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Supplementary Materials for

Renewable lubricants with tailored molecular architecture

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Fig. S20. Overview of cost and impact of raw materials on selling price of lubricants.
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Scheme S1. Strategies for the synthesis of 2-alkylfurans. Strategies for the synthesis of (a) 2-methylfuran and furan [22, 29] (a) and various 2-alkylfurans from furan [23] (b).

Table S1. Properties of commercial solid acid catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Acid density (H⁺ mmol/g)</th>
<th>Surface area (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Form</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aquivion PW98</td>
<td>1.0</td>
<td>&lt;1</td>
<td>-</td>
<td>Coarse powder</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>Nafion NR50</td>
<td>0.89</td>
<td>&lt;1</td>
<td>-</td>
<td>Pellets</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>Amberlyst-15</td>
<td>4.8</td>
<td>42</td>
<td>34.3</td>
<td>Beads</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>Amberlyst-36</td>
<td>5.4</td>
<td>33</td>
<td>32.9</td>
<td>Beads</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>HZSM-5</td>
<td>0.65</td>
<td>425</td>
<td>~0.5</td>
<td>Powder</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>HY</td>
<td>0.31</td>
<td>780</td>
<td>~0.7</td>
<td>Powder</td>
<td>39</td>
</tr>
<tr>
<td>7</td>
<td>Silica-alumina</td>
<td>0.34</td>
<td>569</td>
<td>5.4</td>
<td>Powder</td>
<td>39</td>
</tr>
</tbody>
</table>
Fig. S1. **Catalysts screening for the synthesis of C_{30}-FL1.** Reaction conditions: 10 mmol 2-pentylfuran, 5 mmol lauraldehyde, H^+ 0.05 mmol (e.g., Aquivion PW98 0.05g), 65°C, 6 h.
Fig. S2. Effect of catalyst (Aquivion PW98) amount on the yield of C$_{30}$-FL1 at low and high conversions of reactants. Reaction conditions: (a) 10 mmol 2-pentylfuran, 5 mmol lauraldehyde, 65°C for (a) 6 hr and (b) 1 hr.
Fig. S3. Effect of reaction temperature on the production of C₃₀-FL1.

Reaction conditions: 10 mmol 2-pentylfuran, 5 mmol lauraldehyde, (a) Catalyst: 0.05g for 6 h and (b) Catalyst: 0.02g for 0.5 h
**Fig. S4.** Arrhenius plot for HAA of 2-pentylfuran with lauraldehyde over Aquivion PW98. $E_a=16.0$ kcal/mol (2-pentylfuran), $E_a=16.4$ kcal/mol (lauraldehyde).

**Fig. S5.** Time course of the HAA reaction over Aquivion PW98 catalyst.

Reaction conditions: 10 mmol 2-pentylfuran, 5 mmol lauraldehyde, Aquivion PW98 0.05 g, 65°C.
Scheme S2. Reaction pathway for HAA of 2-alkylfuran with an aldehyde over acid catalyst.

Fig. S6. Recyclability of Aquivion PW98.

Reaction conditions: 10 mmol 2-pentylfuran, 5 mmol lauraldehyde, catalyst: 0.05 g, 6 hr.
Fig. S7. Time course of the HAA reaction for C\textsubscript{30}-FL1 synthesis over the P-SiO\textsubscript{2} catalyst.

Reaction conditions: 10 mmol 2-pentylfuran, 5 mmol lauraldehyde, 0.05 g P-SiO\textsubscript{2}, 65°C.

Fig. S8. Recyclability of P-SiO\textsubscript{2} for the synthesis of C\textsubscript{30}-FL1.

Reaction conditions: 10 mmol 2-allkylfuran, 5 mmol aldehyde, 0.05 g P-SiO\textsubscript{2}, 65°C, 1hr.
Fig. S9. Thermogravimetric profiles of P-SiO$_2$ before and after reaction. Measurement conditions: sample weight ~10 mg, heating rate 10°C/min, in air.
Fig. S10. Hydrogenation of C\textsubscript{30}-FL1 over pretreated Pd/C.

Reaction conditions: 0.5 g C\textsubscript{30}-FL1, 0.03 g Pd/C, 60\textdegree C, Pd/C was reduced under H\textsubscript{2} (50 ml/min) at 200\textdegree C for 1 hr.
Fig. S11. TEM images of Pd/C before reaction (a & b) and after reaction (c & d).

Reaction conditions: 0.5 g C₃₀-FL1, 0.03 g Pd/C, 60°C, 6 MPa H₂, 2 hr.
Fig. S12. Recyclability of Ir-ReO$_x$/SiO$_2$ for the HDO of C$_{30}$-FL1.

Reaction condition: Ir-ReO$_x$/SiO$_2$ (0.15 g), C$_{30}$-FL1 0.3 g, 170°C, H$_2$ 5 MPa, 12 hr.
Fig. S13. TEM images of Ir-ReOₓ/SiO₂ before reaction (a & b) and after 5 cycles (c & d).

Reaction conditions: 0.3 g C₃₀-FL1, 0.15 g Ir-ReOₓ/SiO₂, 170°C, H₂ 5 MPa, 12 hr.
Table S2. HAA reaction of different 2-alkylfurans with aldehydes over P-SiO$_2$.

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>HAA</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl</td>
<td>$n$Undecyl</td>
<td>C$_{22}$-FL1</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl</td>
<td>$n$Undecyl</td>
<td>C$_{24}$-FL1</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>$n$Propyl</td>
<td>$n$Undecyl</td>
<td>C$_{26}$-FL1</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>$n$Butyl</td>
<td>$n$Undecyl</td>
<td>C$_{28}$-FL1</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>$n$Pentyl</td>
<td>$n$Undecyl</td>
<td>C$_{30}$-FL1</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>$n$Hexyl</td>
<td>$n$Undecyl</td>
<td>C$_{32}$-FL1</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>$n$Heptyl</td>
<td>$n$Undecyl</td>
<td>C$_{34}$-FL1</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>$n$Pentyl</td>
<td>Methyl</td>
<td>C$_{20}$-FL1</td>
<td>89</td>
</tr>
<tr>
<td>9</td>
<td>$n$Pentyl</td>
<td>$n$Pentyl</td>
<td>C$_{24}$-FL2</td>
<td>88</td>
</tr>
<tr>
<td>10</td>
<td>$n$Pentyl</td>
<td>$n$Heptyl</td>
<td>C$_{26}$-FL2</td>
<td>89</td>
</tr>
<tr>
<td>11</td>
<td>$n$Pentyl</td>
<td>$n$Nonyl</td>
<td>C$_{28}$-FL2</td>
<td>85</td>
</tr>
<tr>
<td>12a</td>
<td>$n$Pentyl</td>
<td>2-Ethylpentyl</td>
<td>C$_{26}$-FL3</td>
<td>87</td>
</tr>
<tr>
<td>13a</td>
<td>$n$Hexyl</td>
<td>2-Ethylpentyl</td>
<td>C$_{28}$-FL3</td>
<td>86</td>
</tr>
<tr>
<td>14a</td>
<td>$n$Heptyl</td>
<td>2-Ethylpentyl</td>
<td>C$_{30}$-FL2</td>
<td>88</td>
</tr>
</tbody>
</table>

Reaction conditions: HAA reaction of 2-alkylfuran with aldehyde to condensed furan over Aquivion PW98: 10 mmol 2-alkylfuran, 5 mmol aldehyde, 0.05 g catalyst, 65°C, 1.5 h.

a: 3 h.
Fig. S14. Effect of chain length of 2-alkylfurans on the HAA reaction rate at <25% conversion. Reaction conditions: 10 mmol 2-allkylfuran, 5 mmol aldehyde, 0.02 g Aquivion PW98, 65°C.
Fig. S15. Effect of chain length of linear aldehydes on the formation rates of the HAA condensation products at <25% conversion. Reaction conditions: 10 mmol 2-allkylfuran, 5 mmol aldehyde, 0.02 g Aquivion PW98, 65°C.
Fig. S16. Effect of aldehyde branching on the formation rates of the HAA condensation products at <25% conversion. Reaction conditions: 10 mmol 2-alkylfuran, 5 mmol aldehyde, 0.02 g Aquion PW98, 65°C.
Fig. S17. Gas chromatogram trace of C_{30}-BPAOL1 and ExxonMobil PAO4.

Table S3. Simulated kinematic viscosities and viscosity index at 40° and 100°C of C_{30}-BPAOL lubricant base oils.

<table>
<thead>
<tr>
<th>Base oil</th>
<th>KV_{40} (cSt)</th>
<th>KV_{100} (cSt)</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{30} BPAOL3</td>
<td>7.84 ± 0.10</td>
<td>2.73 ± 0.02</td>
<td>227 ± 14</td>
</tr>
<tr>
<td>C_{30} BPAOL4</td>
<td>7.45 ± 0.23</td>
<td>2.26 ± 0.04</td>
<td>116 ± 26</td>
</tr>
<tr>
<td>C_{30} BPAOL1</td>
<td>7.14 ± 0.12</td>
<td>2.23 ± 0.03</td>
<td>126 ± 19</td>
</tr>
<tr>
<td>C_{30} BPAOL5</td>
<td>7.61 ± 0.15</td>
<td>2.41 ± 0.05</td>
<td>150 ± 25</td>
</tr>
<tr>
<td>C_{30} BPAOL2</td>
<td>5.97 ± 0.10</td>
<td>1.98 ± 0.03</td>
<td>130 ± 22</td>
</tr>
</tbody>
</table>
Simulation and Economics

Simulation

Using the available data, a simulation of the production processes is performed using Aspen Plus® V8.8.2. The NRTL method is utilized to predict the liquid-liquid and liquid-vapor behavior. Most of the components involved in the reactions are directly selected from Aspen database. Components not found in the database (i.e., furan compounds and lubricants) are defined by their structures. All missing parameters are estimated by the molecular structures using the UNIFAC Model and Thermo Data Engine (TDE). TDE is a thermodynamic data correlation, evaluation, and prediction tool developed by the collaboration of Aspen plus and the National Institute of Standard and Technology [54]. Production of $p$-xylene is combined with the production of lubricants, as the starting material required is furfural, which is a by-product from $p$-xylene production. The estimates are based on projected large-scale production, rather than the small quantities made in the lab, and as such serve as first estimates.

For the process simulation, we consider the following:

1. The yield and reaction conditions of all the reactions are as shown in Table S4. The furfural flowrate and purity are taken from our previous study of $p$-xylene production [54].
2. The by-products do not affect the conversion and selectivity of any reactions. No separation steps are considered before reaction.
3. Continuous regeneration of catalyst is a well-established process and uses specialized equipment which cannot be designed in Aspen plus and therefore, continuous regeneration of catalyst is not included in the calculation. Hence, the capital cost for the process is underestimated compared to the actual cost of the equipment.
4. The syngas produced is used for the production of electricity via a gas turbine [55].

Table S4. Reaction specifications.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HAA</th>
<th>HDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>65</td>
<td>170</td>
</tr>
<tr>
<td>P (bar)</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>85</td>
<td>86</td>
</tr>
</tbody>
</table>

Economics

All the equipment and operating costs estimated by Aspen Economic Analyzer® V8.8.2 are based on the price of the first quarter in 2014. The discounted cash flow analysis is utilized to perform the economic evaluation of the different processes. The production cost of lubricant is used to determine the minimum cost, which is defined as the selling price of the product when the net present value (NPV) is zero. Some additional assumptions are necessary to perform the economic analysis:

1. The capacity of base scenario is assumed 50 metric ton/h of dried biomass. The cost of biomass is averaged to ($60/metric ton) based on the 2011 data of NREL [56]. From the production of $p$-xylene, 8.25 metric ton/h of furfural is produced.
2. The plant operates in a continuous mode for 8000 hours per year. The economic life of the project is assumed to be 20 years with a recovery period of 10 years. The
internal rate of return (ROR) on investment is assumed as 15%. 35% tax is applied to the profits. The simplest depreciation method -- the straight-line method is used as the salvage value is 10% of the original capital cost after 20 years.

3. The market price of heptane is estimated as $1,500/metric ton and of valeric acid is $3,000/metric ton based on the average prices reported at www.alibaba.com - a worldwide e-commerce market site.

4. The cost of cyclohexane is $1,500/metric ton, of hydrogen is $653/metric ton, of tetrafluoroacetic anhydride is $1,000/metric ton and of lauraldehyde is $2,500/metric ton.

5. The catalyst cost is estimated as that of the precious metal cost plus $11,000/ton of supported catalyst and catalyst manufacturing [57]. The unit price of Pd is $23,262/kg [58]. The Pd/Li-aluminate catalyst that is used in the conversion of furfural to furan consists of 0.5 wt% Pd leading to a price of $127,305/metric ton. The catalyst life taken is 6 months. Similarly, the Ir-ReO\(_x\)/SiO\(_2\) catalyst cost is estimated as that of the precious metal cost plus cost of the support and the catalyst manufacturing. The unit price of Ir and Re are $45,819/kg and $2,844/kg [58], respectively. The Ir-ReO\(_x\)/SiO\(_2\) catalyst of 4 wt% of Ir and the molar ratio of Ir:Re is 2 lead to a price of $2,062,856/metric ton. The catalyst life is taken to be 12 months. It is assumed that the catalyst manufacturer will be able to recover 99% of the metals in the spent catalyst. Therefore, after every 12 months only the cost of the catalyst support, makeup metals and manufacturing cost would be required. The cost of copper chromite catalyst is $110,000/metric ton and the cost of P-SiO\(_2\) is $5,000/metric ton (Alibaba). The total catalyst needed for Ir-ReO\(_x\)/SiO\(_2\), and P-SiO\(_2\) per hour is 6,412 kg and 322 kg, respectively. 4,330 kg of copper chromite is needed for the reaction.

6. Heat integration was not implemented in this analysis. All the utilities are bought from a third party vendor at a fixed cost.

7. Electricity generated is sold at $0.085/kWh.

8. Transportation cost and wastewater treatment have not been included.

9. The minimum price of lubricants is calculated by keeping the selling price of \(p\)-xylene at $1,477/metric ton. A scenario is considered where furfural is bought at market price of $1,000/metric ton (Alibaba).

**Process description**

*Production from lignocellulosic biomass*

The flow diagram for the production of lubricant base oils is shown in Fig. S16. The lignocellulosic biomass was deconstructed by a one-pot depolymerization and saccharification process using molten salt hydrate for the hydrolysis of non-food biomass into C\(_5\) and C\(_6\) sugars [59]. The sugars are then dehydrated to produce furfural and HMF, respectively, in a biphasic reactor with ethyl acetate and water over AlCl\(_3\) catalyst [60]. The production of 2,5-dimethylfuran (DMF) by HDO of HMF over Ni-Cu/C and the subsequent production of \(p\)-xylene from DMF over P-BEA are similar to previous work [61, 26]. The process derived furfural was used for lubricants production, which was first converted to furan by reductive decarbonylation [62]. A 2:1 H\(_2\) to furfural is used with Pd/Li-aluminate catalyst promoted by cesium carbonate at 250 °C. Furfural and hydrogen is fed to reactor (R1)
containing the catalyst at 250 °C. Decarbonylation of furfural produces furan and syngas (stream 1). The overall yield of furan is ~91% at a conversion of 95.2%. Byproducts include furfuryl alcohol and methylfuran with 3.23% and 0.97% selectivity, respectively. The product (stream 1) is introduced into a flash drum (V1) at -30 °C. Syngas is separated and used for electricity generation. The liquid (stream 2) is fed to another flash drum (V2) and then to a distillation column (C1) operated at 2 bar pressure to separate furan from water formed and the byproducts (furfuryl alcohol and methylfuran). The syngas produced is used for electricity production via gas turbine.

Combined anhydride formation and furan acylation of furan is carried out with a fatty acid in the presence of trifluoroacetic anhydride (TFAA) and a solvent at room temperature and pressure with a yield of 95%. For this study, valeric acid is used. In the literature, hexane is used as the solvent for the reaction. However, it was found that hexane is too volatile and thus difficult to handle. Heptane is used as the solvent as the boiling point is higher than hexane and thus easy to handle. Furan is acylated with valeric acid using trifluoroacetic anhydride (TFAA) as the catalyst in heptane as a solvent in reactor (R2) at atmospheric temperature and pressure. The product (stream 5) containing intermediate, TFAA and heptane is fed to a distillation column (C2, C3, C4) to separate intermediate, TFAA and valeric acid. Valeric acid and TFAA are recycled back to R1.

Heptane from the first reaction (stream 12) is carried forward to the next step. The intermediate formed is hydrogenated in the presence of heptane and copper chromite catalyst at 220 °C and 7 bar to form 2-pentylfuran. The yield of the reaction is 91% [16]. The product (stream 15) is fed to a series of flash drum (V3, V4) and a distillation column (C5) to separate 2-pentylfuran. Vapor phase (stream 19) from V4 containing mainly heptane and a small amount of water is combined with distillate (stream 20) from C5. To recycle the solvent, removal of water is necessary to avoid build up in the reactor which can deactivate the catalyst. However, separating the small amount of water is difficult. Hence, to make the separation easier, we add water to the heptane stream and introduce it to another distillation column (C6). The purified heptane is recycled back.

For the production of condensed furan (C$_{30}$-FL1), HAA of 2-pentylfuran and lauraldehyde is carried out at 65°C in the presence of P-SiO$_2$ in reactor (R4). The yield of the reaction is 85%.

The final step is the HDO of C$_{30}$-FL1 in the presence of Ir-ReO$_x$/SiO$_2$ catalyst and cyclohexane as the solvent at 170°C and 50 bar hydrogen pressure in reactor (R5). The yield of the reaction is 86%. The product produced is flashed in a series of flash drum (V6, V7, V8) to separate cyclohexane and water formed from the product. Cyclohexane and water are immiscible and hence a decanter is used for separating them and the purified cyclohexane is then recycled back. The lubricant produced is then purified in a vacuum distillation column (C7) with a purity of 97%.
Fig. S18. Flow diagram for the production of lubricants from furfural.

Results
The capacity of the three processes is based on the flowrate of furfural, which is 65,380 metric tons per year. The amount of total lubricants produced is 78,295 metric tons per year or 9.08 T/hr with 97% purity. Syngas, which is produced during decarbonylation of furan, is the only by-product produced which is used to produce 37,120 MW of electricity per year.

The detailed capital and operating costs of lubricant production are listed in Table S5 and depicted in Fig. S17. The total capital cost and operating cost for the combined production of p-xylene (from cellulose) and lubricants (from hemicelluloses) from an integrated cellulosic biorefinery process is $250 million and $435.5 million per year, respectively.
Table S5. Summary of capital and operating cost for combined production of p-xylene and lubricants.

<table>
<thead>
<tr>
<th>Cost</th>
<th>Cost (million $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital</td>
<td>250.06</td>
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<tr>
<td>Total Capital</td>
<td>250.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost (million$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Chloride</td>
<td>0.82</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>0.12</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>0.01</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>8.55</td>
</tr>
<tr>
<td>Biomass</td>
<td>24</td>
</tr>
<tr>
<td>Ethylene</td>
<td>29.17</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.46</td>
</tr>
<tr>
<td>Water</td>
<td>1.5</td>
</tr>
<tr>
<td>LiBr</td>
<td>19.8</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.5</td>
</tr>
<tr>
<td>Lauraldehyde</td>
<td>118.72</td>
</tr>
<tr>
<td>Valeric Acid</td>
<td>167.71</td>
</tr>
<tr>
<td>TFAA</td>
<td>1.72</td>
</tr>
<tr>
<td>Total Utility Cost</td>
<td>26.24</td>
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<tr>
<td>Total Catalyst Cost</td>
<td>1.37</td>
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<tr>
<td>Labor and Maintenance</td>
<td>27.8</td>
</tr>
<tr>
<td>Total Operating Cost</td>
<td>435.5</td>
</tr>
</tbody>
</table>

Fig. S19. Overview of cost and impact of raw materials on selling price of lubricants.

In the base case scenario, the minimum price of lubricants, which is defined as the price when the NPV equals zero, is $4,535/metric ton. The lignin value (~20 wt% dry weight of biomass) was ignored. We have also considered a scenario where furfural is bought instead of being a by-product of p-xylene production. The detailed capital and operating costs of lubricant
production are listed in Table S6 and depicted in Fig. 18. The total capital and operating cost are $49.38 million and $400.37 million per year, respectively.

**Table S6. Summary of capital and operating cost.**

<table>
<thead>
<tr>
<th>Cost</th>
<th>Cost (million $)</th>
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<td>Labor and Maintenance</td>
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<tr>
<td>Total Operating Cost</td>
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**Fig. S20. Overview of cost and impact of raw materials on selling price of lubricants.**

For the scenario where furfural is bought instead of being produced, the minimum selling price of lubricants is $5,191 /metric ton. The distribution of individual processes to various costs is shown in Fig. S19.
Fig. S21. Distribution of various costs by process.
Identification of Synthesized Compounds

C_{20}\text{-FL1}: HAA of 2-pentylfuran and acetaldehyde

\[ \text{\includegraphics[width=0.5\textwidth]{compound.png}} \]

\[^1H\text{ NMR (400 MHz, CDCl}_3\text{): } \delta=5.80-5.75 \text{ (m, 4H), 4.01 \text{ (q, } J = 7.0 \text{ Hz, 1H), 2.46 \text{ (t, } J=7.6, \text{ 4H), 1.56-1.47 \text{ (m, 4H), 1.45(d, } J=7.0, \text{ 3H), 1.29-1.13 \text{ (m, 8H), 0.79 (t, } J=6.8, \text{ 6H).} \]
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$=155.39, 155.02, 105.24, 105.02, 33.30, 31.54, 28.16, 27.90, 22.57, 18.33, 14.19

HR-MS-LIFDI: C$_{20}$H$_{30}$O$_2$ Calc. Mass 302.2246, found Mass 302.2245
C_{22}-FL1: HAA of 2-methylfuran and lauraldehyde

{H NMR (400 MHz, CDCl3): δ=5.91 (d, J=3.0 Hz, 2H), 5.88-5.82 (m, 2H), 3.90 (t, J = 7.6 Hz, 1H), 2.25 (d, J=0.9, 6H), 1.97-1.87 (m, 2H), 1.36-1.18 (m, 18H), 0.88 (t, J=7.0, 3H).}
\[^{13}\text{C} \text{NMR } (101 \text{ MHz, CDCl}_3): \delta=154.31, 150.71, 106.10, 105.98, 39.10, 33.09, 32.07, 29.80, 29.79, 29.75, 29.62, 29.54, 29.51, 27.55, 22.85, 14.29, 13.77\]

\text{HR-MS-LIFDI: } C_{22}H_{34}O_2 \text{ theoretical mass } 330.2557, \text{ observed mass } 330.2559
C_{24}-FL1: HAA of 2-ethylfuran and lauraldehyde

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\] \delta=5.91 (d, J=3.0 Hz, 2H), 5.88-5.84 (m, 2H), 3.93 (t, J = 7.6 Hz, 1H), 2.59 (q, J=7.5 Hz, 4H), 1.98-1.87 (m, 2H), 1.34-1.15 (m, 24H), 0.88 (t, J=7.0, 3H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta$=156.46, 154.22, 105.85, 104.26, 39.14, 33.27, 32.07, 29.80, 29.79, 29.75, 29.63, 29.54, 29.51, 27.55, 22.85, 21.51, 14.29, 12.29

HR-MS-EI: C$_{24}$H$_{38}$O$_2$ Calc. mass 358.2872, observed mass 358.2877
C24-FL.2: HAA of 2-pentylfuran + hexanal

$^1$H NMR (400 MHz, CDCl3): $\delta=5.94-5.80$ (m, 4H), 3.92 (t, $J = 7.6$ Hz, 1H), 2.56 (t, $J=7.6$ Hz, 4H), 1.97-1.84 (m, 2H), 1.68-1.55 (m, 4H), 1.42-1.21 (m, 14H), 0.96-0.81 (m, 9H).
\[^{13}\text{C} \text{NMR (101 MHz, CDCl3): } \delta=155.23, 154.16, 105.84, 105.03, 39.15, 33.25, 31.76, 31.51, 28.16, 27.92, 27.21, 22.66, 22.58, 14.21, 14.18 \]

HR-MS-LIFDI: \( \text{C}_{24}\text{H}_{38}\text{O}_2 \) Calc. Mass 358.2872, found Mass 358.2876
C<sub>26</sub>-FL1: HAA of 2-propylfuran + lauraldehyde

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ=5.94-5.83 (m, 4H), 3.92 (t, J = 7.6 Hz, 1H), 2.56 (t, J=7.6 Hz, 4H), 1.98-1.87 (m, 2H), 1.69-1.55 (m, 4H), 1.35-1.16 (m, 18H), 0.99-0.83 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta$=155.01, 154.20, 105.83, 105.19, 39.15, 33.28, 32.07, 30.21, 29.81, 29.79, 29.74, 29.63, 29.54, 29.52, 27.53, 22.85, 21.60, 14.29, 13.88

HR-MS-LIFDI: $\text{C}_{26}\text{H}_{42}\text{O}_2$ Calc. Mass 386.3185, found Mass 386.3199
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta=5.83$-$5.71$ (m, 4H), 3.82 (t, $J = 7.6$ Hz, 1H), 2.46 (t, $J=7.6$ Hz, 4H), 1.87-$1.76$ (m, 2H), 1.56-$1.45$ (m, 4H), 1.29-$1.03$ (m, 18H), 0.85-$0.71$ (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta=155.23, 154.16, 105.84, 105.03, 39.15, 33.30, 31.97, 31.51, 29.53, 29.32, 28.16, 27.92, 27.55, 22.80, 22.58, 14.26, 14.19

HR-MS-LIFDI: C$_{26}$H$_{42}$O$_2$ Calc. Mass 386.3185, found Mass 386.3182
C26-FL.3: HAA of 2-pentylfuran + 2-ethylhexanal

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl3): } & \delta=5.99-5.81 (m, 4H), 3.98 (d, J = 7.2 \text{ Hz}, 1H), 2.57 (t, J=7.6 \text{ Hz}, 4H), \\
& 2.01-1.91 (m, 1H), 1.68-1.54 (m, 4H), 1.41-1.10 (m, 16H), 0.96-0.76 (m, 12H).
\end{align*}
\]
$^{13}C$ NMR (101 MHz, CDCl3): $\delta = 154.92, 154.91, 153.30, 153.27, 106.90, 106.68, 105.11, 105.09, 43.06, 42.26, 31.46, 30.38, 29.16, 28.16, 28.01, 28.00, 23.82, 23.11, 22.59, 14.24, 14.18, 11.25$

HR-MS-LIFDI: C$_{26}$H$_{42}$O$_{2}$ Calc. Mass 386.3185, found Mass 386.3189
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$=5.94-5.83 (m, 4H), 3.92 (t, J = 7.6 Hz, 1H), 2.57 (t, J=7.6 Hz, 4H), 1.98-1.87 (m, 2H), 1.64-1.53 (m, 4H), 1.42-1.18 (m, 22H), 0.95-0.84 (m, 9H). 

C$_{28}$-FL1: HAA of 2-butylfuran + lauraldehyde
\(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)): \(\delta=155.19, 154.17, 105.83, 105.03, 39.14, 33.28, 32.07, 30.36, 29.81, 29.79, 29.75, 29.65, 29.56, 29.52, 27.89, 27.54, 22.85, 22.40, 14.29, 14.00\)

HR-MS-LIFDI: C\(_{28}\)H\(_{46}\)O\(_2\) Calc. Mass 414.3476, found Mass 414.3498
C_{28}-FL.2: HAA of 2-pentylfuran + decanal

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$=5.92-5.82 (m, 4H), 3.92 (t, $J$ = 7.6 Hz, 1H), 2.56 (t, $J$=7.6 Hz, 4H), 1.98-1.84 (m, 2H), 1.68-1.55 (m, 4H), 1.39-1.16 (m, 22H), 0.93-0.81 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta=155.23, 154.16, 105.84, 105.03, 39.14, 33.30, 32.05, 31.51, 29.72,$
$29.65, 29.57, 29.47, 28.16, 27.92, 27.55, 22.84, 22.58, 14.29, 14.19$

HR-MS-LIFDI: C$_{28}$H$_{46}$O$_2$ Calc. Mass 414.3476, found Mass 414.3498
C_{28}-FL.3: HAA of 2-hexylfuran + 2-ethylhexanal

1H NMR (400 MHz, CDCl3): δ=5.97-5.81 (m, 4H), 3.99 (d, J = 7.2 Hz, 1H), 2.56 (t, J=7.6 Hz, 4H), 2.01-1.89 (m, 1H), 1.67-1.51 (m, 4H), 1.40-1.11 (m, 20H), 0.97-0.76 (m, 12H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta=154.93, 154.91, 153.29, 153.26, 106.90, 106.87, 105.11, 105.09, 43.05, 42.25, 31.77, 30.37, 29.16, 28.95, 28.29, 28.20, 23.82, 23.11, 22.75, 14.26, 14.24, 11.25

HR-MS-LIFDI: C$_{28}$H$_{46}$O$_2$ Calc. Mass 414.3498, found Mass 414.3490
C_{30}-FL1: HAA of 2-pentylfuran + lauraldehyde

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta=5.92-5.82 (m, 4H), 3.92 (t, J = 7.6 Hz, 1H), 2.56 (t, J=7.6 Hz, 4H), 1.97-1.85 (m, 2H), 1.68-1.54 (m, 4H), 1.39-1.16 (m, 26H), 0.93-0.81 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta=155.23, 154.17, 105.84, 105.03, 39.14, 33.29, 32.07, 31.51, 29.80, 29.78, 29.75, 29.65, 29.56, 29.51, 28.15, 27.91, 27.54, 22.84, 22.57, 14.29, 14.18$

HR-MS-LIFDI: C$_{30}$H$_{50}$O$_2$ Calc. Mass 442.3811, found Mass 442.3814
C₃₀-FL₂: HAA of 2-heptylfuran + 2-ethylhexanal

¹H NMR (400 MHz, CDCl₃): δ=5.98-5.81 (m, 4H), 3.99 (d, J = 7.2 Hz, 1H), 2.56 (t, J=7.6 Hz, 4H), 2.01-1.90 (m, 1H), 1.68-1.51 (m, 4H), 1.40-1.11 (m, 24H), 0.97-0.76 (m, 12H).
$^{13}$C NMR (101 MHz, CDCl₃): $\delta$=154.93, 154.92, 153.29, 153.26, 106.90, 106.88, 105.11, 105.09, 43.06, 42.25, 31.95, 30.38, 29.24, 29.16, 28.34, 28.33, 28.19, 23.82, 23.11, 22.81, 14.27, 14.25, 11.26

HR-MS-LIFDI: C$_{30}$H$_{50}$O$_2$ Calc. Mass 442.3811, found Mass 442.3811
C\textsubscript{32}-FL1: HAA of 2-hexylfuran + lauraldehyde

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) = 5.92-5.81 (m, 4H), 3.92 (t, \( J = 7.6 \) Hz, 1H), 2.56 (t, \( J = 7.6 \) Hz, 4H), 1.97-1.85 (m, 2H), 1.68-1.54 (m, 4H), 1.39-1.16 (m, 30H), 0.95-0.80 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): δ=155.23, 154.16, 105.84, 105.03, 39.14, 33.30, 32.07, 31.76, 29.82, 29.80, 29.77, 29.66, 29.57, 29.52, 29.00, 28.20, 27.55, 22.85, 22.74, 14.29, 14.25

HR-MS-LIFDI: C$_{32}$H$_{54}$O$_2$ Calc. Mass 470.4124, found Mass 470.4112
$^{1}$H NMR (400 MHz, CDCl$_3$): δ=5.92-5.81 (m, 4H), 3.92 (t, J = 7.6 Hz, 1H), 2.56 (t, J=7.6 Hz, 4H), 1.97-1.85 (m, 2H), 1.68-1.54 (m, 4H), 1.38-1.16 (m, 34H), 0.95-0.82 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta = 155.23, 154.16, 105.84, 105.02, 39.15, 33.30, 32.07, 31.95, 29.82, 29.80, 29.77, 29.66, 29.57, 29.52, 29.28, 29.22, 28.25, 28.19, 27.55, 22.85, 22.81, 14.29, 14.26

HR-MS-LIFDI: C$_{34}$H$_{56}$O$_2$ Calc. Mass 498.4437, found Mass 498.4435
C$_{20}$-BPAOL1 from HDO of C$_{20}$-FL1

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$=1.33-1.17 (m, 33H), 0.88 (t, J= 7.6, 6H), 0.84 (d, J=6.6, 3H).
$^{13}$C NMR (101 MHz, CDCl₃): $\delta=37.24, 32.89, 32.09, 30.20, 29.91, 29.83, 29.54, 27.25, 22.86, 19.89, 14.30$

HR-MS-EI: C$_{20}$H$_{42}$ Calc. Mass 282.3287, found Mass 282.3271
C₂₂-BPAOL1 from HDO of C₂₂-FL1

¹H NMR (400 MHz, CDCl₃): δ=1.37-1.13 (m, 37H), 0.92-0.84 (m, 9H).
\(^{13}\)C NMR (101 MHz, CDCl3): δ=37.53, 33.81, 33.77, 32.55, 30.32, 29.89, 29.87, 29.82, 29.53, 26.84, 26.52, 22.90, 22.86, 14.32, 14.30

HR-MS-El: C\(_{22}\)H\(_{46}\) Calc. Mass 310.3600, found Mass 310.3605
C_{24}-BPAOL1 from HDO of C_{24}-FL1

$^1$H NMR (400 MHz, CDCl3): $\delta=$1.37-1.13 (m, 41H), 0.92-0.84 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta=$37.53, 33.83, 33.81, 32.13, 32.09, 30.00, 29.88, 29.83, 29.54, 26.83, 26.82, 22.89, 22.87, 14.31

HR-MS-LIFDI: C$_{24}$H$_{50}$ Calc. Mass 338.3913, found Mass 338.3915
C_{24}-BPAOL2 from HDO of C_{24}-FL2

\[ \text{H NMR (400 MHz, CDCl}_3\text{: } \delta = 1.37-1.14 \text{ (m, 41H), 0.92-0.84 (m, 9H).} \]
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$=37.53, 33.81, 33.78, 32.56, 32.09, 30.32, 29.90, 29.87, 29.83, 29.54, 26.84, 26.52, 22.90, 22.87, 14.30

HR-MS-LIFDI: $^{24}$C$_{24}$H$_{50}$ Calc. Mass 338.3913, found Mass 338.3924
C_{26}-BPAOL1 from HDO of C_{26}-FL1

{\textsuperscript{1}H} NMR (400 MHz, CDCl3): \( \delta = 1.37-1.12 \) (m, 45H), 0.91-0.85 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$=37.52, 33.82, 32.11, 32.09, 30.31, 30.29, 29.89, 29.87, 29.83, 29.57, 29.53, 26.85, 26.84, 22.87, 14.30

HR-MS-LIFDI: C$_{26}$H$_{54}$ Calc. Mass 366.4226, found Mass 366.4212
C_{26}-BPAOL2 from HDO of C_{26}-FL2

^{1}H NMR (400 MHz, CDCl3): \( \delta = 1.37-1.12 \) (m, 45H), 0.91-0.85 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta=37.52, 33.81, 32.11, 32.09, 30.29, 29.89, 29.86, 29.83, 29.57,$
$29.54, 26.85, 26.84, 22.87, 14.30$

HR-MS-LIFDI: C$_{26}$H$_{54}$ Calc. Mass 366.4226, found Mass 366.4225
C_{26}-BPAOL3 from HDO of C_{26}-FL3

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

$^1$H NMR (400 MHz, CDCl3): $\delta$=1.36-1.03 (m, 42H), 0.93-0.80 (m, 12H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta$ = 41.59, 39.28, 32.09, 30.76, 30.74, 30.61, 30.30, 30.25, 30.05, 29.89, 29.87, 29.83, 29.54, 28.29, 28.23, 23.32, 23.28, 22.86, 14.37, 14.30, 12.87

HR-MS-LIFDI: C$_{26}$H$_{54}$ Calc. Mass 366.4226, found Mass 366.4214
$^{1}H$ NMR (400 MHz, CDCl3): $\delta = 1.37$-$1.12$ (m, 49H), 0.91-$0.85$ (m, 9H).
$^1$C NMR (101 MHz, CDCl₃): δ=37.51, 33.82, 32.10, 30.33, 29.90, 29.88, 29.86, 29.83, 29.55, 26.84, 22.87, 14.30

HR-MS-LIFDI: C$_{28}$H$_{58}$ Calc. Mass 394.4539, found Mass 394.4556
C_{28}-BPAOL2 from HDO of C_{28}-FL2

{\textsuperscript{1}H} NMR (400 MHz, CDCl\textsubscript{3}): \delta=1.37-1.12 (m, 49H), 0.91-0.85 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): $\delta=37.51, 33.81, 32.09, 30.32, 29.89, 29.86, 29.83, 29.54, 26.83, 22.86, 14.30$

HR-MS-LIFDI: $\text{C}_{28}\text{H}_{58}$ Calc. Mass 394.4539, found Mass 394.4554
$C_{28}$-BPAOL3 from HDO of $C_{28}$-FL3

$\text{H NMR (400 MHz, CDCl}_3\text{): } \delta=1.36-1.03 \text{ (m, 46H), 0.93-0.80 (m, 12H).}$
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$=41.59, 39.27, 32.09, 30.75, 30.73, 30.61, 30.32, 30.25, 30.05, 29.87, 29.82, 29.53, 28.22, 23.32, 23.28, 22.86, 14.37, 14.30, 12.87

HR-MS-LIFDI: C$_{28}$H$_{58}$ Calc. Mass 394.4539, found Mass 394.4511
$^{1} \text{H NMR (400 MHz, CDCl3)}: \delta=1.37-1.12 \text{ (m, 53H), 0.91-0.85 (m, 9H).}$
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta=37.51$, 33.81, 32.10, 30.32, 29.90, 29.88, 29.84, 29.54, 27.06, 26.84, 22.87, 14.30

HR-MS-LIFDI: C$_{30}$H$_{62}$ Calc. Mass 422.4852, found Mass 422.4856
$^1$H NMR (400 MHz, CDCl3): δ=1.36-1.03 (m, 50H), 0.93-0.80 (m, 12H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta=41.59, 39.27, 32.09, 30.75, 30.73, 30.61, 30.29, 30.25, 30.04, 29.87, 29.82, 29.53, 28.28, 28.22, 23.32, 23.28, 22.86, 14.37, 14.30, 12.87\)

HR-MS-LIFDI: C\(_{30}\)H\(_{62}\) Calc. Mass 422.4852, found Mass 422.4852
$^{1}$H NMR (400 MHz, CDCl3): $\delta$=1.35-1.12 (m, 57H), 0.91-0.85 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): δ=37.50, 33.80, 32.08, 30.31, 29.88, 29.83, 29.53, 26.83, 22.86, 14.30

HR-MS-LIFDI: C$_{32}$H$_{66}$ Calc. Mass 450.5165, found Mass 450.5165
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 1.37 - 1.12$ (m, 61H), 0.91 - 0.85 (m, 9H).
$^{13}$C NMR (101 MHz, CDCl3): δ=37.50, 33.80, 32.09, 30.31, 29.89, 29.87, 29.83, 29.53, 26.83, 22.86, 14.30

HR-MS-LIFDI: $\text{C}_{34}\text{H}_{70}$ Calc. Mass 478.5478, found Mass 478.5472
C_{30}-SFL1 from hydrogenation of C_{30}-FL1

\[ \text{H NMR (400 MHz, CDCl3): } \delta=4.07-3.57 \text{ (m, 4H), 2.02-1.72 (m, 4H), 1.68-1.49 (m, 4H), 1.48-1.15 (m, 37 H), 0.94-0.78 (m, 9H).} \]

HR-MS-LIFDI: C_{30}H_{58}O_{2} Calc. Mass 450.4437, found Mass 450.4442