Supporting Information for

Triacetic Acid Lactone as a Potential Biorenewable Platform Chemical

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1. Experimental methods

1.1 Catalyst preparation

5 wt% Pd/Nb_2O_5 was prepared by incipient wetness impregnation of an aqueous solution of $Pd(NO_3)_2 \cdot xH_2O$ (Aldrich) with commercial niobia (HY-340, CBMM, Brazil). The catalyst was dried in air at 373 K, calcined in 60 cm^3(STP)/min flowing air at 573 K for 5 h, reduced in 60 cm^3(STP)/min flowing H_2 at 623 K for 5 h, and then passivated with 60 cm^3(STP)/min flowing 2% O_2 in He for 2 h at room temperature. 10 wt% Pd/C (Alfa Aesar) was used as-received. Amberlyst™ 70 (Rohm and Haas) was washed with deionized water, dried in air at 373 K, and mechanically crushed to a fine powder. The powder was then sifted through a sieve (standard US size 45) to remove large particulates.

1.2 Batch reactor studies

Reactions were carried out using a 50 mL pressure vessel (Hastelloy C-276, Model 4792, Parr Instrument). After loading the reactant solution, catalyst, and magnetic stirrer bar into the reactor, the vessel was sealed, purged with 22 bar He, and pressurized with He or H_2. Mechanical stirring was maintained using a magnetic stirrer plate (500 rpm).

1.3 Analytical methods

Concentrations of species in liquid solutions were determined using a gas chromatograph (Shimadzu GC-2010) equipped with a FID, and a high performance liquid chromatograph (Waters Alliance 2695) equipped with a photodiode array detector (Waters 996). Separation in the GC was achieved with a DB-5 column (Agilent Technologies), and the HPLC column was a reversed-phase Agilent Zorbax SB-C18 (4.6 x 300mm, 5µm) using 5 mM H_2SO_4 as the aqueous phase with acetonitrile as the organic modifier. Gas phase products were collected in a gas bag and analyzed using a Shimadzu GC (GC-8A) equipped with a TCD and a Varian GC (Star 3400 CX) equipped with a FID. Identification of all intermediates and products in the liquid phase, except **6**, was performed using a gas chromatograph-mass spectrometer (Shimadzu Corp., GCMS-QP2010S) equipped with a SHRXI-5MS capillary column (30 m × 0.25 mm × 0.25 µm). MS were verified against purchased compounds (Sigma Aldrich) and the NIST MS library and confirmed to at least 95% similarity. All MS are presented in Section 4. For **7**, the MS was compared against the literature[2], and the fragmentation pattern was confirmed against all significant mass ions, such as the high mass ion peaks, m/z 112, m/z 97, m/z 68, and lower mass peaks centred around m/z 40. Identification of **6** was performed using NMR and the spectra compared to literature values[3] (Section 3).

Identification of all products was verified by NMR (Section 3). NMR spectra of all reaction products were obtained using a Varian Mercury 300 spectrometer (^{1}H NMR, 300 MHz), and referenced internally with respect to tetramethyl silane (TMS, Sigma-Aldrich, 99.9+%, NMR Grade), $CDCl_3$ (Aldrich, 100%, ≥99.96 atom% D), or residual solvent impurities (shifts based on literature values[4]).

10% D_2O (Aldrich) was added directly to the final reaction mixture for compounds **2**, **4**, and **5** to provide solvent lock, and Varian's PRESAT solvent presaturation program was used to suppress the H_2O resonance.

Compound **6** was synthesized from the hydrogenation of **1** over 10 wt% Pd/C using ethanol as the solvent. 5 g of **1** was dissolved in 185 g ethanol and hydrogenated over 0.5 g of 10 wt% Pd/C at 34 bar H_2 for 20 h. **6** was isolated using a rotary evaporator, with the sample heated in a water bath controlled at 333 K. 4.9 g of **6** was isolated, corresponding to 95% molar yield with respect to **1**, consistent with experimental results presented in Table 3. The isolated sample was dissolved in $CDCl_3$ prior to analysis by NMR.

Compounds **3**, **7**, **8**, and **12** were isolated using a Water HPLC equipped with a reversed-phase Agilent Zorbax SB-C18 (4.6 x 300mm, 5μm) using Milli-Q water as the aqueous phase with methanol as the organic modifier. Isolated compounds were collected using a Waters Fraction Collector connected to the column outlet. Samples were extracted with an equal volume of dichloromethane. The organic phase was separated and dried over sodium sulfate prior to rotary evaporation. The residue was then dissolved $CDCl_3$ prior to analysis by NMR.

Compound **11** was isolated by HPLC and fractionation as described above (i.e., for compounds **3**, **7**, **8**, and **12**); the residue obtained after rotary evaporation was dissolved in D_2O, and spectra were taken using a Varian INOVA 500 spectrometer (^{1}H NMR, 500 MHz). Multiple solvent suppression (WET1D) was used to suppress resonance of both the H_2O and methanol residue left from sample isolation.

2. Computational studies

Gaussian 03[1] software was used for the calculation of gas-phase thermodynamic properties of **10**, **11**, and **12**. Geometry optimizations and frequency calculations were performed using B3LYP/6-31+G. Frequency calculations were used to provide estimates of standard changes in enthalpy, entropy, and Gibbs free energy.

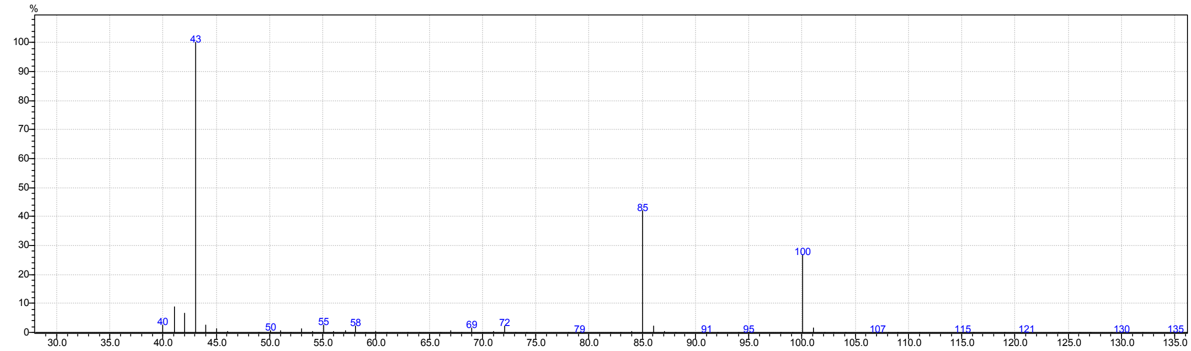
3. NMR data

2 δ_H(300 MHz; D_2O; *i*-PrOH) 2.3 (6 H, s, 1-H, 5-H), 3.9 (3 H, s, 3-H). **3** δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.5 (2 H, d, J = 6.3 Hz, Me), 2.8-2.4 (2 H, m, 5-H), 3.7-3.3 (2 H, m, 3-H), 4.8 (1 H, dqd, J = 11.3, 6.3, 2.8 Hz, 6-H). **4** δ_H(300 MHz; D_2O; *i*-PrOH) 1.9 (3 H, dd, J = 6.8, 1.7 Hz, 5-H), 2.3 (3 H, s, 1-H), 6.2 (1 H, dq, J = 15.9, 1.7 Hz, 4-H), 7.1 (1 H, dq, J = 15.9, 6.8 Hz, 3-H). **5** δ_H(300 MHz; D_2O; *i*-PrOH) 1.2 (3 H, d, J = 6.3 Hz, 5-H), 2.2 (3 H, s, 1-H), 2.7 (2 H, d, J = 6.3 Hz, 3-H), 4.3 (1 H, h, J = 6.3 Hz, 4-H). **6** δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.4 (3 H, d, J = 6.3 Hz, Me), 1.6-1.5 (1 H, m, 5-*H*H), 2.3 (dddd, J = 13.7, 5.5, 3.0, 1.4 Hz, 5-H*H*), 2.5 (1 H, dd, J = 17.1, 7.8 Hz, 3-

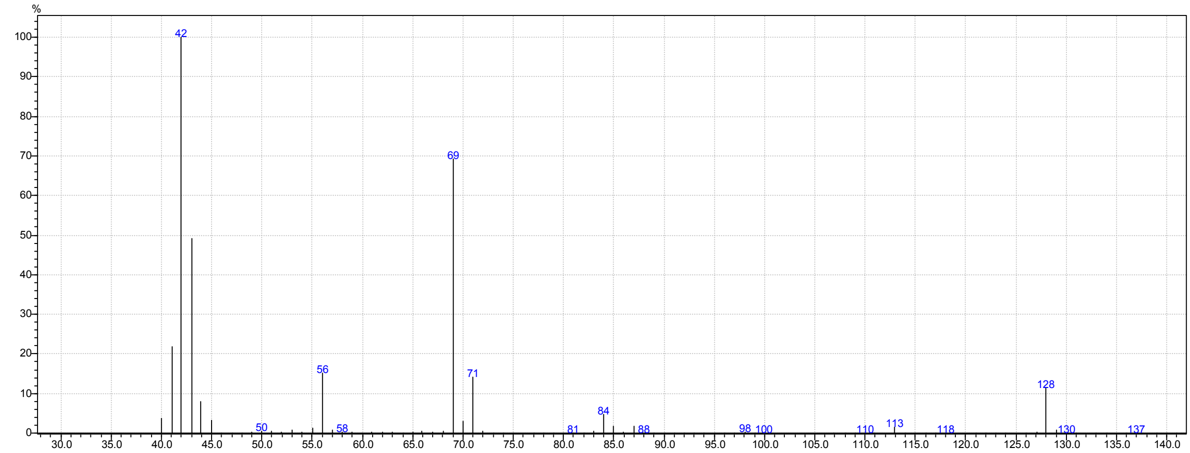
*H*H), 2.9 (1 H, ddd, J = 17.1, 5.9, 1.4 Hz, 3-H*H*), 4.3-4.2 (1 H, m, 4-H), 4.4-4.3 (1 H, m, 6-H). **7** δ_H(300 MHz; $CDCl_3$; CH_2Cl_2) 1.5 (3 H, d, J = 6.3 Hz, Me), 2.3-2.4 (2 H, m, 5-H), 4.7-4.5 (1 H, m, 6-H), 6.0-5.9 (1 H, m, 4-H), 6.9-6.8 (1 H, m, 3-H). **8** δ_H(300 MHz; D_2O; MeOH) 1.8 (3 H, d, J = 4.9 Hz, Me), 6.1-5.8 (1 H, m, 5-H), 6.4-6.2 (2 H, m, 3-H & 4-H), 7.3-7. (1 H, m, 2-H). **11** δ_H(500 MHz; D_2O; MeOH) 1.6 (3 H, d, J = 6.0 Hz, Me), 2.2 (2 H, q, J = 7.1 Hz, 3-H), 2.3 (2 H, t, J = 7.1 Hz, 2-H), 5.6-5.4 (2 H, m, 4-H & 5-H). **12** δ_H(300 MHz; $CDCl_3$) 1.0 (3 H, t, J = 7.4 Hz, Me), 2.6-1.5 (6 H, m, 3 x CH_2), 4.5-4.3 (1 H, m, 5-H).

4. MS for intermediates and compounds

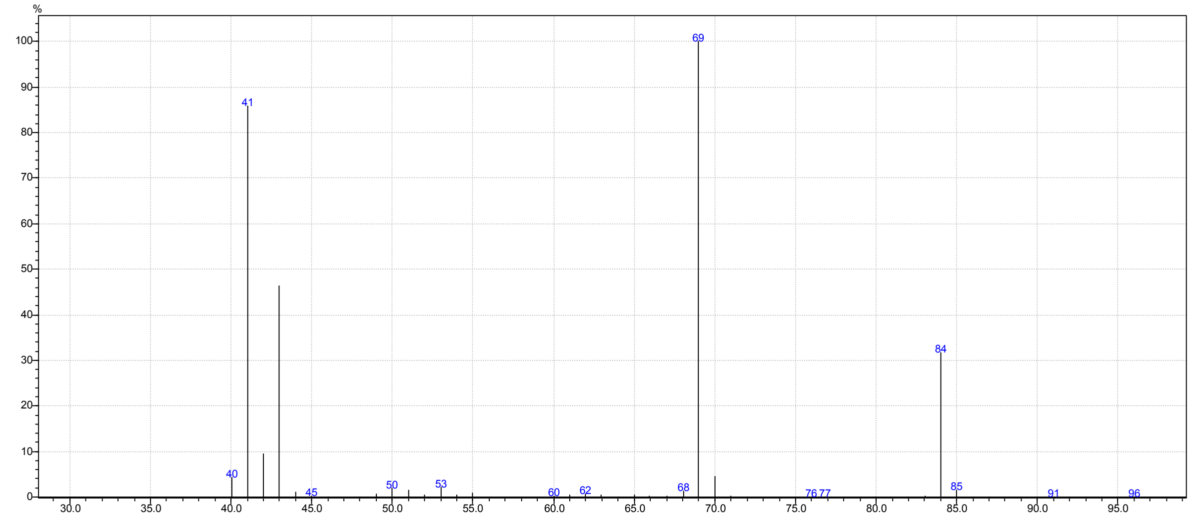
2,4-pentanedione (**2**)



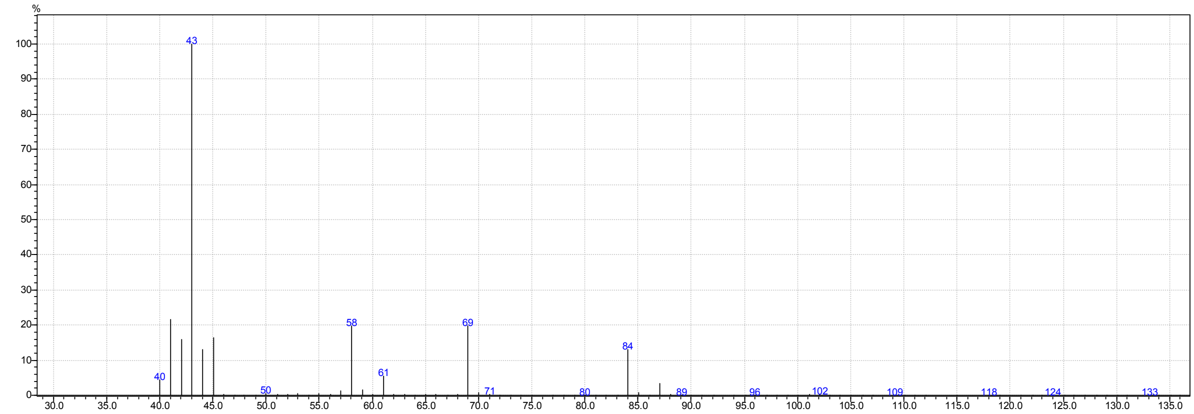
5,6-dihydro-4-hydroxy-6-methyl-2H-pyran-2-one (**3**)



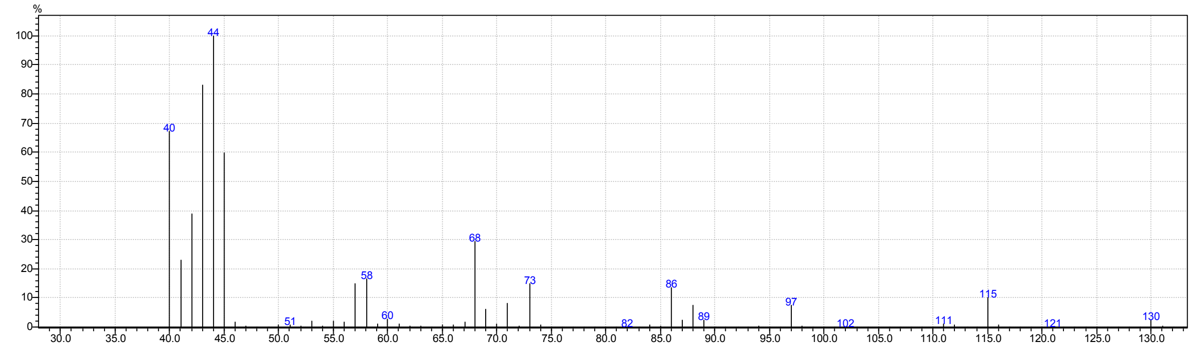
3-penten-2-one (**4**)



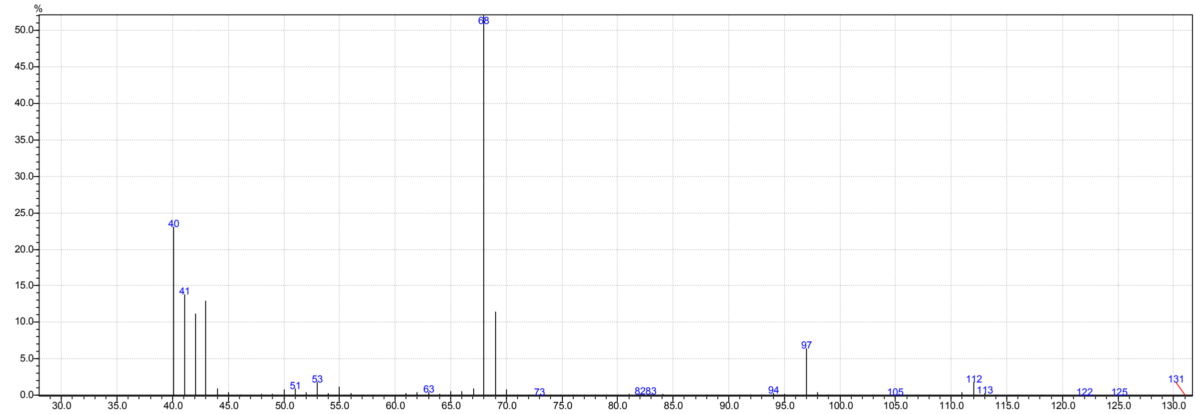
4-hydroxy-2-pentanone (**5**)



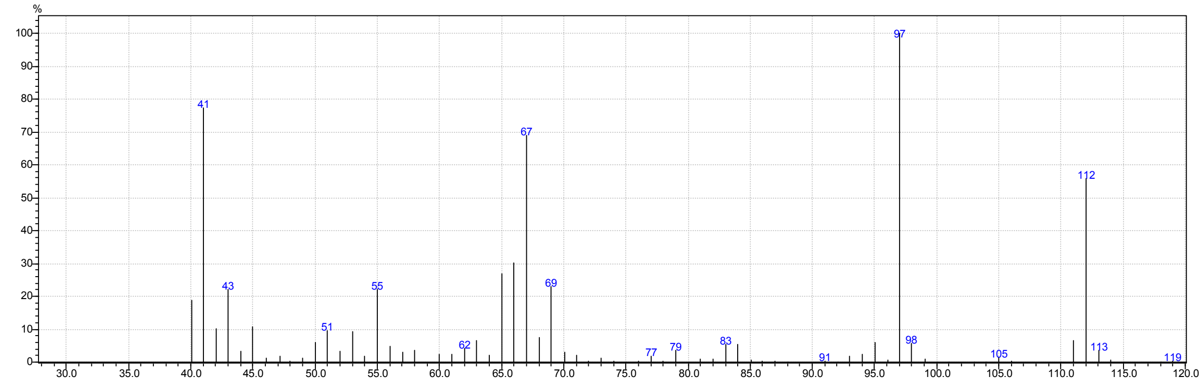
4-hydroxy-6-methyltetrahydro-2-pyrone (**6**)



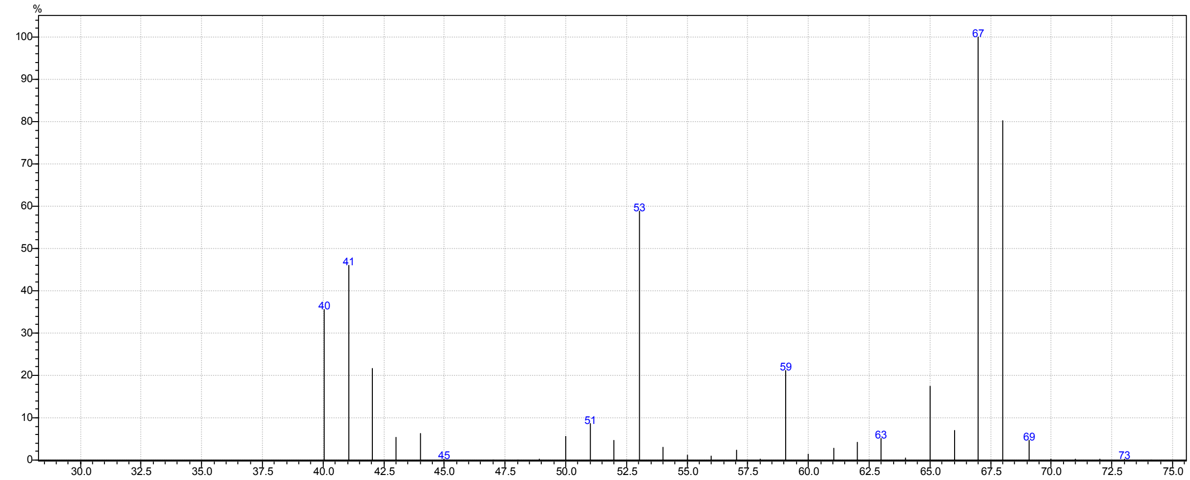
parasorbic acid (**7**)



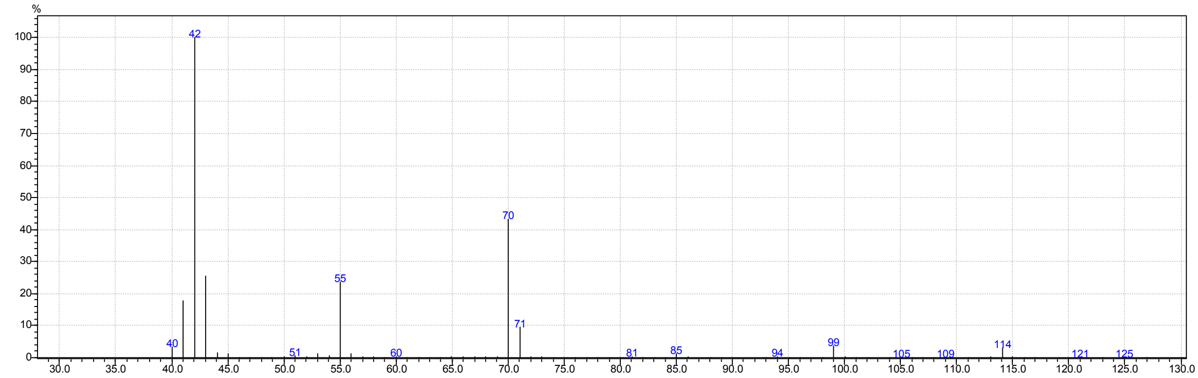
sorbic acid (**8**)



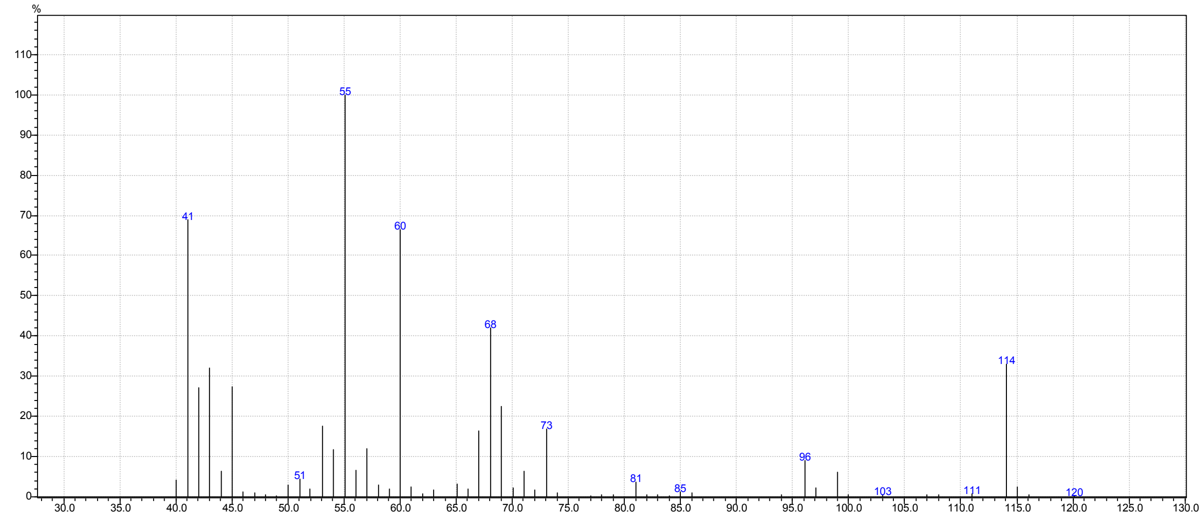
1,3-pentadiene (**9**)



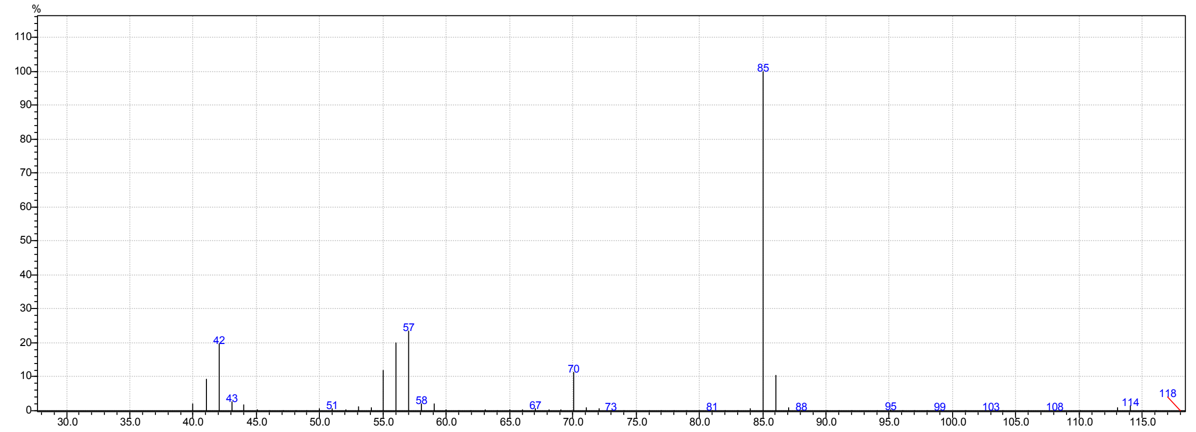
δ-hexalactone (**10**)



4-hexenoic acid (**11**)



γ-caprolactone (**12**)



5. Catalyst recycling study for the dehydration of 6 to 7 over Amberlyst™ 70

Table S1. Dehydration of **6** to **7** over Amberlyst™ 70.[a]

Recycle No.	Conversion of 6 (%)[b]	Specific rate of consumption of 6 (µmol g^{-1} min^{-1})[b]

0	27±2	66±4
1	24±1	55±3
2	20±1	41±1
3	18±3	37±3

[a] Batch reactions. Reaction conditions: 1 h, 373 K, 22 bar He, 2 wt% **6** in THF, mass ratio **6**:catalyst = 2:1. Spent catalyst was filtered and dried at 100 °C before being reused for the next reaction cycle. Quantitative selectivity to **7** in all cases. [b] Conversion and rate values averaged over two runs.

References

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