**SUPPLEMENTARY INFORMATION**

Mild decarboxylation of neat muconic acid to levulinic  
 acid: A combined experimental and computational mechanistic study

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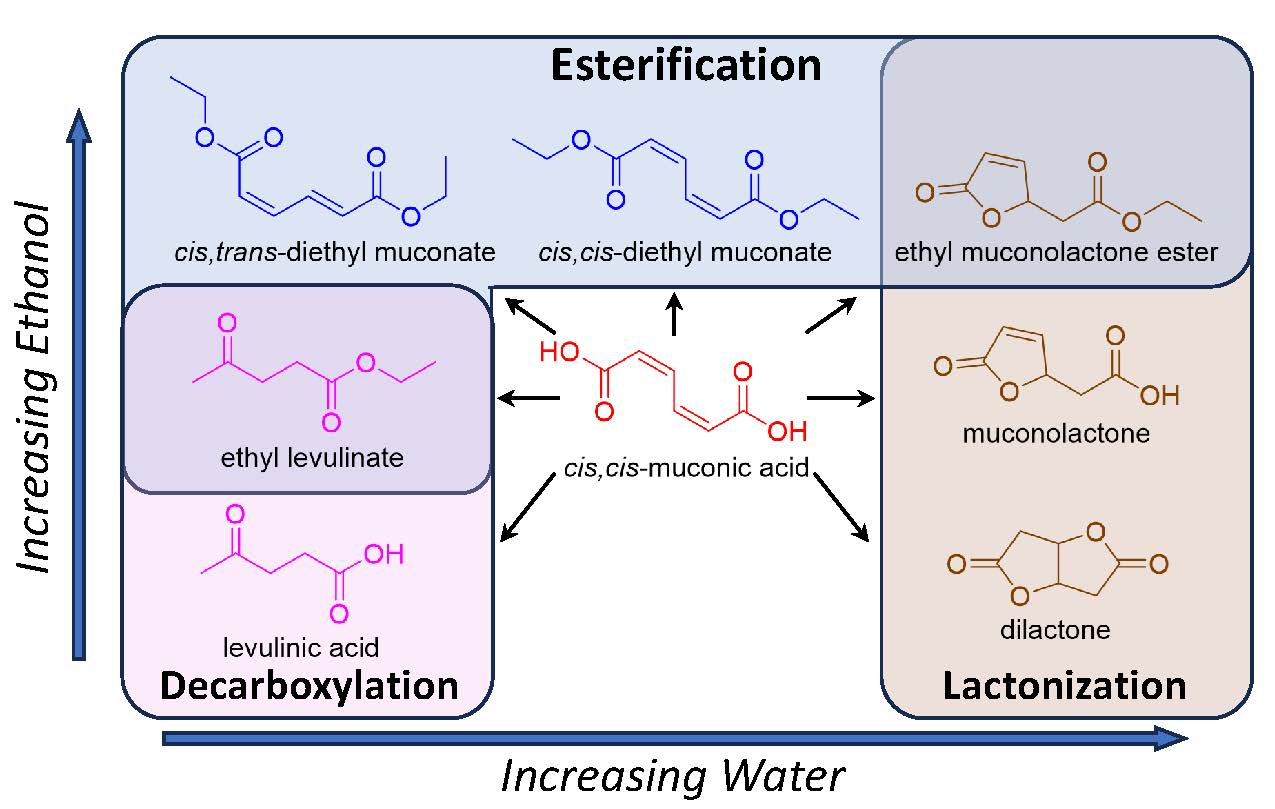


Fig S1 – Family of acid catalyzed reactions of *cis,cis-*muconic acid.

A graph showing different colored lines

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Fig S2 – Trends of muconolactone (MLac) conversion over increasing temperature with respect to levulinic acid (LA)/ethyl levulinate (EL) formation. Notation: *cis,cis*-muconic acid (*cc*MA), *cis,trans*-muconic acid (*ct*MA), and dilactone (Dilac).



Fig S3 – 1H-NMR (600 MHz, CDCl3) of levulinic acid synthesized under solvent-free conditions with raw muconic acid catalyzed by 1wt% sulfuric acid at 110 C for 16hrs- δ(ppm): 2.17(s, 3H), 2.59(t, 2H), 2.73(t, 2H).



Fig S4 – GCMS spectra of levulinic acid. (Reaction conditions- LA was synthesized in the absence of ethanol and water at 80 C for 16hrs in the presence of 30.5 wt.% sulfuric acid).



Fig S5 – 1H-NMR (600 MHz, CDCl3) of muconolactone - δ(ppm): 1.32(t, 3H), 2.68(d, 2H), 2.87(d, 2H), 2.77(t, 2H), 4.23(m, 2H), 5.42(m, 1H), 6.21(d, 1H), 7.62(d, 1H) and esters of muconic acid.



Fig S6 – 1H-NMR (600 MHz, CDCl3) of ethyl levulinate synthesized at 80C for 16hrs in chloroform, ethanol, water and sulfuric acid – δ(ppm): 1.27(t, 3H), 2.21(s, 3H), 2.59(t, 2H), 2.77(t, 2H), 4.15(q, 2H).



Fig S7 - 1H-NMR (600 MHz, CDCl3) of levulinic acid synthesized at 80Cfor 16hrs in chloroform without ethanol and water – δ(ppm): 2.22(s, 3H), 2.66(t, 2H), 2.78(t, 2H).



Fig S8 – HSQC NMR(600 MHz, CDCl3) for the intermediates. (Reaction Conditions- deuterated chloroform and deuterated sulfuric acid was used for LA synthesis at 75 C for 16hrs).



Fig S9 – GCMS spectra of tautomer.



Fig S10 – HCOSY NMR (600 MHz, CDCl3) of dilactone and levulinic acid. (Reaction Conditions- deuterated chloroform and deuterated sulfuric acid was used for LA synthesis at 90 C for 16hrs).



Fig S11 – Effect of time on MLac formation. (Reaction Conditions- chloroform, ethanol, water and sulfuric acid was used for MLac synthesis at 80 C).



Fig S12 – GCMS spectra of levulinic acid and ethyl levulinate. (Reaction conditions- LA was synthesized in the presence of ethanol and water at 80 C for 16hrs in the presence of 30.5 wt.% sulfuric acid).

A screenshot of a computer screen

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Fig S13 – Elementary steps considered and corresponding B3LYP 6-311G++(d,p) calculated reaction free energies (eV) for *cis,cis*-muconic acid reduction to levulinic acid and ethyl levulinate via pathway-1.

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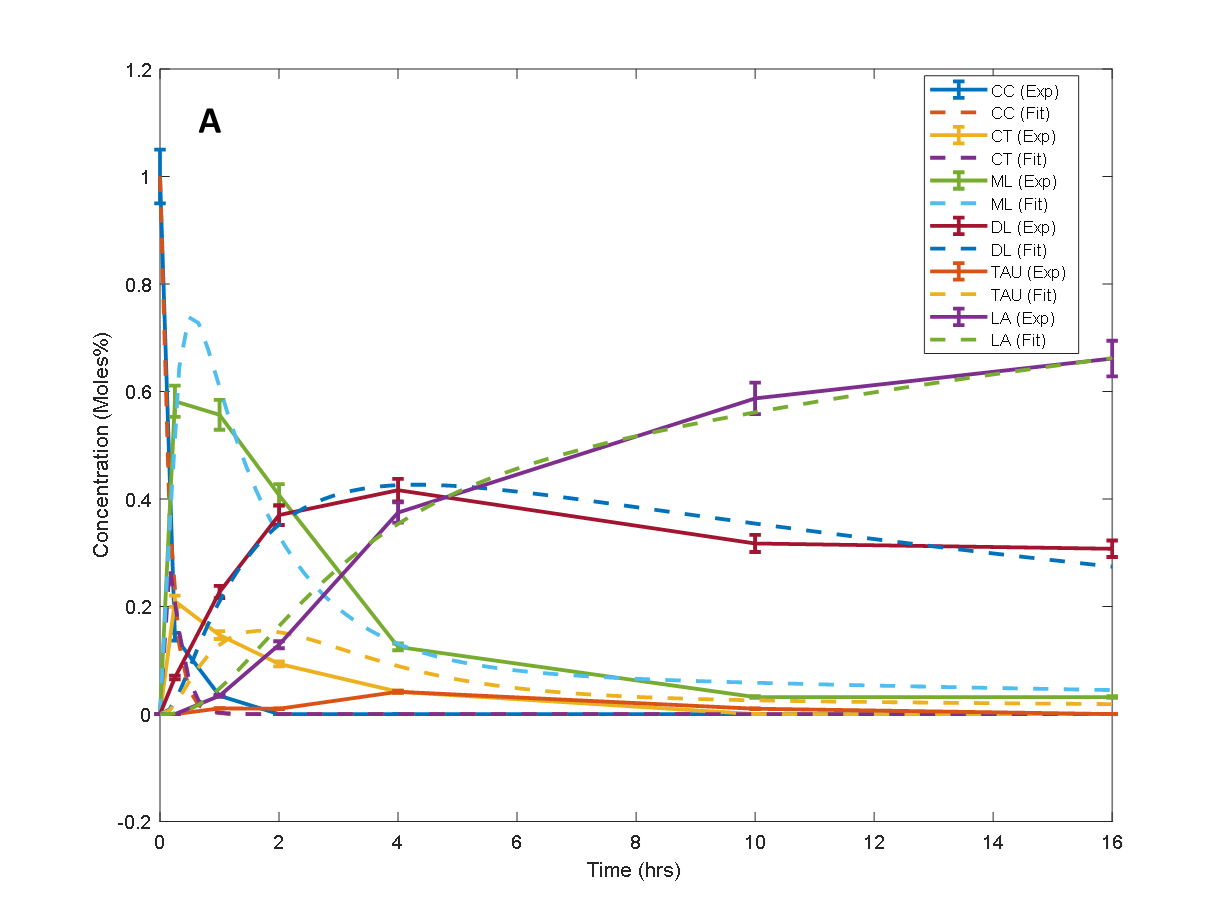
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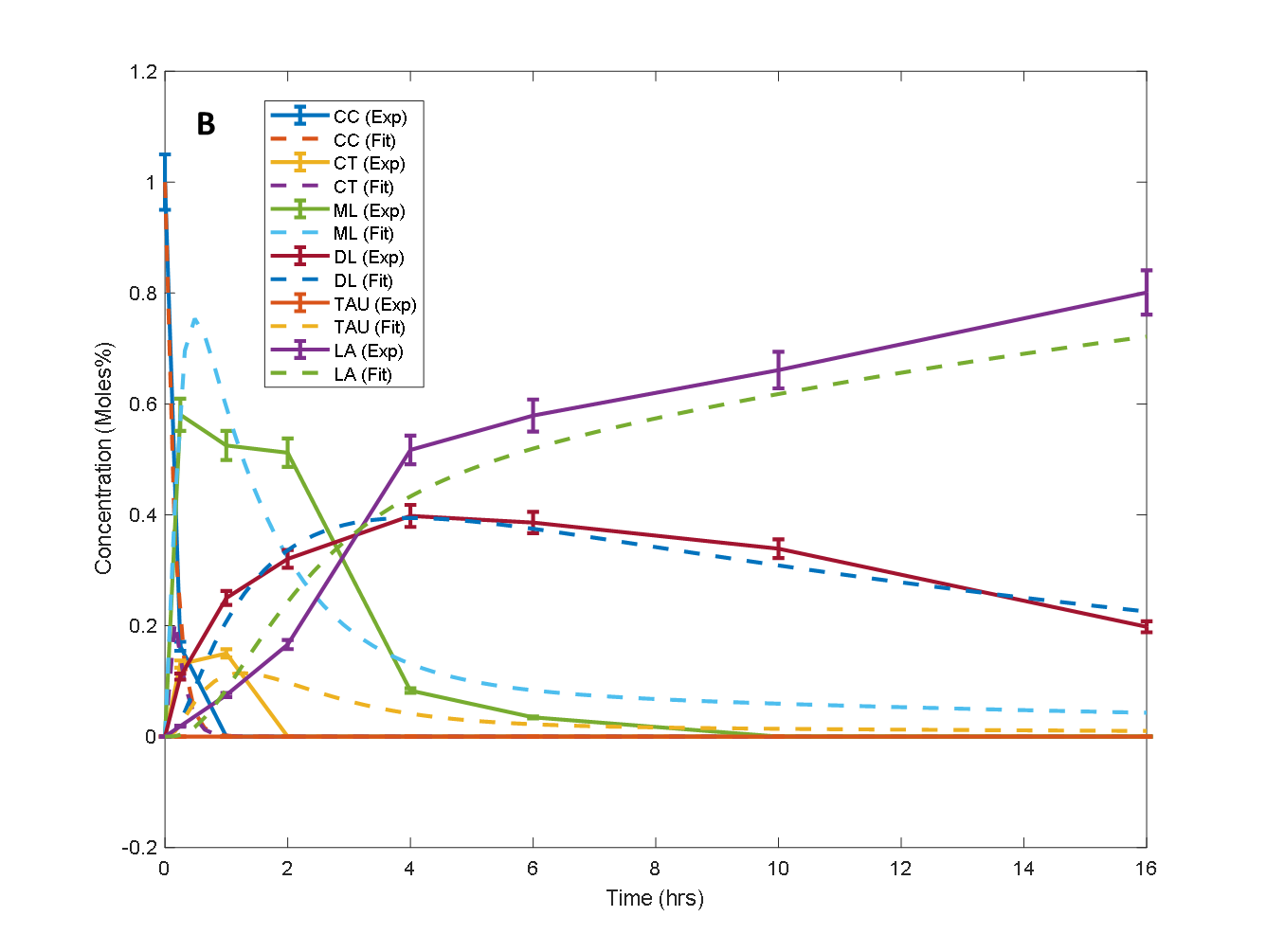
Fig S14 – Elementary steps considered and corresponding B3LYP 6-311G++(d,p) calculated reaction free energies (eV) for *cis,cis*-muconic acid reduction to levulinic acid and ethyl levulinate via pathway-2.

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Fig S15 – Elementary steps considered and corresponding B3LYP 6-311G++(d,p) calculated reaction free energies (eV) for *cis,cis*-muconic acid reduction to levulinic acid and ethyl levulinate via pathway-3.





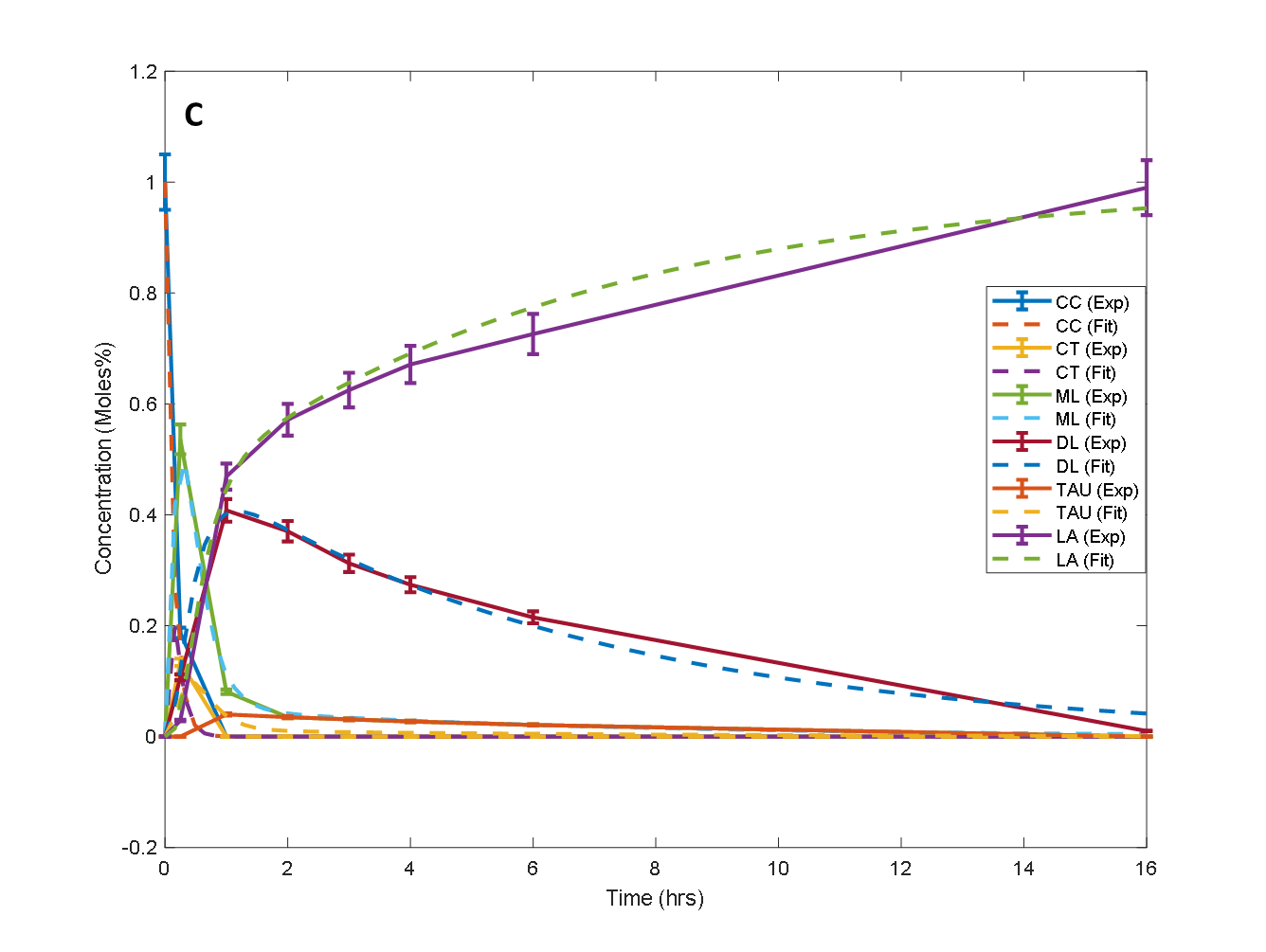


Fig S16 – MATLAB experimental (exp) and simulated fitted (fit) data of levulinic acid (LA) and *cis,cis-*muconic acid (CC) to first order differential rate equation at 75C (A), 80C (B) and 90C (C). The error bars were calculated by non-linear regression with a fixed 5% uncertainty.

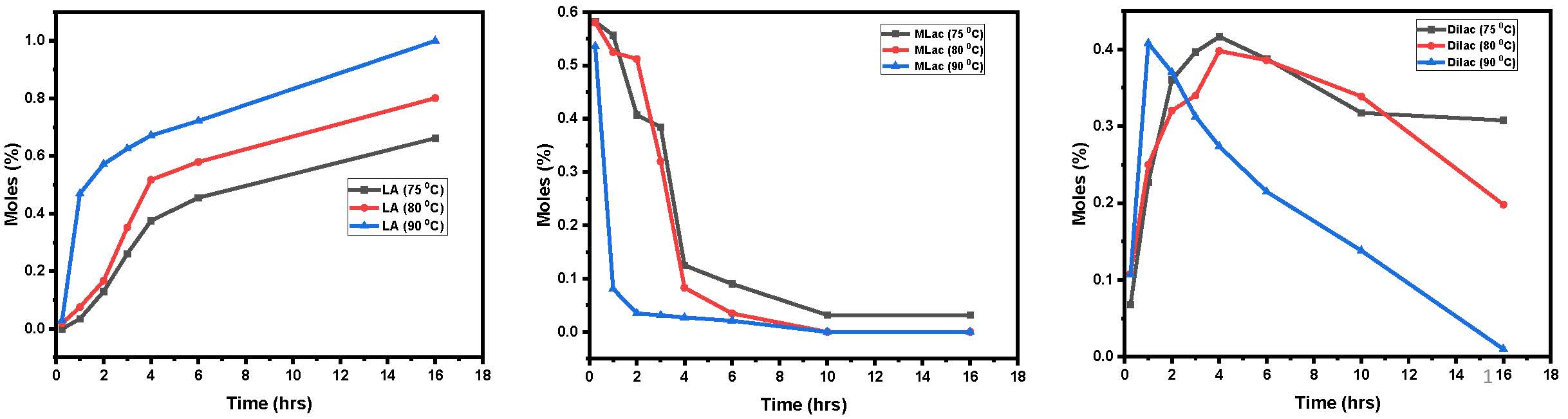
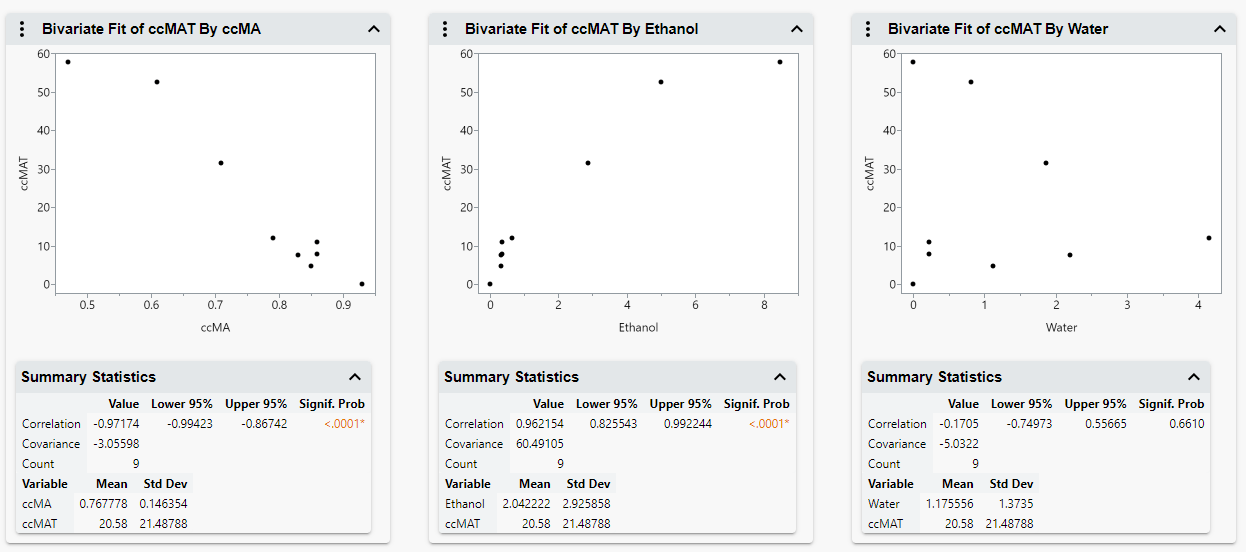


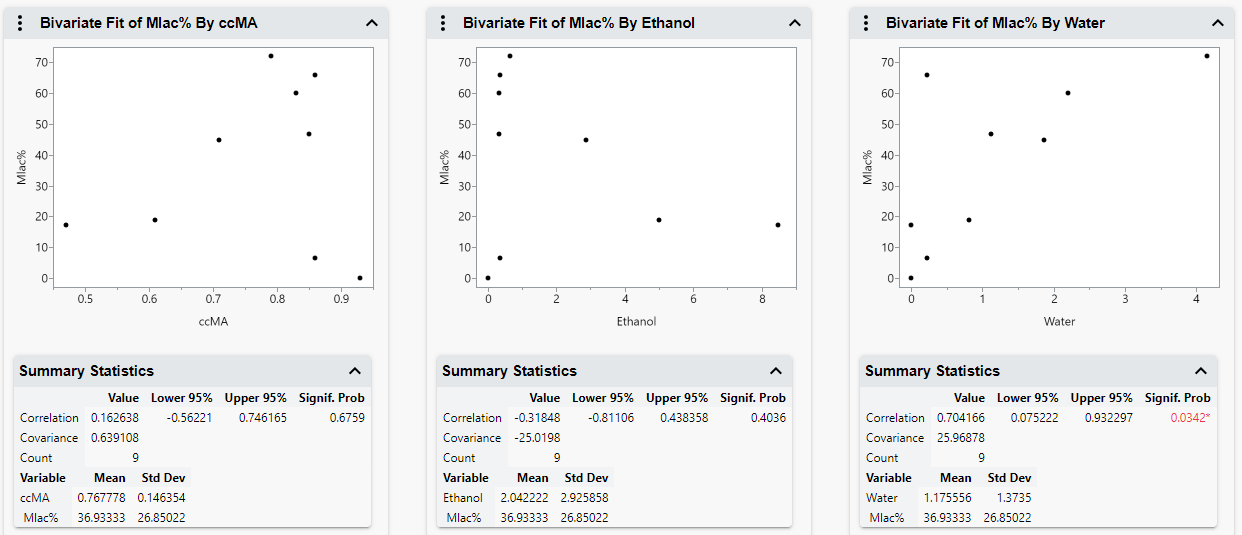
Fig S17 – Effect of temperature on the formation rates of levulinic acid (LA), muconolactone (MLac), and dilactone (Dilac)

A

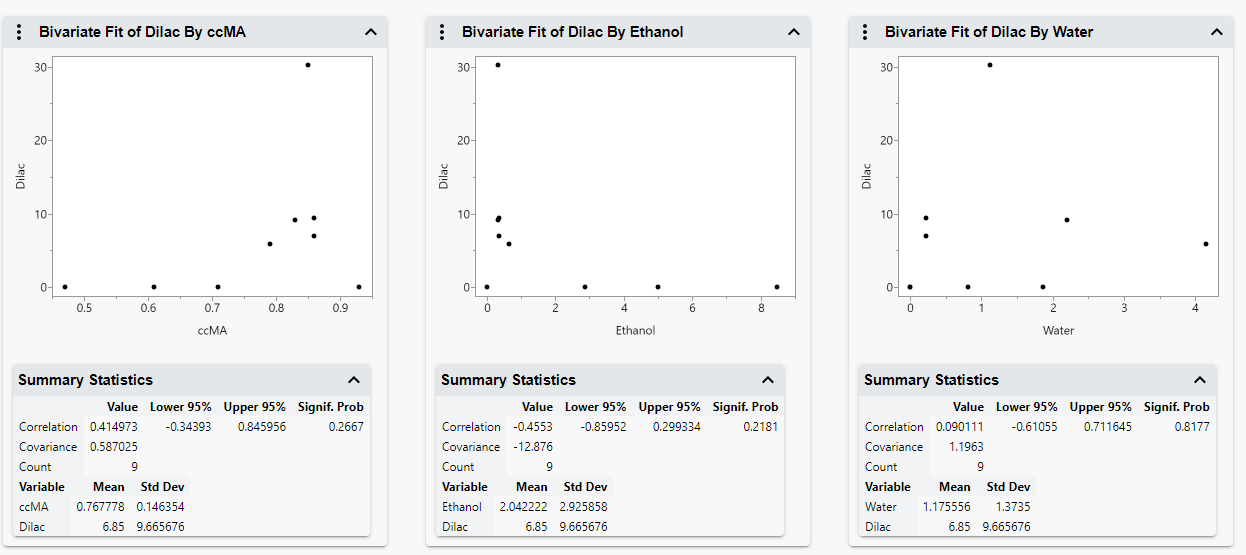
B



C



D



E

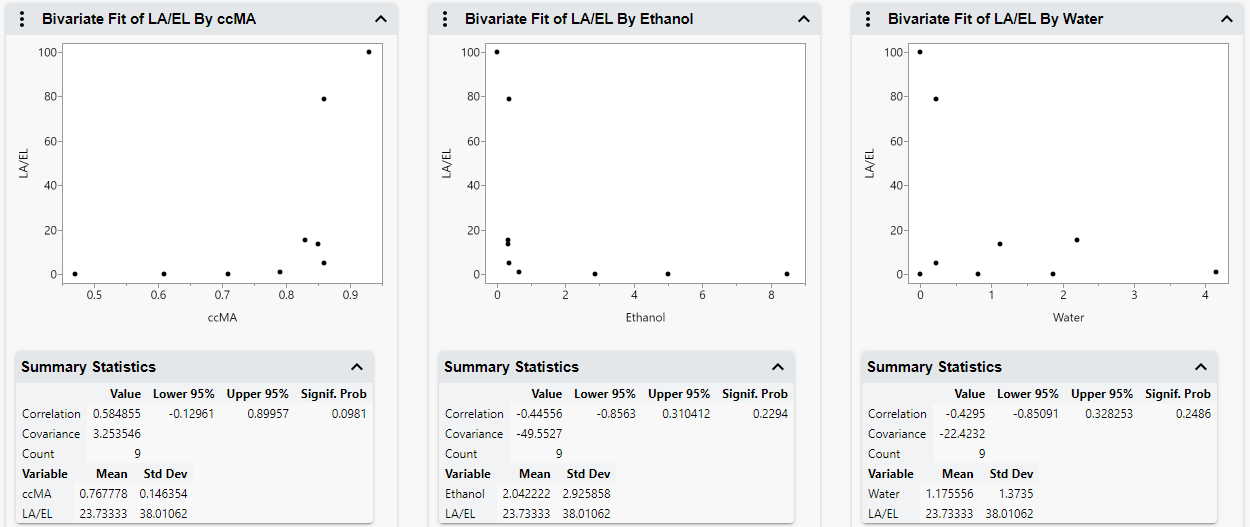


Fig S18 – Bivariate analysis of the relationship between ***cc*MA**, **ethanol**, and **water** concentrations and the formation of **MLac**, **Dilac**, **LA/EL**, ***cc*MAT**, and **ctMAT**. In **A**, **MLac** shows a significant positive correlation with **water** (r = 0.7042, p = 0.0342). **B** illustrates that **LA/EL** has no significant correlations (p > 0.05). **C** shows no significant correlations for **Dilac** (p > 0.05). In **D**, ***ct*MAT** is negatively correlated with ***cc*MA** (r = -0.8925, p = 0.0012) and positively with **ethanol** (r = 0.8453, p = 0.0041). In **E**, ***cc*MAT** is negatively correlated with ***cc*MA** (r = -0.9177, p < 0.0001) and positively with **ethanol** (r = 0.9622, p < 0.0001).

Table S1 – Calculated free energies of elementary steps (∆G, eV) involved in *cis,cis*-muconic acid(*cc*MA) reduction to levulinic acid (LA)/ethyl levulinate (EL)in chloroform at 353.15 K using B3LYP 6-311++G(d,p) (B3LYP), B3LYP 6-311++G(d,p) + DFT-D3 (B3LYP+D3), and CBS-QB3 methods. Isolated H3O+ and H2O in implicit chloroform are used as references for calculating ∆G of protonation/deprotonation steps. Notations: muconolactone (MLac), dilactone (Dilac).

|  |  |  |  |
| --- | --- | --- | --- |
| Elementary steps | B3LYP | B3LYP+D3 | CBS-QB3 |
| *cc*MA 🡪 *ct*MA | -0.16 | -0.14 | -0.14 |
| *ct*MA 🡪 MLac | -0.02 | -0.06 | -0.33 |
| MLac 🡪 Dilac | -0.03 | -0.04 | -0.17 |
| MLac + H+ 🡪 I-1 | 0.80 | 0.76 | 1.05 |
| MLac + H+ 🡪 I-2 | -0.62 | -0.64 | -0.55 |
| I-2 🡪 tautomer + H+ | 1.22 | 1.28 | 1.17 |
| tautomer + H+ 🡪 I-3 | -0.90 | -0.92 | -0.86 |
| I-3 🡪 P-2 + H+ | 0.38 | 0.39 | 0.35 |
| P-2 + H2O 🡪 3-hydroxyhex-3-ene | 0.27 | 0.18 | 0.30 |
| 3-hydroxyhex-3-ene + H+ 🡪 I-4 | -1.11 | -1.18 | -1.13 |
| I-4 🡪 keto adipic acid + H+ | 0.65 | 0.69 | 0.61 |
| keto adipic acid 🡪 LA + CO2 | -0.87 | -0.75 | -0.24 |
| LA + C2H5OH 🡪 EL + H2O | -0.11 | -0.14 | -0.81 |
| I-1 + OH- 🡪 MLac-H2O | -0.26 | -0.37 | -0.72 |
| MLac-H2O 🡪 P-2 + H2O | -0.46 | -0.28 | -0.22 |
| MLac-H2O + H+ 🡪 I-4 | -1.31 | -1.28 | -1.05 |

Table S2 – Calculated zero-point energies (ZPE), entropies (S), and free energies (G) of reaction intermediates involved in *cis,cis*-muconic acid(*cc*MA) reduction to levulinic acid (LA)/ethyl levulinate (EL)in chloroform at 353.15 K. Free energies are referenced to isolated *cc*MA (ZPE: 3.16 eV, S: 456.2 J/(mol\*K)), H3O+ (ZPE: 0.93 eV, S: 208.5 J/(mol\*K)), H2O (ZPE: 0.57 eV, S: 200.2 J/(mol\*K)), CO2 (ZPE: 0.25 eV, S: 228.0 J/(mol\*K)), and C2H5OH (ZPE: 2.16 eV, S: 282.4 J/(mol\*K)) in implicit chloroform. Notations: muconolactone (MLac), dilactone (Dilac).

|  |  |  |  |
| --- | --- | --- | --- |
| Chemical species | ZPE (eV) | S (J/(mol\*K)) | G (eV) |
| *cis,cis*-muconic acid | 3.16 | 456.2 | 0.00 |
| *cis,trans*-muconic acid | 3.15 | 453.9 | -0.16 |
| muconolactone | 3.19 | 417.9 | -0.18 |
| dilactone | 3.25 | 388.5 | -0.21 |
| I-1 | 3.42 | 429.3 | 0.62 |
| I-2 | 3.54 | 423.1 | -0.80 |
| tautomer | 3.15 | 448.9 | 0.42 |
| MLac-H2O | 3.95 | 457.0 | 0.36 |
| I-3 | 3.50 | 424.2 | -0.47 |
| I-3-anion | 2.80 | 425.7 | 3.39 |
| P-2 | 3.16 | 427.1 | -0.10 |
| 3-hydroxyhex-3-ene | 3.89 | 500.3 | 0.17 |
| I-4 | 4.22 | 464.5 | -0.95 |
| I-4-anion | 3.51 | 491.3 | 3.56 |
| keto adipic acid | 3.88 | 501.3 | -0.29 |
| LA | 3.45 | 429.3 | -1.17 |
| EL | 4.97 | 507.5 | -1.27 |

Table S3 – Statistical analysis of the relationship between experimental parameters (**ccMA**, **ethanol**, and **water**) and the concentrations of key intermediates and products (**ccMAT**, **ctMAT**, **MLac**, **Dilac**, and **LA/EL**). The table provides the mean, standard deviation (Std Dev), correlation coefficient (r), 95% confidence intervals (CI) for correlation, and p-values for each relationship. Statistically significant correlations (p < 0.05) are marked with an asterisk (\*). Significant positive correlations suggest that increasing the experimental parameter enhances product formation, while significant negative correlations indicate consumption of the reactant (**ccMA**) during the reaction. Non-significant relationships imply that the experimental parameters do not strongly influence the formation of certain compounds, such as **Dilac** and **LA/EL**.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Compound | Experimental Parameter | Mean | Std Dev | Correlation (r) | Lower 95% CI | Upper 95% CI | p-Value |
| ccMAT | ccMA | 20.58 | 21.49 | -0.9177 | -0.9942 | -0.8674 | <0.0001\* |
|  | Ethanol | 20.58 | 21.49 | 0.9622 | 0.8255 | 0.9922 | <0.0001\* |
|  | Water | 20.58 | 21.49 | -0.1705 | -0.7498 | 0.5567 | 0.661 |
| ctMAT | ccMA | 11.87 | 10.89 | -0.8925 | -0.9773 | -0.5609 | 0.0012\* |
|  | Ethanol | 11.87 | 10.89 | 0.8453 | 0.4132 | 0.9667 | 0.0041\* |
|  | Water | 11.87 | 10.89 | 0.01997 | -0.6528 | 0.6751 | 0.9593 |
| MLac | ccMA | 36.93 | 26.85 | 0.1626 | -0.5622 | 0.7462 | 0.6759 |
|  | Ethanol | 36.93 | 26.85 | -0.3148 | -0.8111 | 0.4384 | 0.4036 |
|  | Water | 36.93 | 26.85 | 0.7042 | 0.0752 | 0.9323 | 0.0342\* |
| Dilac | ccMA | 6.85 | 9.67 | 0.4148 | -0.3439 | 0.846 | 0.2667 |
|  | Ethanol | 6.85 | 9.67 | -0.4553 | -0.8596 | 0.2993 | 0.2181 |
|  | Water | 6.85 | 9.67 | 0.0901 | -0.6106 | 0.7116 | 0.8177 |
| LA/EL | ccMA | 23.73 | 38.01 | 0.5849 | -0.1296 | 0.9 | 0.0981 |
|  | Ethanol | 23.73 | 38.01 | -0.4456 | -0.8563 | 0.3104 | 0.2294 |
|  | Water | 23.73 | 38.01 | -0.4295 | -0.8509 | 0.3283 | 0.2486 |