

Supplementary Materials for

Selective Synthesis of Levulinic Ester from Furfural Catalyzed by Hierarchical Zeolites

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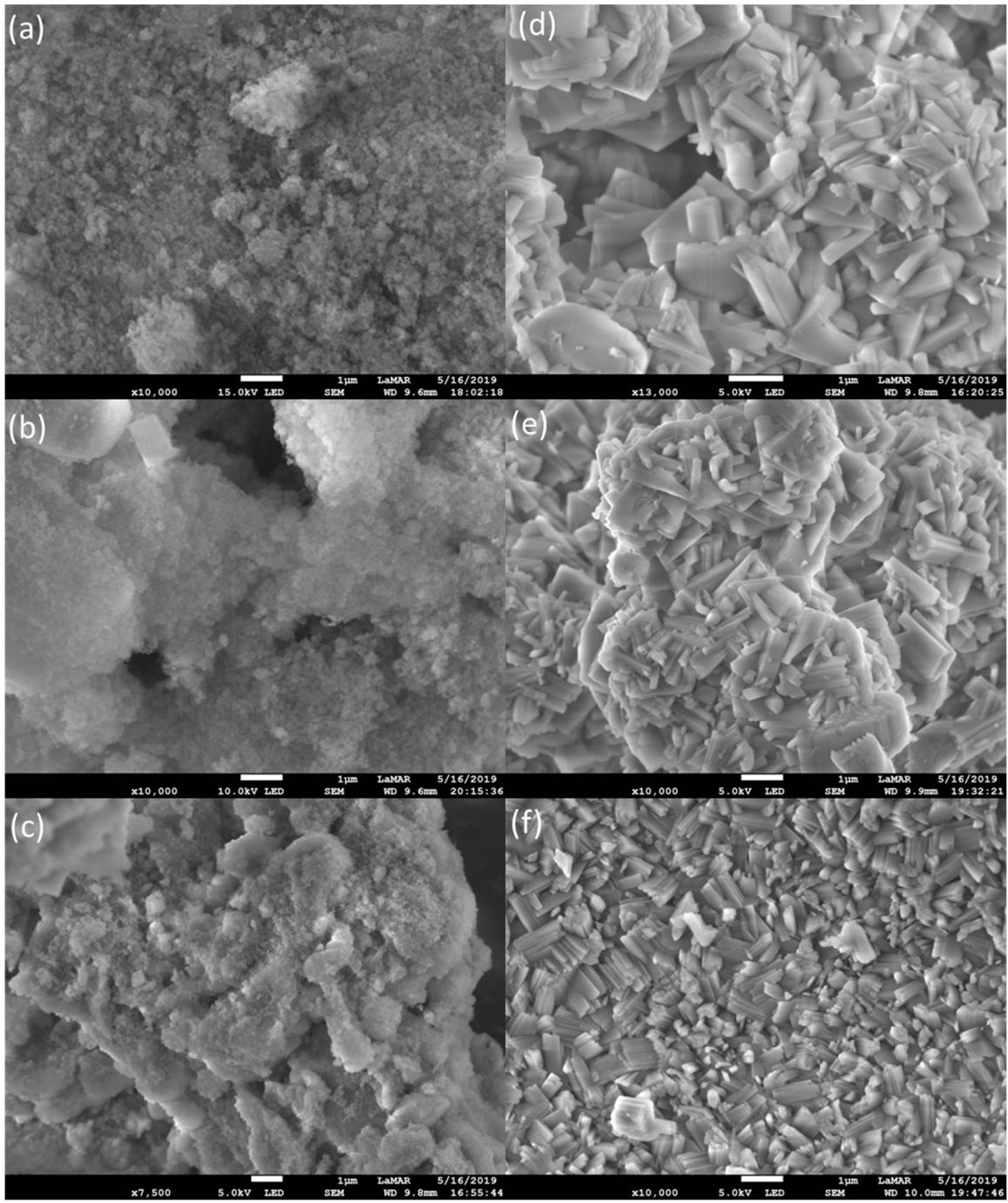


Figure S1. SEM images for the (a,b,c) beta and (d,e,f) mordenite samples.

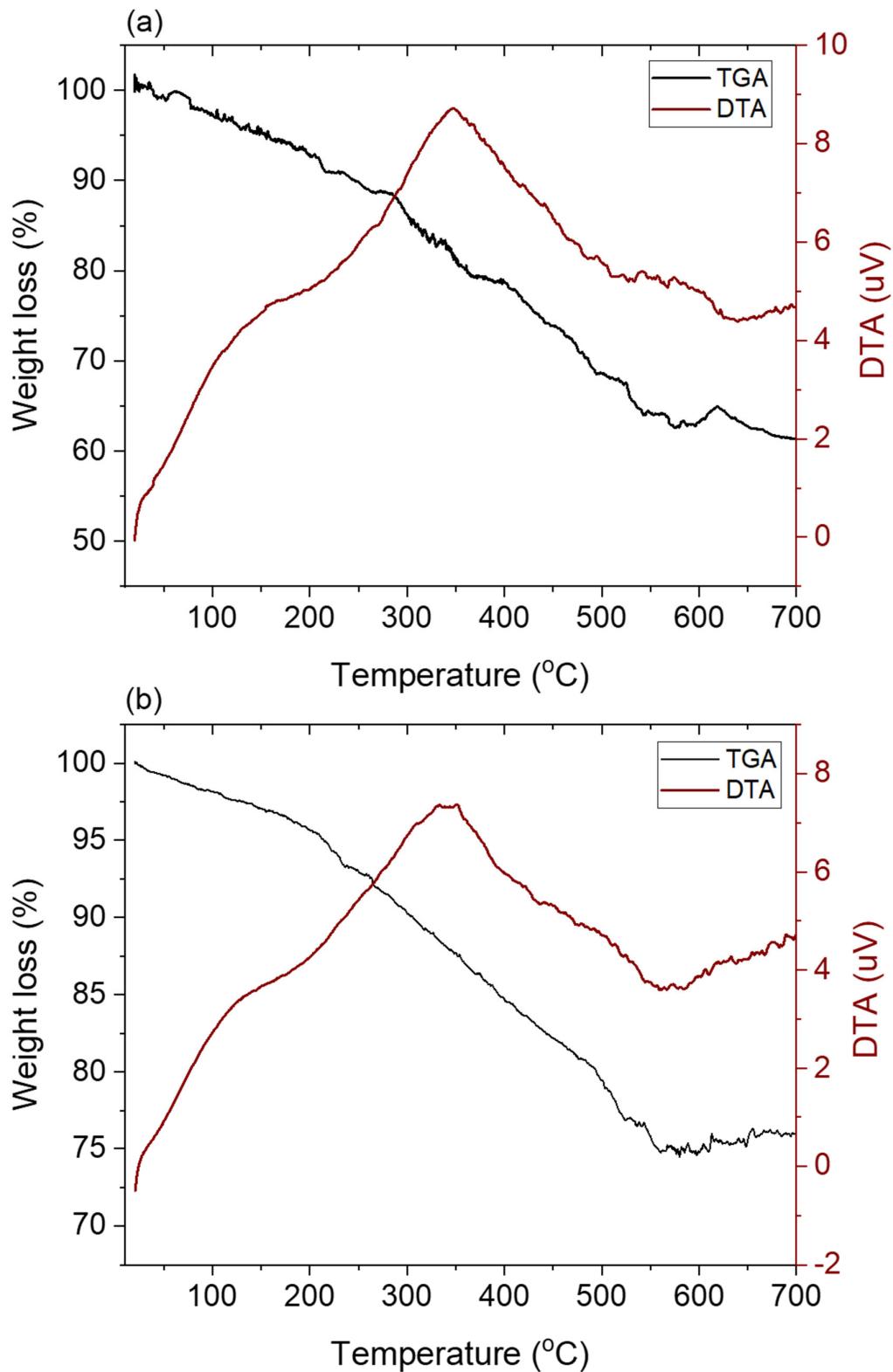


Figure S2. TGA analyses of the (a) commercial beta zeolite and (b) alkali-treated beta zeolite after the 2nd reuse in the furfural upgrading reaction.

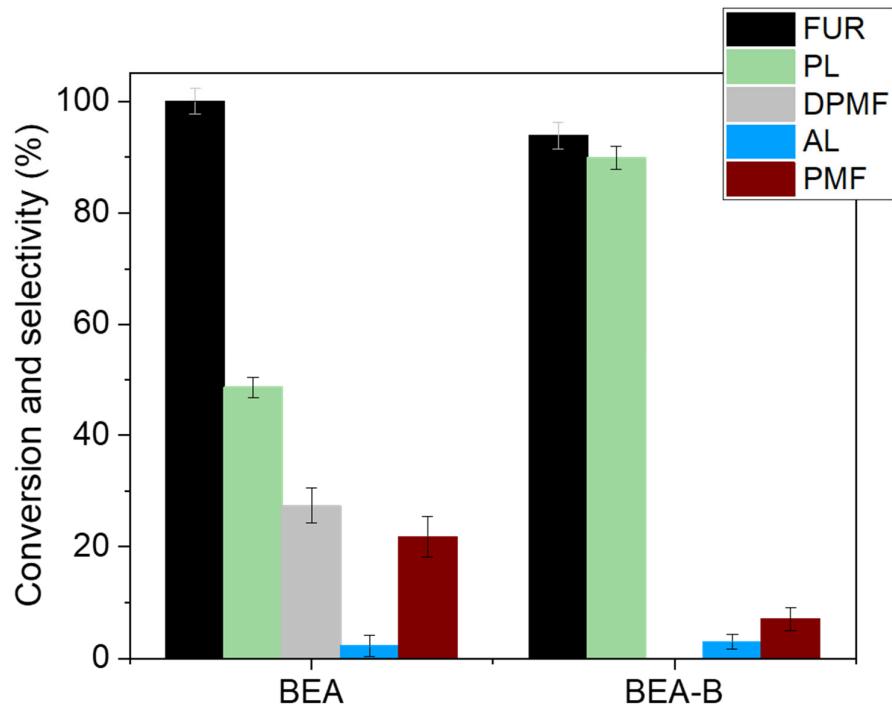


Figure S3. Experiments performed in triplicate for the commercial beta zeolite and alkali-treated beta zeolite in the furfural upgrading reaction.

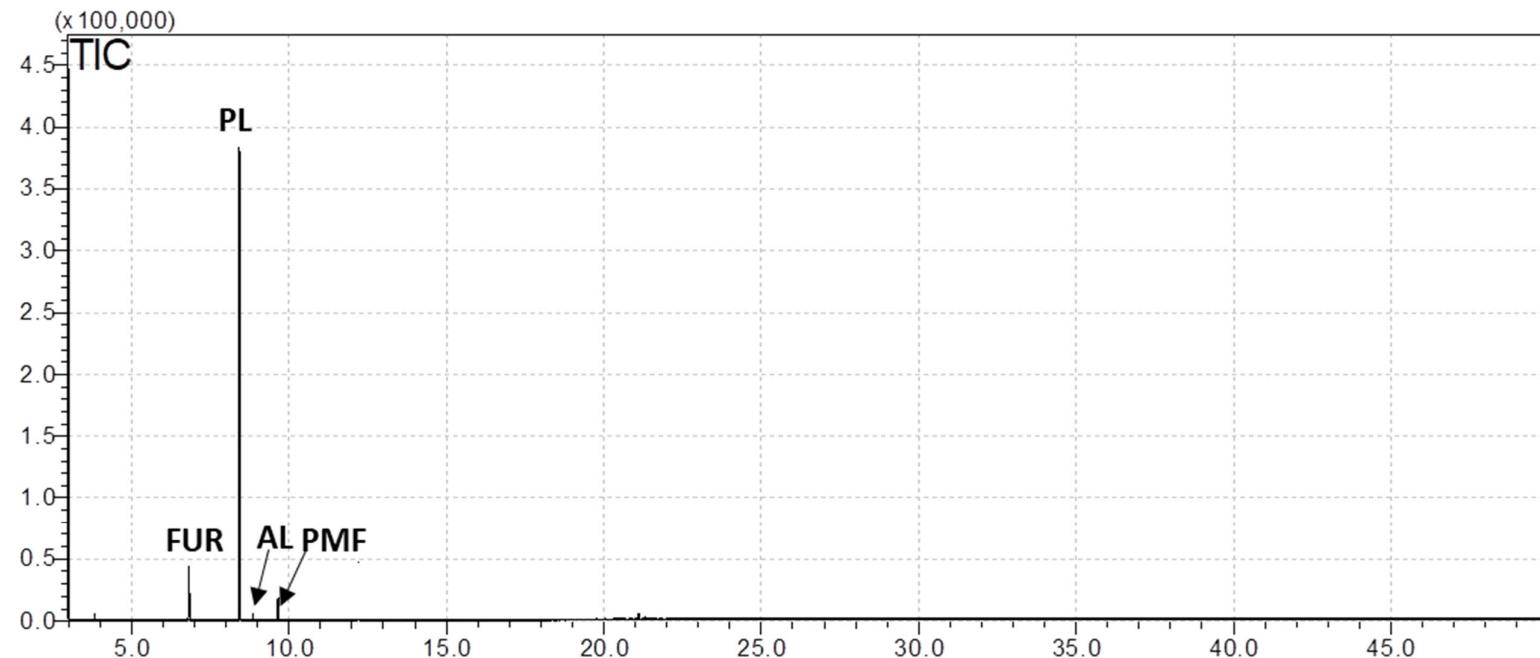


Figure S4. Typical chromatogram for the catalytic upgrading of furfural via domino reaction using BEA-B as a catalyst.

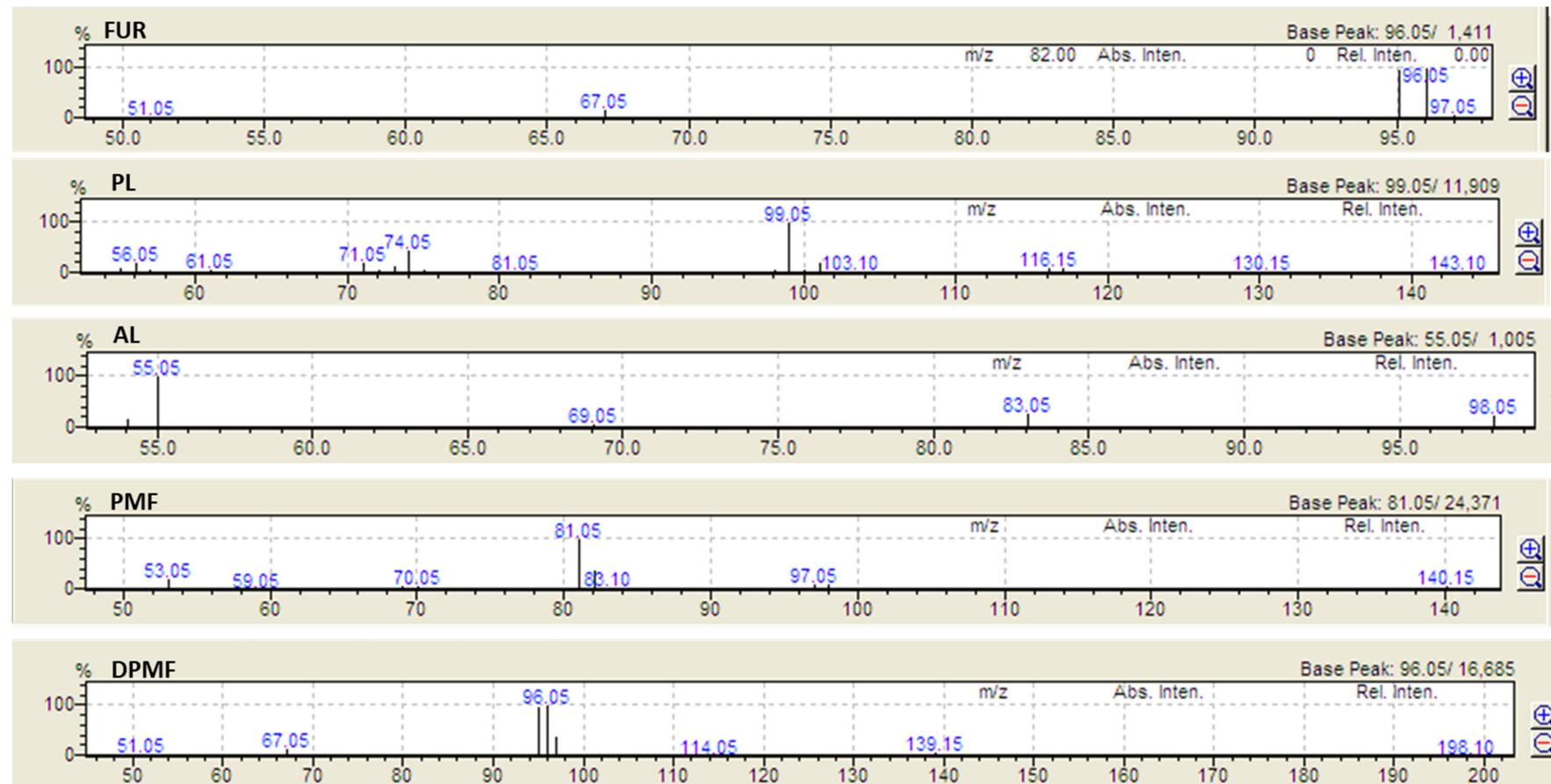


Figure S5. Mass spectra of the products detected in the catalytic upgrading of furfural via domino reaction zeolites as catalysts.

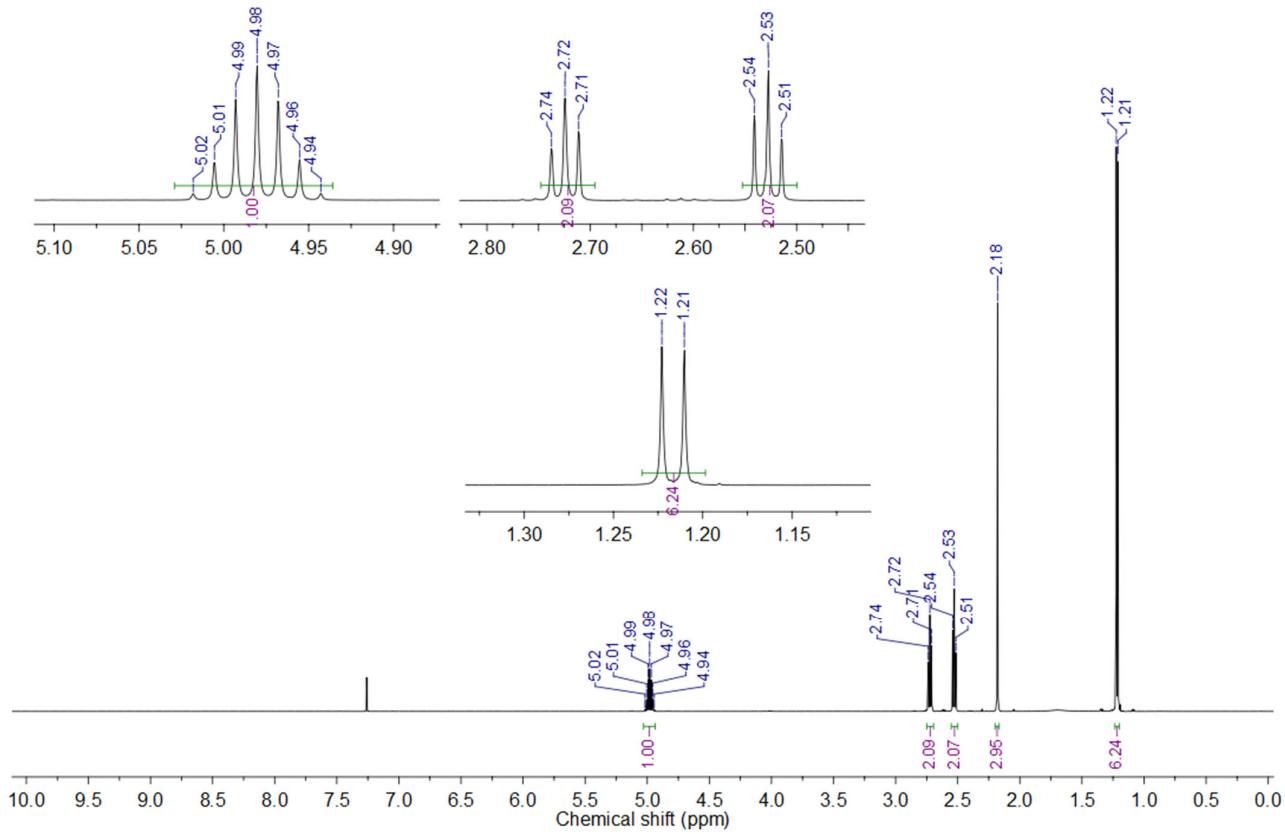


Figure S6. ¹H-NMR spectrum of isopropyl levulinate obtained from the reaction performed at optimized conditions using BEA-B as a catalyst. (500 MHz, CDCl₃). δ 4.98 (hept, J = 6.3 Hz, 1H), 2.72 (t, J = 6.6 Hz, 2H), 2.53 (t, J = 6.6 Hz, 2H), 2.18 (s, 3H), 1.22 (d, J = 6.3 Hz, 6H).

1. Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*; Elsevier, 1999; ISBN 9780125989206.
2. Tamura, M.; Shimizu, K.; Satsuma, A. Comprehensive IR Study on Acid/Base Properties of Metal Oxides. *Appl. Catal. A Gen.* **2012**, *433–434*, 135–145, doi:10.1016/j.apcata.2012.05.008.
3. Jorge, E.Y.C.; Lima, T. de M.; Lima, C.G.S.; Marchini, L.; Castelblanco, W.N.; Rivera, D.G.; Urquieta-González, E.A.; Varma, R.S.; Paixão, M.W. Metal-Exchanged Magnetic β -Zeolites: Valorization of Lignocellulosic Biomass-Derived Compounds to Platform Chemicals. *Green Chem.* **2017**, *19*, 3856–3868, doi:10.1039/C7GC01178D.
4. Jorge, E.Y.C.; Lima, C.G.S.; Lima, T.M.; Marchini, L.; Gawande, M.B.; Tomanec, O.; Varma, R.S.; Paixão, M.W. Sulfonated Dendritic Mesoporous Silica Nanospheres: A Metal-Free Lewis Acid Catalyst for the Upgrading of Carbohydrates. *Green Chem.* **2020**, *22*, 1754–1762, doi:10.1039/C9GC03489G.