS-74 before and after 4 catalytic cycles.

Table S2. Yield and selectivity for the conversion of glycerol to solketal in different conditions. G:A 1:4, 10 mg catatyst, 80°C, 16h

	Yield (%)	Selectivity (%)
Pure	61	98

t-butanol	57	97
Methanol	53	95
H_2O	47	98

Table S3. Catalytic results for the conversion of glycerol to solketal in different simulated crude glycerol composition mixture. G:A 1:4, 10 mg catalyst, 80°C, 2h.

	Yield (%)	Selectivity (%)	Conversion (%)	TON
Pure Glycerol	38	90	41	1418
H_2O (10 wt. %)	25	92	27	1089
CH_3OH (0.75 wt.%)	36	87	41	1624
CH_3OH (10 wt.%)	35	95	34	1484
NaCl 10g/L (10 wt. %)	20	94	22	929
NaCl 180 g/L (10 wt. %)	15	90	16	589

CHARACTERIZATION OF THE FUNCTIONALIZATION

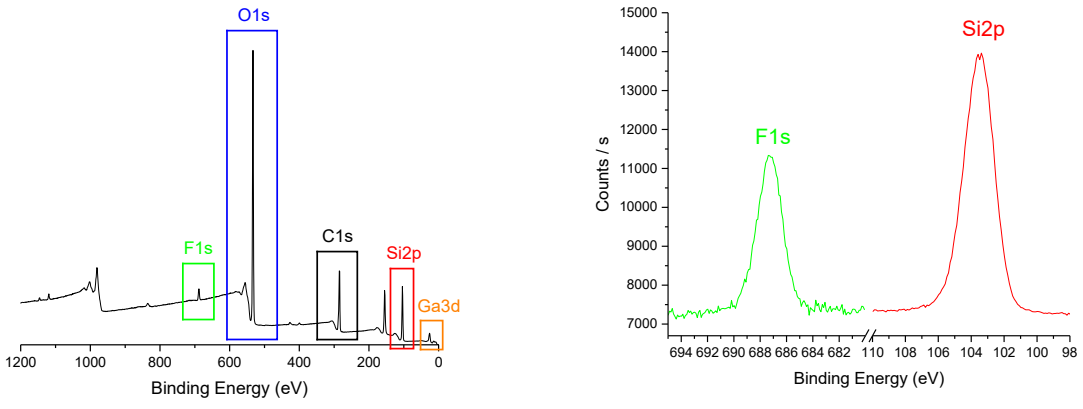

Figure S14. (a) XPS spectrum of Ga-NS-74-F and (b) highlight of the F1s peak and of the Si2p peak of Ga-NS-74-F

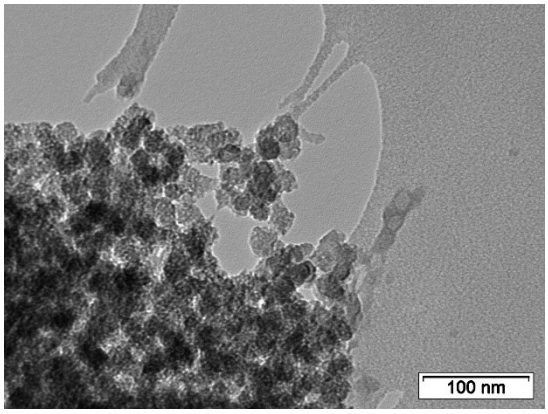

Figure S15. TEM image of Ga-NS-74-F

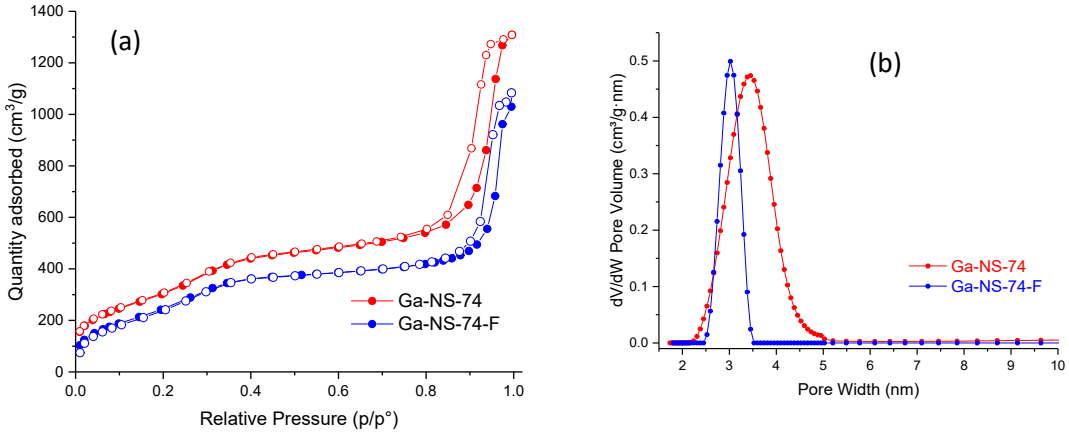

Figure S16. N_2 physisorption isotherms (a) and pore size distribution (b) of functionalized (Ga-NS-74) and non functionalized gallosilicates (Ga-NS-74-F)

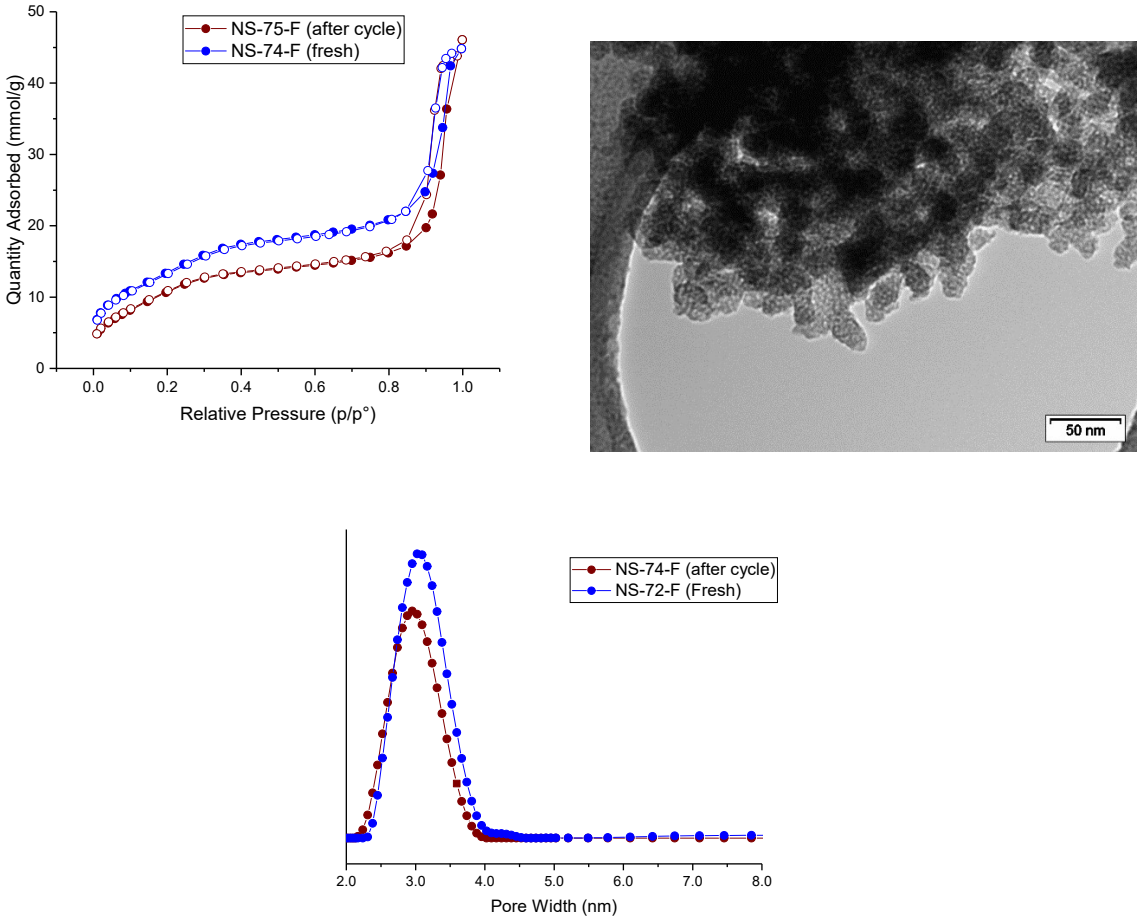

Figure S17. N_2 physisorption isotherms (a), TEM images (b) and Pore size distribution (c) of GA-NS-74-F recovered after the use, washed 3X with iso-propanol and calcined 2 hours at 450°C.

Table S4. Textural properties of Ga-NS-74-F before and after recovering from catalytic cycle.

	NS-74-F (Fresh)	NS-74-F (After cycle)
S_{BET} (m^2/g)	1000	975
Pore size (nm)	3.0	2.9
Si/Ga ratio (ICP-OES)	73	73

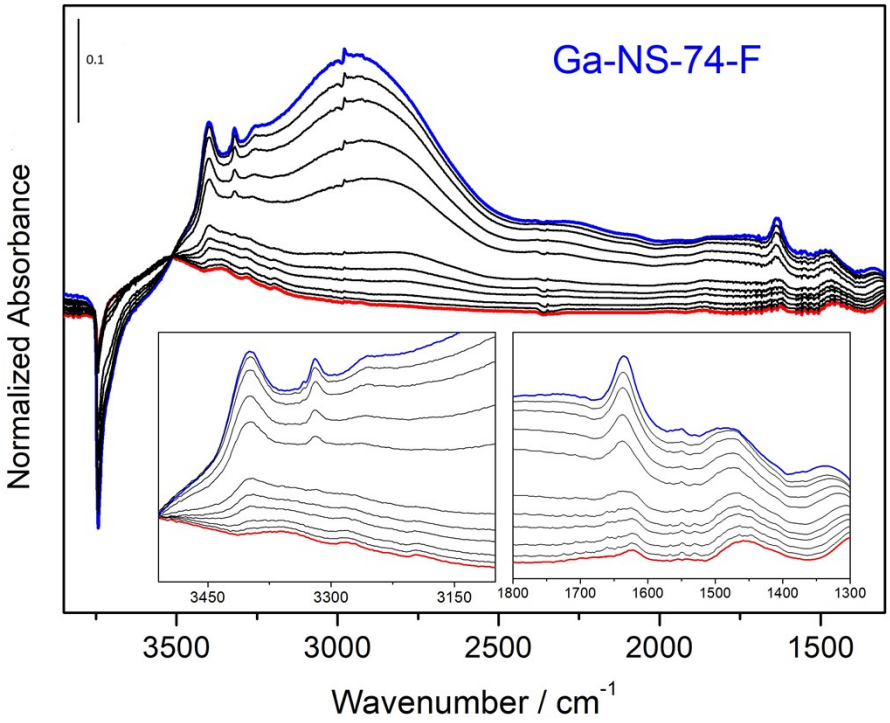

Figure S18. Difference spectra of NH_3 dosages on Ga-NS-74-F, blue curve refers to the highest dosage and red curve refers to the lowest dosage. Insets are related to the magnification of the stretching (left) and bending region (right) of ammonia

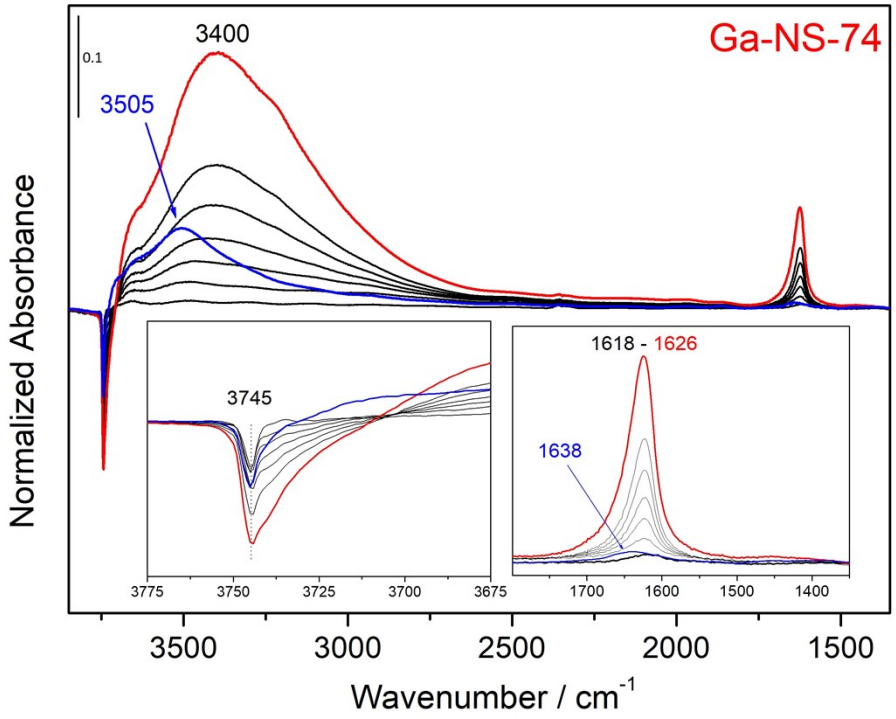

Figure S19. Difference spectra of H_2O dosage on Ga-NS-74

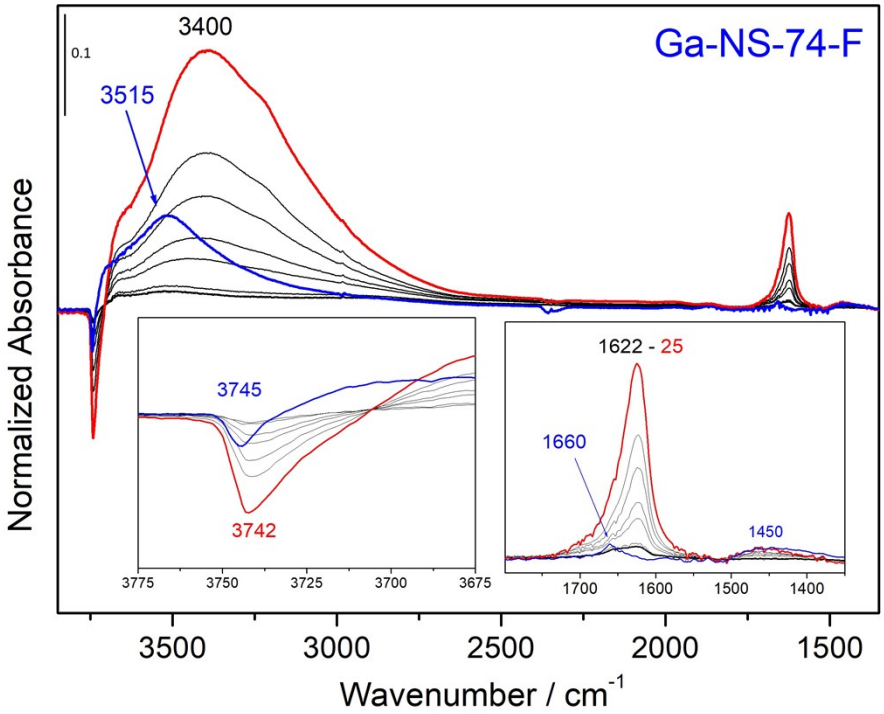

Figure S20. Difference spectra of H_2O dosages on Ga-NS-74-F

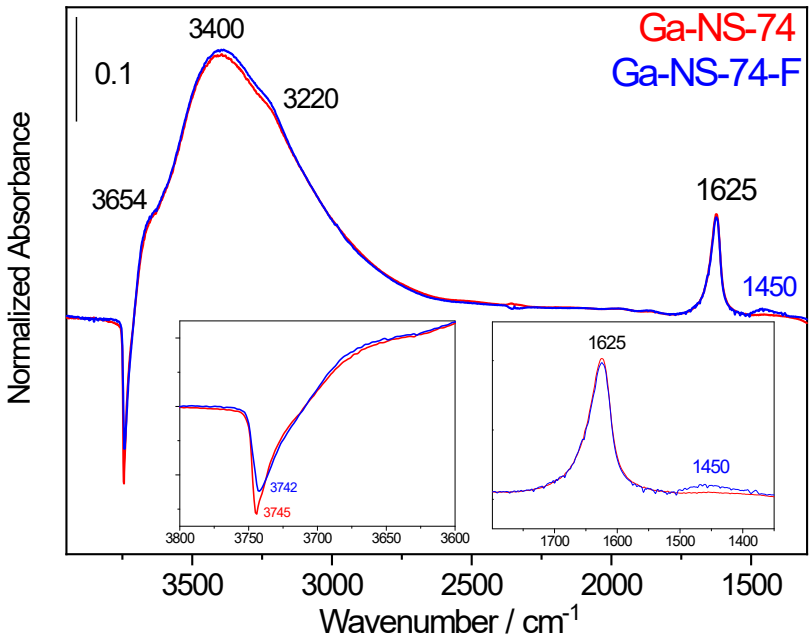

Figure S21. Difference spectra of Ga-NS-74 and Ga-NS-74-F both in contact with 5 mbar equilibrium pressure of water

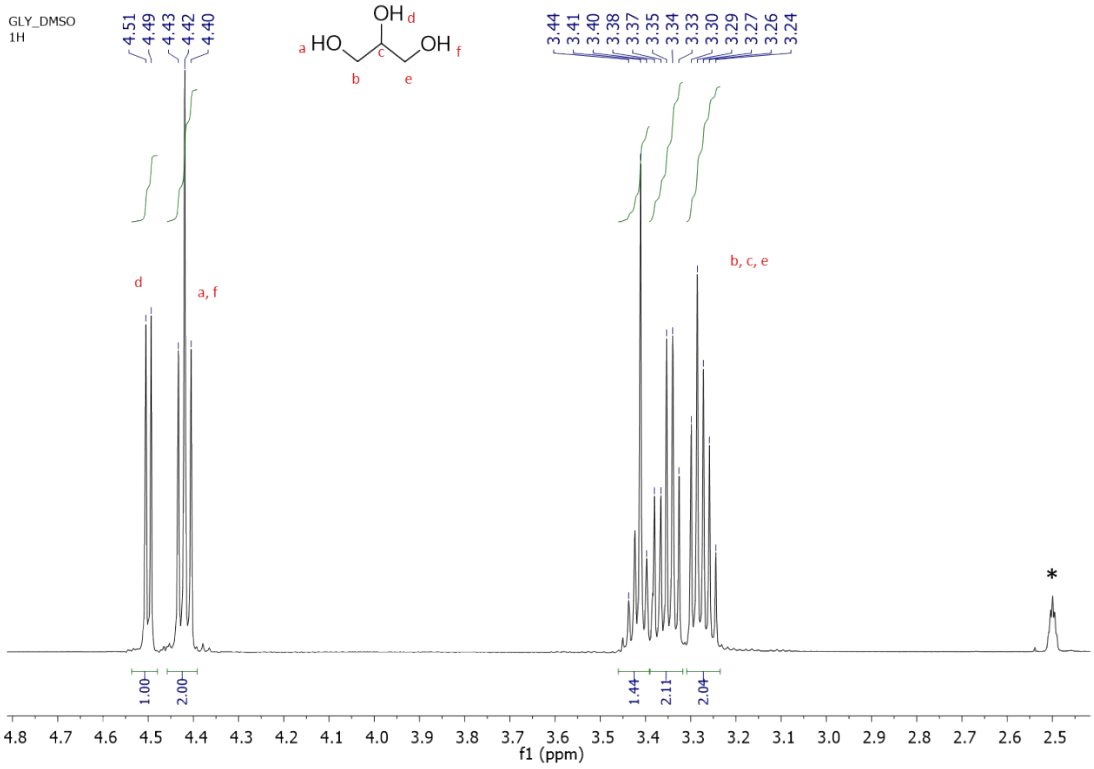

Figure S22. ^{1}H liquid state NMR spectrum registered at 9.4T of pure glycerol. *residual solvent peak (DMSO)

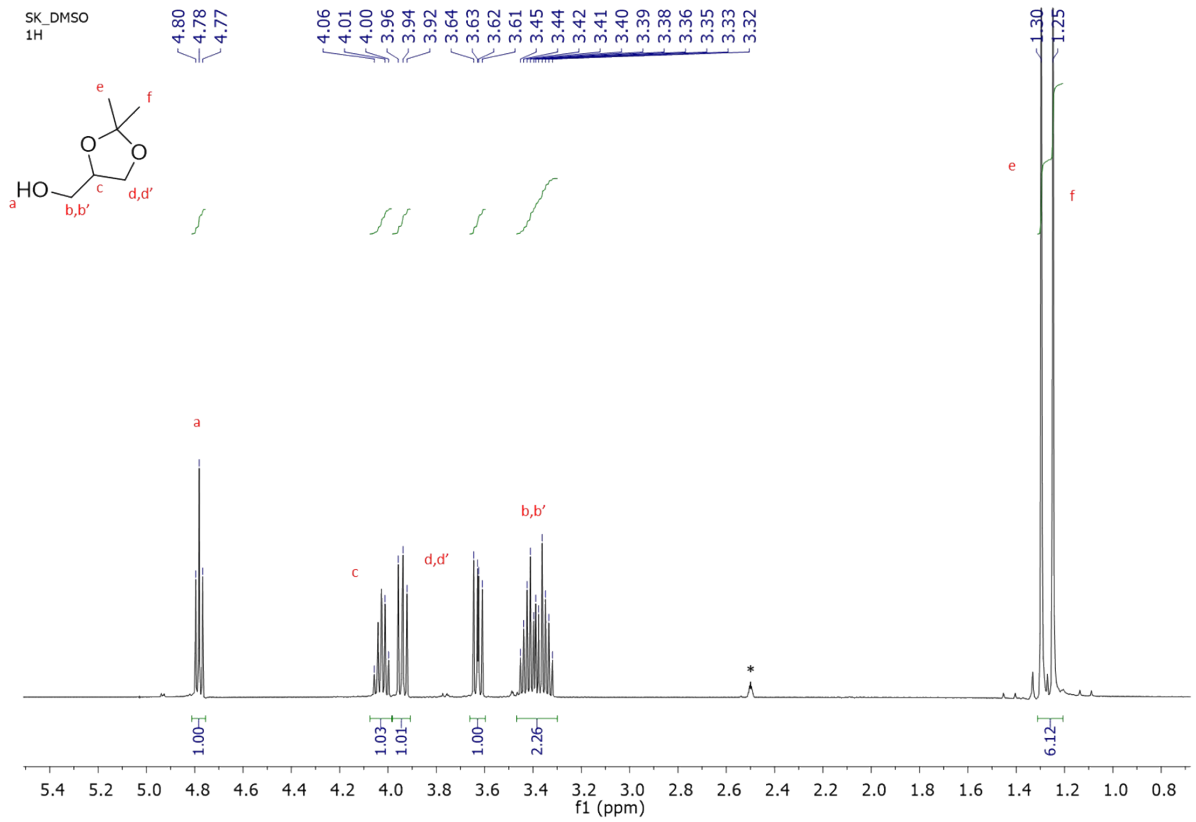

Figure S23. ^{1}H liquid state NMR spectrum registered at 9.4T of pure solketal. *residual solvent peak (DMSO)

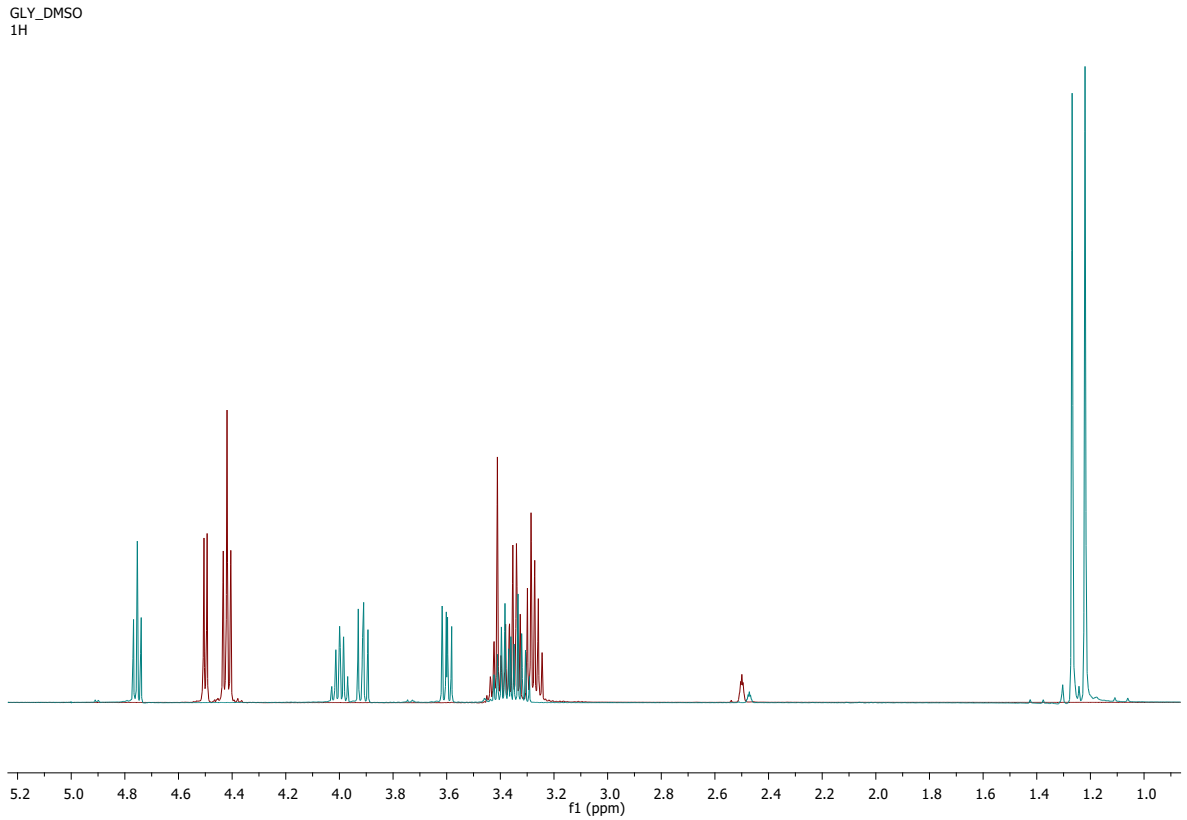

Figure S24. Superposition of ^{1}H liquid state NMR spectra registered at 9.4T of pure glycerol (in red) and pure solketal (in blue).Solvent (DMSO)

REFERENCES

1. Bourque, J. L.; Biesinger, M. C.; Baines, K. M., Chemical state determination of molecular gallium compounds using XPS. *Dalton Trans* **2016,** *45* (18), 7678-96.
2. Li, L.; Korányi, T. I.; Sels, B. F.; Pescarmona, P. P., Highly-efficient conversion of glycerol to solketal over heterogeneous Lewis acid catalysts. *Green Chemistry* **2012,** *14* (6), 1611-1619.