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Supporting Information

Clays as Effective Solid Acid Catalysts for the Preparation of Sugar Esters with Surfactant Properties

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Author Contributions

V.P. Methodology:Equal

Supporting Information

Table of content

Experimental Section

All the reagents, solvents and catalysts were purchased from the Sigma-Aldrich (Merck) except for D-glucose that was purchased from Carlo Erba reagents. They were used without further purification.

Synthesis of D-glucose palmitate esters.

In a one necked flask provided with a reflux condenser, palmitic acid (molar ratio D-glucose:palmitic acid 1:2) and acetylacetone (0.5 ml of each mmol of D-glucose) were added at the selected temperature (80 or 100 °C) and the reaction mixture was stirred (500 rpm) for about 30 minutes. Subsequently, the catalyst (10% w/w on the total reaction weight) was added and the mixture was stirred for another 30 minutes. Finally, D-glucose was added and the reaction was carried out for 7 hours under vigorous stirring. The progress of reaction was monitored by TLC analysis by using *n*-hexane and ethyl acetate in 6:4 ratio as eluent. The decrease in intensity of the spot corresponding to palmitic acid was concomitant with the increase in intensity of several spots with very similar Rf. After 7 hours the reaction was stopped. The reaction mixture was cooled to room temperature. Then dichloromethane was added (10 ml for 1 mmol of D-glucose) and stirred for about one hour. The organic phase was roughly separated from the solid residue and washed with 10 ml of saturated $NaHCO_3$ for three time to remove unreacted palmitic acid. The organic phase solvent was evaporated under vacuum. The solid was then purified through flash chromatography (gradient eluent *n*-hexane:ethyl acetate, from 6:4 to 1:2 ratio) to isolate the products. Although the reaction mixture was purified by repeated flash chromatography, only one product, the most abundant one (**1**), was obtained in pure form and characterized by using NMR and mass spectrometry analyses.

Catalyst cation exchanging procedure.

Montmorillonite K10 (5 g) was stirred with 200 ml of a 0.5 M solution of $Fe(NO_3)_3$ for 24 h. Then the solid was filtered and washed repeatedly with distilled water. Finally, it was dried at 100 °C for three hours. The obtained solid was tested for the esterification reaction.

Gas Chromatography Analysis.

Determination of palmitic acid was performed with GC methods of Cramer and co-workers[1] with slight modification. The analysis was performed on an Agilent 6890 Gas Chromatography system by using a Alltech Heliflex® AT-5 capillary column (30m×0.32mm ID×0.25 m), with split injection and FID detection. Before injection, palmitic acid and products were silylated according to Degn and coworkers.[2] The conversion was determined on 5-10 mg of the dried crude reaction mixture, separate from the unreacted sugar and the catalyst in order to have only the unreacted free palmitic acid and the product mixture in the sample. This was then silylated using N,O-bis(trimethylsilyl)trifluoroacetamide activated with 1% of chlorotrimethylsilane for 20' at 70°. The sample were immediately injected using heptadecane as standard.
Conversion was determined on palmitic acid using the following formula assuming that if the reaction has not proceeded at all, thus if the conversion was 0%, the derivatized sample consist only in palmitic acid. Subtracting the residual PA moles in the sample obtained by GC analysis to the total moles of PA, corresponding to the 0% conversion, we obtain the reacted PA moles:

$$\text{Conv \%} = \frac{\left(\text{mol PA at 0\% conversion - mol PA determined by GC}\right)}{\left(\text{mol PA in the sample}\right)} \times 100$$

Catalysts Characterization.

IR spectroscopy. The FT-IR studies of probe molecules (pyridine) adsorption and desorption were carried out with a BioRad FTS-60 (Segrate, Italy) spectrophotometer equipped with a mid-IR MCT detector. The experiments were performed on a sample disk of 20 mg after a simple calcination treatment at 180 °C, 20 minutes at ambient pressure and 30 minutes under vacuum. One spectrum

was collected before the adsorption of the probe molecule as a blank experiment. Therefore, pyridine adsorption was carried out at room temperature, and the following desorption steps were performed from room temperature to 250 °C. The spectrum of each desorption step was acquired every 50 °C after cooling the sample. For quantitative analysis, the amount of adsorbed pyridine ($mmol_{Py}/g_{cat}$) was calculated on the basis of the relationship reported by Emeis[3] from the integration of diagnostic bands evaluated in the spectra registered at 150 °C.

BET analysis. The morphology studies on the catalysts were studied by N_2 adsorption and desorption isotherms measured at liquid nitrogen temperature with an automatic surface area analyzer (Sorptomatic 1900 instrument). The surface area was calculated using BET equation that considers N_2 molecular area of 16.2 $Å^2$.

Structural characterization of D-glucose palmitate esters.

NMR Spectroscopy. NMR Spectroscopy ^1H, ^{13}C NMR and spectra were acquired at 400.33 and 100.95 MHz, respectively, on a Bruker Advance 400 spectrometer (Bruker, Karlsruhe, Germany) interfaced with a workstation running a Windows operating system and equipped with a TOPSPIN software package. The analysis was performed dissolving 15 mg of products in 0.6 ml of $CDCl_3$ and the spectra were recorded at 25 °C. Chemical shifts given in parts per million (ppm) and referenced to the solvent signals (7.25 and 77.4 ppm from tetramethylsilane, for ^1H and ^{13}C, respectively). ^{13}C NMR signal multiplicities were based on attached proton test (APT) spectra and assigned on the basis of ^1H-^{13}C correlation experiments (Heteronuclear Single Quantum Correlation spectroscopy, HSQC, and Heteronuclear Multiple Bond Correlation spectroscopy, HMBC). ^1H signals were assigned by using ^1H–^1H correlation experiments (Correlation SpectroscopY, COSY).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 8.6 Hz, 6H, -$(CH_2)_{12}$-C**H$_3$**), 1.15 – 1.40 (br s, 48H, -(C**H$_2$**)$_{12}$-), 1.42 (s, 3H, C**H$_3$**$^{1'}$), 1.58 – 1.67 (m, 4H, C**H$_2$**$^{\beta}$), 2.28 (s, 3H, C**H$_3$**$^{6'}$), 2.34 (t, J = 10.0 Hz, 4H, C**H$_2$**$^{\alpha}$), 2.39 (s, 3H, C**H$_3$**$^{5'}$), 2.57 (s, 3H, C**H$_3$**$^{10'}$), 2.94 (s, 2H, C**H$_2$**$^{8'}$), 3.89 (dd, J = 14.5, 4.8 Hz, 1H, H^{6b}), 4.07 (br d, J = 14.4 Hz, 1H, H^{6a}), 4.92 - 5.03 (m, 3H, H^3, H^4, H^5), 5.05 (br s, 1H, H^2), 6.48 (br s, 1H, H^1).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.53(-$(CH_2)_{12}$-**C**H_3), 14.90 (**C**$H_3^{10'}$), 24.18 (**C**$H_3^{1'}$), 25.09 (**C**H_2^{β}), 29.42 (**C**$H_3^{5'}$), 29.46, 29.64, 29.76, 29.83, 29.99, 30.08 (-(**C**H_2)$_{12}$-), 32.01 (**C**$H_3^{6'}$), 34.34 (**C**H_2^{α}), 53.43 (**C**$H_2^{8'}$), 73.05 (C^6), 79.84 (C^2), 81.64 (C^3, C^4), 83.89 (C^5), 108.96 (C^1), 112.22 ($C^{2'}$), 149.52 (C=**C**$^{3'}$), 159.30 (C=**C**$^{9'}$), 179.80 (**C**OO), 194.27 (O=**C**$^{4'}$), 205.93 (O=**C**$^{7'}$).

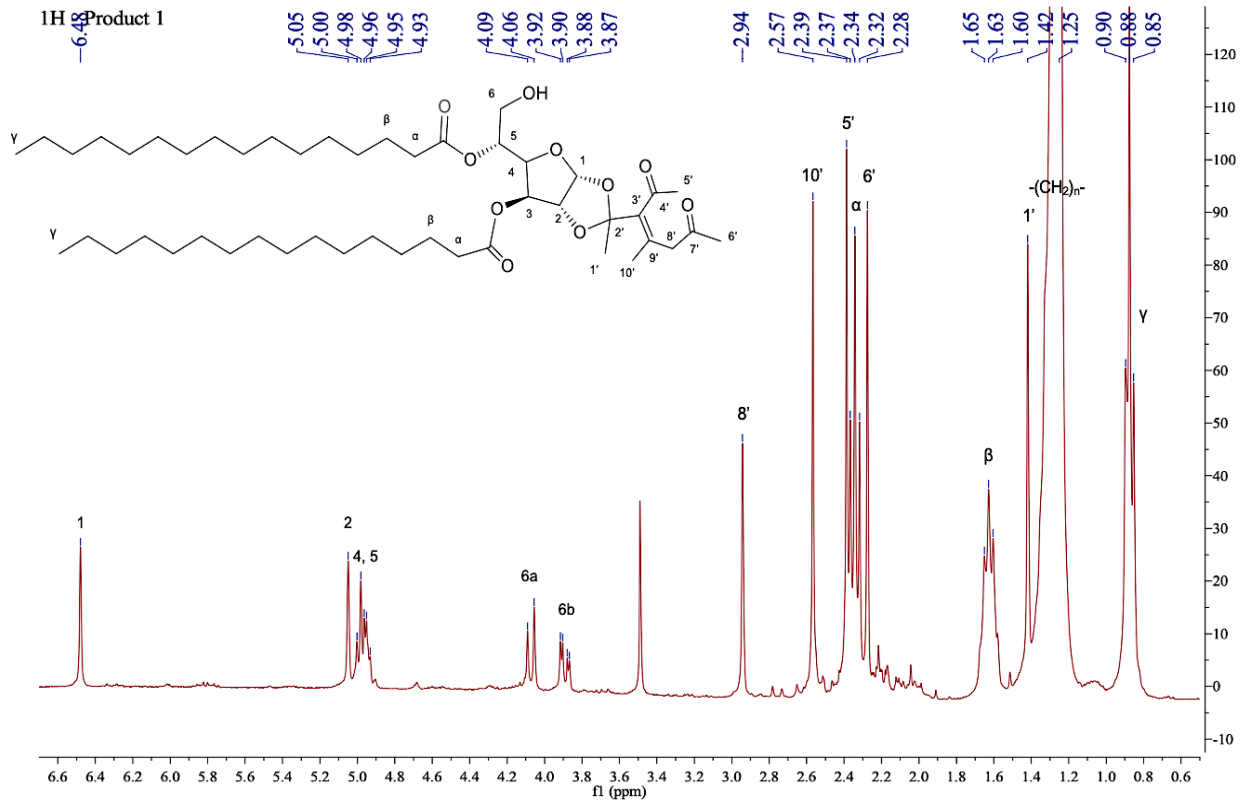
Mass Spectroscopy. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo Finnigan LCQ Advantage spectrometer (Hemel Hempstead, Hertfordshire, U.K.) using a positive and negative ion mode. The sample was injected to the mass spectrometer in a MeOH solution. MALDI ionization mass spectra were recorded on a Microflex apparatus using a HCCA matrix type (α-cyano-4-hydroxycinnamic acid).
ESI-MS negative-ion mode, *m/z*: 801.79 $[M - H2O - H]^-$. MALDI (HCCA): *m/z:* 860.8 $[M + K + H]^+$.

Interfacial tension analysis. The surface properties of the synthesized crude surfactant were measured by a Gibertini Tensiometer (equipped with a platinum ring), using the Du Noüy method.[4,5] Specifically, the interfacial tension ($\gamma_{O/W}$) of sunflower/double distilled water system was measured as a function of the bio-surfactant concentration (0.002 – 0.500% w/v) at a constant temperature (22.0 ± 0.2 °C). These measurements were performed in triplicate to limit the standard deviation (less than 0.7 mN m^{-1}). From these results, the apparent critical micelle concentration (CMC) and the interfacial tension at the CMC (γ_{CMC}) were extrapolated.

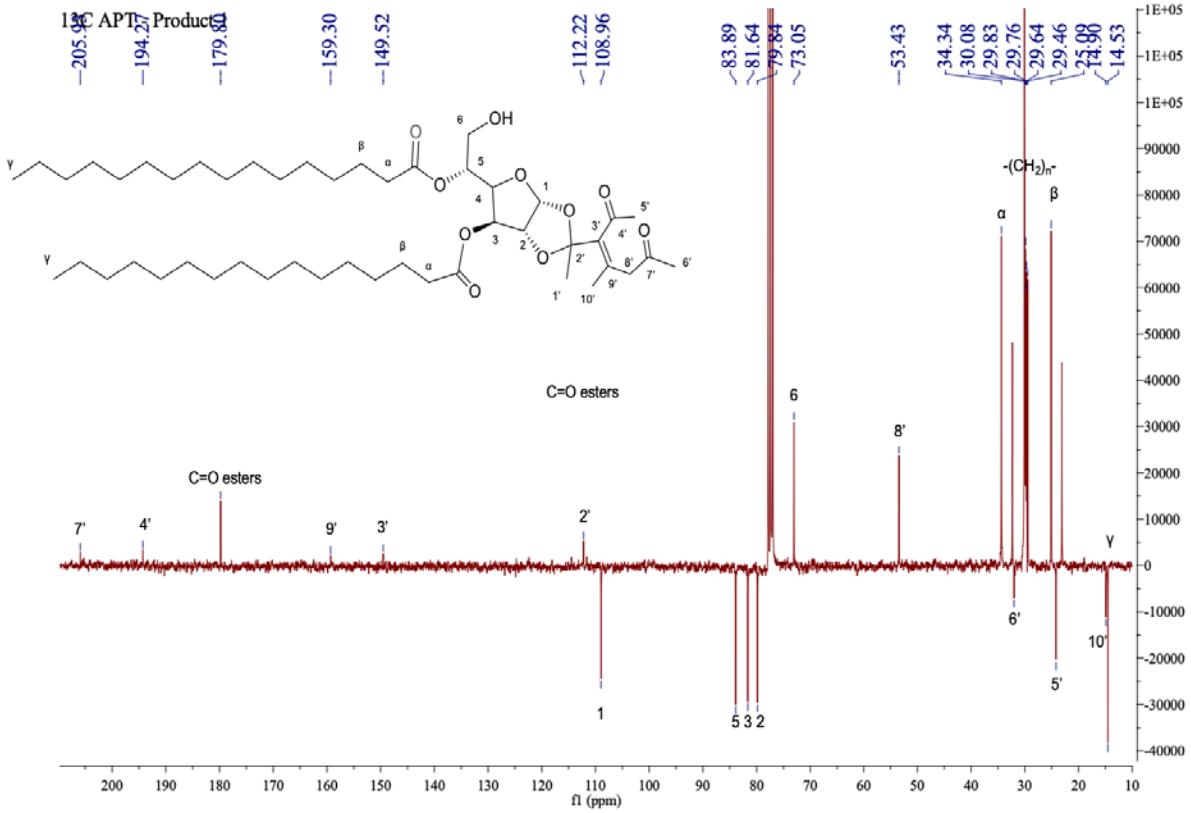
[1] J. F. Cramer, M. S. Dueholm, S. B. Nielsen, D. S. Pedersen, R. Wimmer, L. H. Pedersen, *Enzyme Microb. Technol.* **2007**, *41*, 346–352.
[2] P. Degn, L. H. Pedersen, J. Duus, W. Zimmermann, *Biotechnol. Lett.* **1999**, *21*, 275–280.
[3] C. A. Emeis, *J. Catal.* **1993**, *141*, 347–354.
[4] L. P. Du Nouy, *J. Gen. Physiol.* **1925**, *7*, 625–631.
[5] A. Olietti, E. Pargoletti, A. Diona, G. Cappelletti, *J. Mol. Liq.* **2018**, *261*, 199–207

NMR Spectra

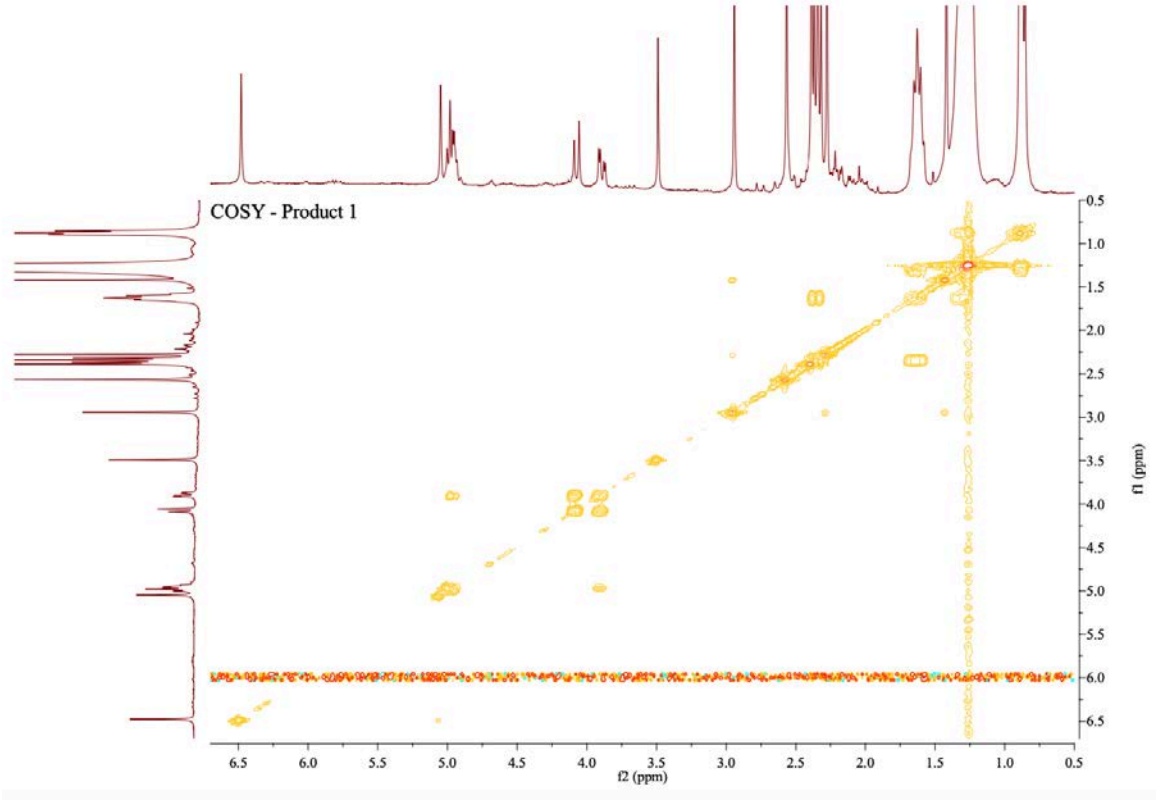
^{1}H-NMR – Product **1**



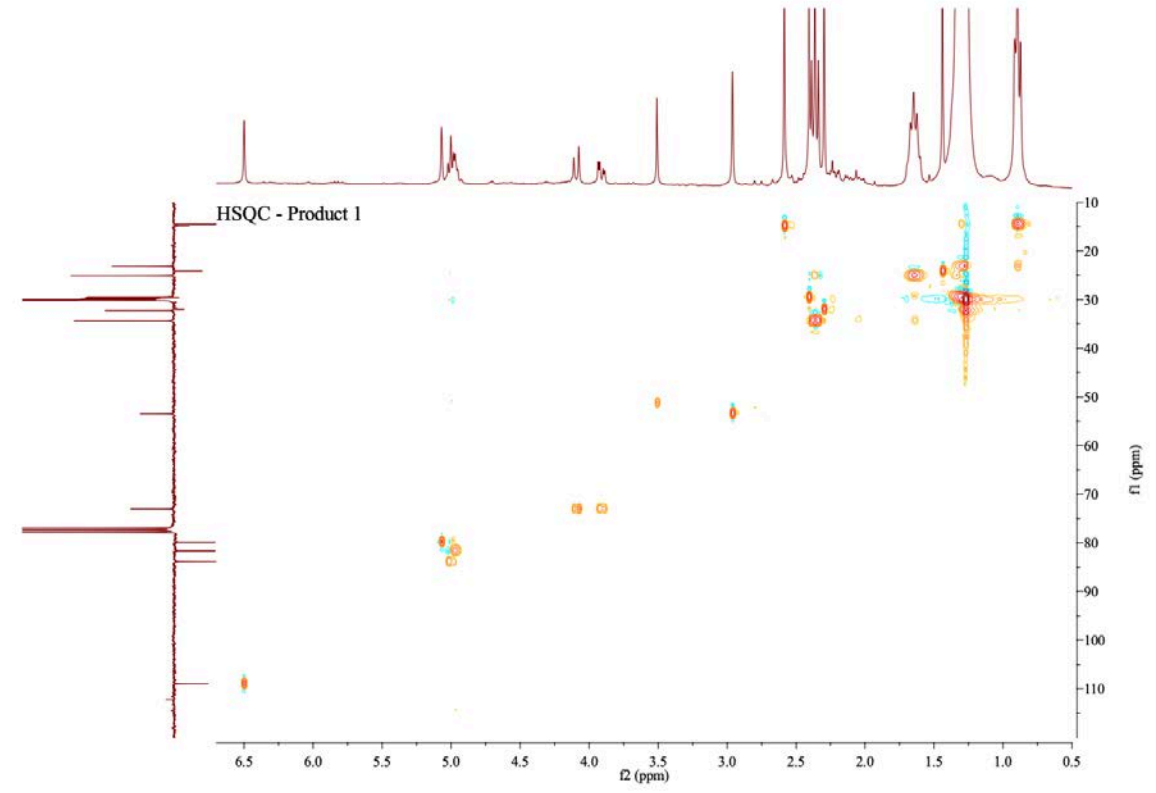
^{13}C-NMR – Product **1**



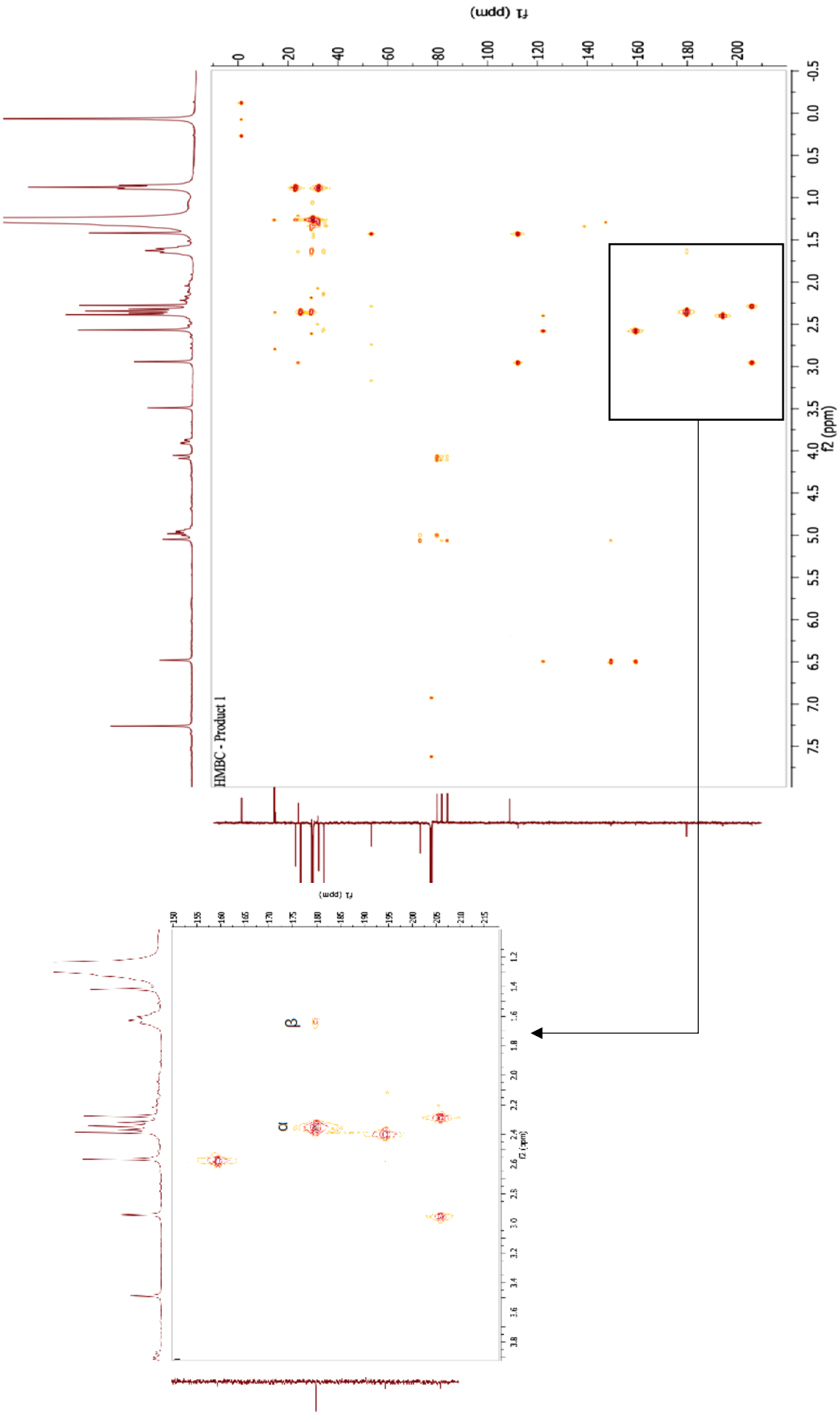
^{1}H-^{1}H COSY – Product **1**



^{1}H-^{13}C HSQC – Product **1**

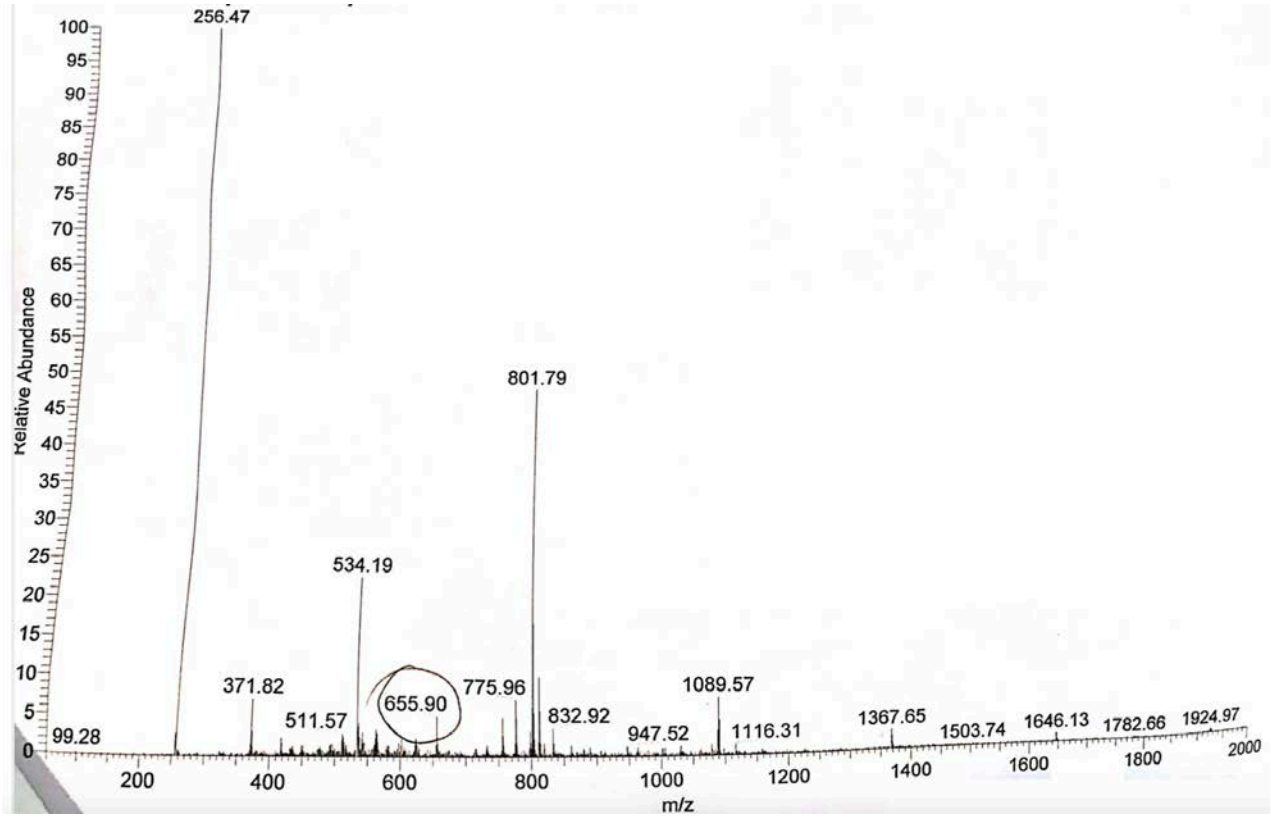


^{1}H-^{13}C HMBC Product **1**

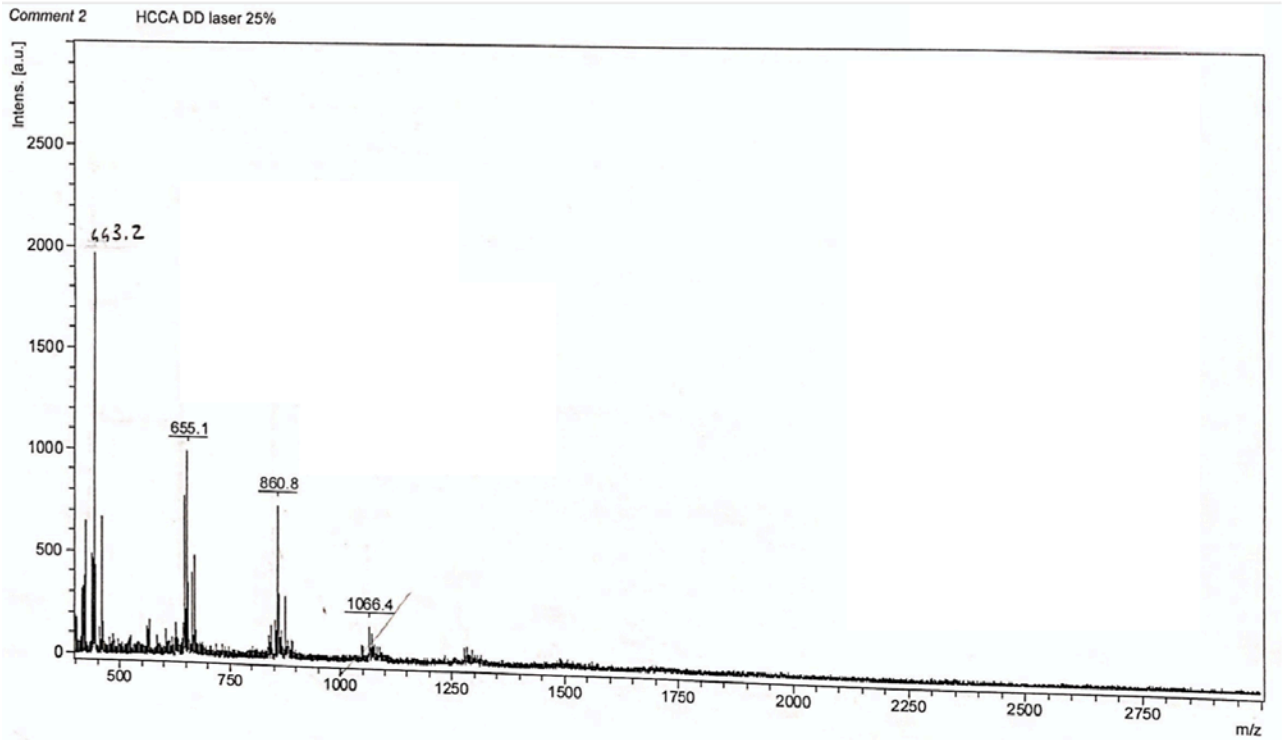


Mass Spectra

(-) ESI-MS

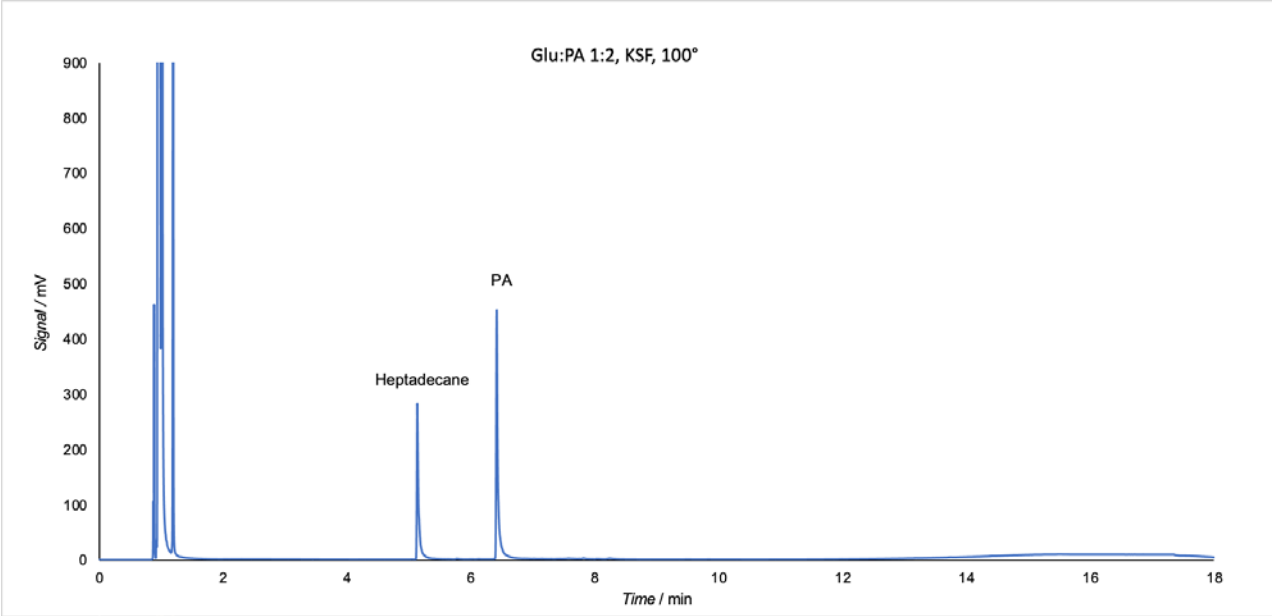


MALDI - HCCA

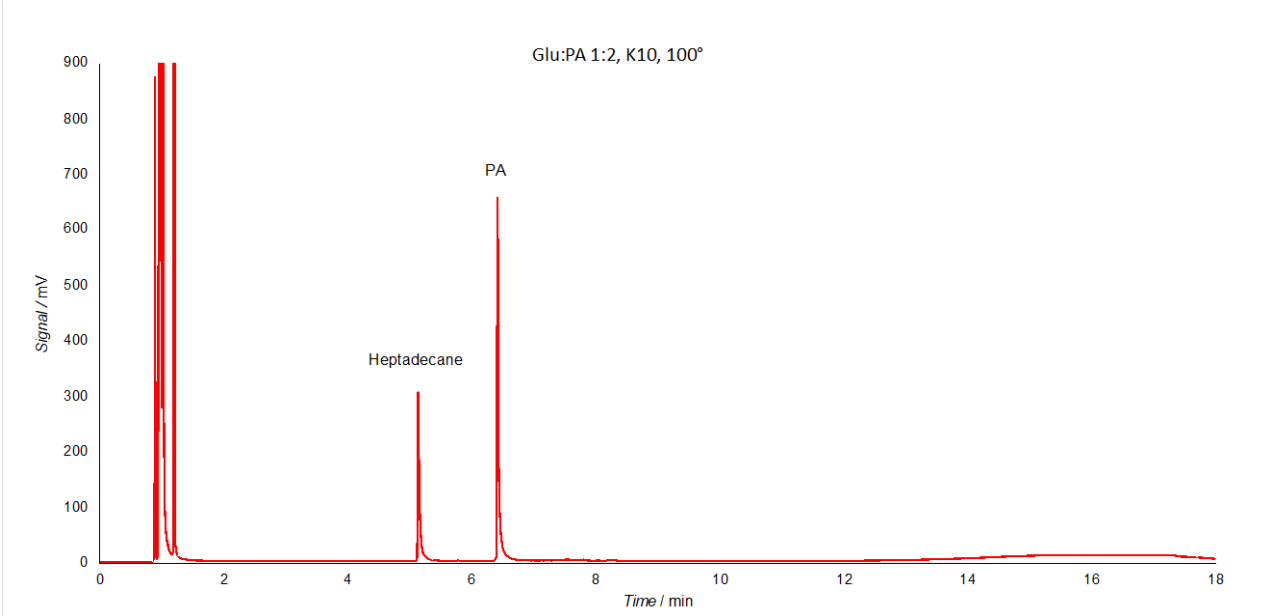


GC Chromatograms

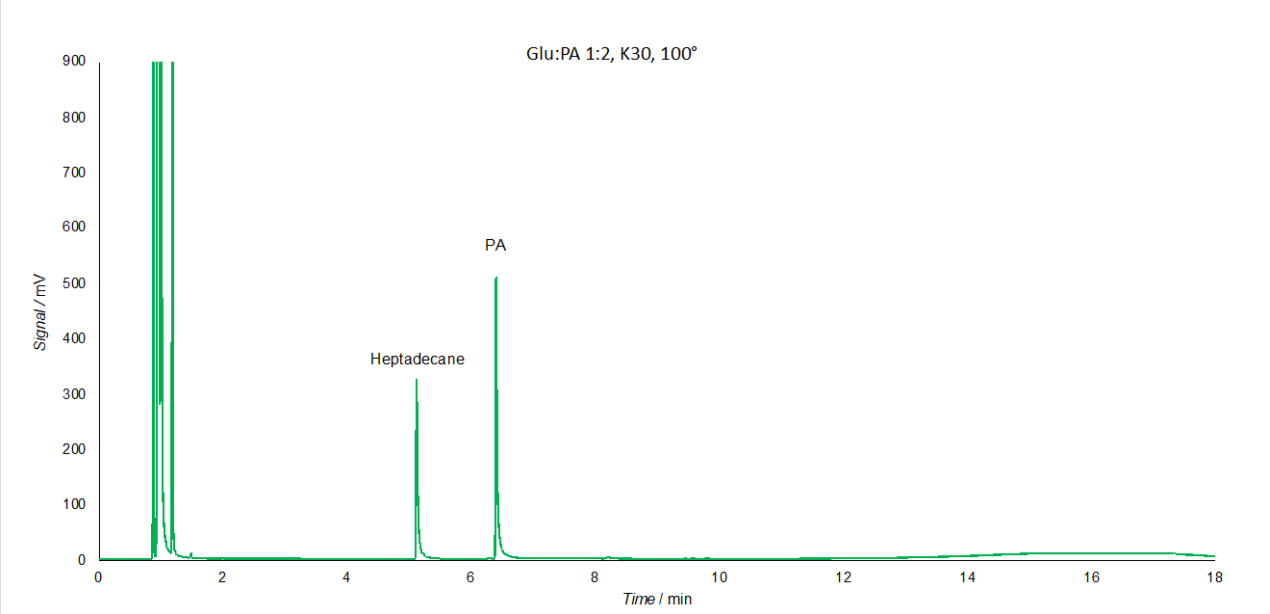
Glu:PA 1:2, KSF, 100°



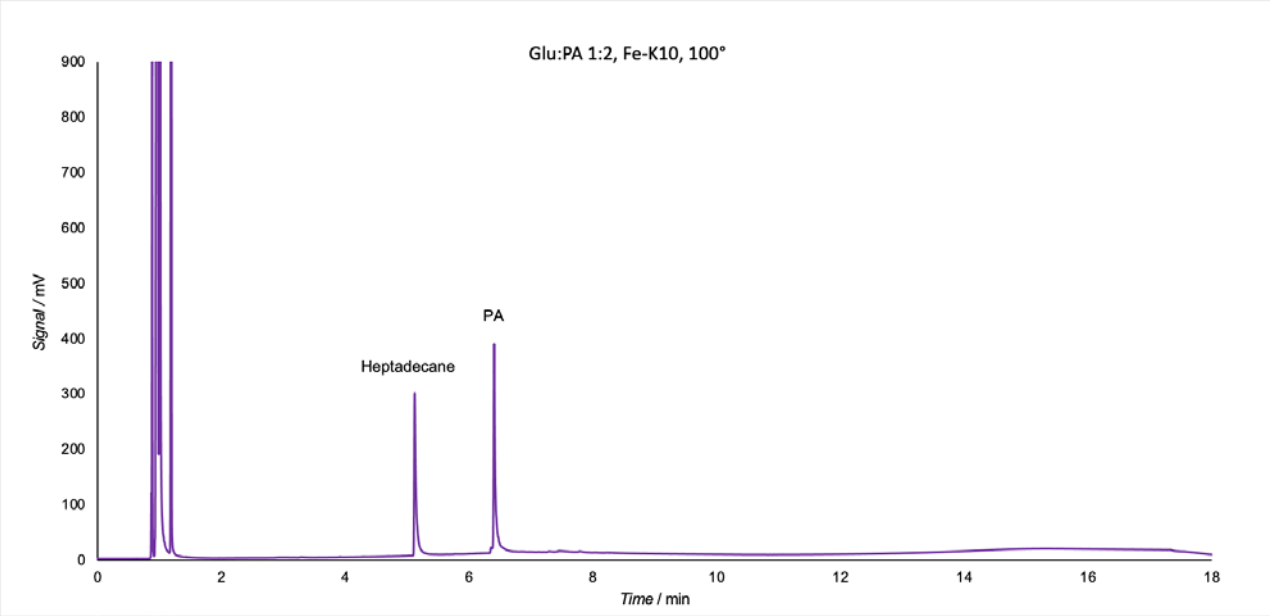
Glu:PA 1:2, K10, 100°



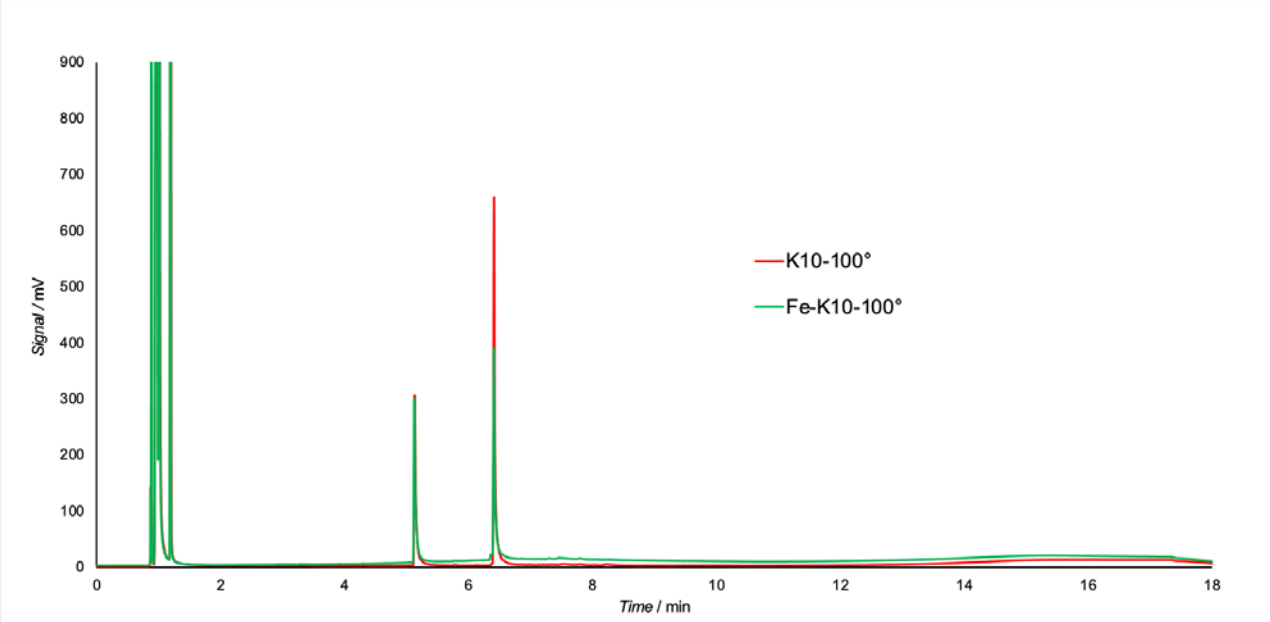
Glu:PA 1:2, K30, 100°



Glu:PA 1:2, Fe-K10, 100°



Glu:PA 1:2, K10 vs Fe-K10, 100°



K10

Heptadecane t= 5,13 min area 647,00 [mVs^{-1}] 35%
Palmitic Acid t= 6,41 min area 1161,06 [mVs^{-1}] 64%
[A_H/A_{PA}]= 0,56

Fe-K10

Heptadecane t= 5,12 min area 623,64 [mVs^{-1}] 48 %
Palmitic Acid t= 6,41 min area 670,66 [mVs^{-1}] 52%
[A_H/A_{PA}]= 0,93