Supporting Information

Acid-Catalyzed Conversion of Furfuryl Alcohol to Ethyl Levulinate in Liquid Ethanol

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Fragmentation Analysis

Protonated EL $[M+H]^+$ has a m/z of 145.0 (MW = 144), and the fragmentation pattern is: MS(1) 145.0 → MS(2) 99 .1 → MS(3) 71.5→ MS(4) 43.8. Both intermediate 1 and intermediate 2 have similar mass spectra, but the fragmentation patterns of these intermediates are different. Intermediate 1 starts by fragmenting the 113.0 ion. It fragments the following way: MS(1) 113.0 → MS(2) 81.4, 71.6 → MS(3) 53.9; MS(2) 71.6 →MS(3) 41.8, 43.9; in the case of intermediate 2 the 127.0 m/z ion is fragmented the following way: MS(1) 127.0 → MS(2) 99.1→MS(3) 71.5 → MS(4) 43.8. A FAL molecule or a ring-opened molecule with the same MW as FAL, i.e. 98, that reacts with ethanol and loses one water molecule has a MW of 126, 127 m/z when protonated. The ethyl group is not very stable inside the ion trap, therefore giving a 113.0 m/z ion as the most abundant ion, followed by 127.0 m/z (see figures 3 to 5 of the article).

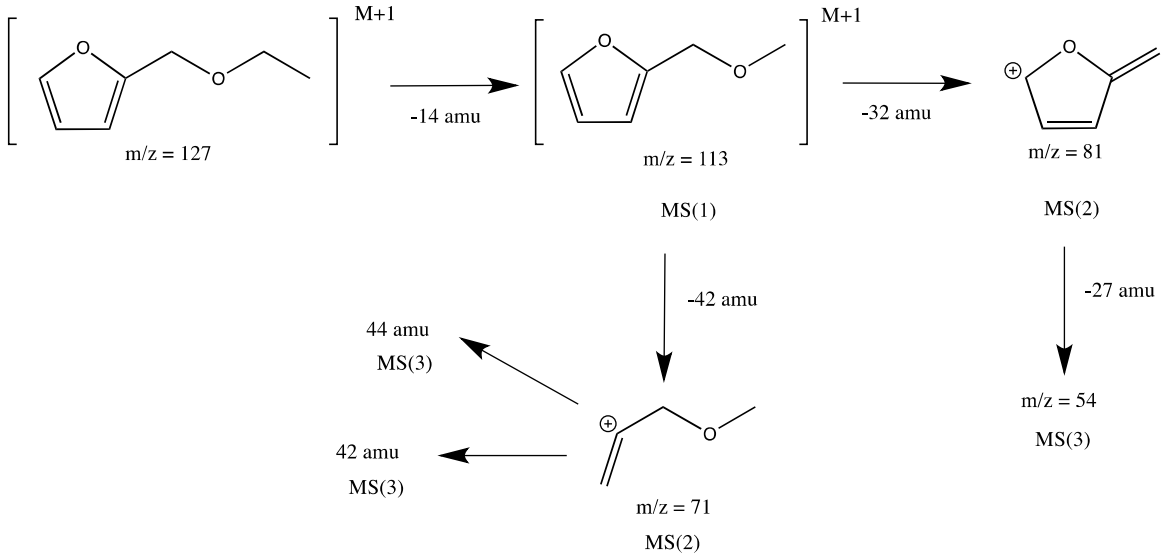


Figure S 1. Proposed Fragmentation MS(n) Pattern for Intermediate 1

Intermediate 3 has the following fragmentation: MS(1) 158.9 → MS(2) 85.0 → MS(3) 58.7, 46.1. Ion 172.9, shown in Figure 5 of the article, was not fragmented initially. From 172.9 to 158.9 a mass of 14 is lost, similar to the case for intermediate 1 and 2.

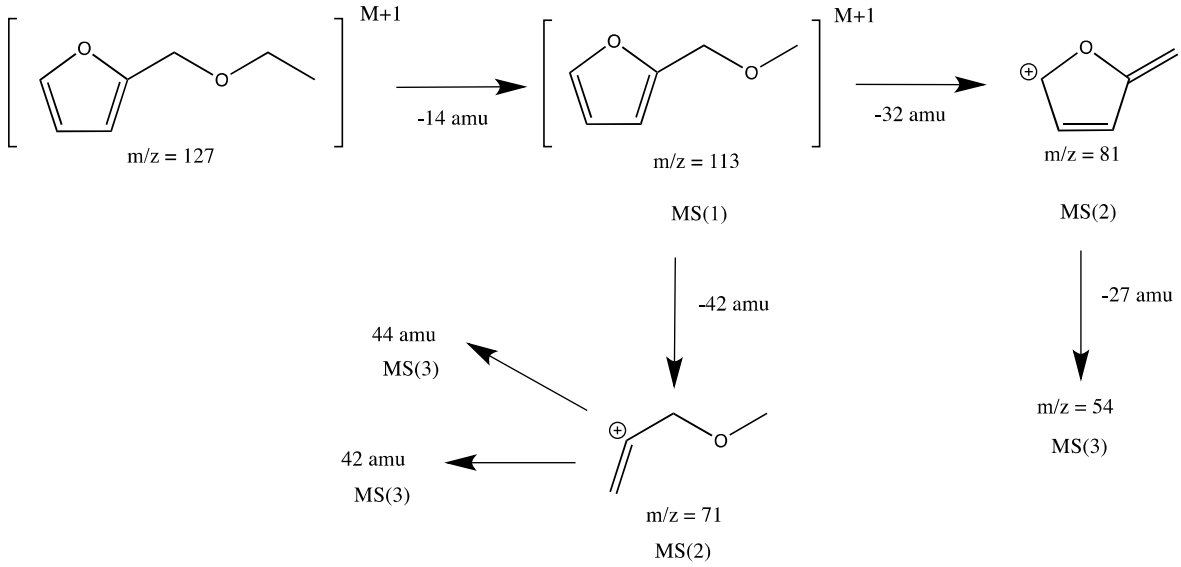


Figure S 2. Proposed Fragmentation MS(n) Pattern for Intermediate 2

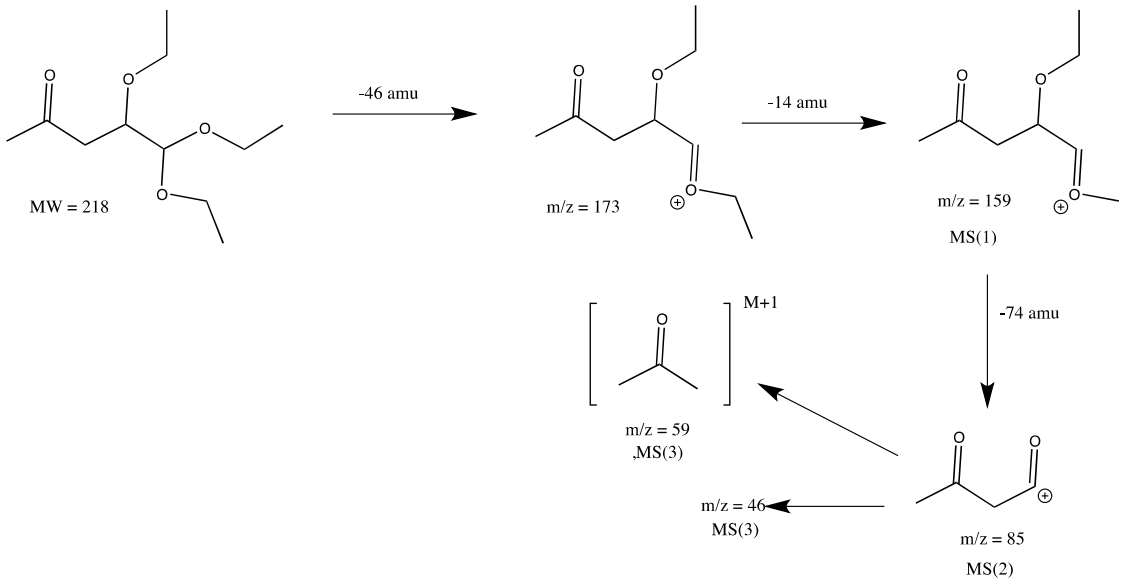
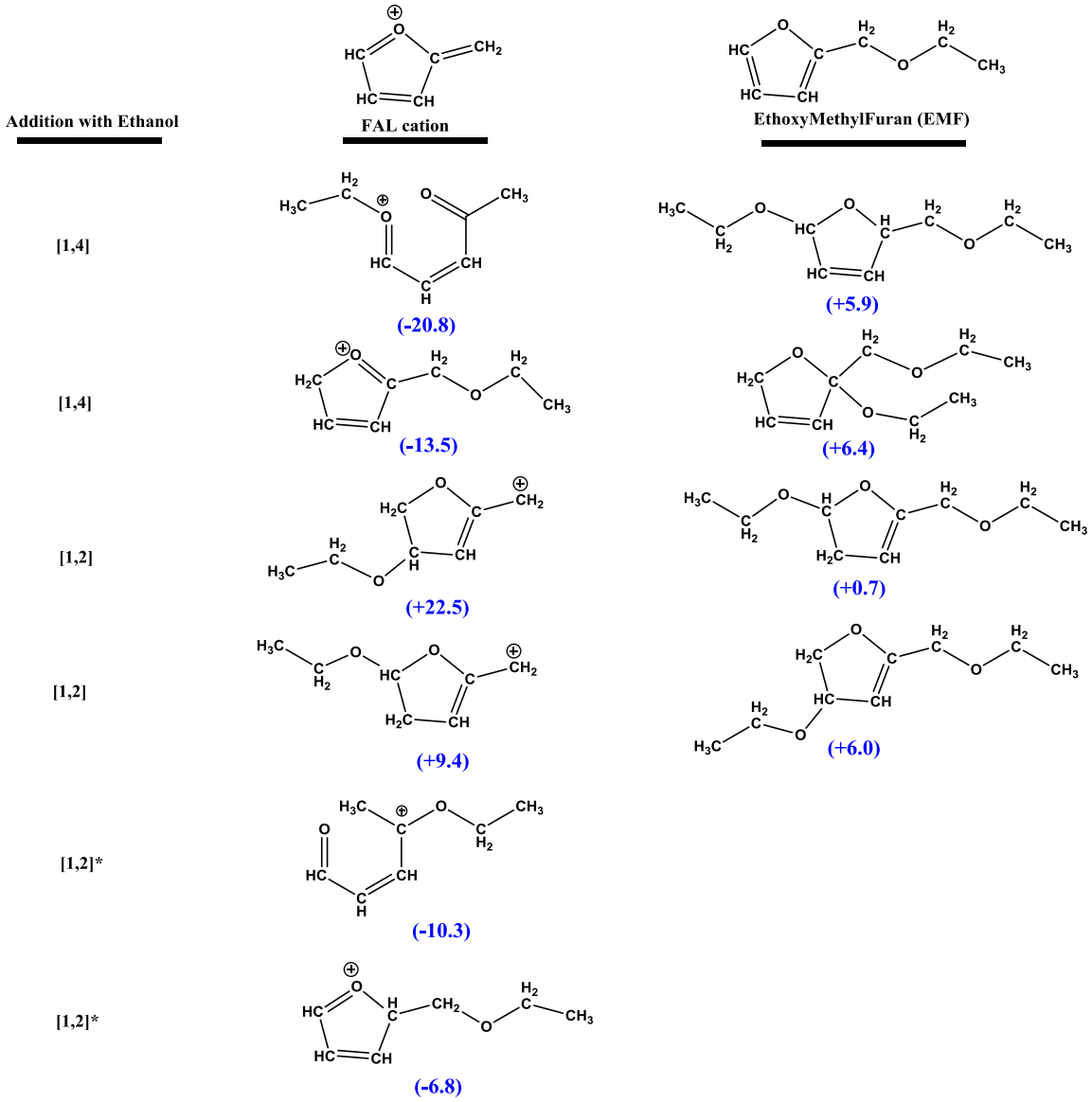
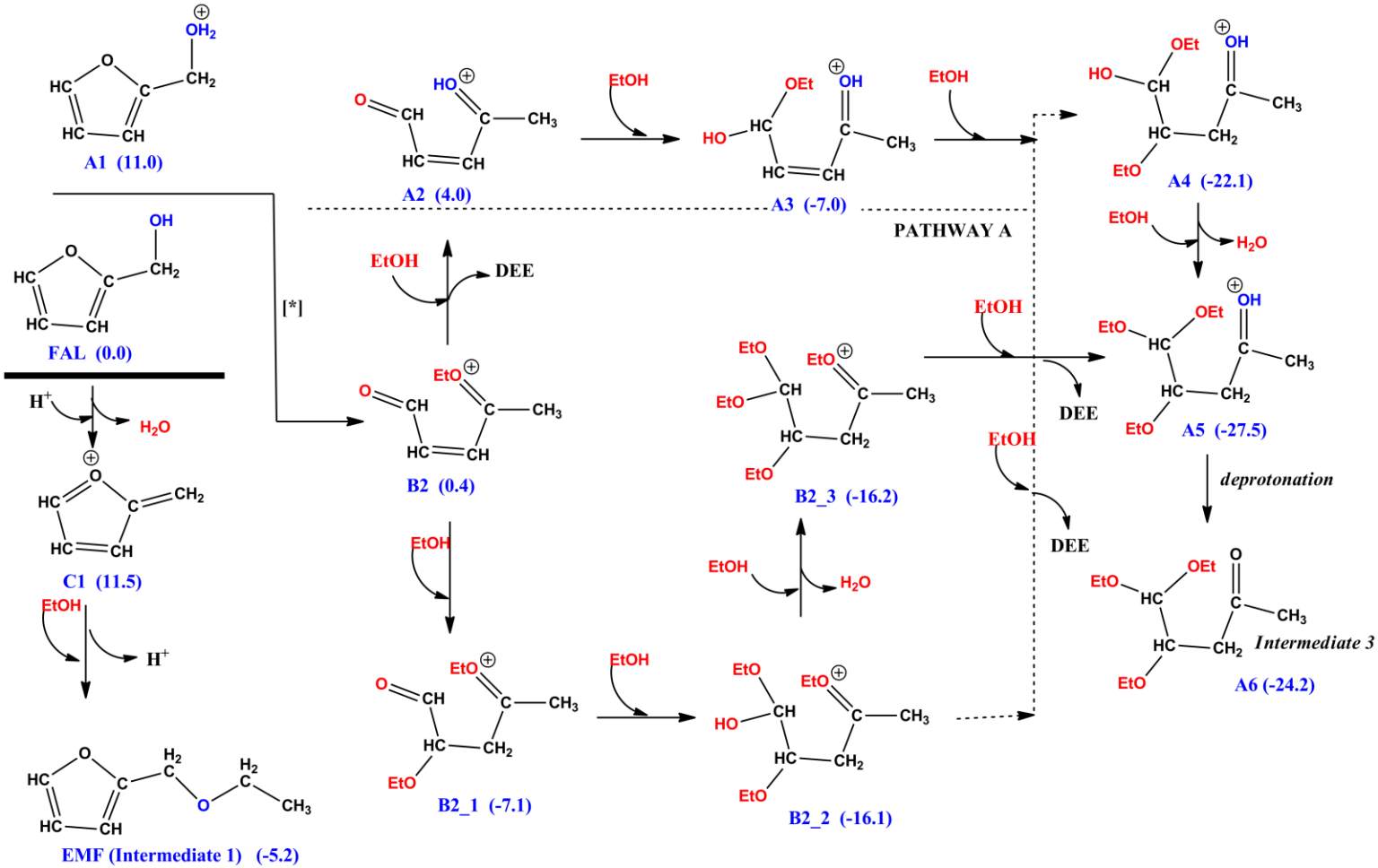


Figure S 3. Proposed fragmentation pathway for Intermediate 3. Note that the original the m/z detected by the ion trap is the 173m/z but the ion that is first fragmented is 159 m/z. See the NMR analysis for more details on this molecule with MW = 218.

Theoretical Studies



Scheme S 1. Schematic representation of addition products of FAL cation (C1) and ethoxy-methyl-furan (EMF) with ethanol. The computed free energies of the reactions (kcal/mol) at the B3LYP/6-31G(2df,p) level of theory is also given. (*) indicates the addition reaction is C=CH_2 bond.



Scheme S 2. Schematic representation for the formation of Intermediate 1 and Intermediate 3 from FAL. The computed relative free energies (kcal/mol) of all species w.r.t FAL is also shown.

NMR Spectra

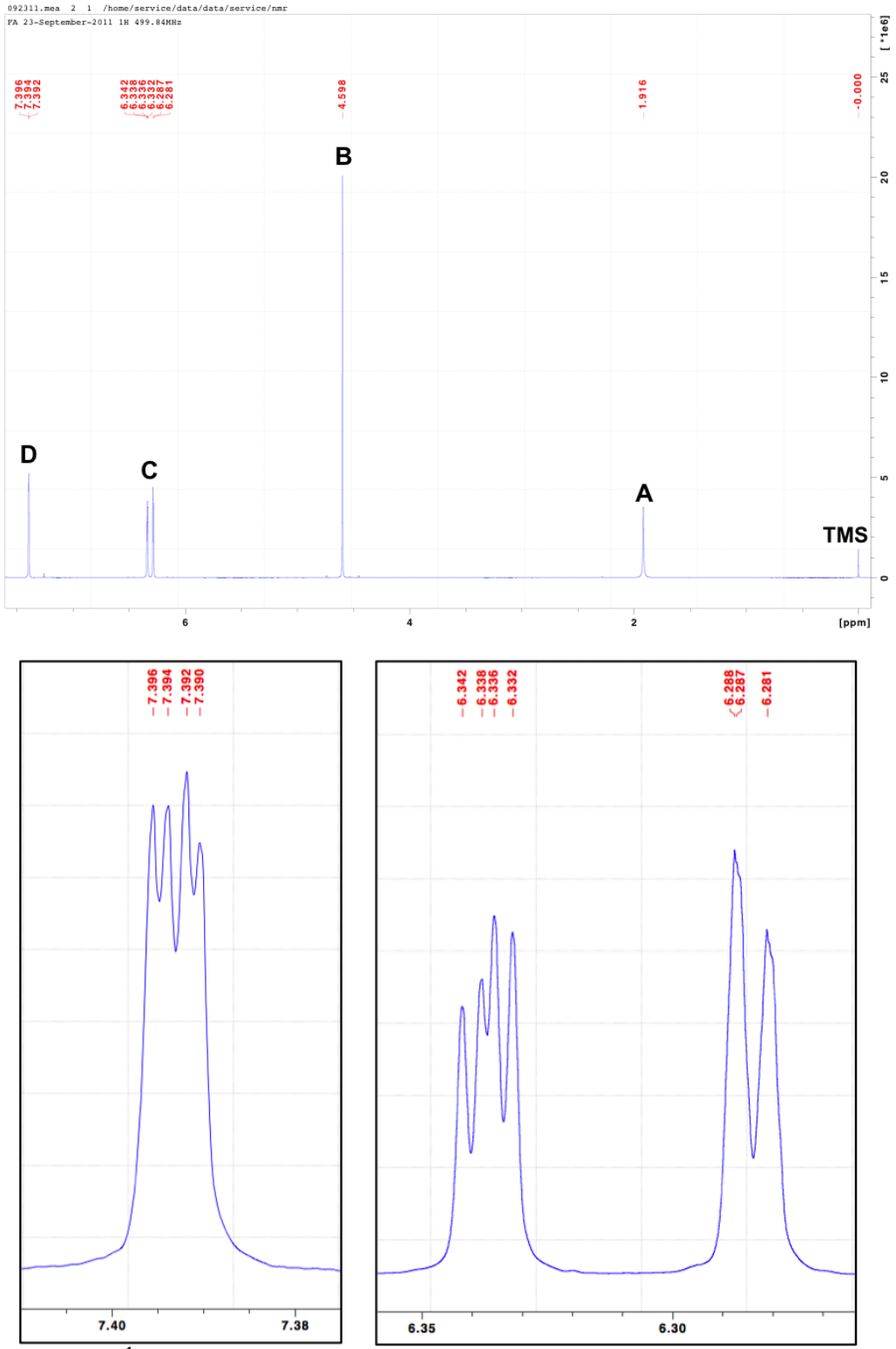


Figure S 4. FAL ^{1}HNMR in CDCl3. Full spectrum (top), zoom in doublet and multiplets (bottom). TMS was used as a reference.

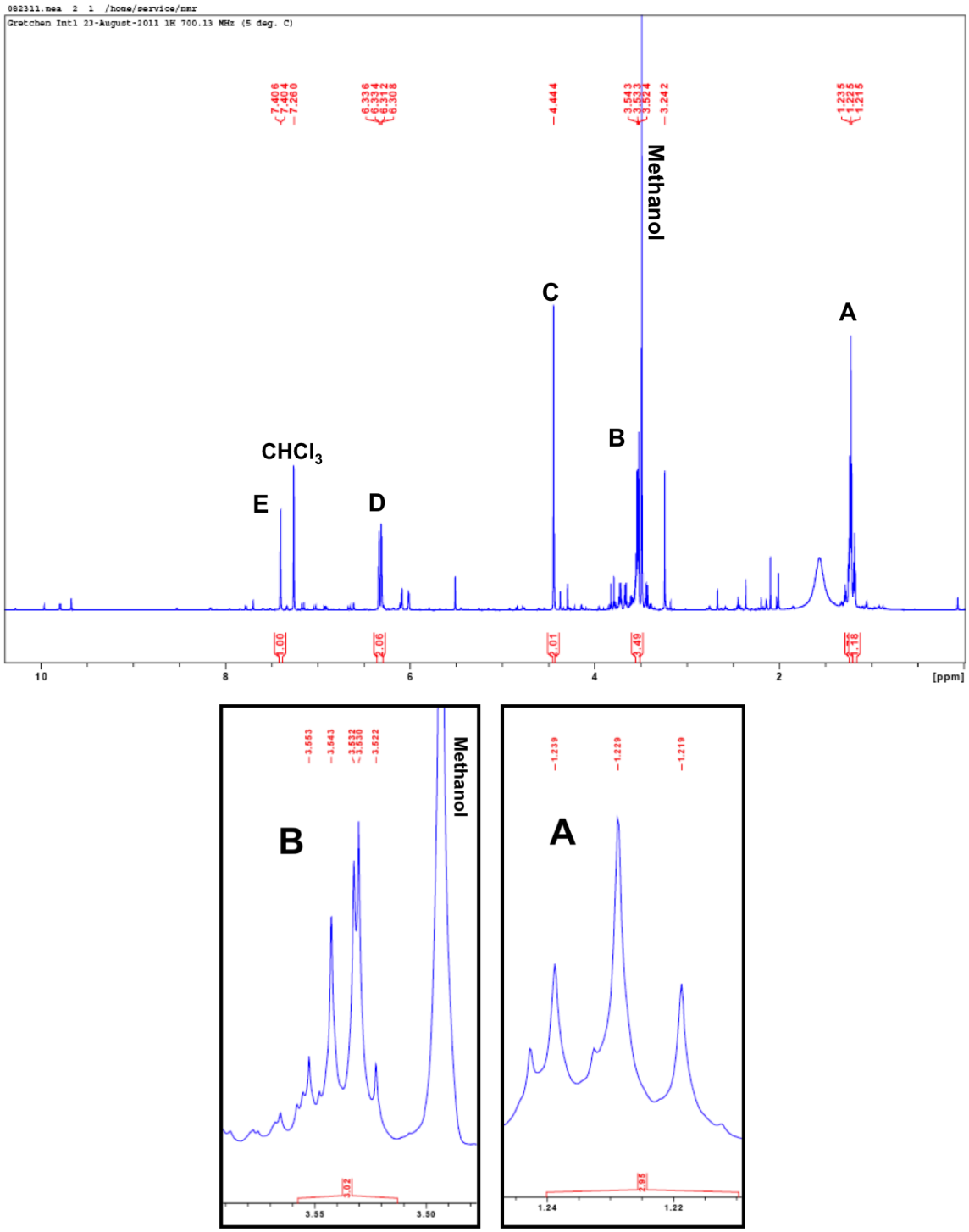


Figure S 5. ^{1}HNMR of EMF (intermediate 1) in $CDCl_3$ (top). Zoom in of quartet and triplet resonances (bottom).

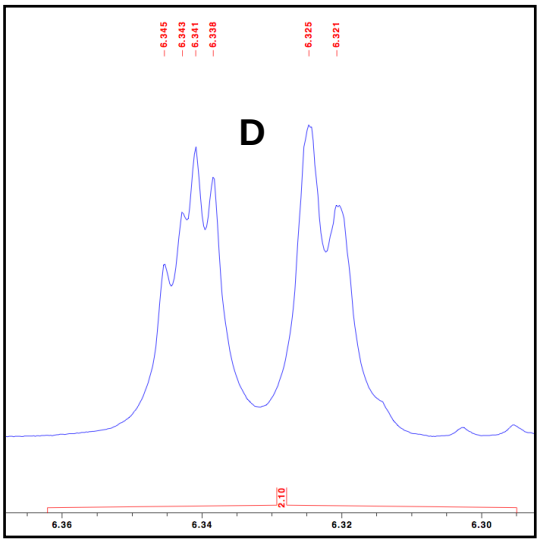


Figure S 6. Intermediate 1 (EMF) Zoom in on group D

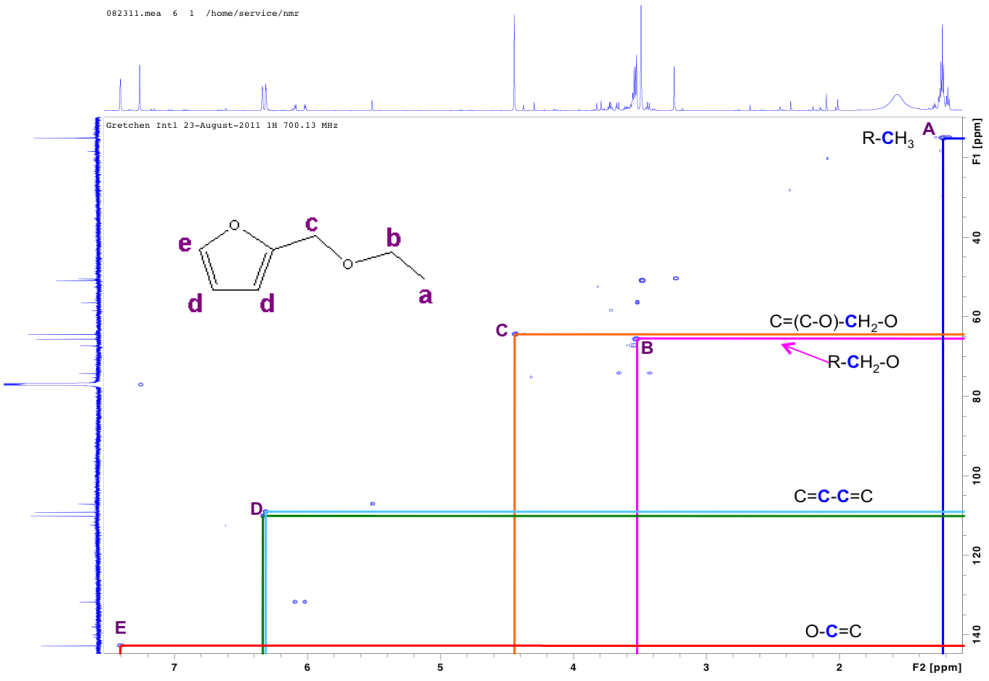


Figure S 7 HSQC NMR for EMF (intermediate 1)

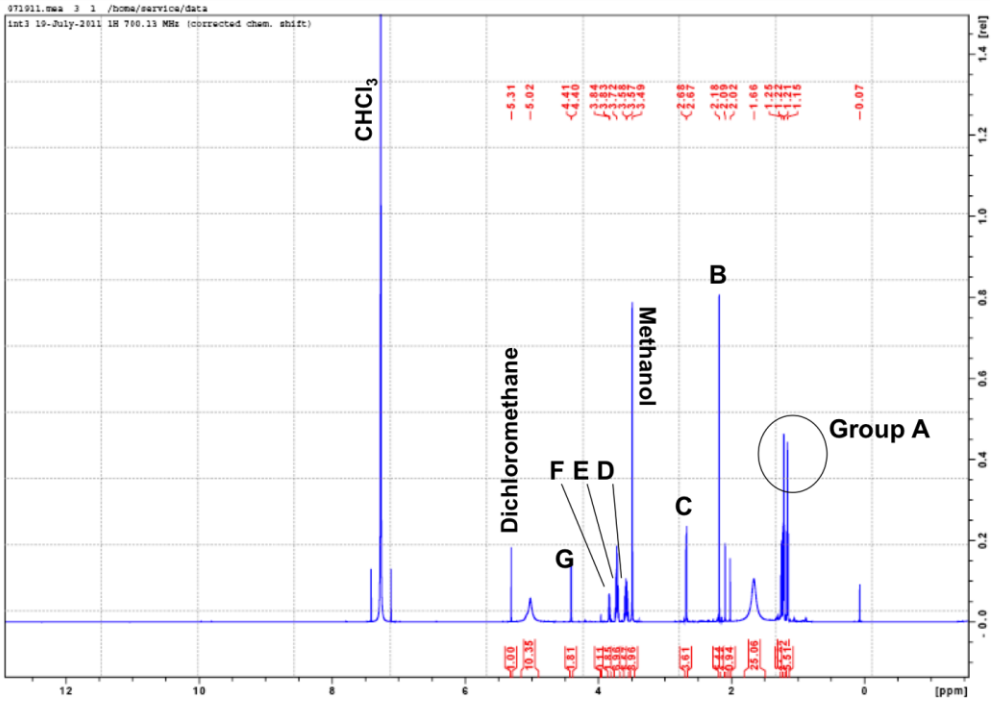


Figure S 8 ^{1}HNMR of intermediate 3 in $CDCl_3$. Dichloromethane, methanol, and chloroform are impurities from the isolation process. Dichloromethane was present in the low-pressure evaporation environment from a previous experiment.

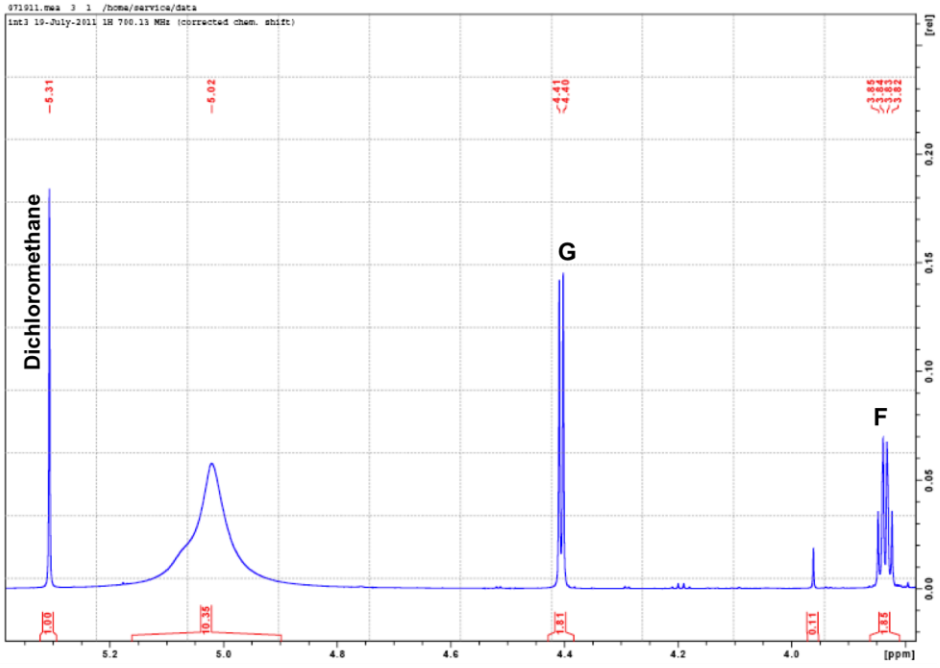


Figure S 9 Zoom in of ^{1}H NMR spectrum of intermediate 3 at 3.8 - 5.4 ppm

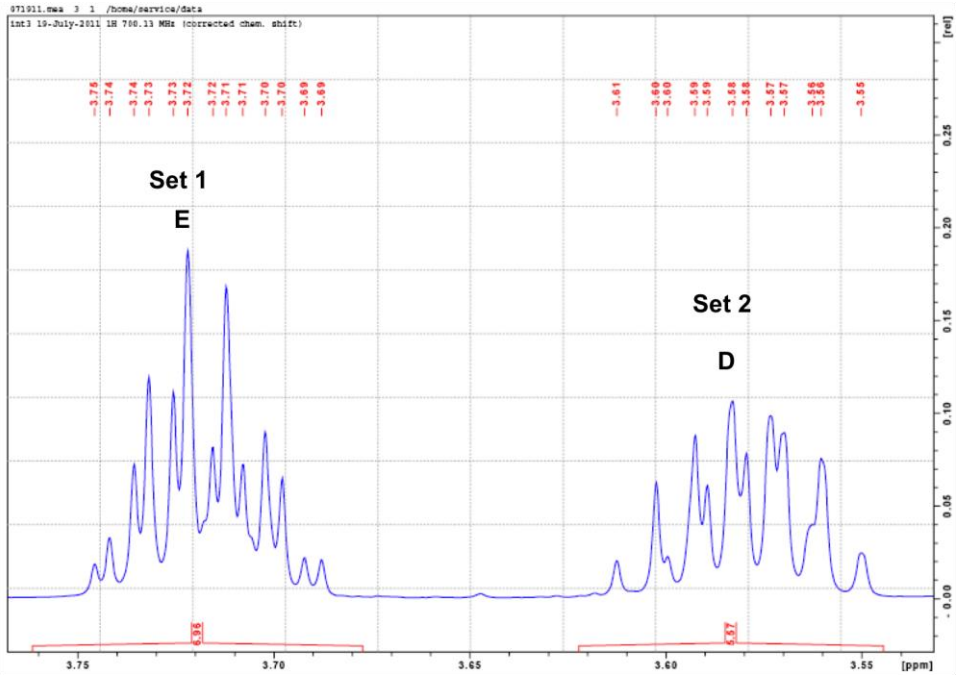


Figure S 10 Zoom in of multiplets of ^{1}H NMR spectrum of intermediate 3 from 3.5 – 3.8 ppm

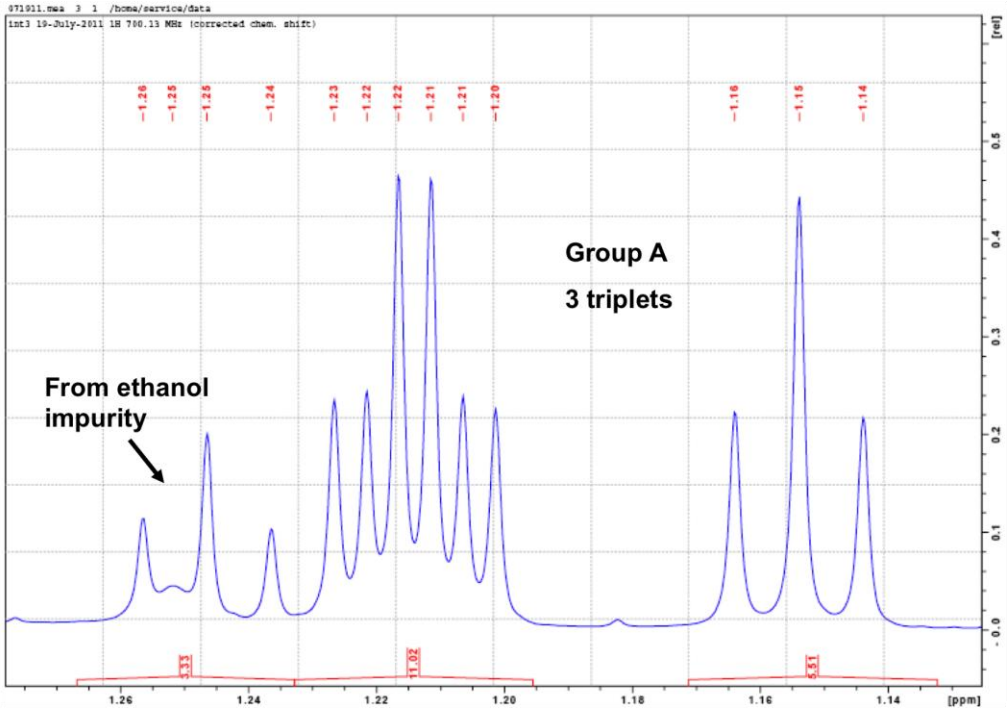


Figure S 11 Zoom in of ^{1}HNMR spectrum of intermediate 3 at 1.1-1.3 ppm

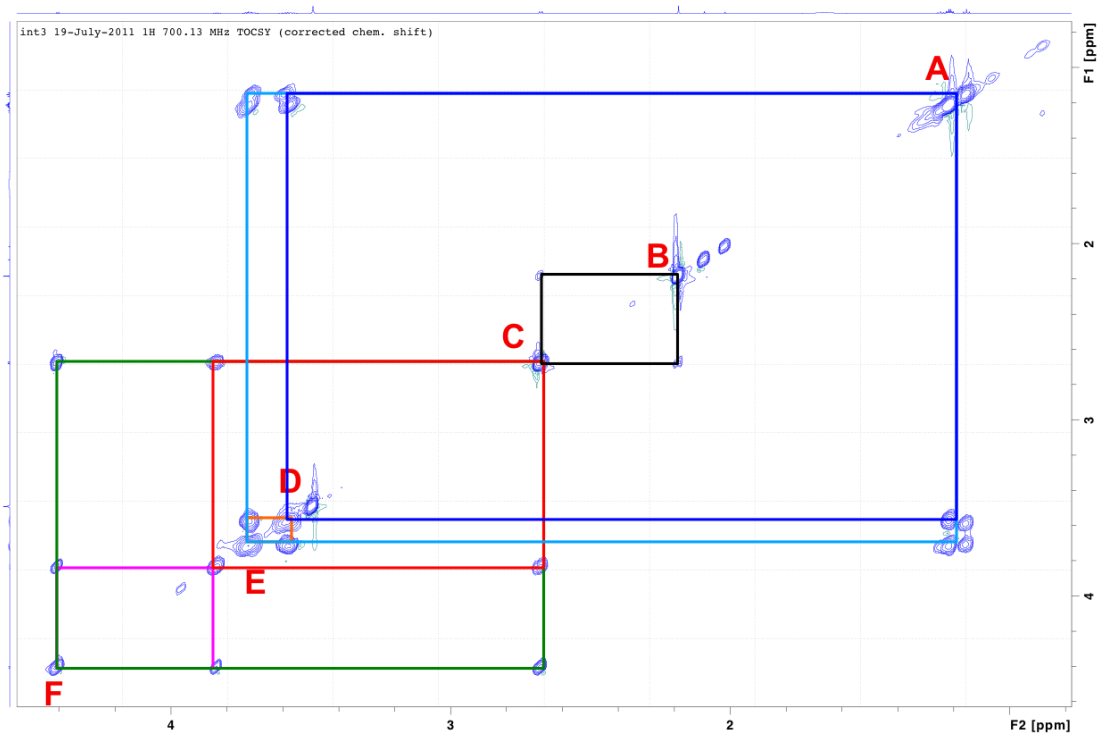


Figure S 12 TOCSY NMR for 4,5,5-triethoxypentan-2-one (intermediate 3)

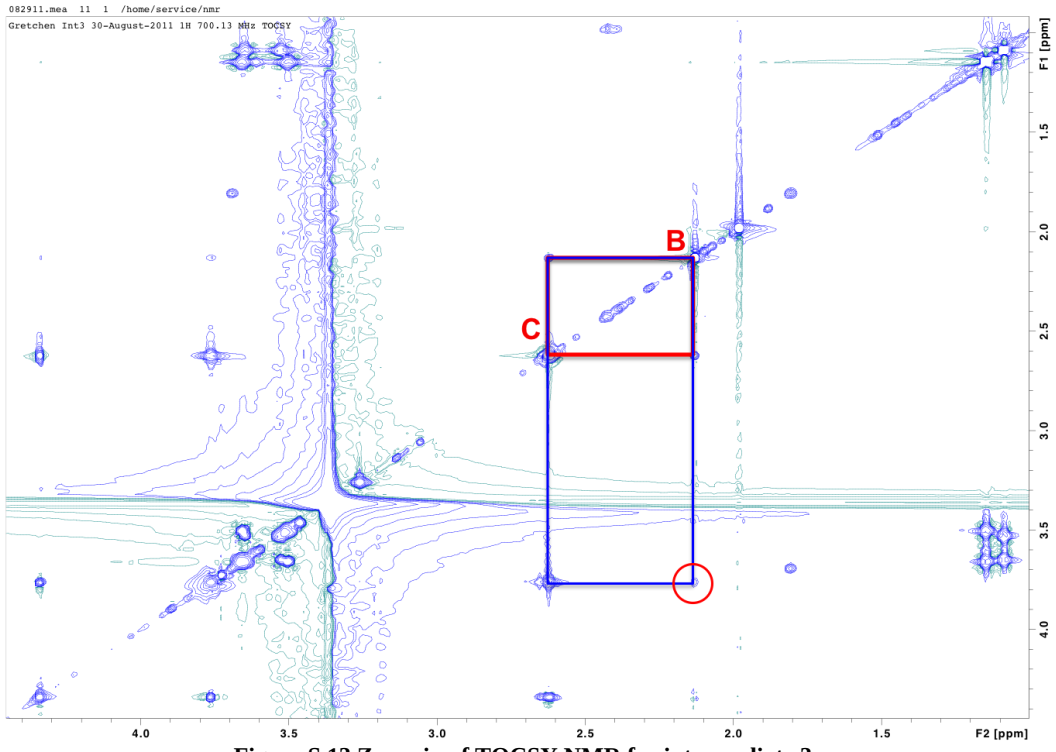


Figure S 13 Zoom in of TOCSY NMR for intermediate 3.

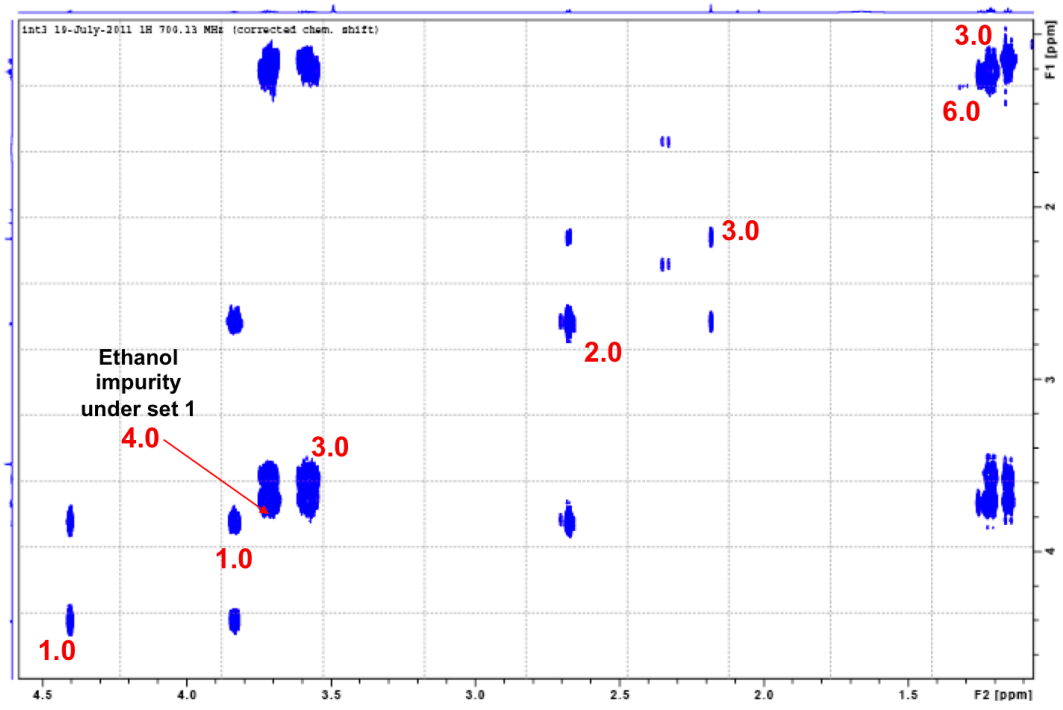


Figure S 14 COSY NMR for intermediate 3. The red numbers represent the number of protons.

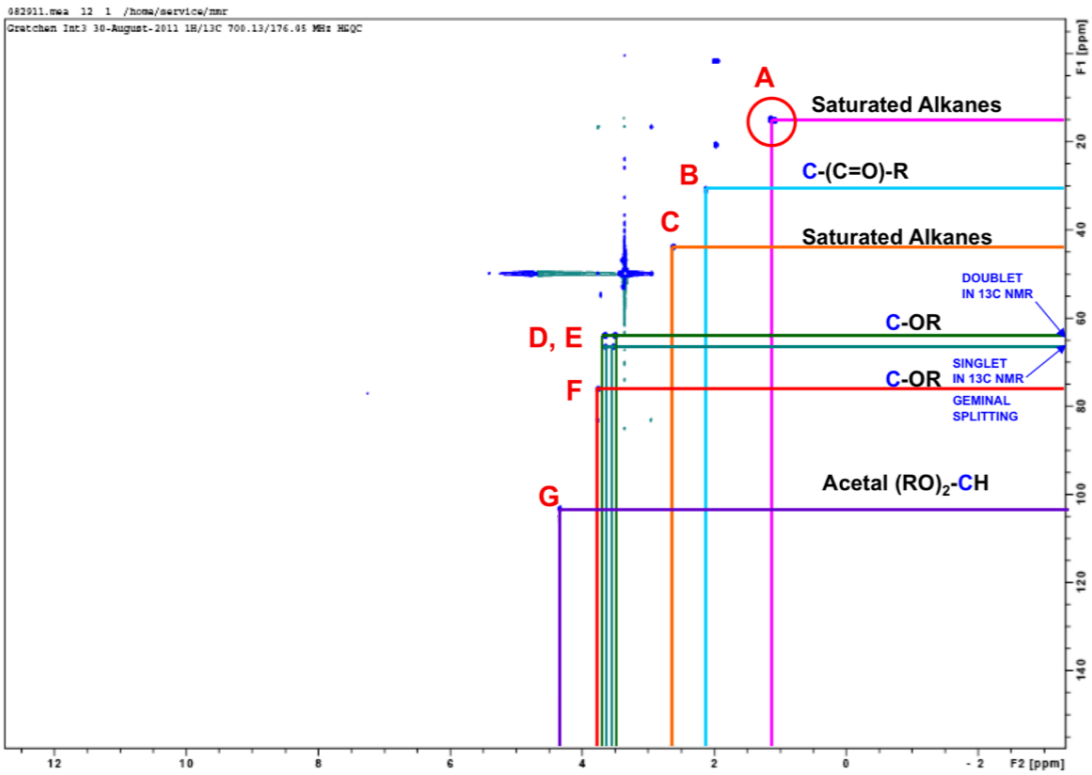


Figure S 15 HSQC NMR for intermediate 3.

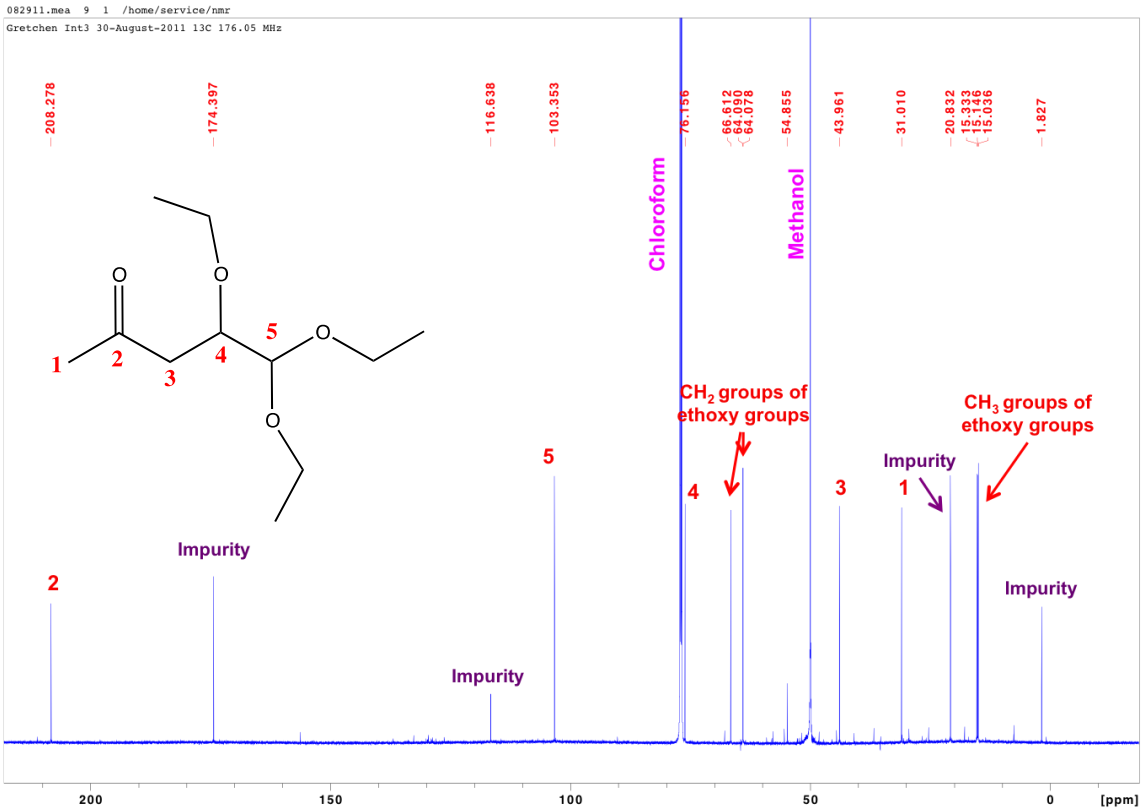


Figure S 16 ^{13}C NMR for Intermediate 3