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Electronic Supplementary Information (ESI)

Mechanistic study on -C-O- and -C-C- hydrogenolysis over Cu catalysts: identification of reaction pathways and key intermediates

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^{13}C-NMR and GC data for identification of 3-deoxy and 6-deoxy hexitols is shown in Figure S-1, S-2, S-3, S-4, and S-5.

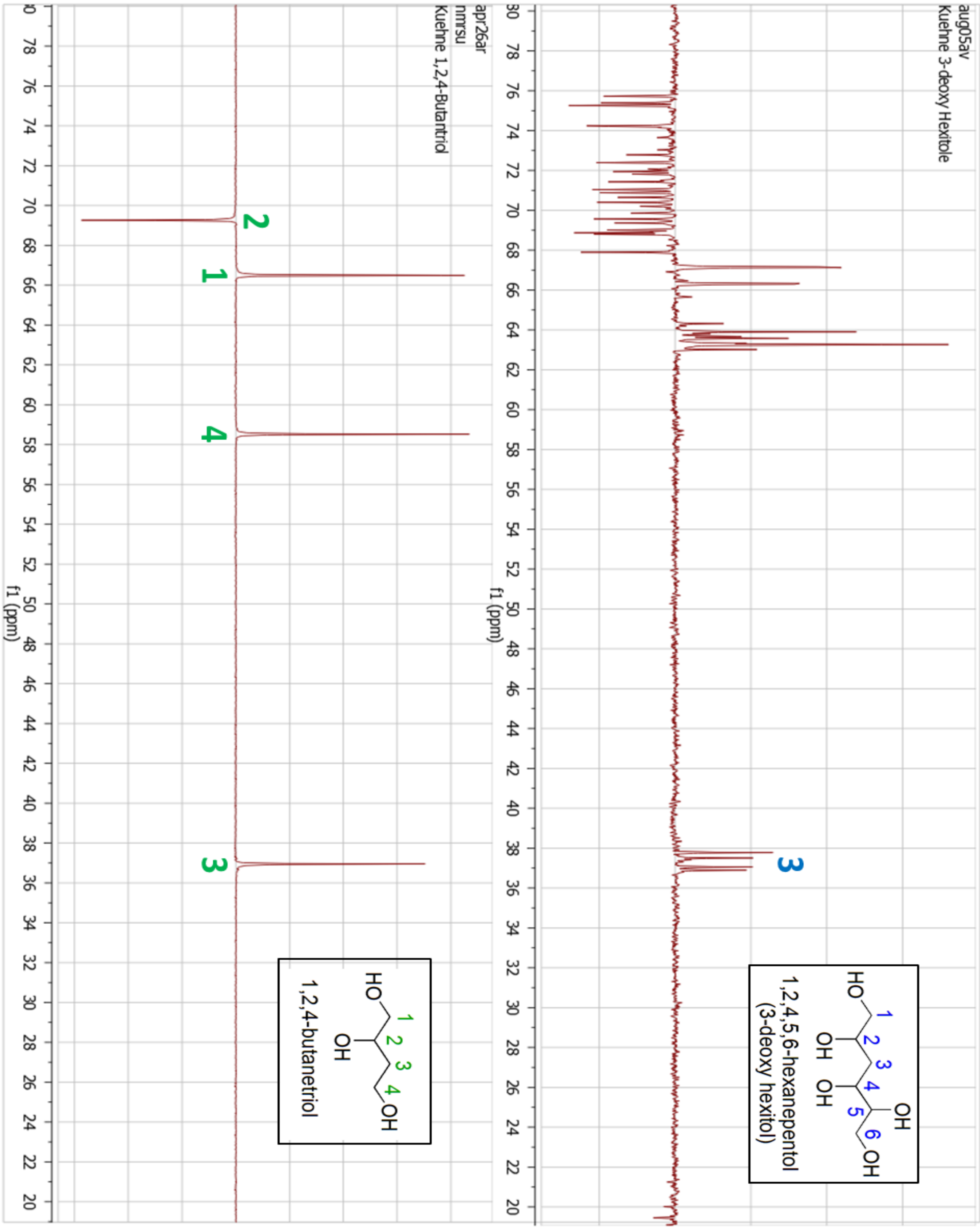

Figure S-1: Identification of 3-deoxy hexitols (1,2,4,5,6-hexanepentols) by ^{13}C-NMR analysis (DEPT) in comparison with 3-deoxy tetritols (1,2,4-butanetriol, a standard purchased from Sigma-Aldrich as reference). Carbon atoms with one or three C-H bonds are facing down from the base line, while carbon atoms with two C-H bonds face upwards. The 3-deoxy hexitol shows four different isomeric carbon atoms at the 3-position that result from three chiral carbon atoms (3^2 = 8 diastereomers: however, enantiomers are not separated which results in four visible diastereomers). The corresponding GC chromatogram is shown in **Figure S-2**.

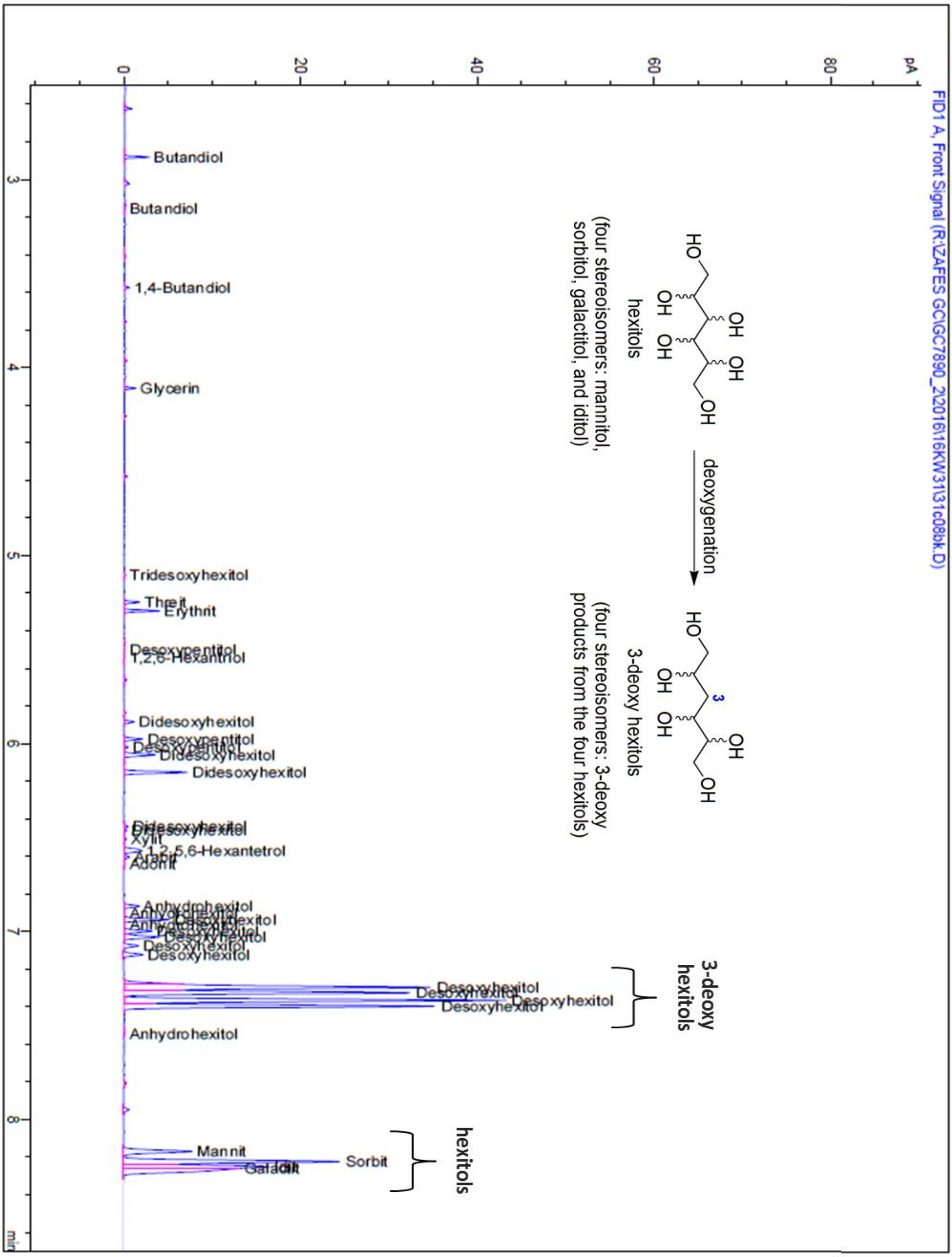

Figure S-2: GC chromatogram of the polyol mixture that was analyzed by NMR analysis for identification of the 3-deoxy hexitols (1,2,4,5,6-hexanepentols). The polyol mixture was isolated by chromatography from a reaction mixture resulting from hydrogenolysis of sorbitol using a Cu-Raney catalyst at 180 °C, 150 bar H_2 and 5 h reaction time (**Figure S-3**). Four different monodeoxy hexitols are detected at about 7.4 min retention time, which are identified as 3-deoxy hexitols by ^{13}C-NMR analysis (see **Figure S-1**).

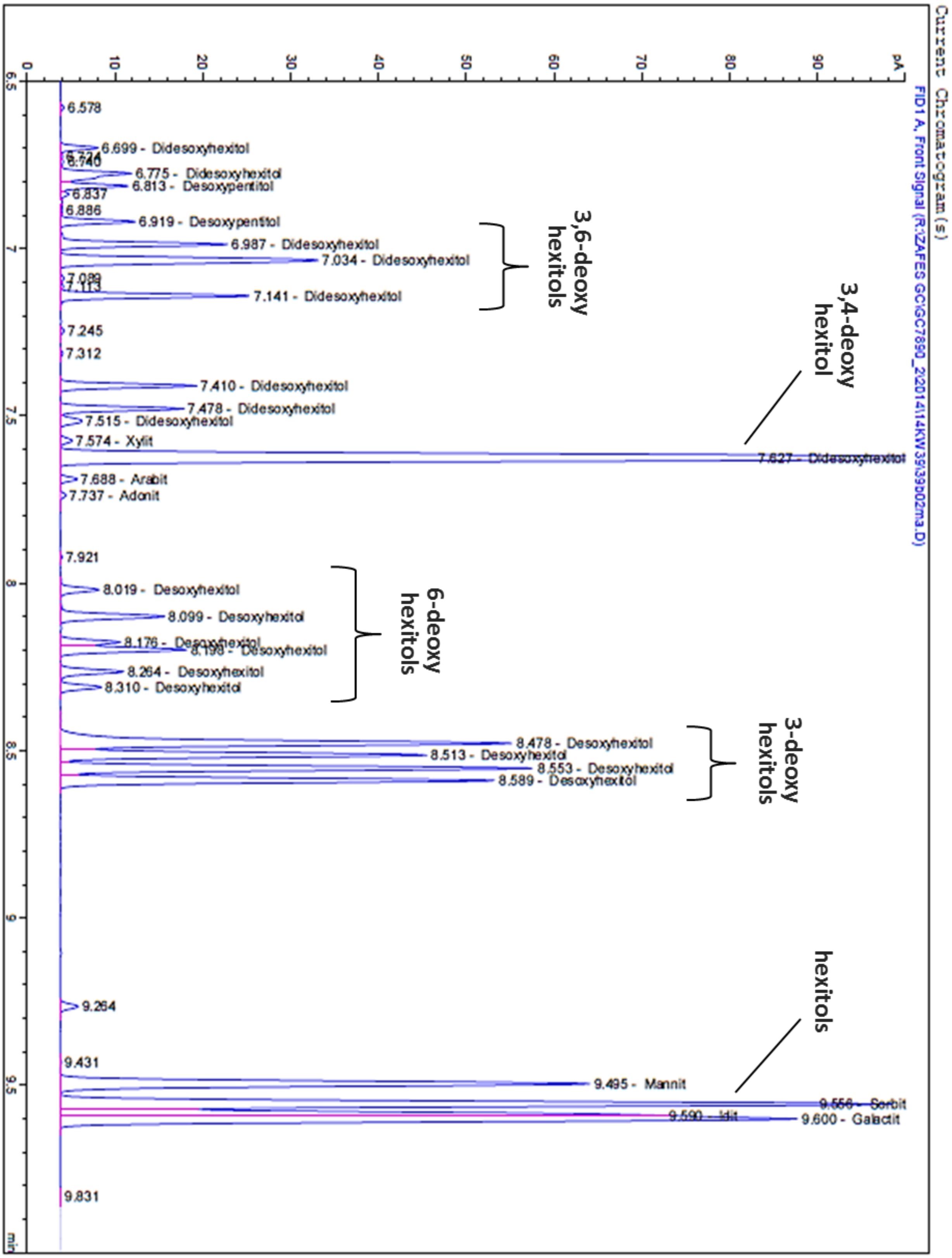

Figure S-3: GC chromatogram for the conversion of mannitol over Cu-Raney at 180 °C, 150 bar H_2 and 5 h reaction time. Four stereoisomers of 3-deoxy hexitols (1,2,4,5,6-hexanepentols) are detected at a retention time of 8.5 to 8.6 min. Six stereoisomers of 6-deoxy hexitols (1,2,3,4,5-hexanepentols) are detected at 8.0 to 8.3 min. The same 6-deoxy stereoisomers are obtained from rhamnose hydrogenation as shown in **Figure S-4**.

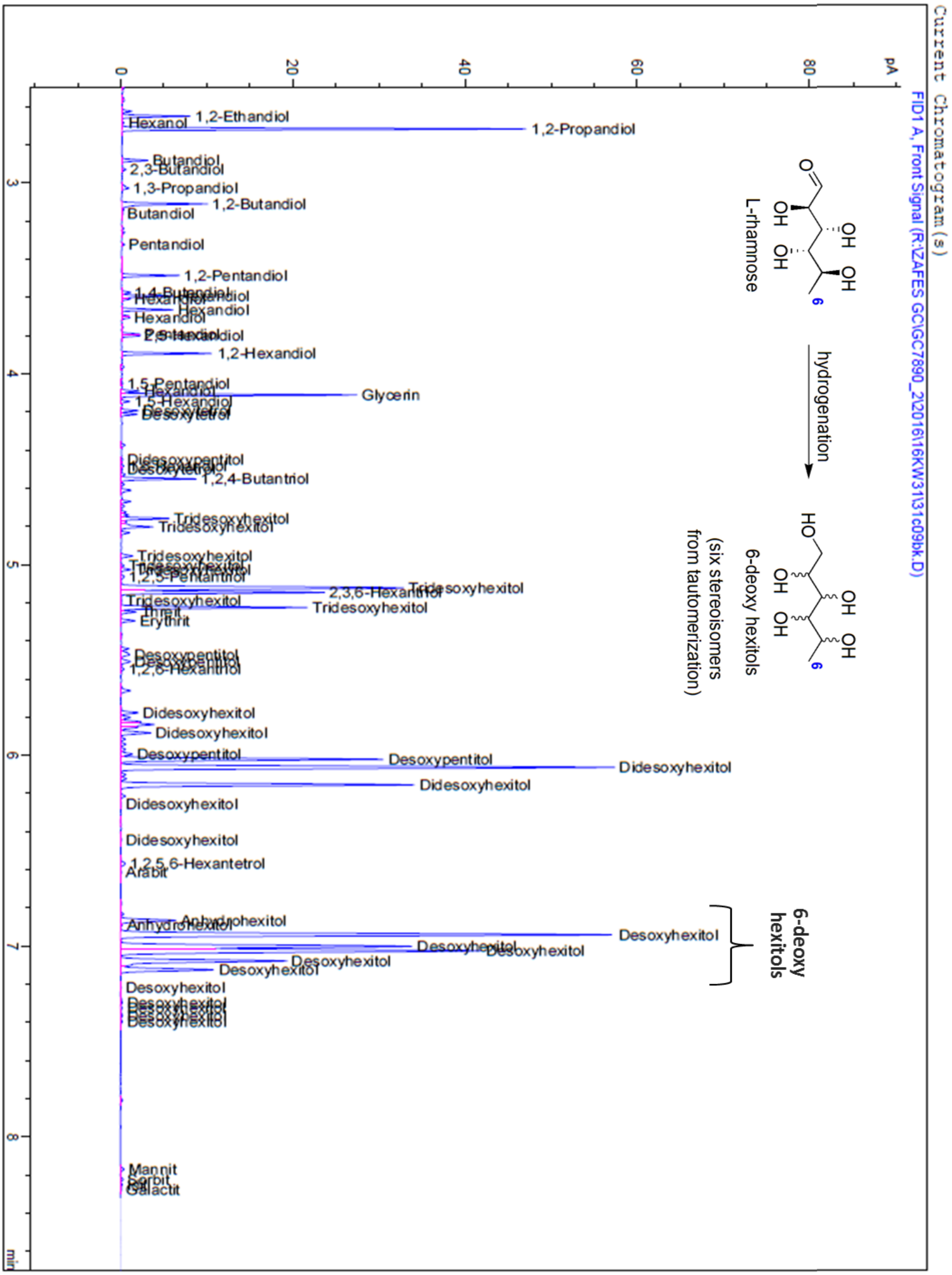

Figure S-4: GC chromatogram of the product mixture obtained from rhamnose hydrogenation to 6-deoxy hexitols (1,2,3,4,5-hexanepentols, catalyst: Cu-Raney at 70 °C and 150 bar H_2) and subsequent hydrogenolysis at 180 °C, 150 bar H_2 and 5 h reaction time. Six different stereoisomers of 6-deoxy hexitols are formed from the 6-deoxy sugar rhamnose.

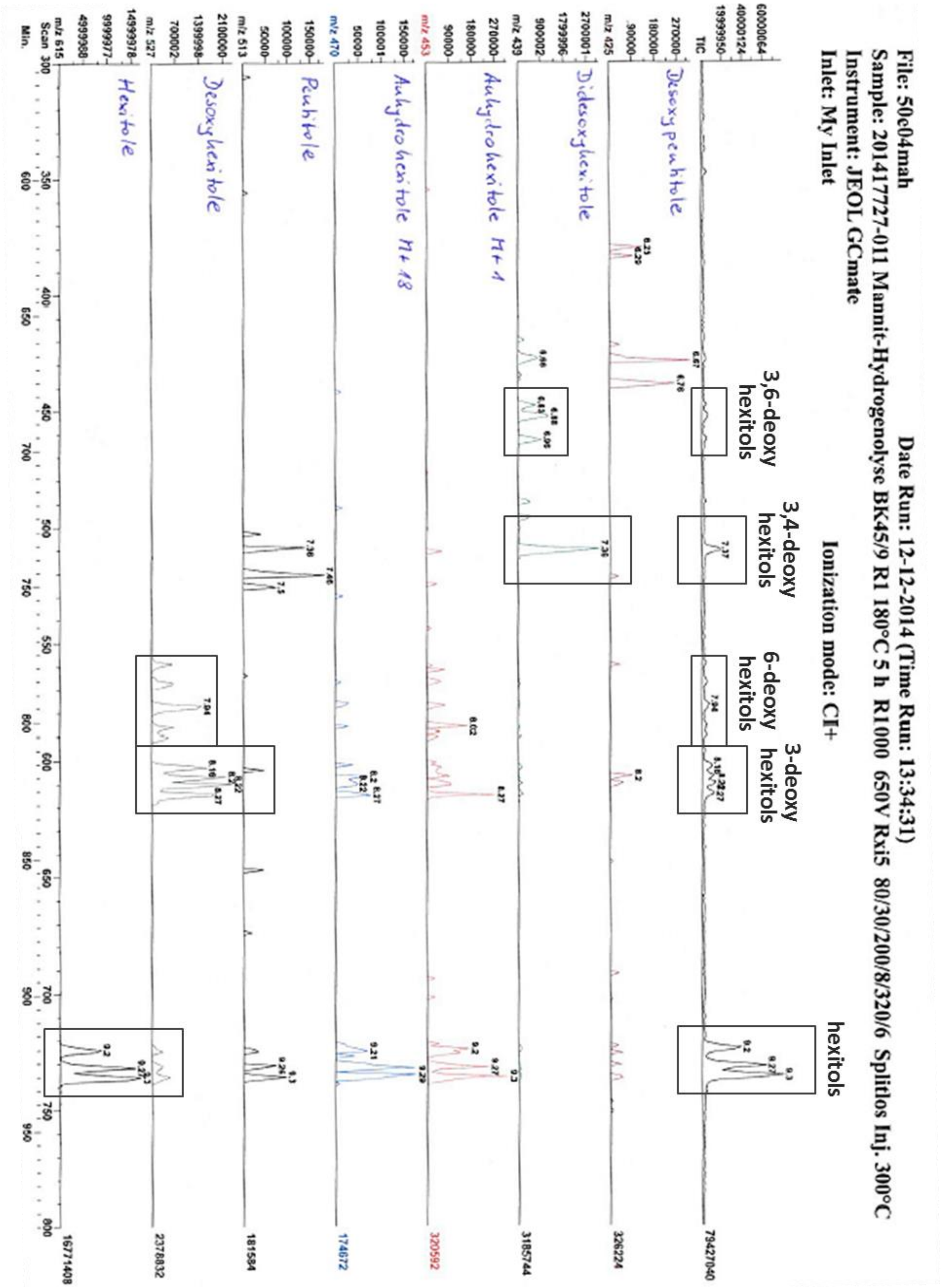

Figure S-5: GC-MS analysis of the polyol mixture shown in **Figure S-3**. 3-deoxy and 6-deoxy hexitols (labeled as Desoxyhexitole) are detected with a mass-to-charge-ratio of 527 m/z which accounts for the M+1 form (with an added proton) of the TMS-derivatives (see experimental section for silylation). The M+1 species of the 3,4-deoxy and 3,6-deoxy hexitols (as Didesoxyhexitole) are detected with a 439 m/z ratio.

^{13}C-NMR and GC data for identification of 3,4-deoxy hexitols (1,2,5,6-hexanetetrol) is shown in Figure S-6, S-7, and S-8.

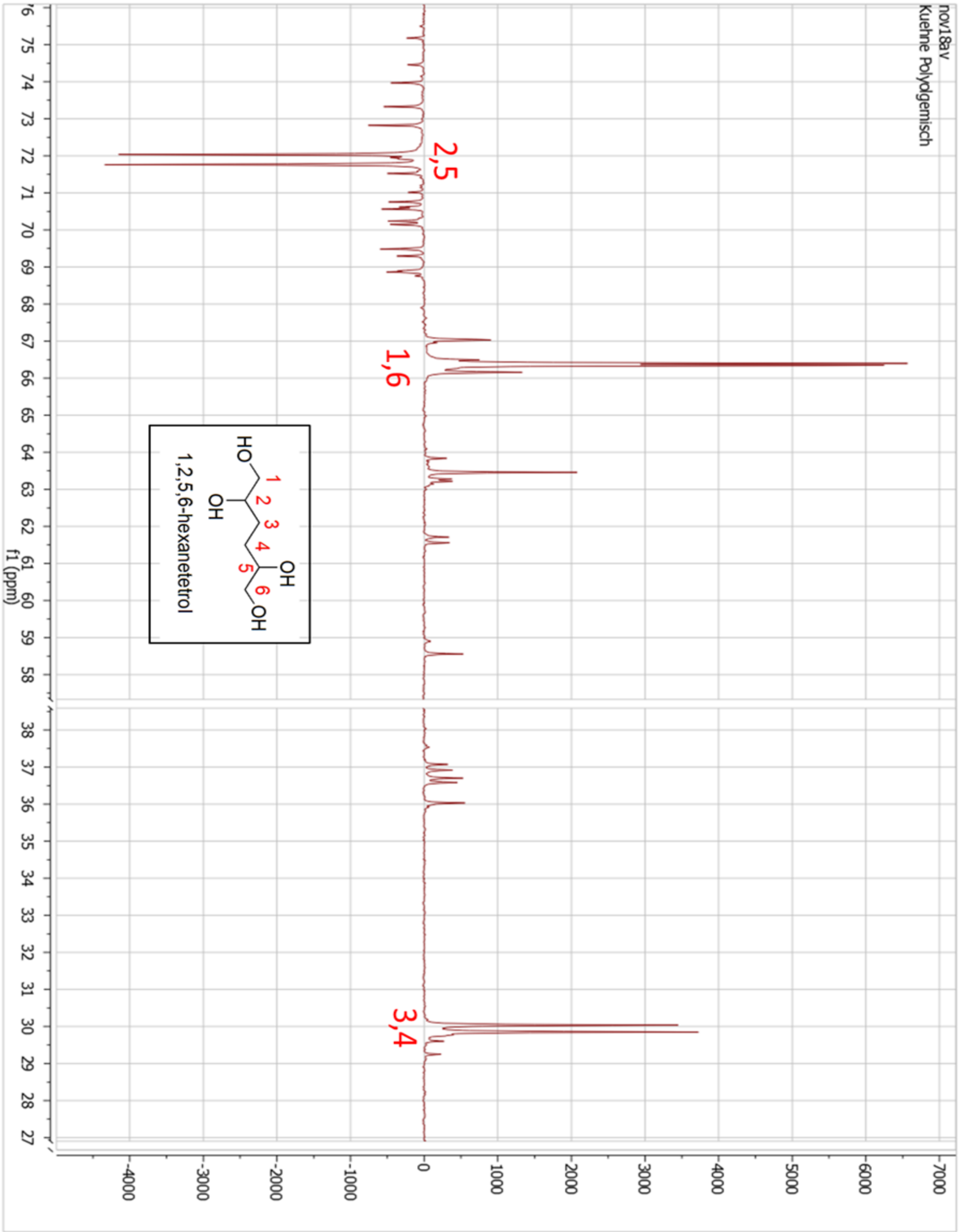

Figure S-6: Identification of the 3,4-dideoxy hexitol (1,2,5,6-hexanetetrol) by ^{13}C-NMR analysis (DEPT). Carbon atoms with one or three C-H bonds are facing down from the base line, while carbon atoms with two C-H bonds face upwards. The 1,2,5,6-hexanetetrol shows two different isomeric carbon atoms for each position in the molecule that result from two chiral carbon atoms (2^2 = 4 diastereomers: however, enantiomers are not separated which results in two visible diastereomers). The GC chromatogram is shown in **Figure S-7**.

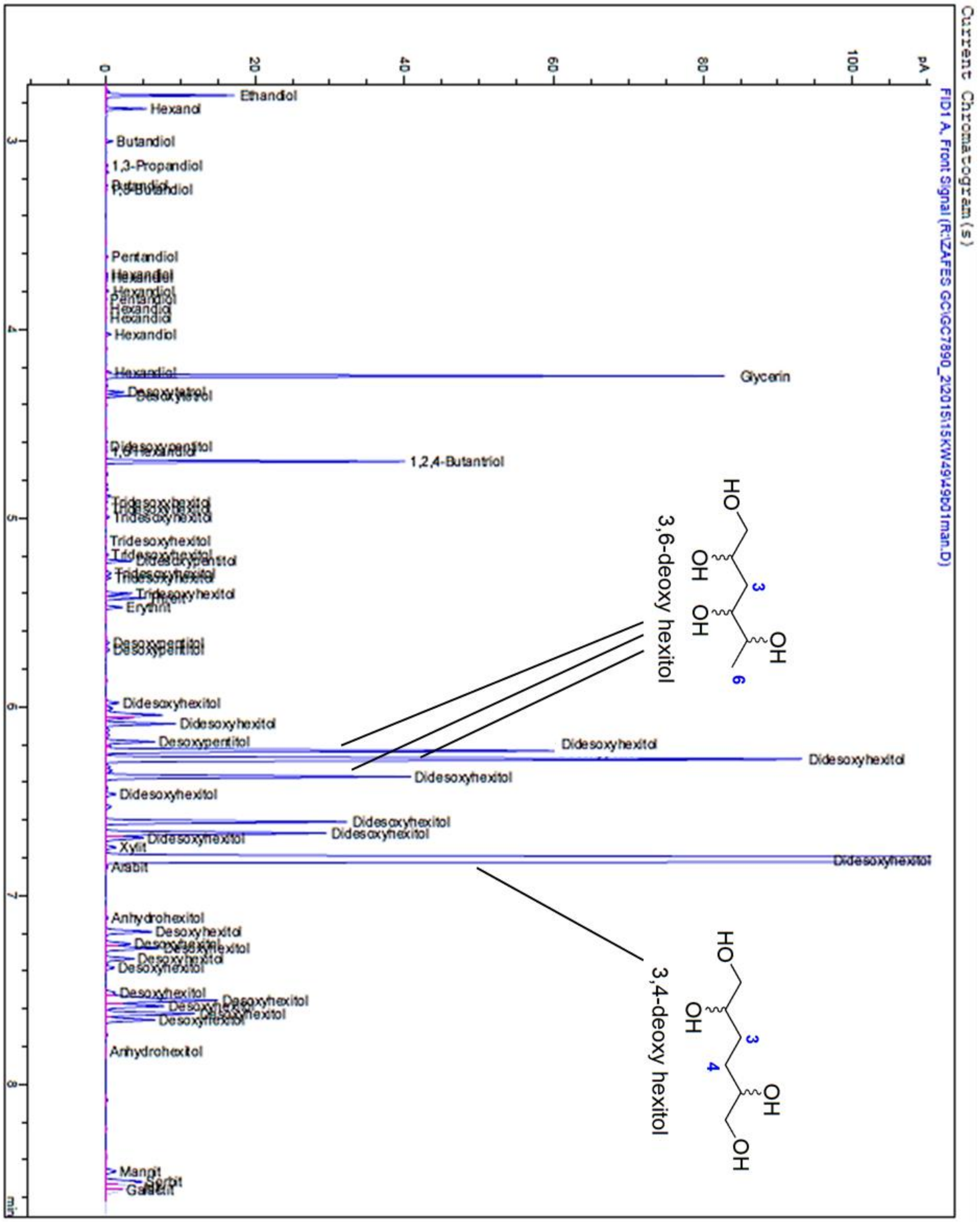

Figure S-7: GC chromatogram of the polyol mixture that was analyzed by NMR analysis for identification of the 3,4-deoxy hexitols (1,2,5,6-hexanetetrol). The polyol was isolated by chromatography from a reaction mixture resulting from hydrogenolysis of sorbitol using a Cu-Raney catalyst at 180 °C, 150 bar H_2 and 40 h reaction time. The 3,4-deoxy hexitol (1,2,5,6-hexanetetrol) is detected at a retention time of 6.8 min and was identified by NMR analysis as shown in **Figure S-6**.

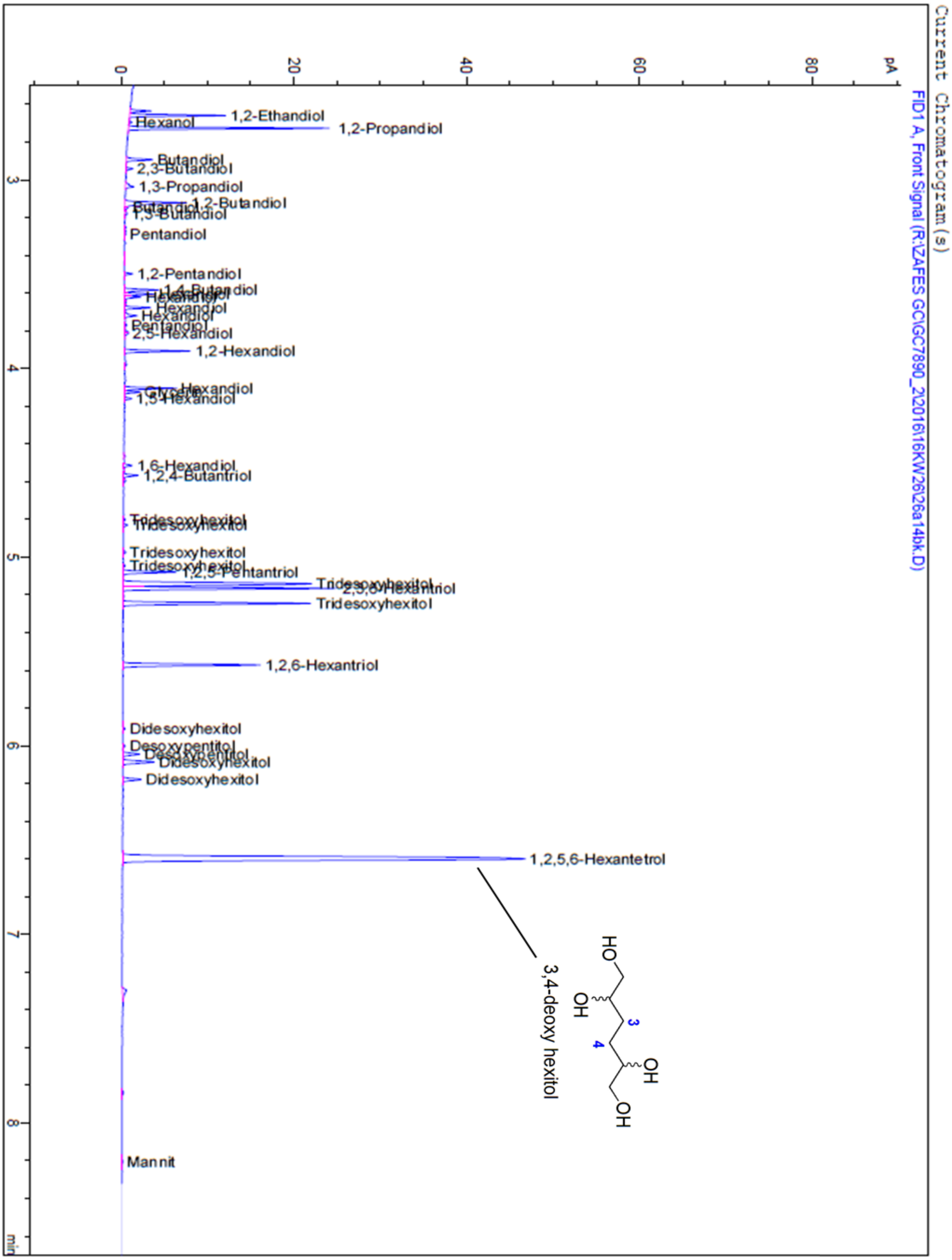

Figure S-8: GC chromatogram for the conversion of mannitol over Cu-Raney at 180 °C, 150 bar H_2 and 40 h reaction time. The 3,4-deoxy hexitol (1,2,5,6-hexanetetrol) is detected at a retention time of 6.6 min. The polyol mixture shown in **Figure S-7** was obtained by chromatographic separation from this aqueous polyol solution.

^{13}C-NMR and GC data for identification of 3,6-deoxy hexitols (1,2,4,5-hexanetetrol) is shown in Figure S-9, S-10, and S-11.

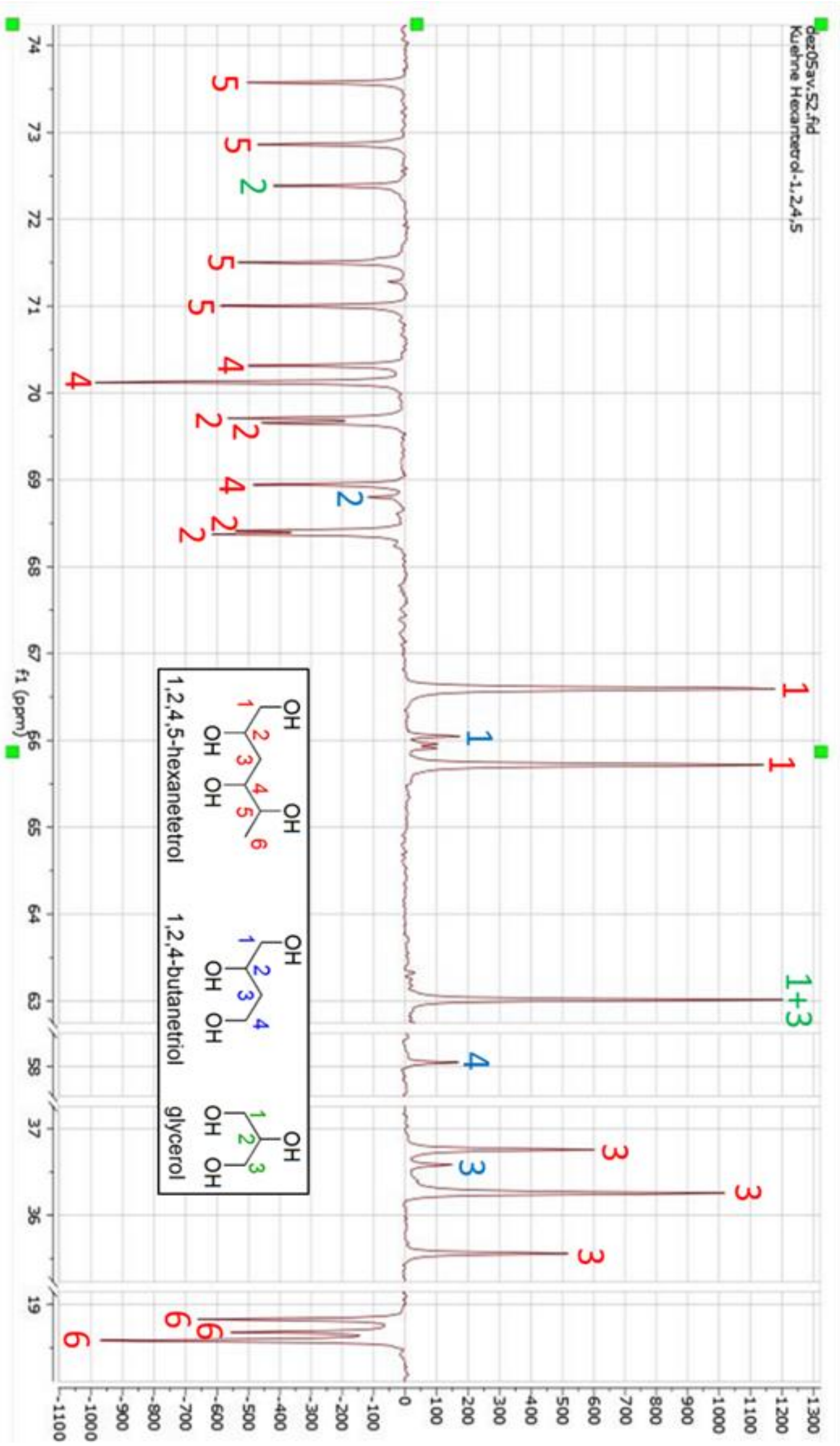

Figure S-9: Identification of the 3,6-dideoxy hexitol (1,2,4,5-hexanetetrol) along with 1,2,4-butanetriol and glycerol by ^{13}C-NMR analysis (DEPT). Carbon atoms with one or three C-H bonds are facing down from the base line, while carbon atoms with two C-H bonds face upwards. 1,2,4,5-hexanetetrol shows four different isomeric carbon atoms for each position in the molecule that result from three chiral carbon atoms ($2^3 = 8$ diastereomers: however, enantiomers are not separated which results in four visible diastereomers). The GC chromatogram is shown in **Figure S-10**.

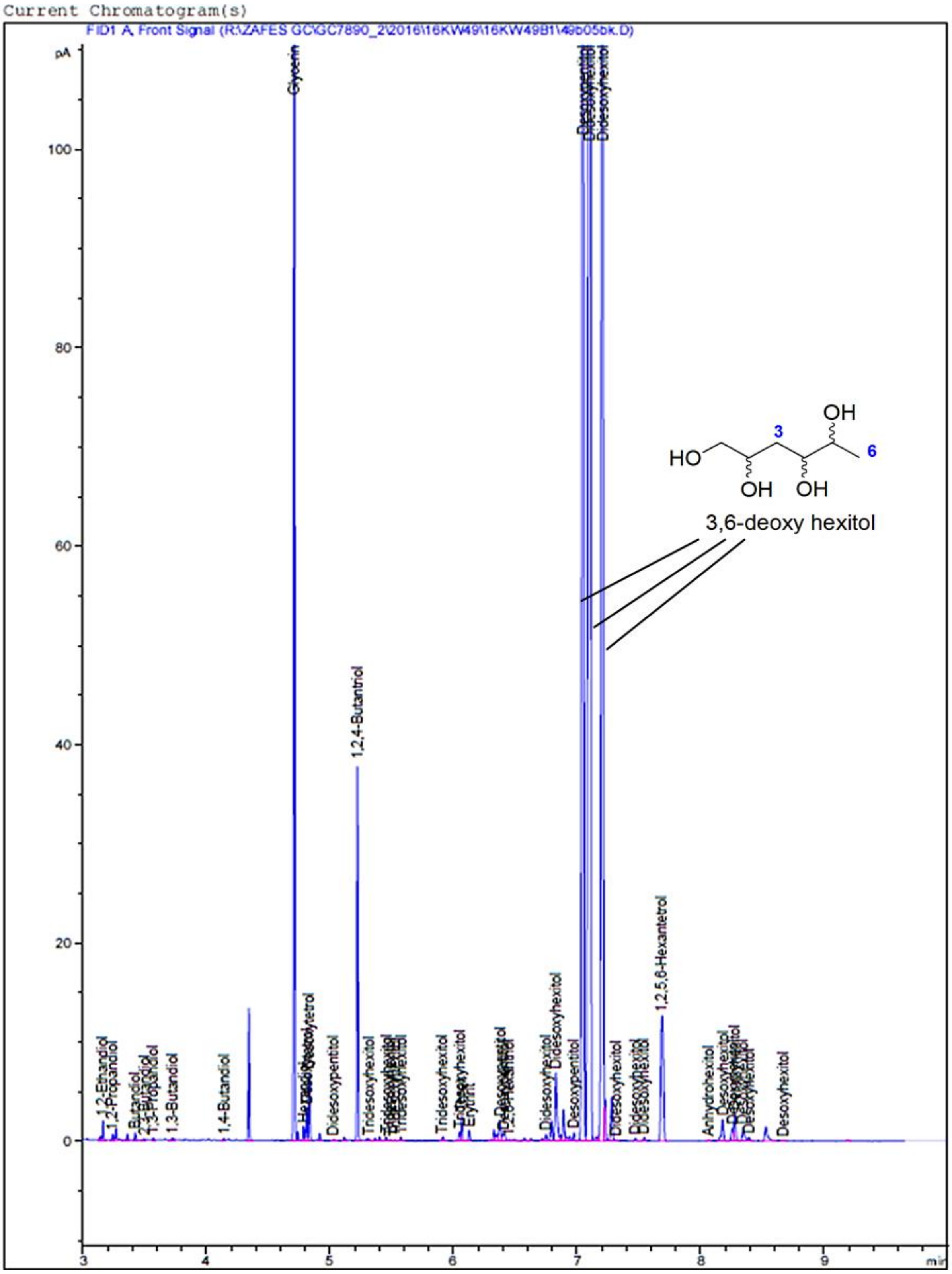

Figure S-10: GC chromatogram of the polyol mixture that was analyzed by NMR analysis for identification of the 3,6-deoxy hexitols (1,2,4,5-hexanetetrols). The polyols were isolated by chromatography from a reaction mixture resulting from hydrogenolysis of rhamnose over a Cu-Raney catalyst at 180 °C, 150 bar H_2 and 20 h reaction time. The 3,6-deoxy hexitols are detected at a retention time of 7.0 to 7.2 min and were identified by NMR analysis as shown in **Figure S-9**.

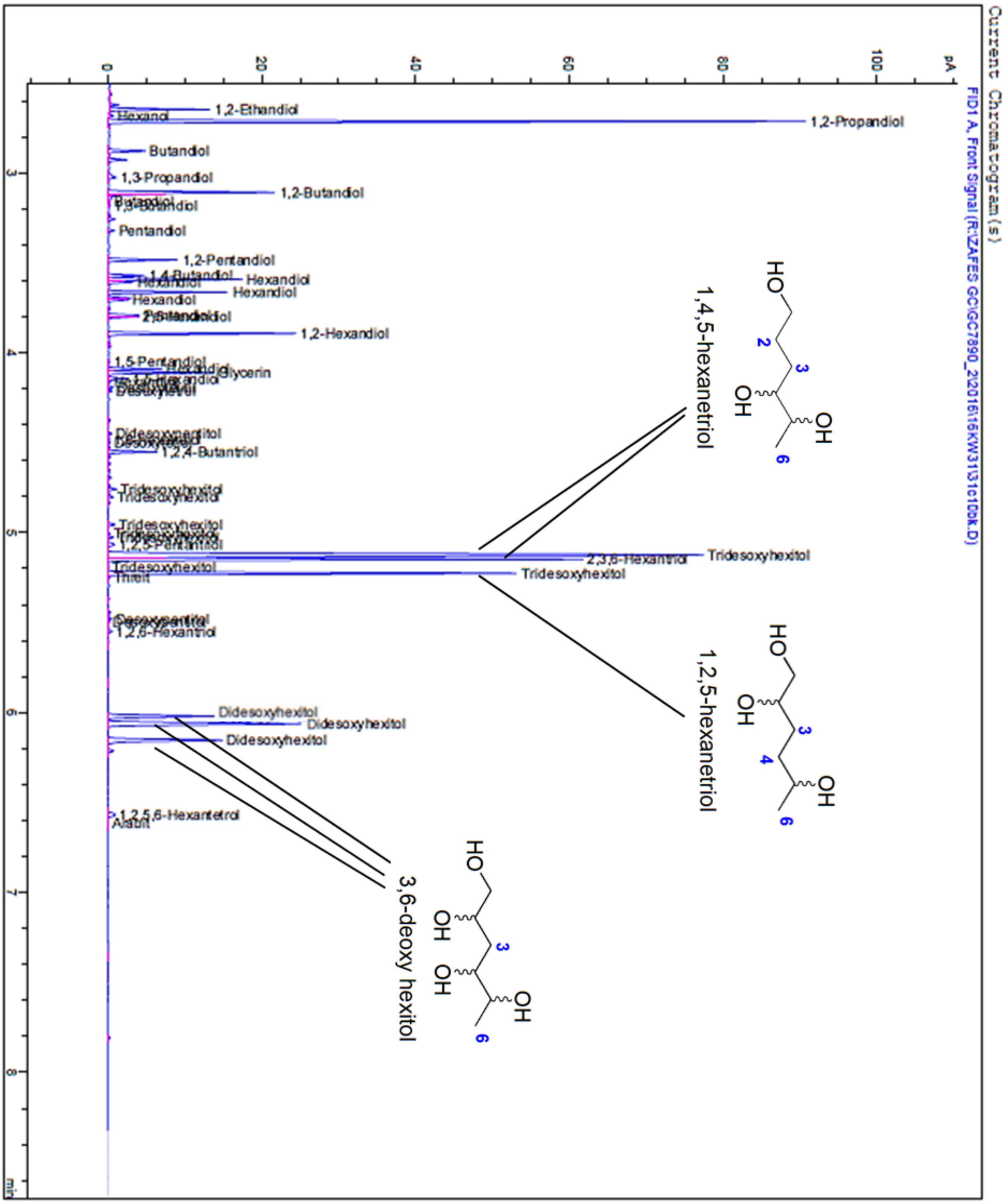

Figure S-11: GC chromatogram for a polyol solution obtained from rhamnose hydrogenolysis over Cu-Raney at 180 °C, 150 bar H_2 and 20 h reaction time. Three peaks for 3,6-deoxy hexitols (1,2,4,5-hexanetetrols) are detected at a retention time of 6.0 to 6.2 min. The peak in the middle is twice as large as the two others which is a clear indication that two stereoisomers are co-eluted which means that four stereoisomers are formed. This is in line with the detected four stereoisomers in NMR analysis as shown in **Figure S-9**. The same three 3,6-deoxy hexitols are obtained as intermediate products from hexitols (**Figure S-3** and **Figure S-5**).

^{13}C-NMR and GC data for identification of the hexanetriols (1,2,5-, 1,2,6-, and 1,4,5-hexanetriol) is shown in Figure S-12, S-13, S-14, and S-15.

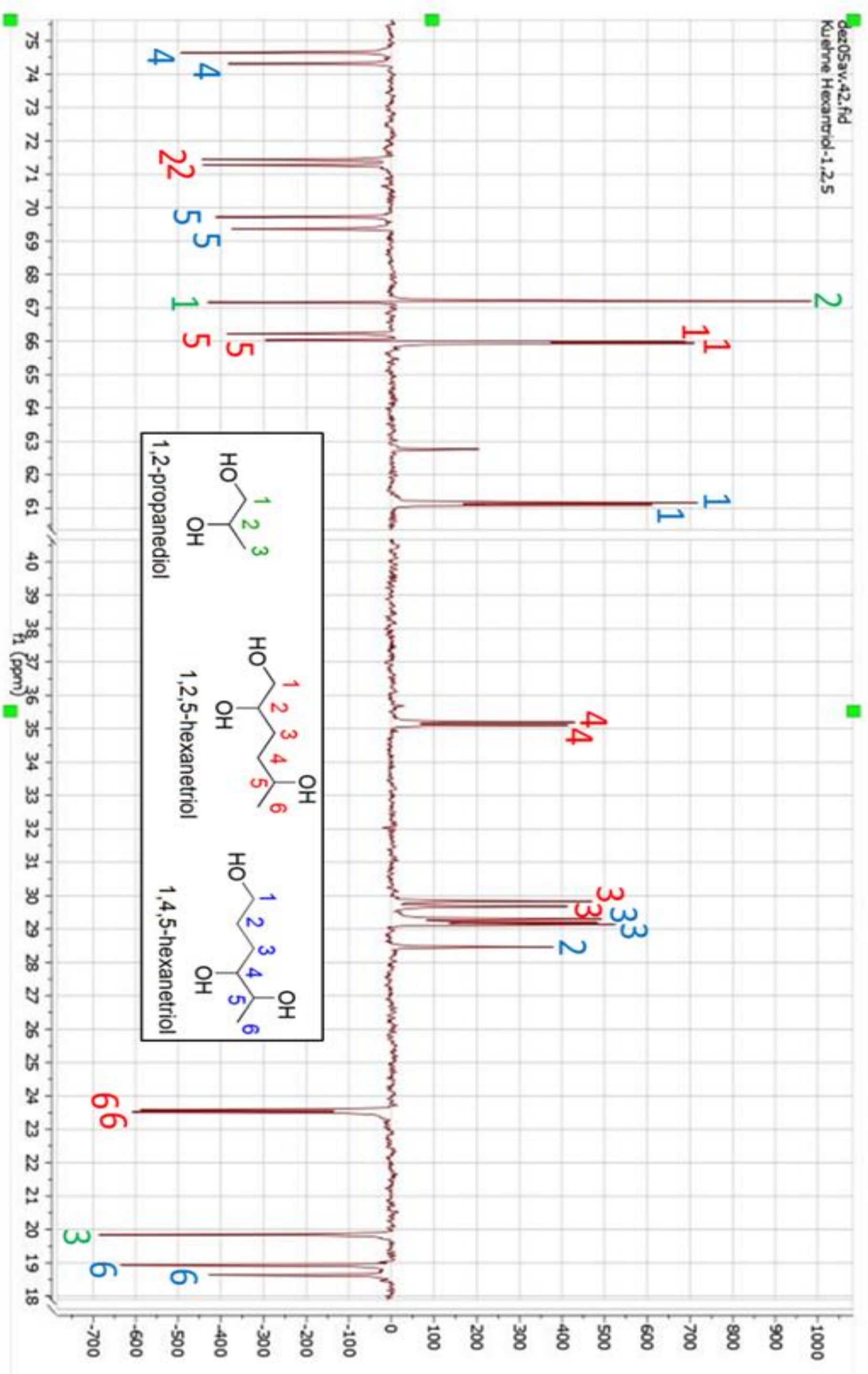

Figure S-12: Identification of the two hexanetriol isomers 1,2,5-hexanetriol and 1,4,5-hexanetriol along with 1,2-propanediol by ^{13}C-NMR analysis (DEPT). Carbon atoms with one or three C-H bonds are facing down from the base line, while carbon atoms with two C-H bonds face upwards. Both hexanetriols show two different isomeric carbon atoms for each position in the molecule that result from two chiral carbon atoms (2^2 = 4 diastereomers: however, enantiomers are not separated which results in two visible diastereomers). The GC chromatogram is shown in **Figure S-13**.

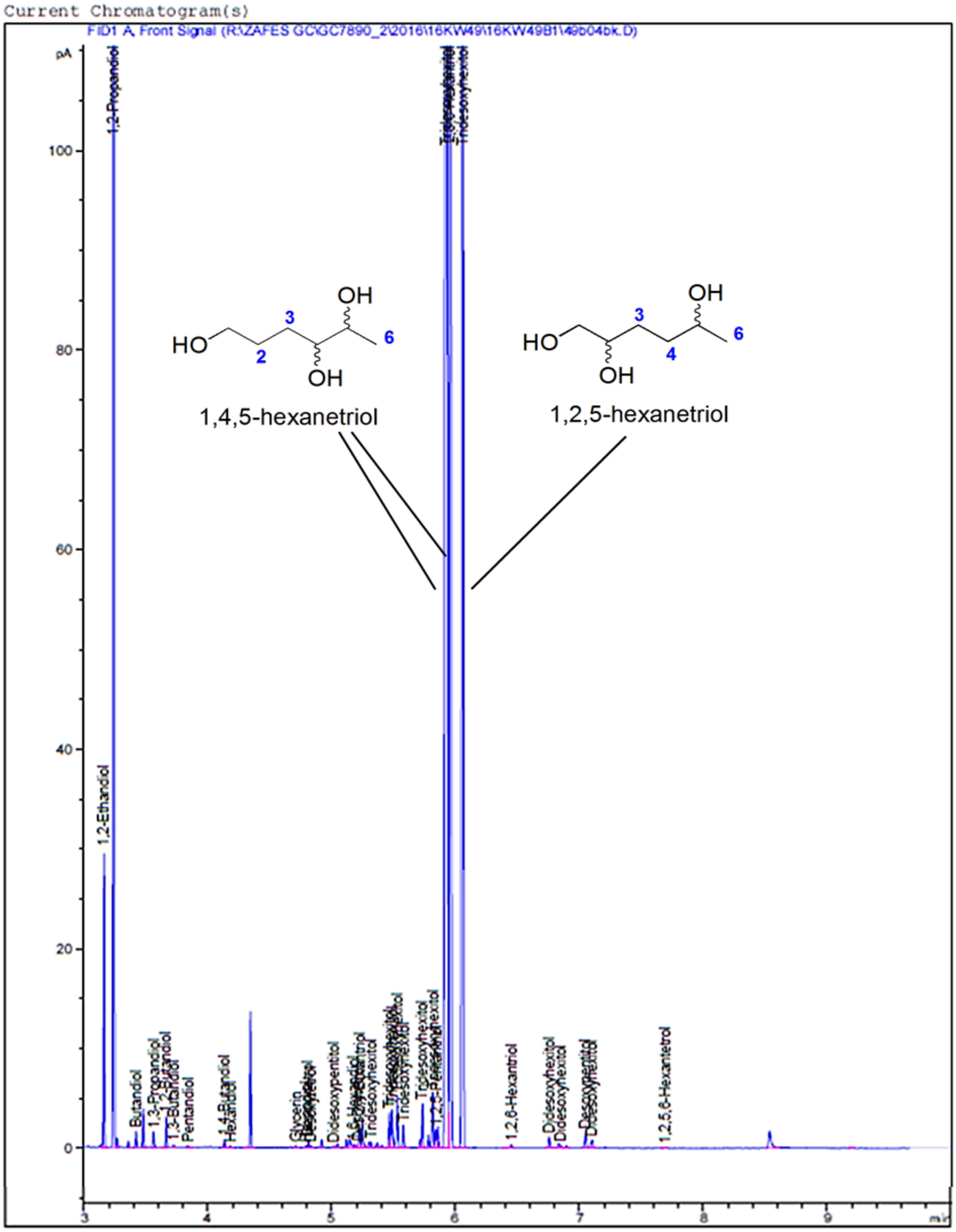

Figure S-13: GC chromatogram of the polyol mixture that was analyzed by NMR analysis for identification of the 1,2,5- and 1,4,5-hexnaetriols. The polyols were isolated by chromatography from a reaction mixture resulting from mannitol hydrogenolysis over Cu-Raney at 180 °C, 150 bar H_2 and 40 h (**Figure S-8**). The hexanetriols are detected at a retention time of 5.9 to 6.1 min and were identified by NMR analysis as shown in **Figure S-12**. Three peaks are detected, similar to the reaction mixture shown in **Figure S-8** at a retention time of 5.2 min. The first two peaks are partly co-eluted (no base line separation) which indicates that the two compounds are stereoisomers. **Figure S-14** and **Figure S-15** show that the co-eluted stereoisomers are the 1,4,5-hexanetriol.

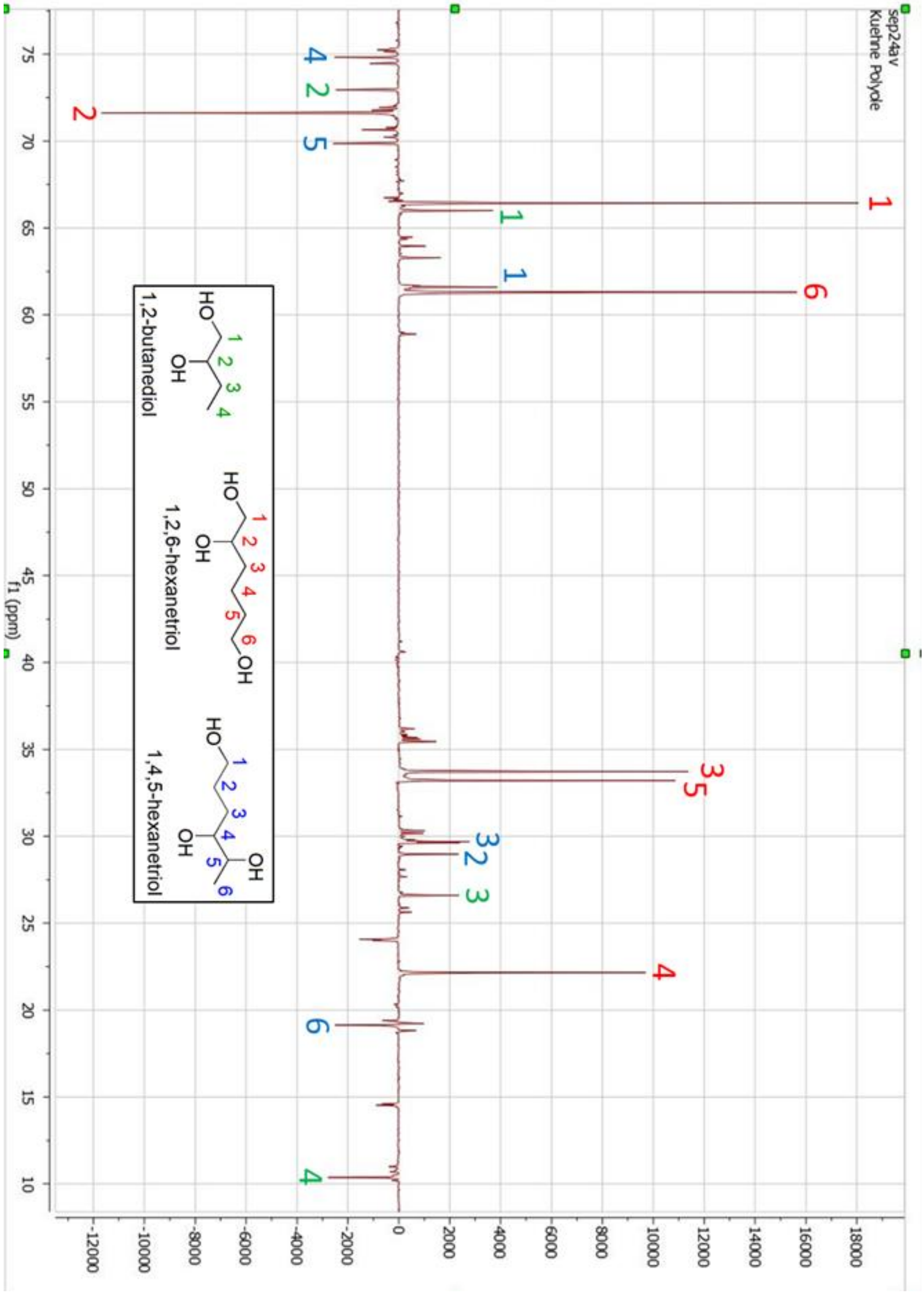

Figure S-14: Identification of the two hexanetriol isomers 1,2,6-hexanetriol and 1,4,5-hexanetriol along with 1,2-butanediol by ^{13}C-NMR-analysis (DEPT). Carbon atoms with one or three C-H bonds are facing down from the base line, while carbon atoms with two C-H bonds face upwards. The GC chromatogram is shown in **Figure S-13**.

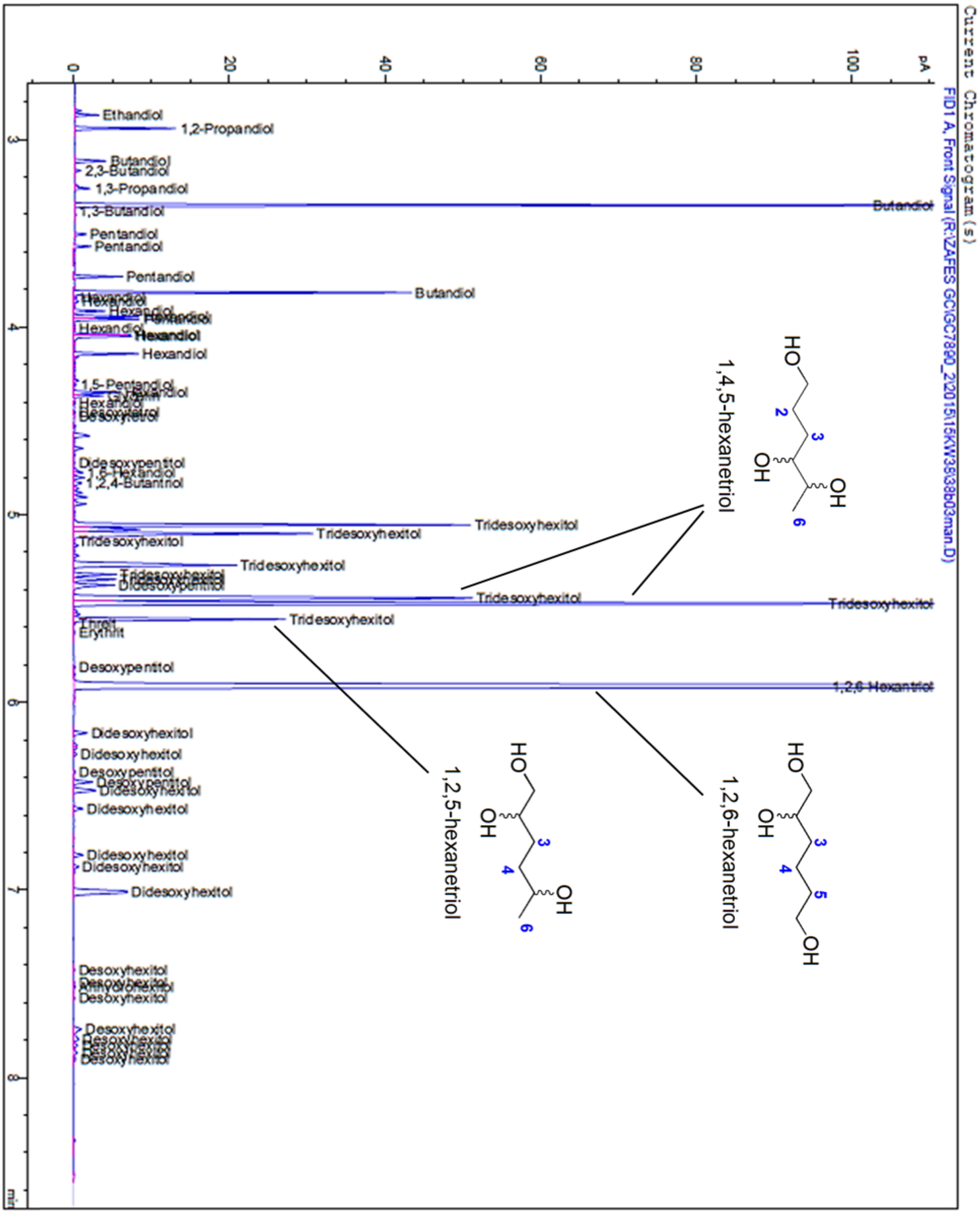

Figure S-15: GC chromatogram of the polyol mixture that was analyzed by NMR analysis for identification of the 1,2,6- and 1,4,5-hexanetriols (**Figure S-15**). The polyols were isolated by chromatography from a reaction mixture resulting from hydrogenolysis of mannitol using a Cu-Raney catalyst at 180 °C, 150 bar H_2 and 40 h reaction time as shown in **Figure S-8**. 1,4,5- and 1,2,6-hexanetriols are the main components and detected at a retention time of about 5.5 and 5.9 min, respectively. The 1,2,6-hexanetriol was identified using a standard reference, purchased from Sigma-Aldrich.

GC-MS data for identification of saccharinic acids (deoxy aldonic acid) is shown in Figure S-16.

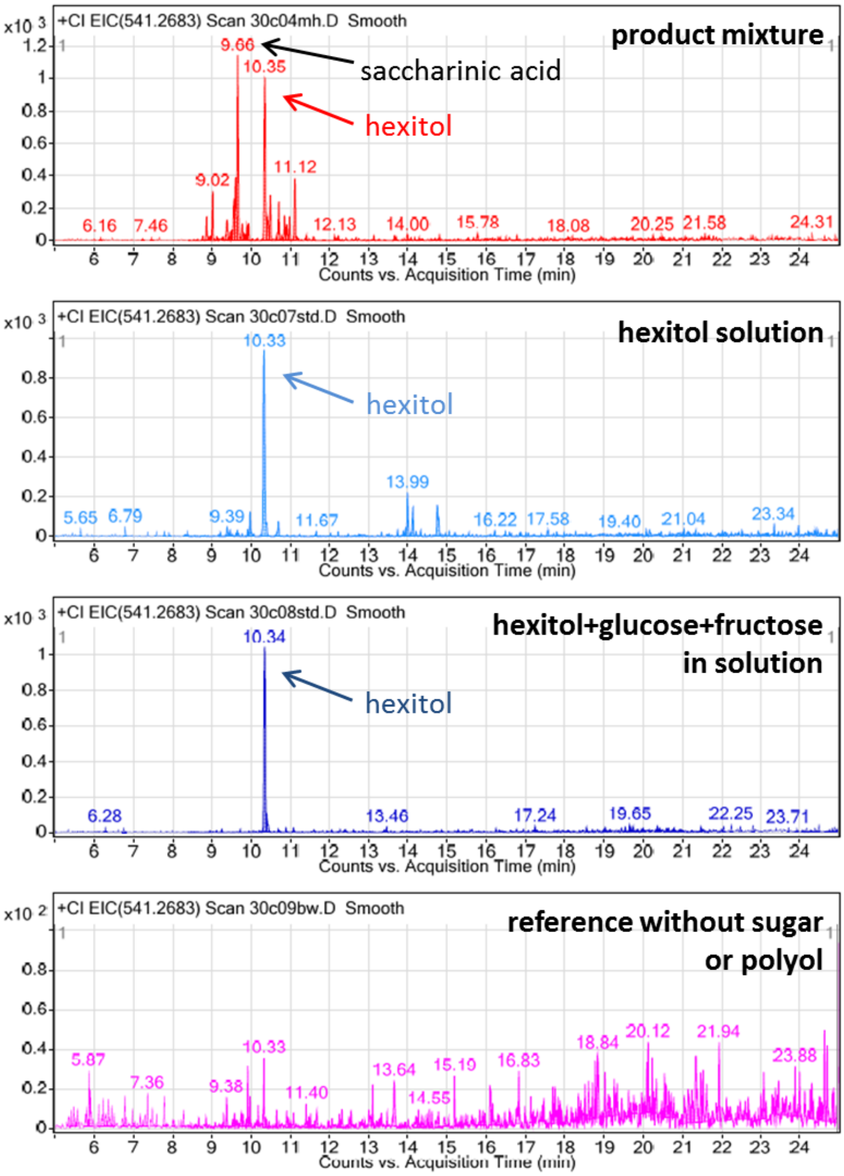

Figure S-16: Identification of saccharinic acids with a mass of 541,2 m/z for the TMS-derivated molecule (OH-groups protected with trimethylsilyl-groups, see chapter **Fehler! Verweisquelle konnte nicht gefunden werden.**) via GC-MS. The mass-to-charge-ratio only fits a deoxygenated aldonic acid (saccharinic acid, M+1 ion after addition of a proton) and is only detected in the product mixture. Hence, formation of an unknown artifact from hexitols or sugars such as glucose or fructose can be excluded.

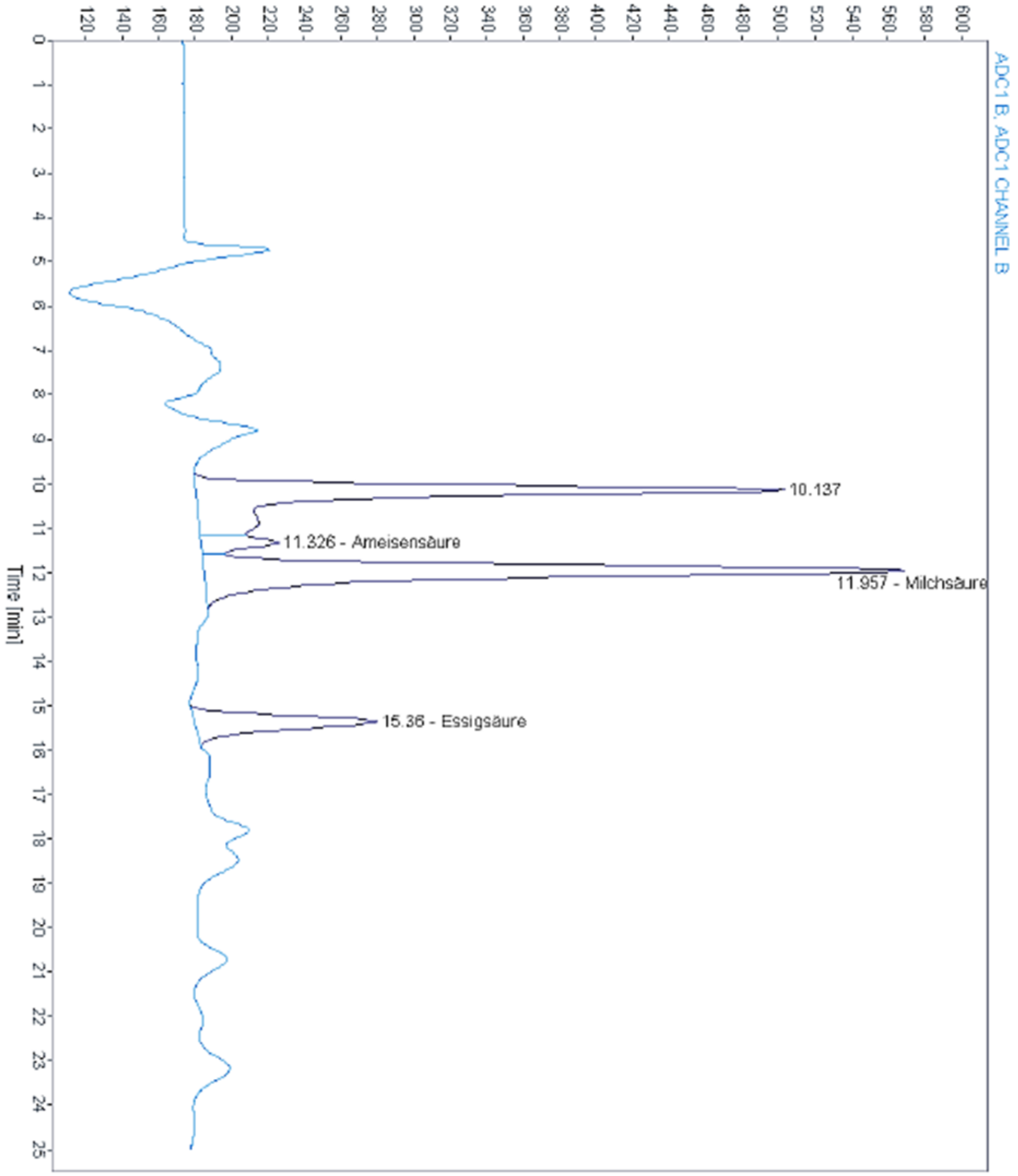

Figure S-17: Verification of formic acid (at 11 min retention time), acetic acid (15,5 min), and lactic acid formation (12 min) with HPLC-analysis. One additional unidentified acid is detected at a retention time of 10 min. The product mixture was obtained from mannitol hydrogenolysis over Cu-Raney at 180 °C without H_2 atmosphere (instead 25 bar N_2 were used) and 5 h reaction time.

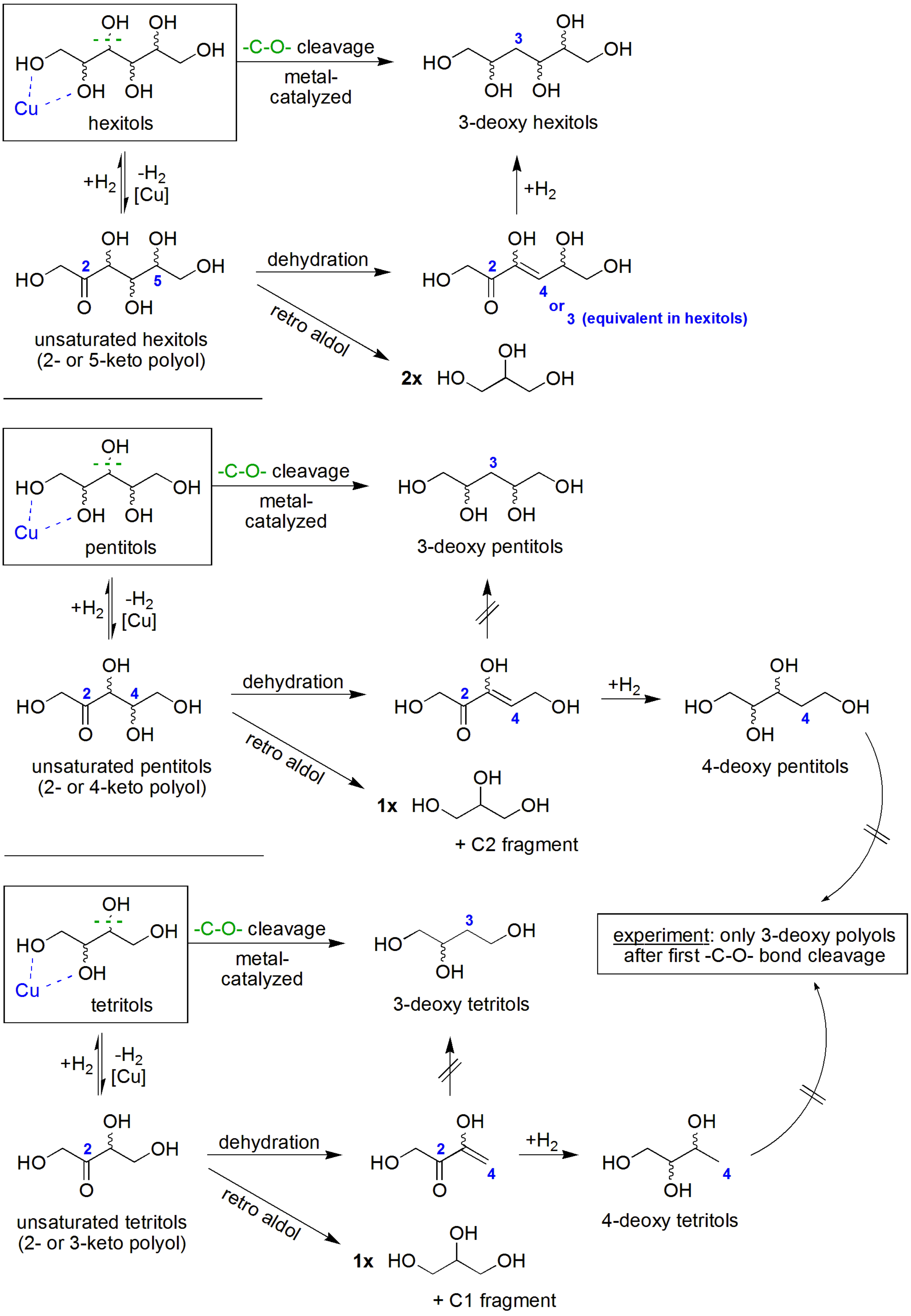

Figure S-18: Comparison of metal-catalyzed -C-O- bond cleavage and dehydration from unsaturated intermediates shows that different deoxy polyols are obtained. Hence, the metal-catalyzed reaction has to be the most dominant pathway.

The selective formation of 3-deoxy polyols after the first -C-O- bond cleavage is a strong indication that the deoxygenation reaction is metal-catalyzed as shown in Figure 8 and Figure 11 in the revised manuscript. Another known pathway for the formation of deoxy compounds is dehydrogenation to unsaturated intermediates and dehydration as shown in Figure S-18. This route is most commonly proposed for -C-O- hydrogenolysis from glycerol to 1,2-propanediol [12,16,23]. In fact, 3-deoxy hexitols could be formed along this pathway as well. The predominant unsaturated species after adsorption has to be the 2-keto (or 5-keto) intermediate. We conclude this from the product distribution shown in Figure 1 which clearly shows that the major side products are C3 polyols, in particular glycerol. Cleavage between the C3 and C4 bond, which yields two equivalents of glycerol, can only occur via such a 2-keto (or 5-keto) polyol. However, the adaptation of this dehydrogenation/dehydration pathway is not possible for the selective -C-O- bond cleavage of pentitols and tetritols. This route would lead to 4-deoxy products from such 2-keto (or 5-keto) intermediates. However, hydrogenolysis of tetritols (e.g. erythritol) and pentitols (e.g. xylitol) reveals that 3-deoxy products are formed after the first -C-O- bond cleavage step as shown in Figure 15 in the revised manuscript. Hence, deoxygenation over Cu seems to be a metal-catalyzed reaction.