Supporting Information

# Fully Recyclable Brønsted Acid Catalyst Systems

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The change in free energy of the esterifications is approximated as the change in enthalpy of the reaction, as the entropy change of two molecules going to two molecules is likely to be small (equation 1). The Heat of formations of the reactants are subtracted from the heat of formation for the products to give this approximate ΔG (Equation 2). This approximated delta G is then used to calculate the equilibrium constant at the reaction temperature of 70 ℃ (Equation 3). This equilibrium constant can then be used to calculate the concentration of products in solution using (equation 4) which can be simplified to (equation 5).

$$\Delta G = \Delta H - T\Delta S \approx \Delta H \quad \text{(Equation 1)}$$

$$\Delta G \approx \Delta H = \Sigma \Delta_f H^o_{\text{Liquid of Products}} - \Sigma \Delta_f H^o_{\text{Liquid of Reactants}} \quad \text{(Equation 2)}$$

$$Keq = e^{\frac{\Delta G}{RT}} \quad \text{(Equation 3)}$$

$$Keq = \frac{[ester][water]}{[alcohol][acid]} \quad \text{(Equation 4)}$$

$$[ester] = \frac{1}{1 + \sqrt{\left(\frac{1}{Keq}\right)}} \quad \text{(Equation 5)}$$

Values for heats of formation were found using data readily available from NIST below.

| Compound | $\Delta_f H^o_{\text{Liquid (KJ/mol)}}$ |
|---|---|
| Water[1] | -285.83 |
| Methanol[2] | -238.4 |
| Ethanol[3] | -276 |
| Acetic Acid[4] | -483.52 |
| Hexanoic Acid[5] | -581.8 |
| Octanoic Acid[6] | -636.80 |
| Methlyl Acetate[7] | -445.89 |
| Ethyl Acetate[8] | -480.57 |
| Methyl Hexanoate[9] | -540.2 |
| Ethyl Hexanoate[10] | -579.1 |
| Methyl Octanoate[11] | -590.6 |

[1] https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=2#Thermo-Condensed. Accessed 10/21/20
[2] https://webbook.nist.gov/cgi/cbook.cgi?ID=C67561&Mask=2#Thermo-Condensed. Accessed 10/21/20
[3] https://webbook.nist.gov/cgi/cbook.cgi?ID=C64175&Mask=2#Thermo-Condensed. Accessed 10/21/20
[4] https://webbook.nist.gov/cgi/cbook.cgi?ID=C64197&Mask=2#Thermo-Condensed. Accessed 10/21/20
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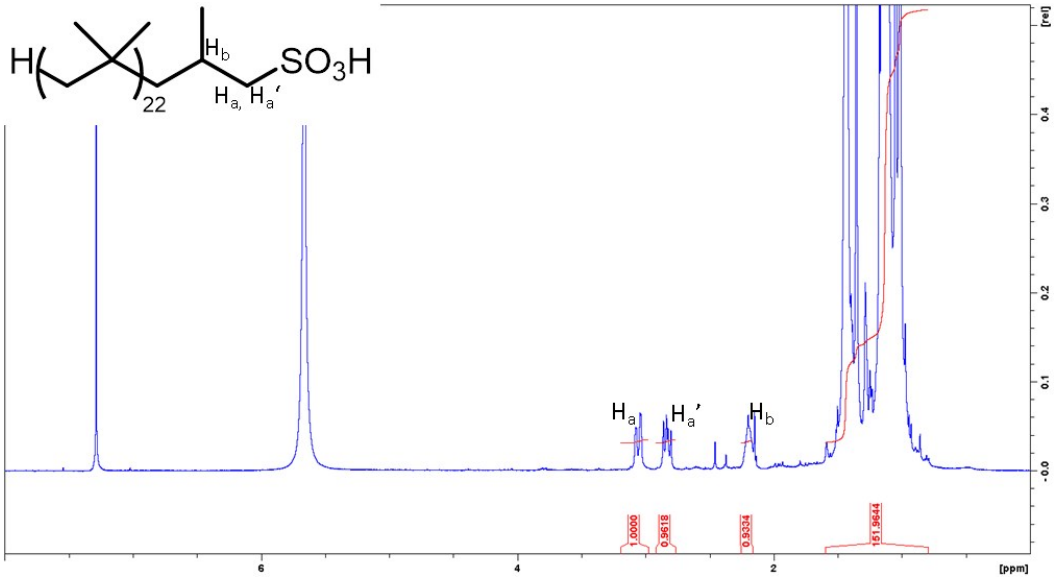
[11] https://webbook.nist.gov/cgi/cbook.cgi?ID=C111115&Mask=2#Thermo-Condensed. Accessed 10/21/20

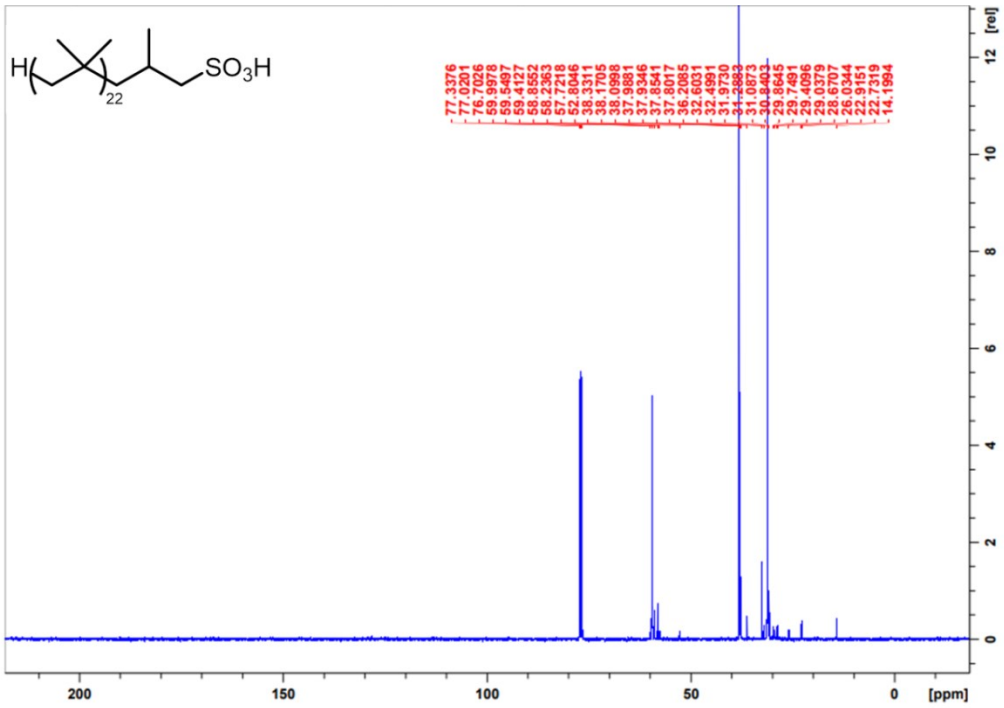
| | |
|---|---|
| Ethyl Octanoate[12] | -629.5 |

$^{1}$H NMR Spectrum of PIB-$CH_2SO_3H$ **2**. This sample of **2** was derived from **1**, $PIB_{1000}$ with a degree of polymerization of 17 as shown in Scheme 1. Titration indicated that this PIB-$CH_2SO_3H$ **2** had a degree of polymerization of 22 and that is what is shown in the NMR caption below.

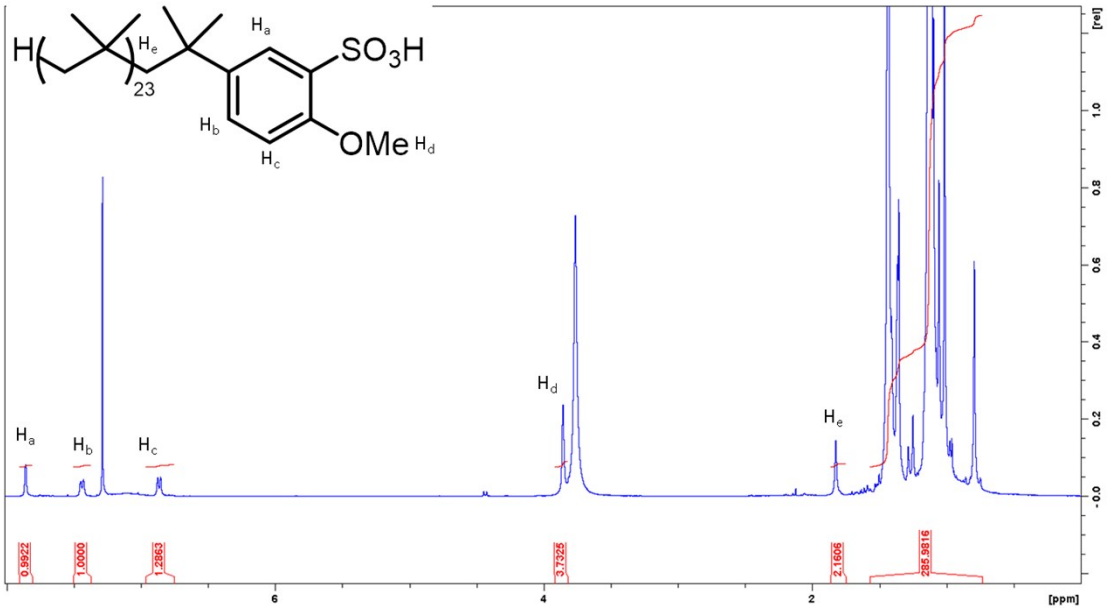



$^{13}$C NMR Spectrum of PIB-$CH_2SO_3H$ **2**. This sample of **2** was derived from **1**, $PIB_{1000}$ with a degree of polymerization of 17 as shown in Scheme 1. Titration indicated that this PIB-$CH_2SO_3H$ **2** had a degree of polymerization of 22 and that is what is shown in the NMR caption below.

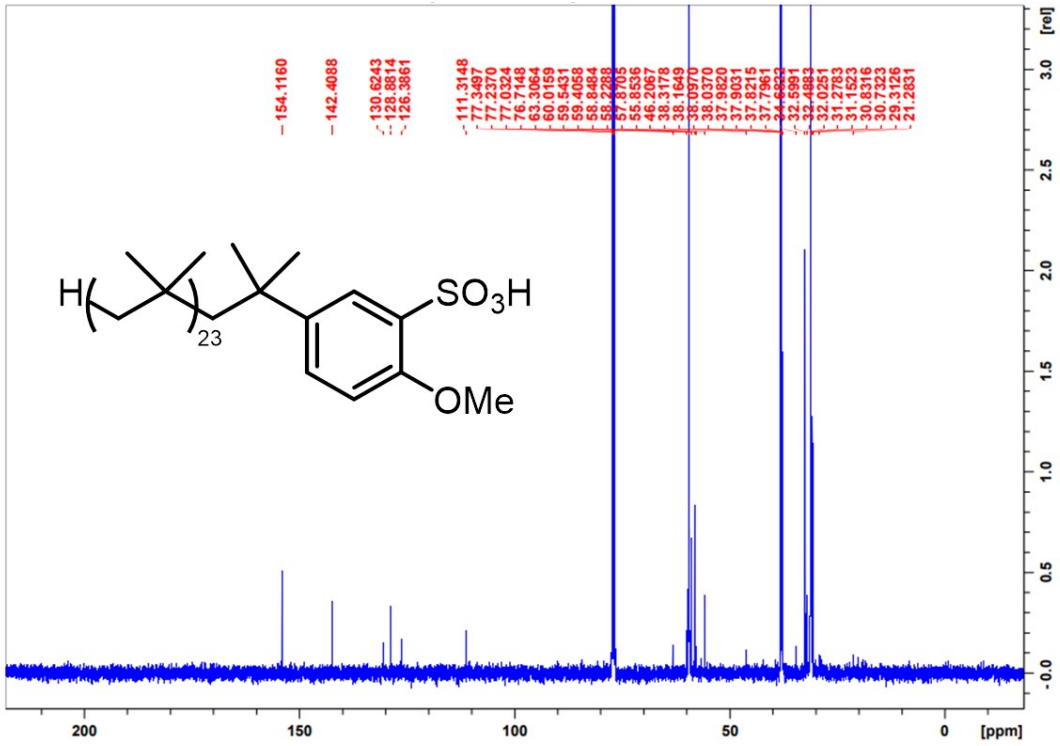
[12] https://webbook.nist.gov/cgi/cbook.cgi?ID=C106321&Mask=2#Thermo-Condensed. Accessed 10/21/20



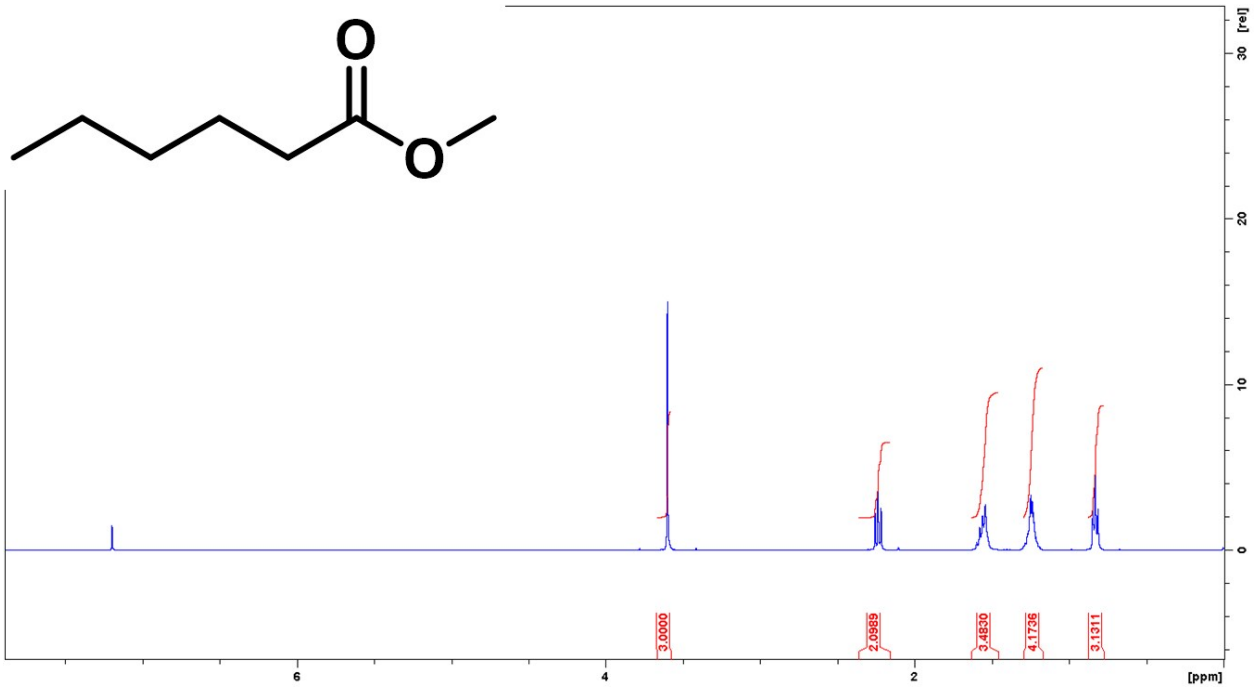

$^{1}$H NMR Spectrum of PIB-Ar$SO_3$H **3**. This sample of **3** was derived from **1**, $PIB_{1000}$ with a degree of polymerization of 17 as shown in Scheme 1. Titration indicated that this PIB-Ar$SO_3$H **3** had a degree of polymerization of 23 and that is what is shown in the NMR caption below.



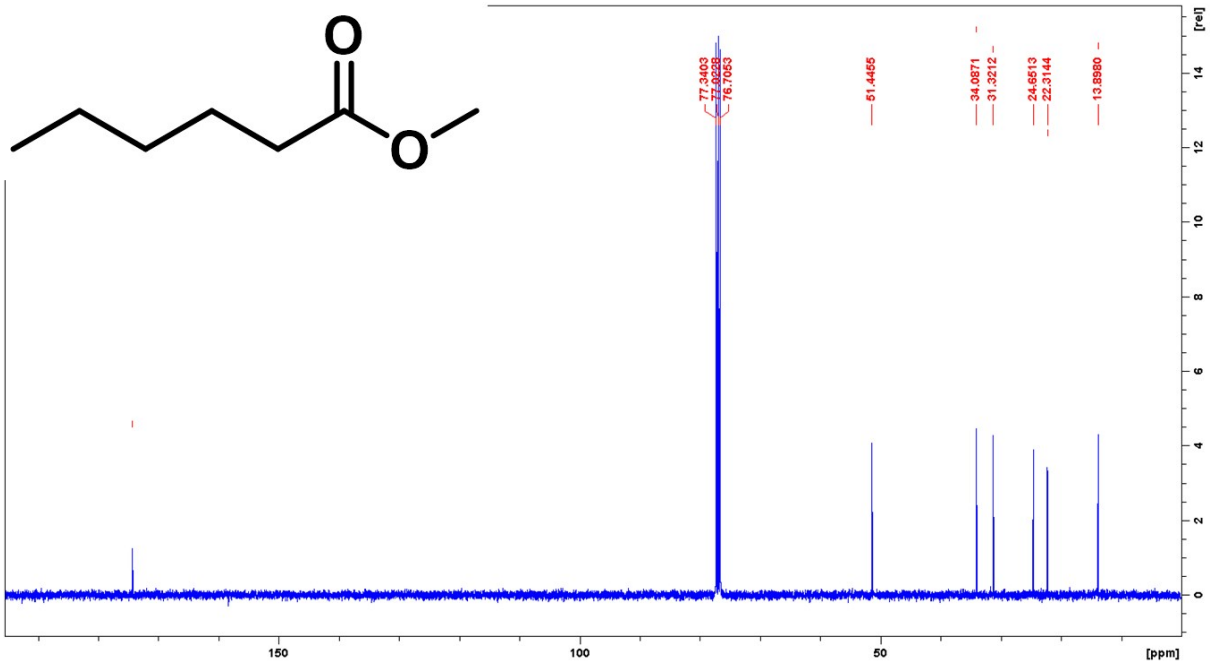

$^{13}$C NMR Spectrum of PIB-Ar$SO_3$H **3**. This sample of **3** was derived from **1**, $PIB_{1000}$ with a degree of polymerization of 17 as shown in Scheme 1. Titration indicated that this PIB-Ar$SO_3$H **3** had a degree of polymerization of 23 and that is what is shown in the NMR caption below



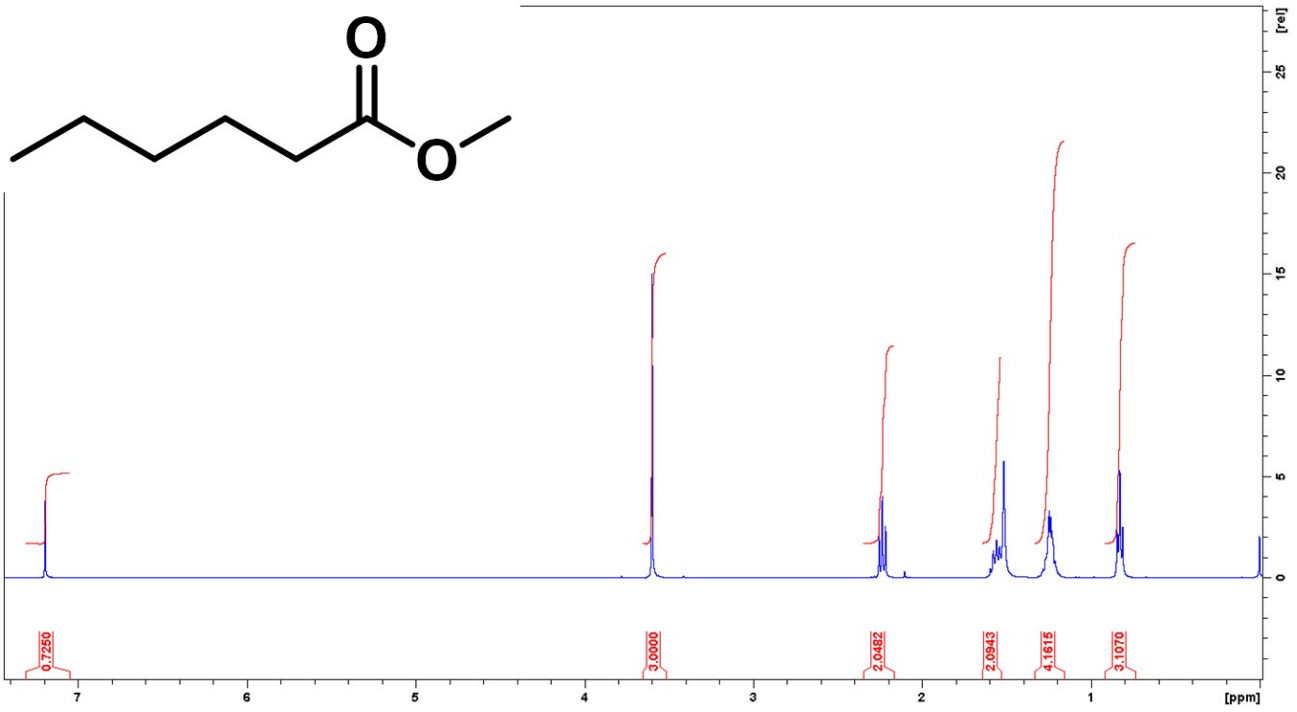

$^{1}$H NMR Spectrum of Methyl Hexanoate Product Catalyzed by **2**



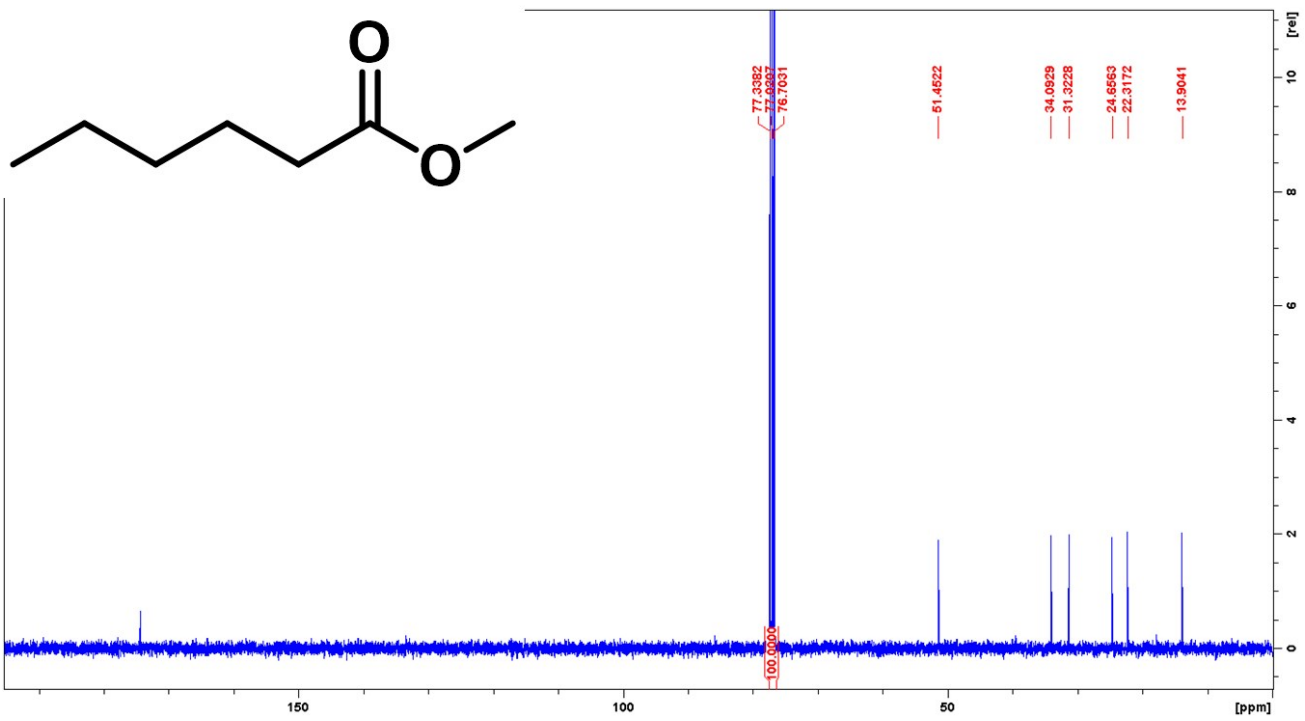

$^{13}$C NMR Spectrum of Methyl Hexanoate Product Catalyzed by **2**


77.3403
77.0228
76.7053
51.4455
34.0871
31.3212
24.6513
22.3144
13.8980
[rel]
[ppm]
150
100
50

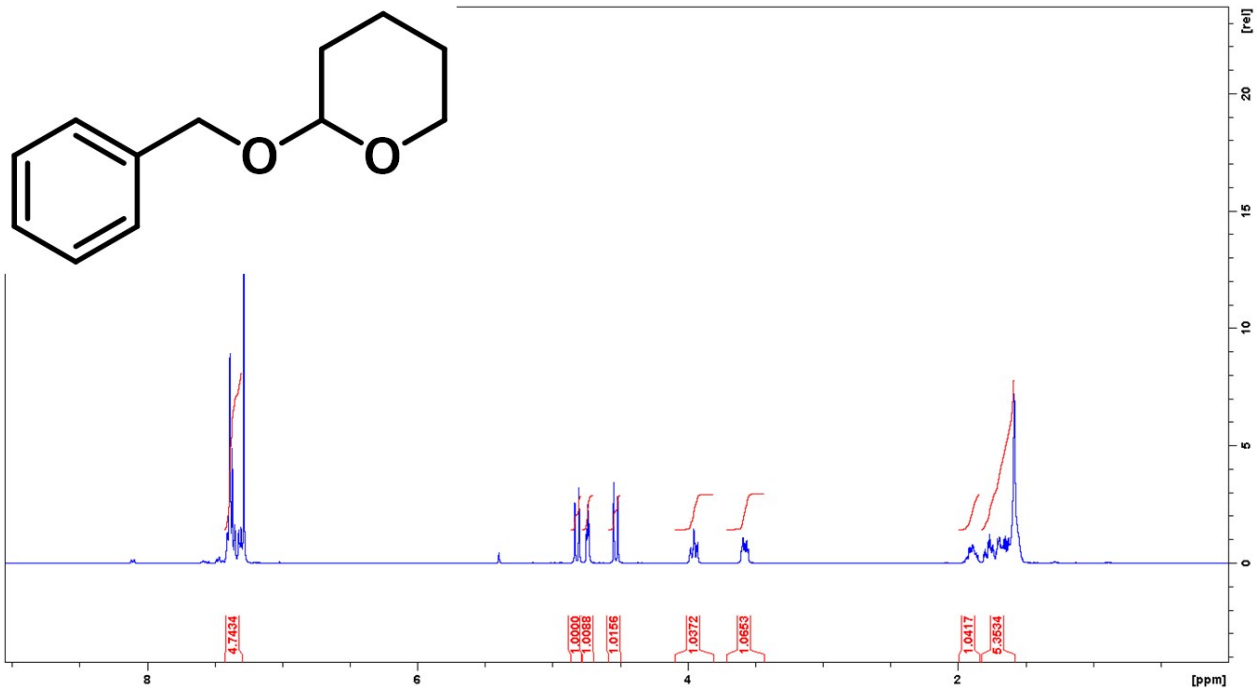
$^{1}$H and Spectrum of Methyl Hexanoate Product Catalyzed by **3**



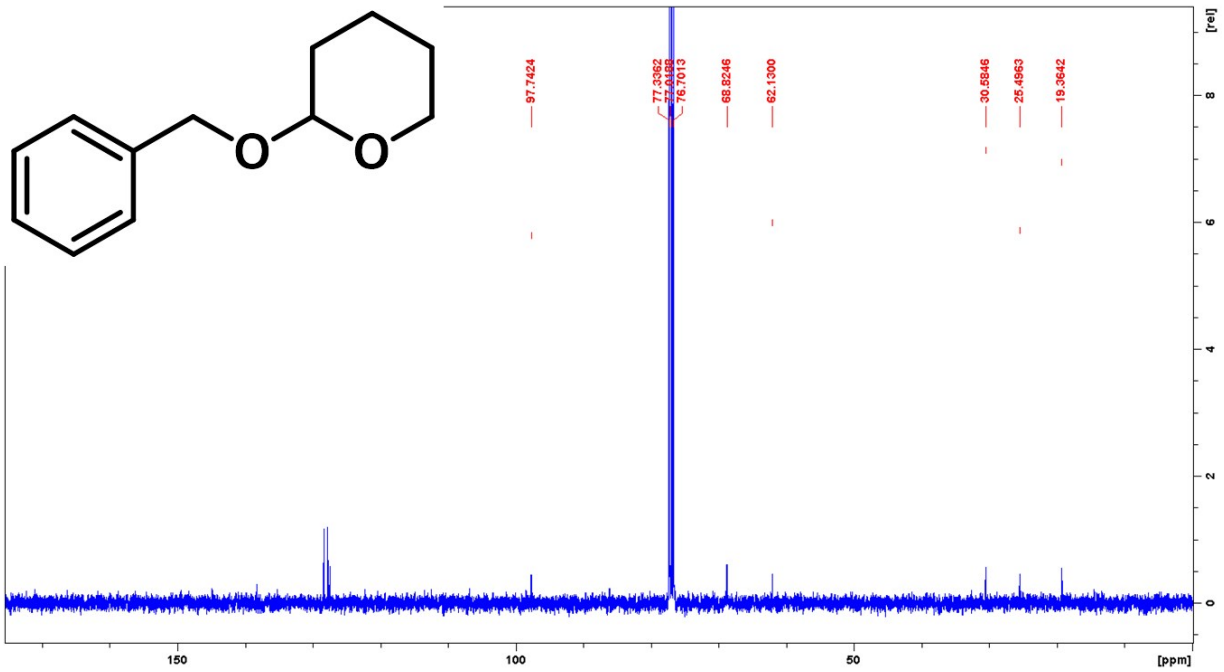

$^{13}$C NMR Spectrum of Methyl Hexanoate Product Catalyzed by **3**



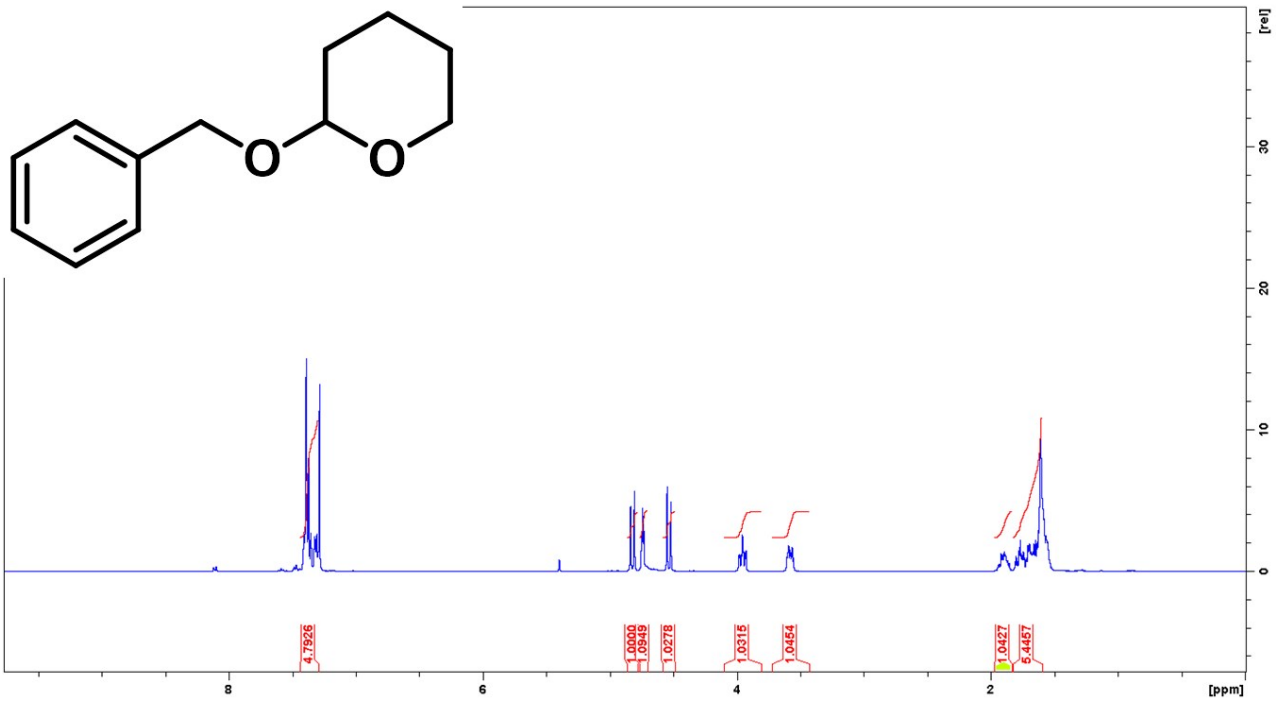
$^{1}$H Spectrum of Tetrahydropyran Protected Benzyl Alcohol Product Catalyzed by **2**



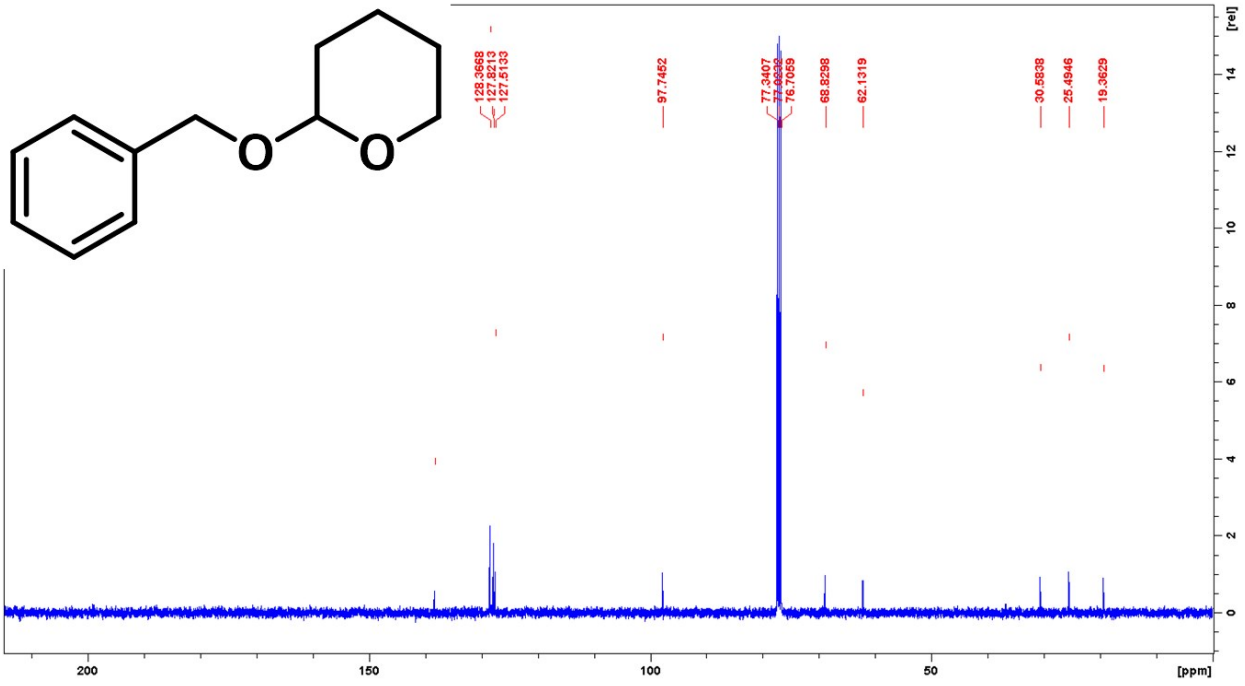

$^{13}$C NMR Spectrum of Tetrahydropyran Protected Benzyl Alcohol Product Catalyzed by **2**



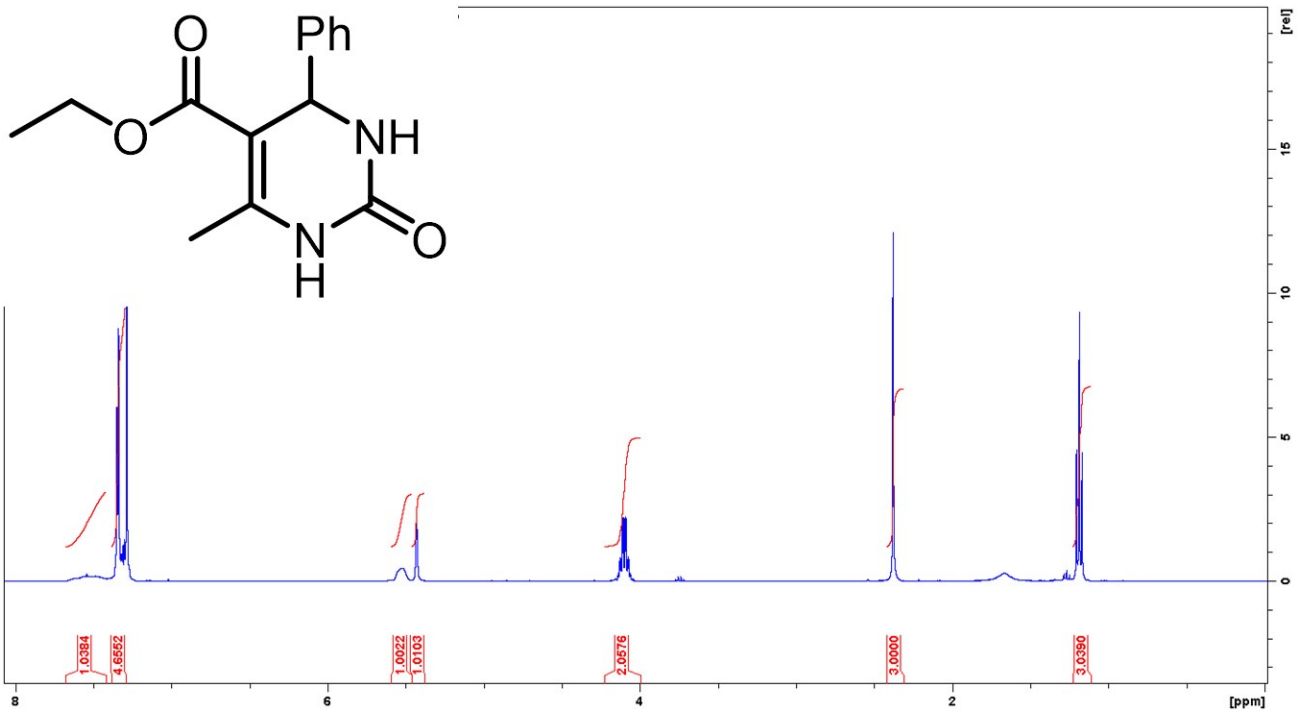
$^{1}$H Spectrum of Tetrahydropyran Protected Benzyl Alcohol Product Catalyzed by **3**



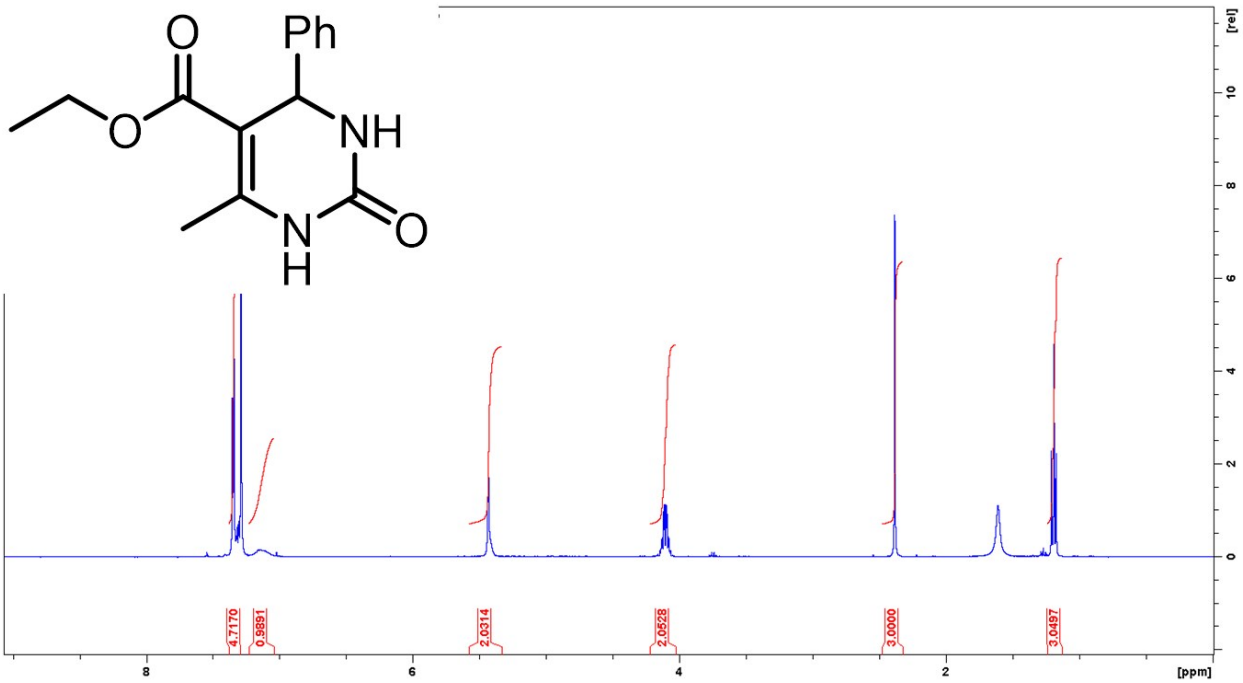

$^{13}$C NMR Spectrum of Tetrahydropyran Protected Benzyl Alcohol Product Catalyzed by **3**



$^{1}$H NMR Spectrum of 3,4-Dihydropyrimidin-2-one Product Catalyzed by **2**

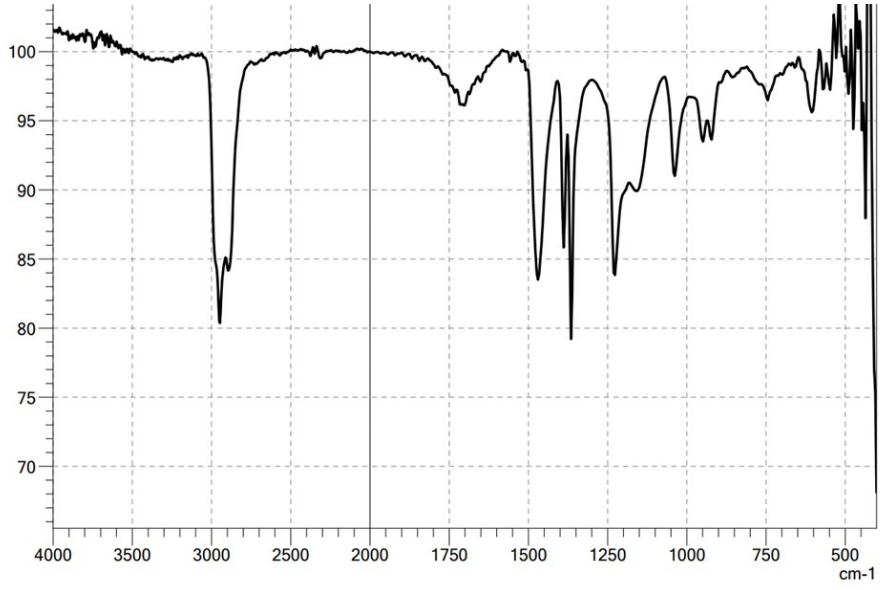



$^{1}$H NMR Spectrum of 3,4-Dihydropyrimidin-2-one Product Catalyzed by **3**

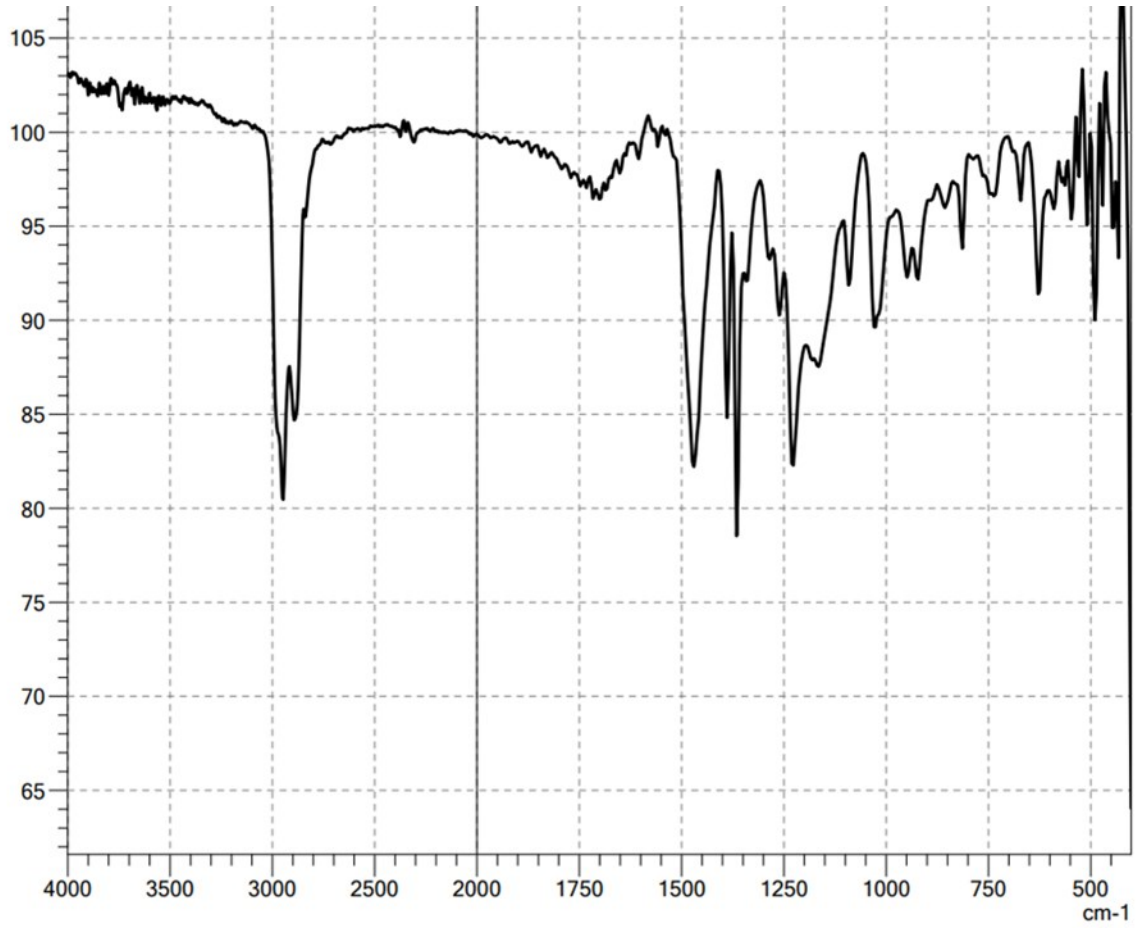


IR Spectrum of the starting alkene-terminated $PIB_{1000}$ **1**.


IR Spectrum of PIB-Bound Alkyl Sulfonic Acid **2**.



IR Spectrum of PIB-Bound Aromatic Sulfonic Acid **3**



GPC Trace of PIB Alkene **1,** PIB-Bound Alkyl Sulfonic Acid **2,** and PIB-Bound Aromatic Sulfonic Acid **3**