Green Approaches in the Synthesis of Furan-based Diepoxy Monomers

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Results and discussion

Glycidylation of furan-2,5-dicarboxylic acid with epichlorohydrin

Monodimensional ^{1}H-NMR and ^{13}C-NMR analysis

The reaction between acidic groups of FDCA and ECH to form the glycidyl ester through a single-step reaction proceeds through the addition of the carboxylate group of FDCA to the epoxy ring of epichlorohydrin. Initially, the mixture had an almost neutral pH, being a white opaque suspension of FDCA. When heated up to 90 °C, the pH decreased to a value of 5.25, suggesting the dissociation of FDCA. The reaction was left to proceed until the pH of the mixture got back to neutrality, indicating the complete transformation of the carboxylate ion into the halohydrin intermediate; as a further evidence, the solution became a limpid yellow liquid and the insoluble portion of FDCA dissolved. Temperature was then lowered, a slight vacuum applied, and the second synthetic step was started adding dropwise the alkaline solution; the latter is needed to allow the ring closure, resulting in the formation of NaCl as by-product. As soon as NaOH was added, a white solid precipitated instantaneously. As the alkaline solution addition started, the reaction was left to proceed for a total of 6 hours, then it was stopped. The reacting mixture was filtered, the organic phase washed with water, separated, anhydrified with magnesium sulfate and dried with a rotary evaporator. The crude product, pale yellow viscous, obtained after the synthesis results impure as can be noticed by the ^{1}H-NMR spectra reported in Figure 1S, where it is compared with the spectra of BOFD after purification.

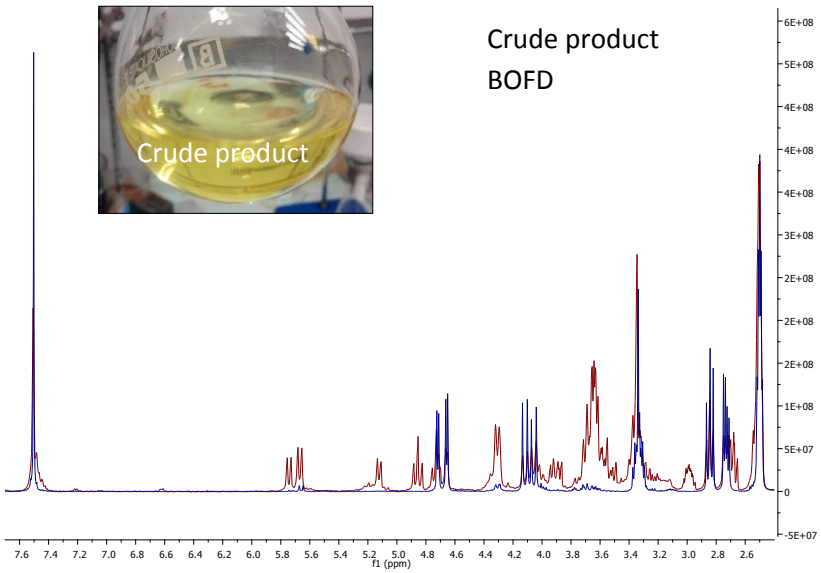

Figure 1S ^{1}H-NMR spectra for the crude product of FDCA glycidylation (red line) and BOFD (blue line)

Once obtained the pure BOFD and characterized by monodimensional ^{1}H-NMR and ^{13}C-NMR the structure was elucidated by performing further mono- and multi-dimensional NMR spectroscopy. Distortionless Enhancement by Polarization Transfer at 90° (DEPT 90) and Distortionless Enhancement by Polarization Transfer at 135° (DEPT 135) spectroscopy were performed while, as for multidimensional analysis, homonuclear correlation spectroscopy (COSY), heteronuclear single-quantum correlation spectroscopy (HSQC) and heteronuclear multiple-bonds correlation spectroscopy (HMBC) were carried out. DEPT 90 gives signals only from tertiary carbons and DEPT 135 gives primary and tertiary carbons signals as positive peaks while secondary carbons are represented as negative peaks. In DEPT 90 and DEPT 135 spectra for BOFD obtained by glycidylation, reported in Figure 2S, are present two positive peaks at 119.16 ppm and 49.24 ppm confirming the previous assignments of these respectively to furanic and oxirane CH. Peaks at 66.16 ppm and 44.95 are then confirmed to be secondary carbons, the first from glycidyl and the second on the oxirane ring.

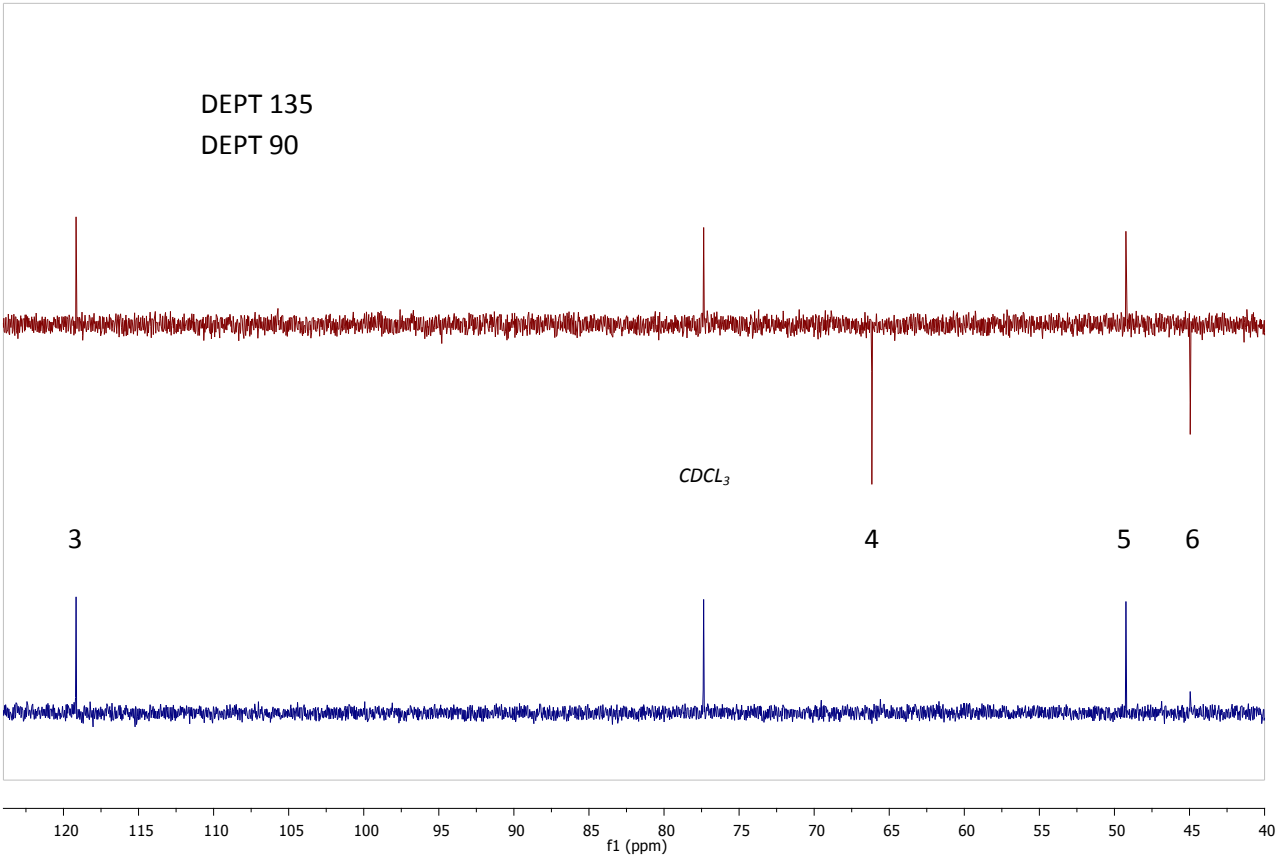

Figure 2S DEPT 90 (blue line) and DEPT 135 (red line) NMR analysis for BOFD obtained by glycidylation

Multidimensional NMR analysis

COSY spectroscopy shows the homonuclear interactions between hydrogens and thanks to this analysis is possible to identify the protons linked to carbons separated by a single bond. Heteronuclear HSQC and HMBC spectroscopy relate in different ways ^{1}H-NMR and ^{13}C-NMR spectra. Single quantum correlation (HSQC) gives strong information about heteronuclear atoms directly connected by a single bond helping to assign at each carbon the chemical shift of the hydrogens bonded. HSQC spectroscopy, reporting only the correlation between carbons and hydrogens directly linked, is usually represented in function of DEPT 135; quaternary carbons in fact do not give signal in this kind of spectroscopy because not linked to any hydrogen. Complementary to this analysis is the multiple-bond correlation (HMBC) that relates nuclei separated by about 2 to 4 bonds. This analysis gives the last information about the molecular structure, especially to assign definitely the chemical shifts related to quaternary carbons. In fact, peaks related to this kind of carbons are present only in the HMBC multidimensional analysis, reported in function of ^{13}C-NMR as f_1. It has to be reminded also that in HMBC spectroscopy are present signals related to $^{1}J_{CH}$ correlations too, but they appears as doublets.

The COSY spectroscopy, reported in Figure 3S, shows the interactions between adjacent protons and in both axes are reported ^{1}H spectra. In this case the cross-peaks highlighted by green circles confirm the relation between protons of methylene linked at the ester group (b,c) and methyne protons on oxirane ring (d), while the cross-peaks highlighted by blue circles prove the correlation between this last proton (d) and methylene protons on oxirane ring (e,f). However the two types of methylene protons (b,c and e,f) were not directly related to each other, as expected.

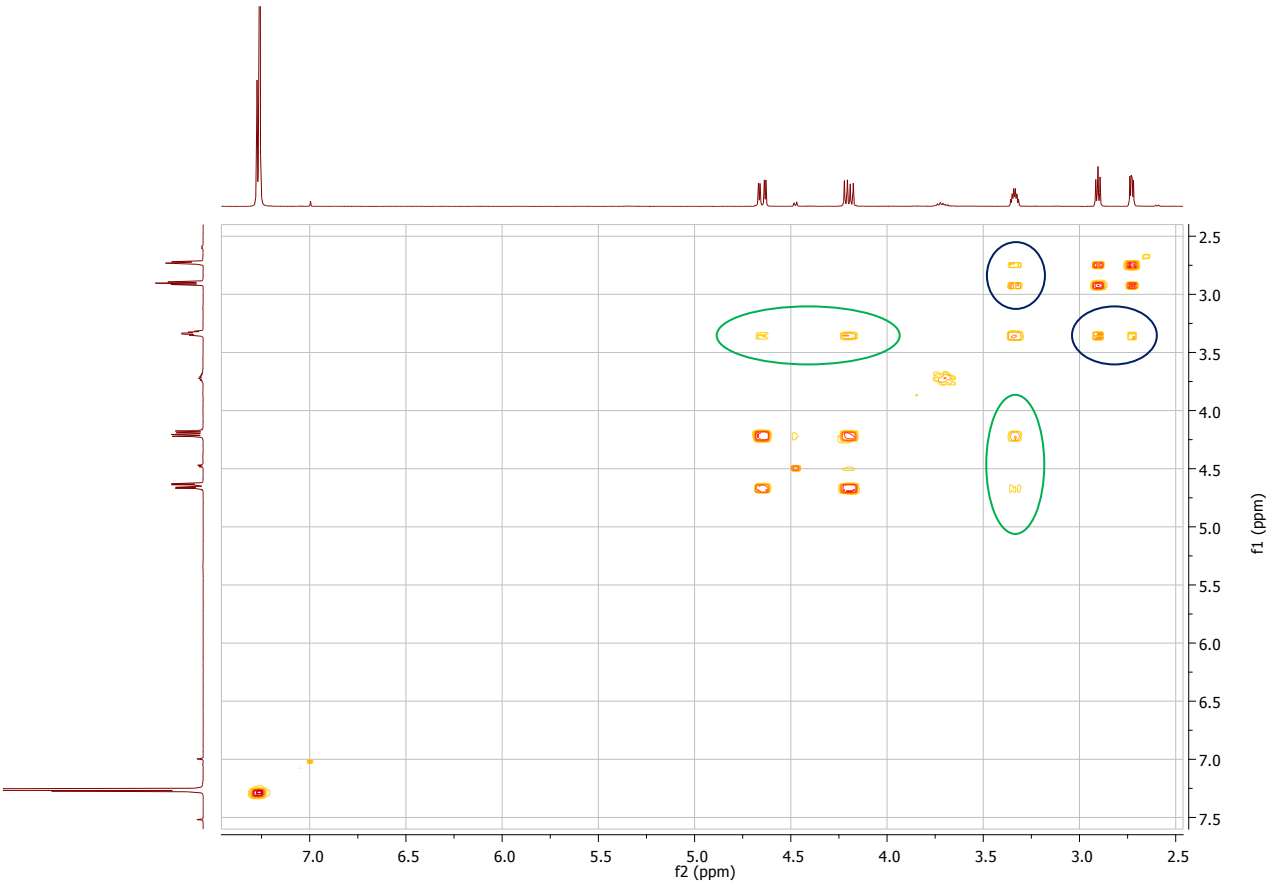

Figure 3S COSY analysis of BOFD obtained by glycidylation

HSQC spectroscopy investigates on $^{1}J_{CH}$ correlations and gives information about nuclei of two different species connected by a bond. Results of HSQC spectroscopy for BOFD are reported in Figure 4S as function of DEPT 135 and ^{1}H-NMR analysis. Through this analysis the CH_2 glycidyl carbons (4), represented by a negative peak at 66.16 ppm on f_1, can be directly correlated to protons of methylene linked to the ester group (b,c; purple circle). Analogously the CH carbons at 49.19 ppm (5, positive on f_1) result bonded with the methyne protons of the oxirane ring (d; green circle) and the CH_2 carbons on oxirane ring (6, negative peak at 44,95 ppm on f_1) are bonded to the external methylene protons of the oxirane ring (e,f; orange circle). Also the in the furanic moiety of

the molecule the bond between the CH carbons (3, positive peak at 119,16 ppm on f_1) and hydrogens (a) are shown by a peak highlighted with a red circle.

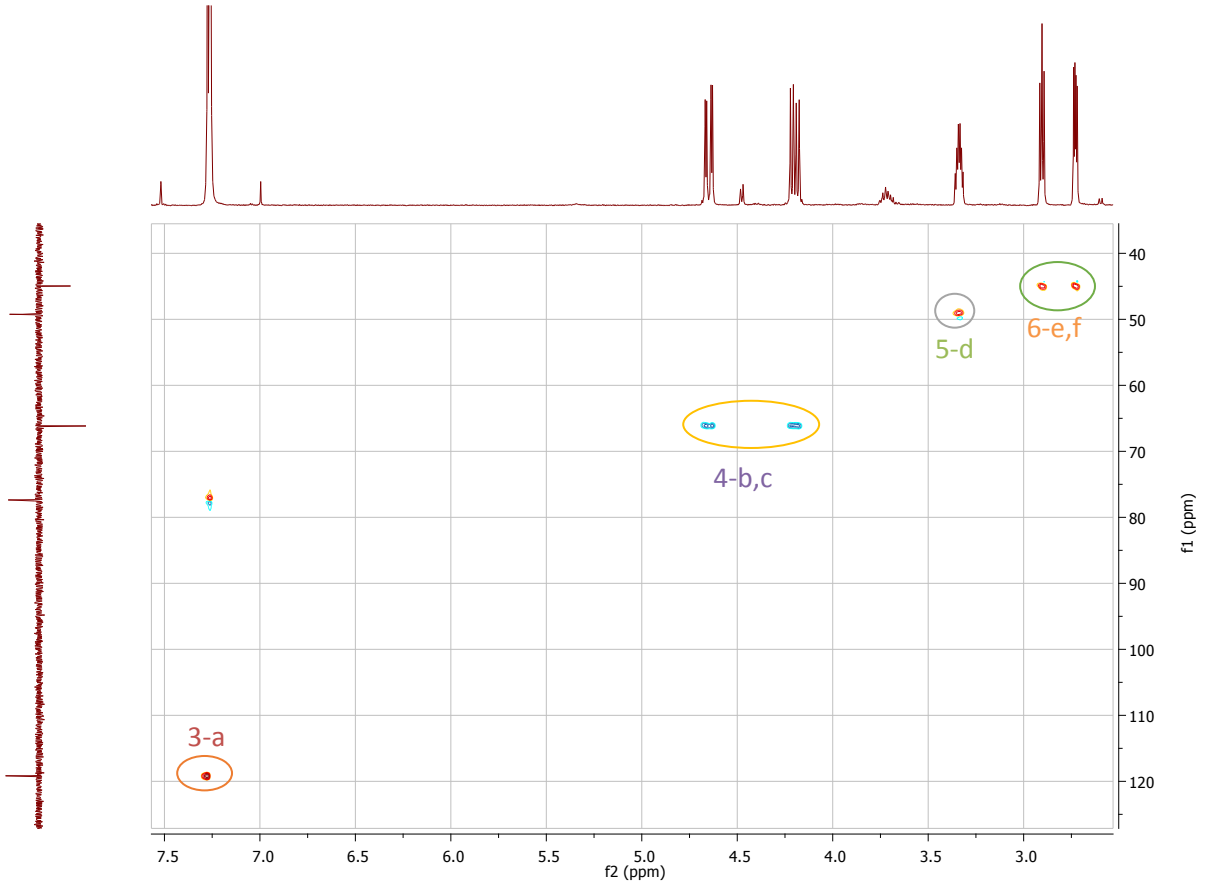

Figure 4S HSQC analysis of BOFD obtained by glycidylation

Figure 5S reports the HMBC spectroscopy for BOFD sample. In the graph a correlation of the C=O carbon (1) with the furanic (a) and the glycidyl (b,c) protons are evidenced. The furanic protons result correlated also to the furanic quaternary carbon, while glycidyl protons are also correlated to the carbons on the oxirane ring. Methylene protons of the oxirane ring are correlated to the tertiary carbon of oxirane ring and the glycidyl carbon directly linked with the ester group.

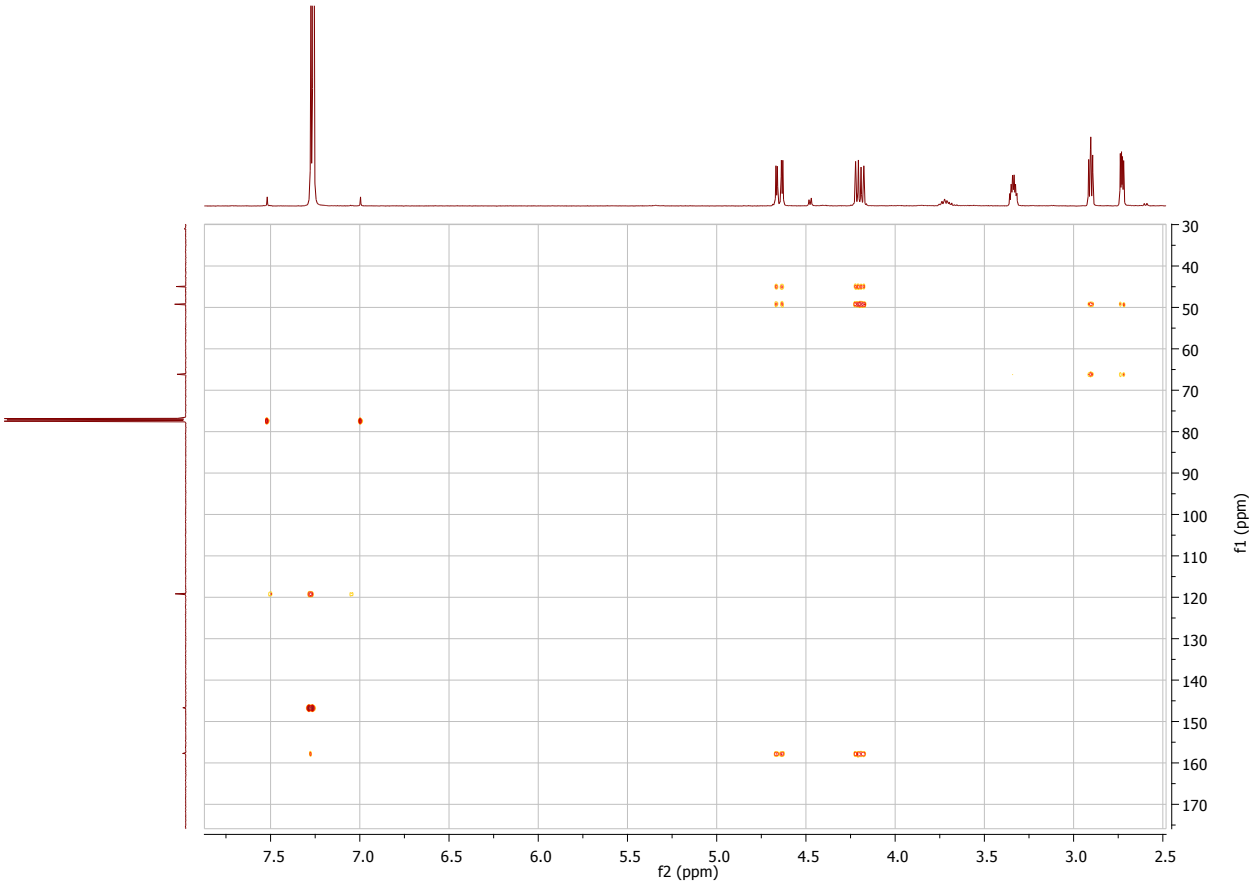

Figure 5S HMBC analysis of BOFD obtained by glycidylation

Transesterification of dimethyl 2,5-furandicarboxylate and glycidol

The procedure proposed for the production of BOFD by transesterification of DM-FDCA and glycidol results much more convenient than the glycidylation process both in terms of synthetic conditions and in terms of yield. Transesterification indeed does not need a large excess of reagents and is performed at lower temperature and for shorter time than glycidylation. The crude product obtained in this case is a white crystalline product and the main impurity is easily identified by ^{1}H-NMR analysis (Figure 6S) being unreacted DM-FDCA. Also in this case, the ^{1}H-NMR spectrum of BOFD displays the characteristic peaks of furanic proton at 7.27 ppm, the two double doublets at 4.65 ppm and 4.19 ppm due to the protons of methylene linked to the ester group, a sextet at 3.34 from methyne protons on oxirane ring, a triplet at 2.90 and a double doublet 2.73 due to protons of methylene on oxirane ring. These signals are in agreement with those reported for BOFD obtained by glycidylation, and in this case can be noticed also a decrease of the intensity of signals given by oligomeric impurities at 4.47 and 3.70 ppm.

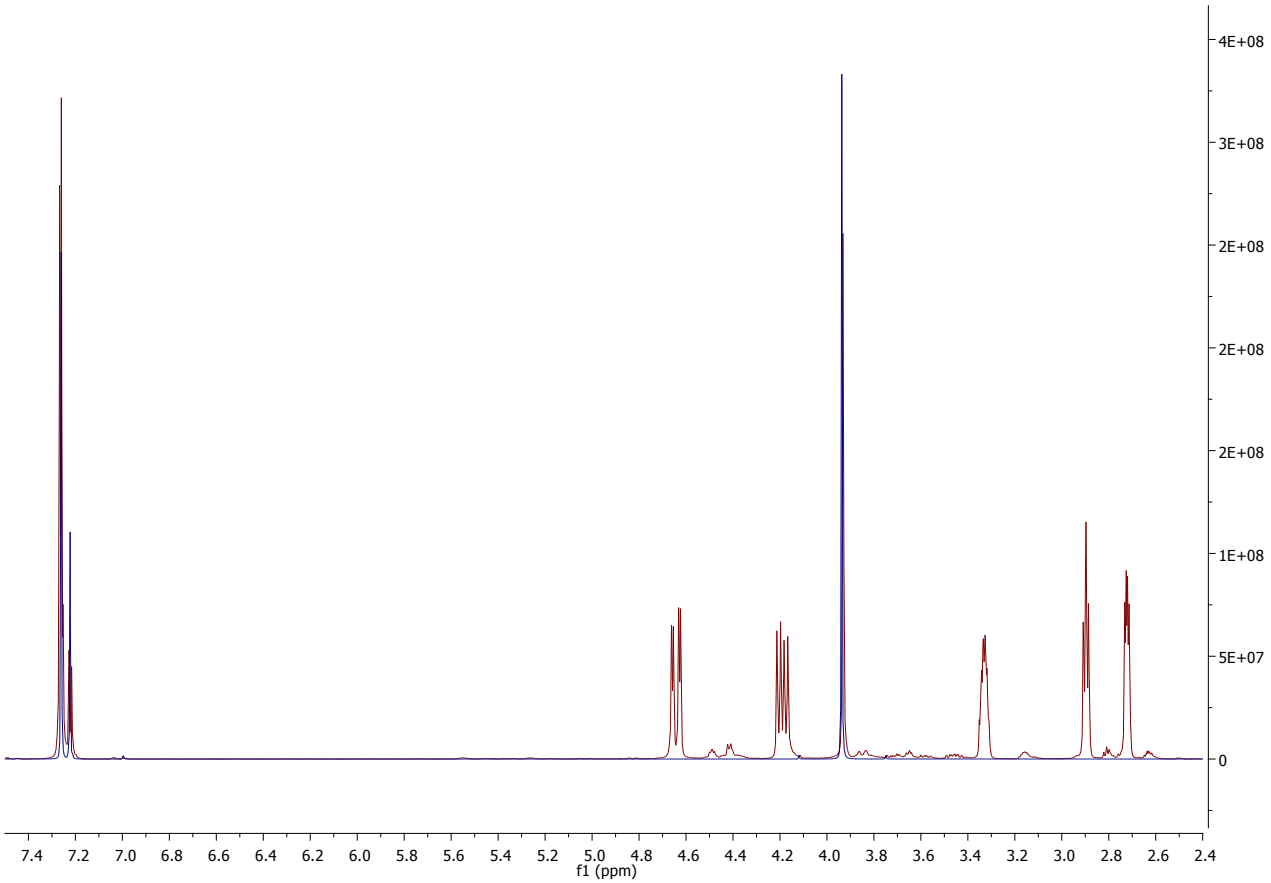

Figure 6S ^{1}H-NMR spectra for the crude product of transesterification (red line) and DM-FDCA (blue line)

In Figure 7S reports FTIR spectra for DM-FDCA and purified BOFD obtained by transesterification.

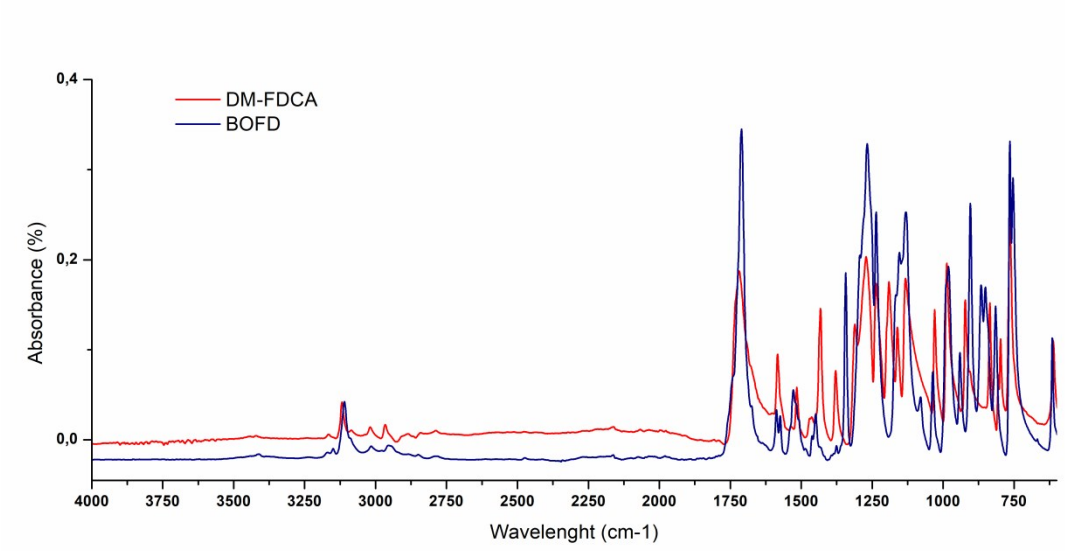

Figure 7S FTIR spectra for DM-FDCA and BOFD obtained by transesterification