Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Catalytic Production of Renewable Lubricant Base Oils from Bio-Based 2-Alkylfurans and Enals

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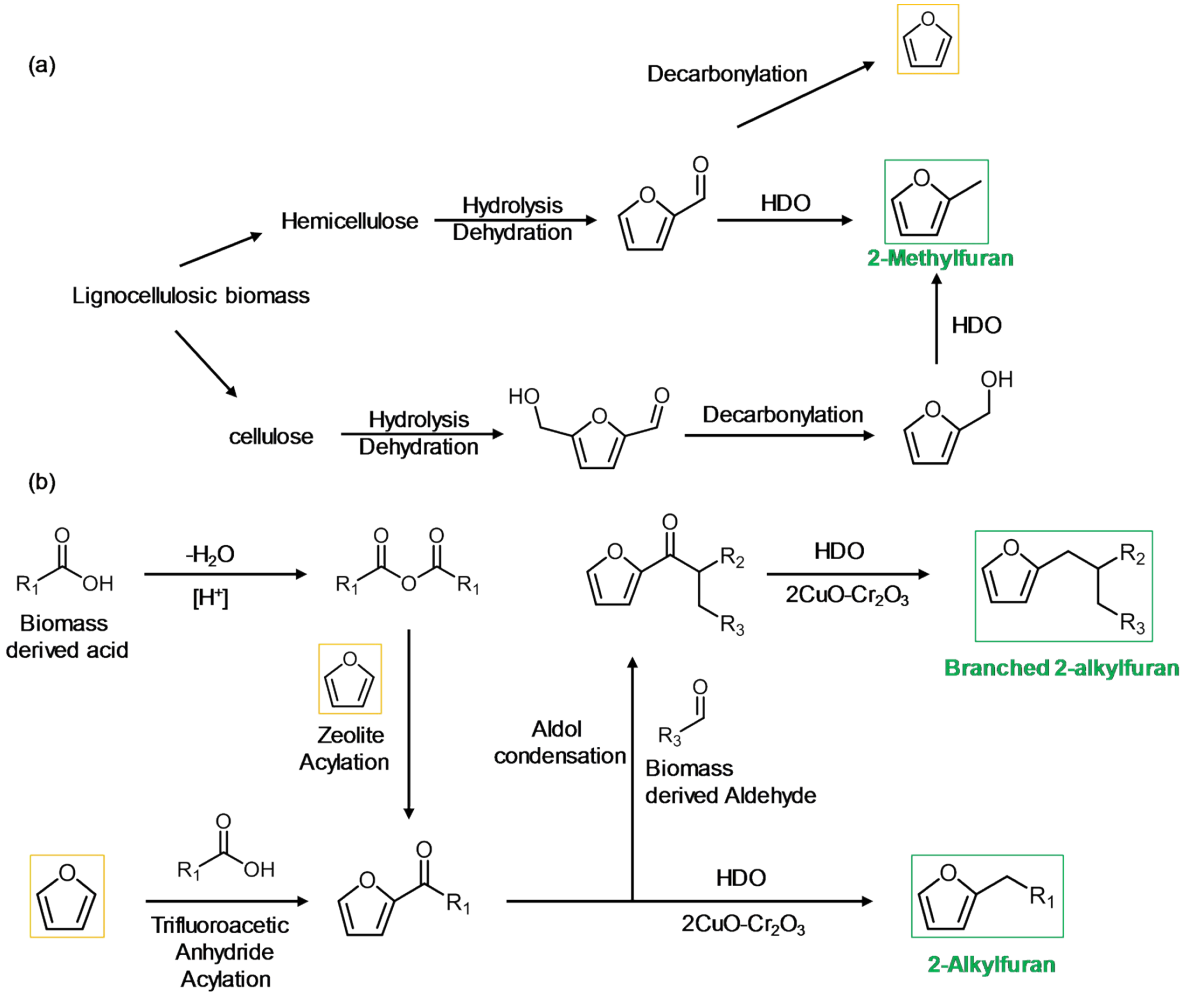
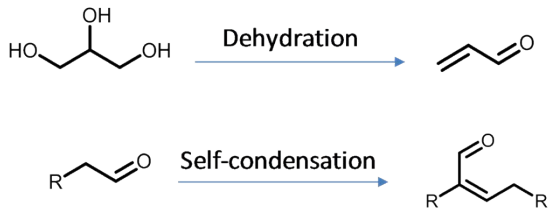


Scheme S1. Strategies for the synthesis of various 2-alkylfurans.
(a) 2-Methylfuran is produced by one-step hydrodeoxygenation (HDO) of biomass-derived furfural or in two steps from 2-hydroxymethylfurfural (HMF) involving decarbonylation of HMF to furfuryl alcohol, followed HDO of furfural alcohol over metal-based catalysts with over 90% yield. Furan is obtained by decarbonylation of furfural over a Pd/HY catalyst with the yield of 99% (ACS Catal., 2013, 3, 2655-2668).
(b) 2-Alkylfurans are synthesized by acylation of furan with carboxylic acids over a liquid catalyst (trifluoroacetic anhydride) or anhydrides of the carboxylic acids over zeolite catalysts, followed by HDO of the acylated intermediate over a commercial copper chromite (2CuO-Cr_2O_3) catalyst. The yield of the product in each step is above 90% with an overall yield of 2-alkylfurans of 87%. (ACS Cent. Sci., 2016, 2 (11), 820–824)



Scheme S2. Strategies for the synthesis of various enals.

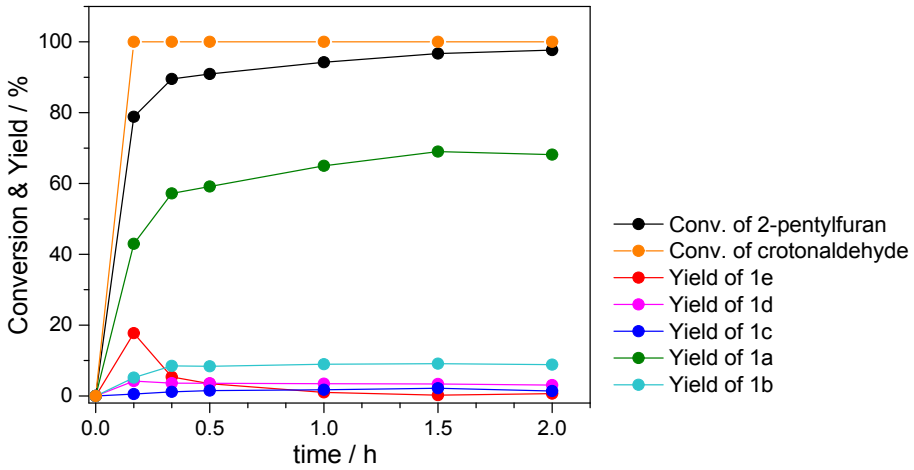


Fig. S1 Time course of condensation of 2-pentylfuran and crotonaldehyde over Aquivion PW79S. Reaction conditions: 6 mmol 2-pentylfruan, 2 mmol crotonaldehyde, 0.05 g Aquivion PW79S and 65 ^{o}C.

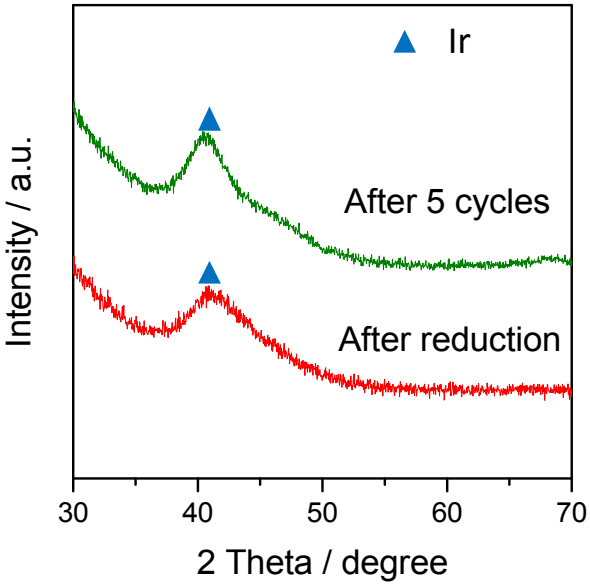


Fig. S2 XRD patterns of the Ir-ReO_x/SiO_2 (Re/Ir=2) catalyst. a: after reduction, b: after 5 cycles.

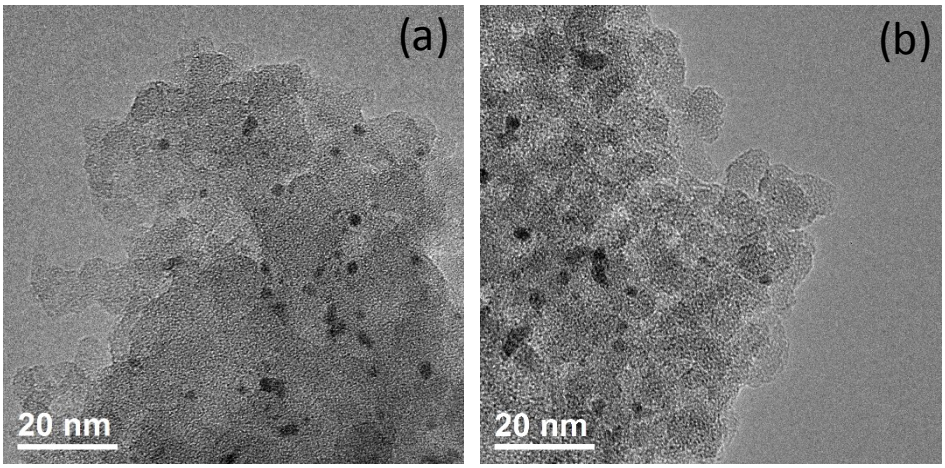
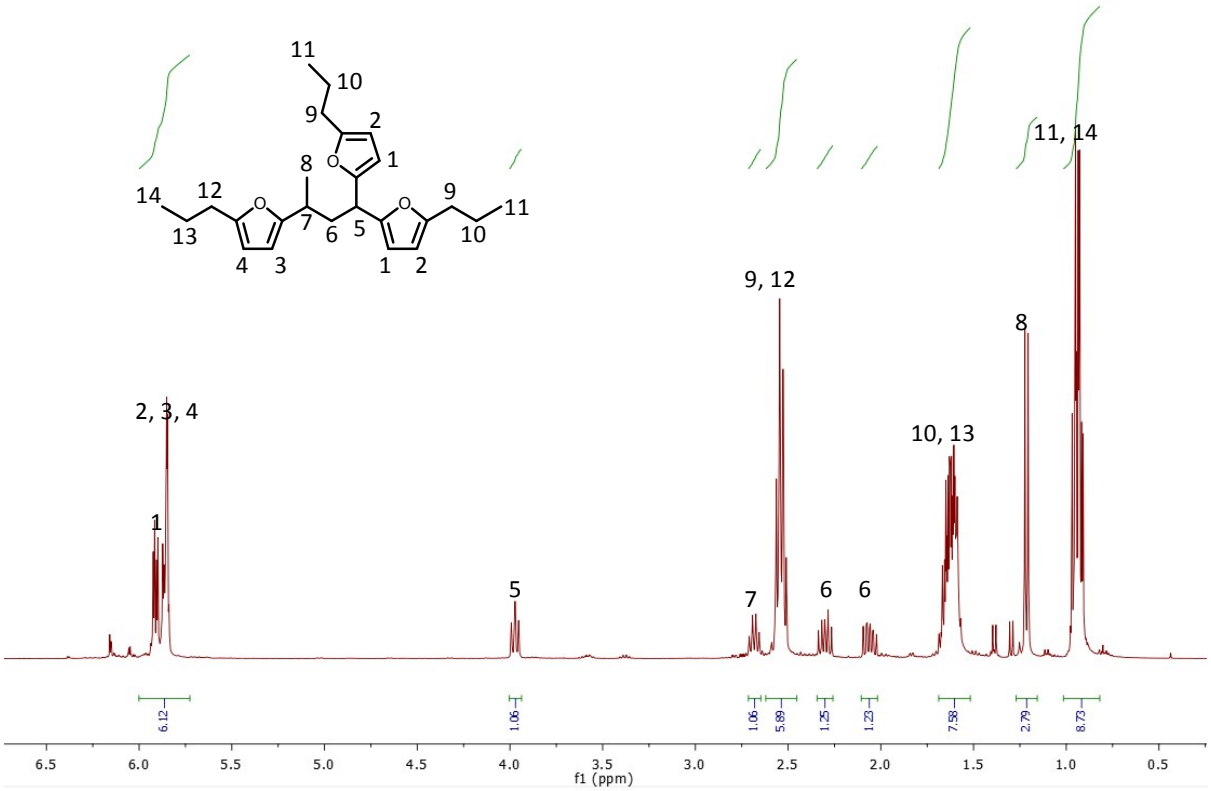


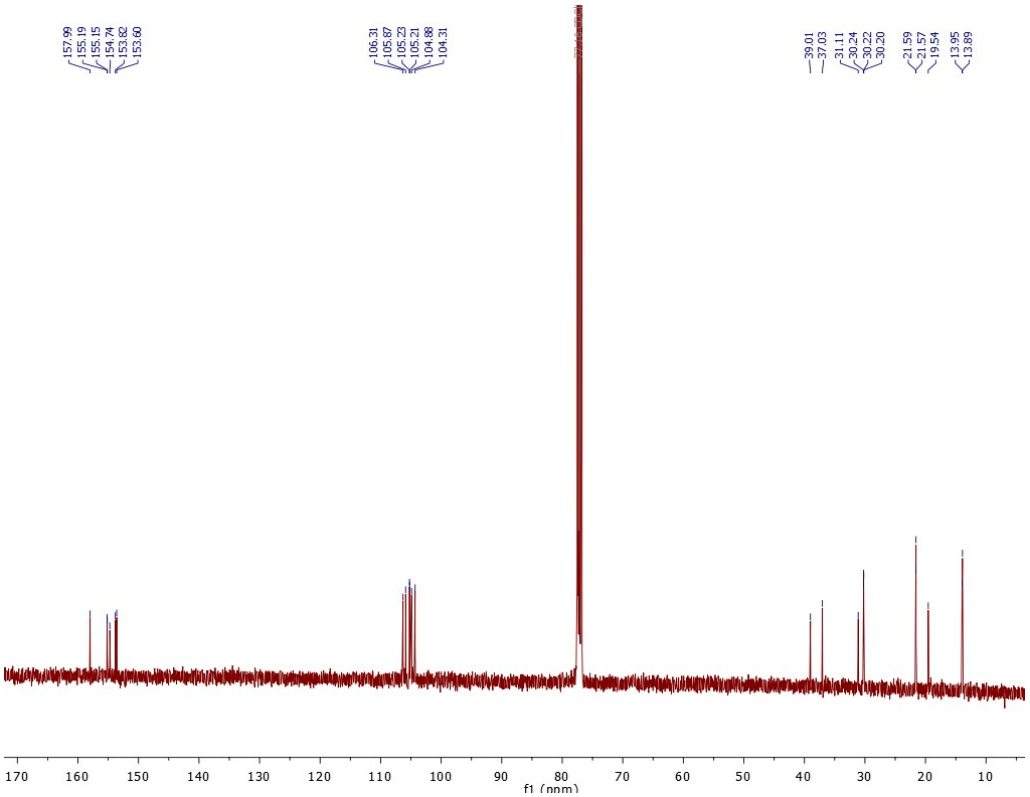
Fig. S3 TEM images of the Ir-ReO_x/SiO_2 (Re/Ir=2) catalyst. (a): after reduction, (b): after 5 cycles.

Identification of the synthesized compounds

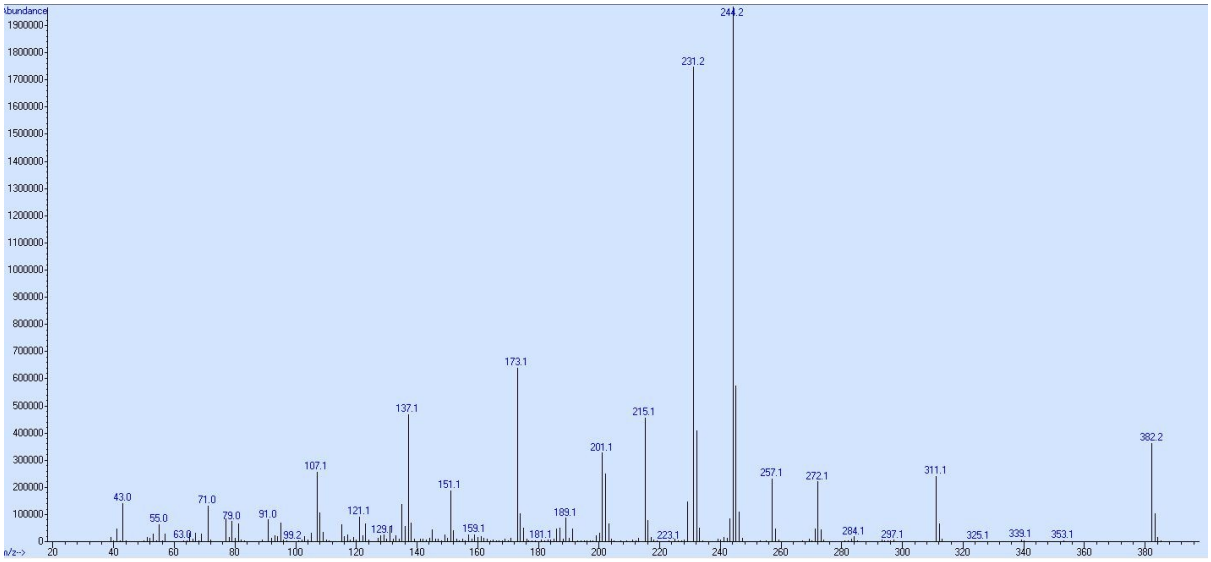
C_{25} condensed furan: CA-HAA of 2-propylfuran + crotonaldehyde

^{1}H and ^{13}C-NMR spectra





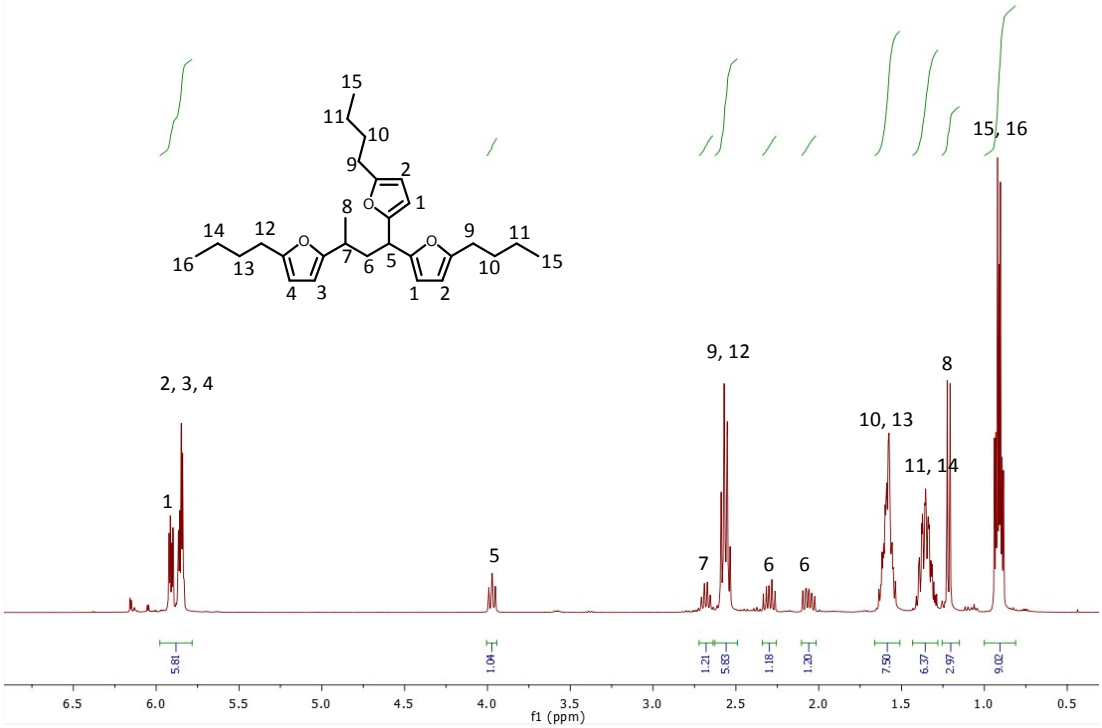
GC-MS (MS spectrum)

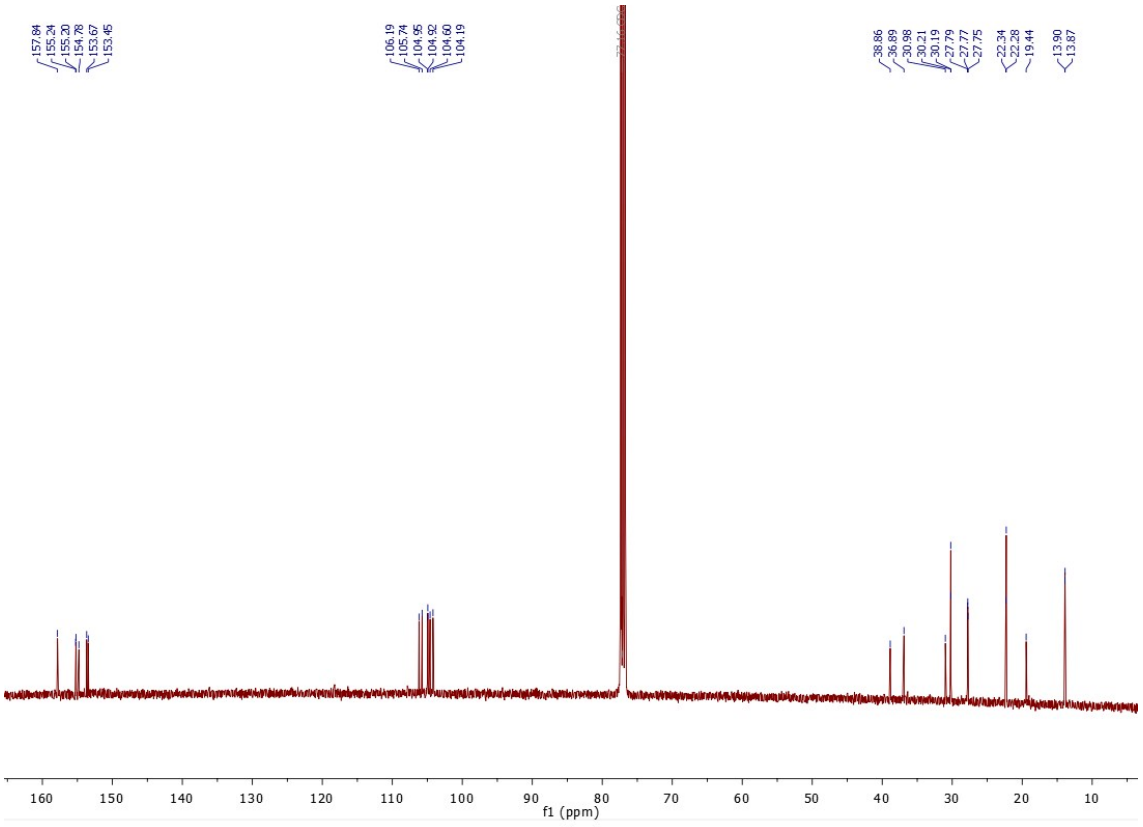


HR-MS-LIFDI: $C_{25}H_{34}O_3$ Calc. mass 382.2508; found mass 382.2514.

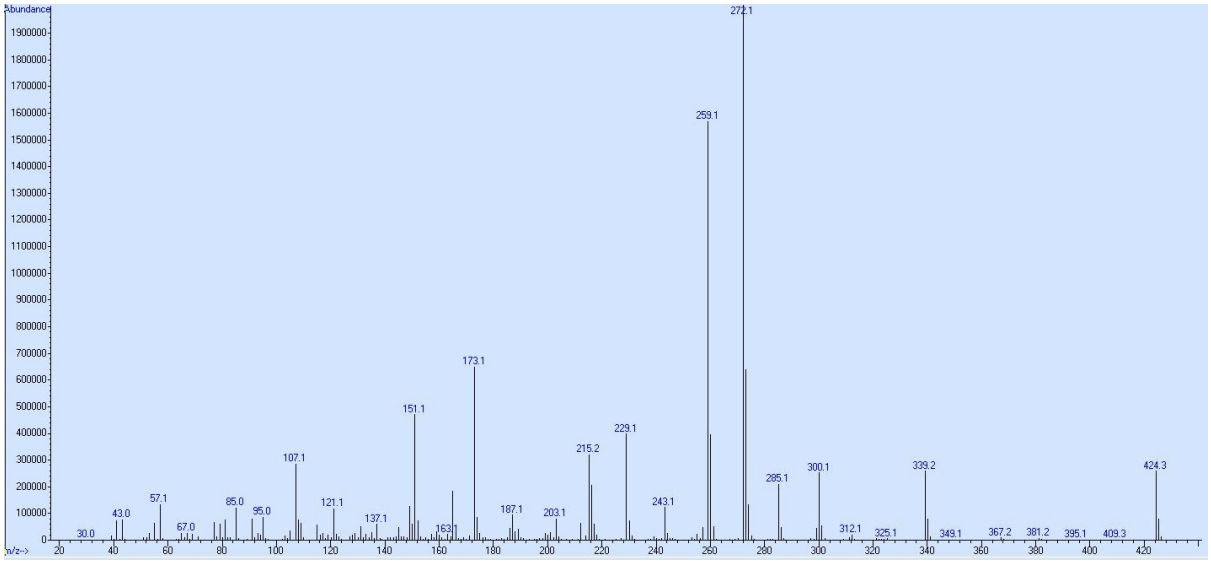
C_{28} condensed furan: CA-HAA of 2-butylfuran + crotonaldehyde

^{1}H and ^{13}C-NMR spectra





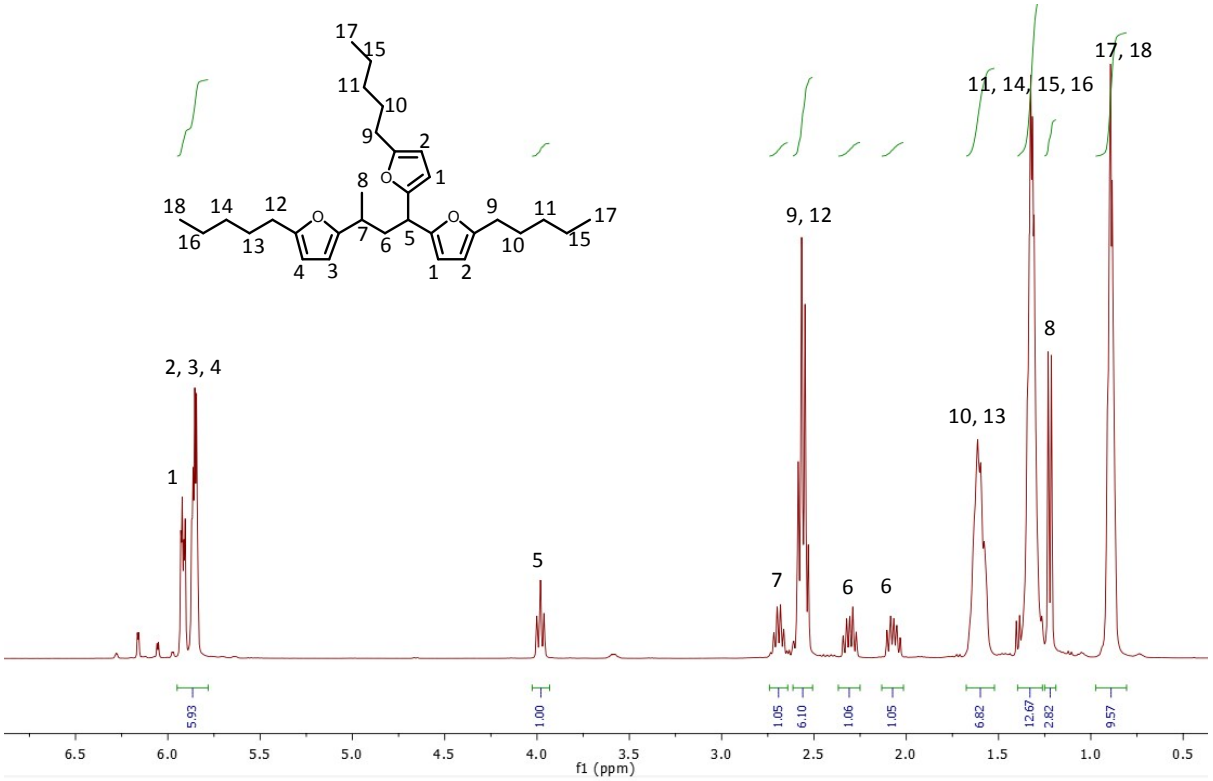
GC-MS (MS spectrum)

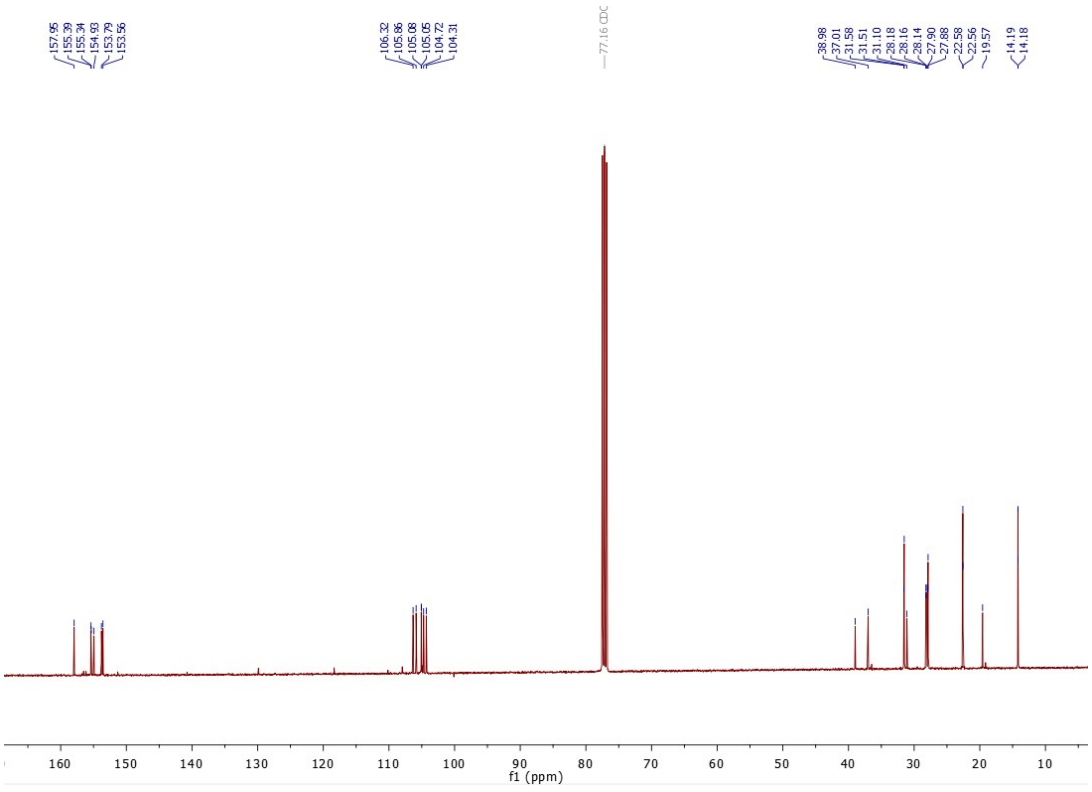


HR-MS-LIFDI: $C_{28}H_{40}O_3$ Calc. mass 424.2977; found mass 424.2959.

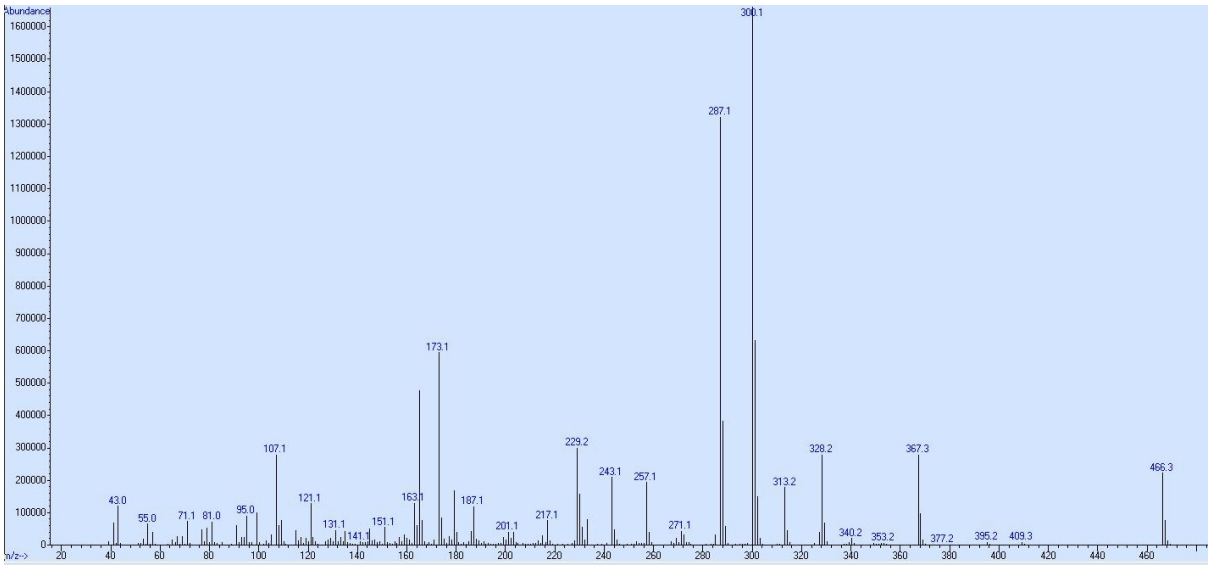
C_{31} condensed furan: CA-HAA of 2-pentylfuran + crotonaldehyde

^{1}H and ^{13}C-NMR spectra





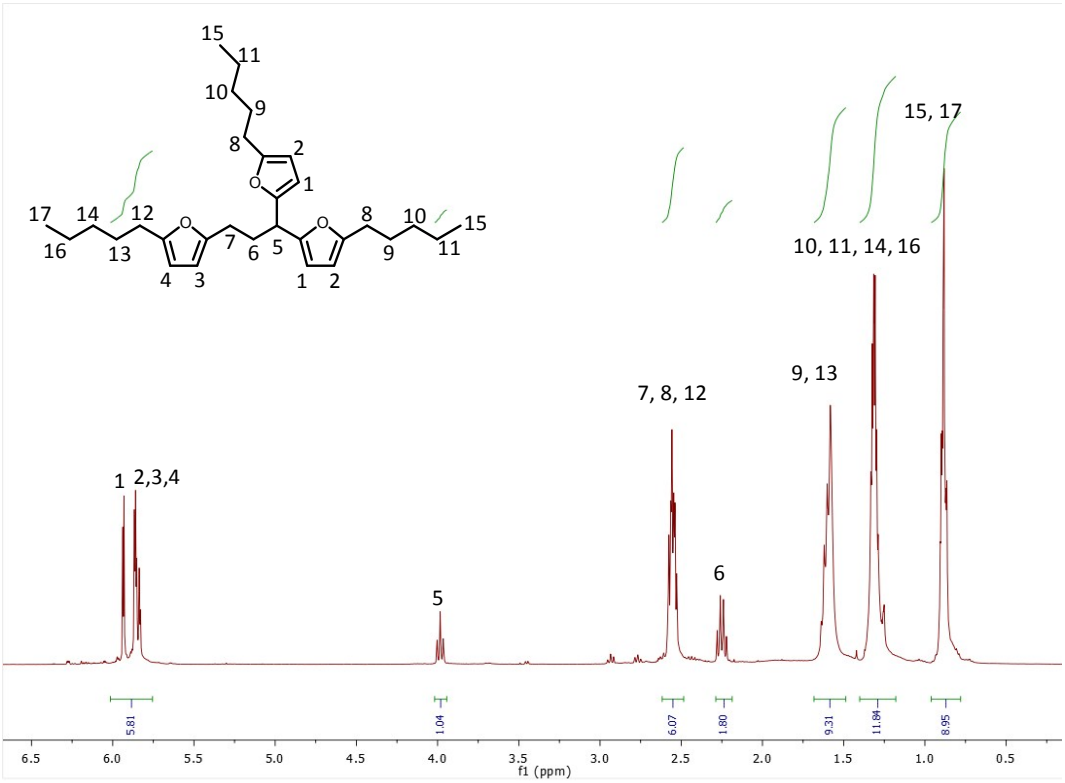
GC-MS (MS spectrum)

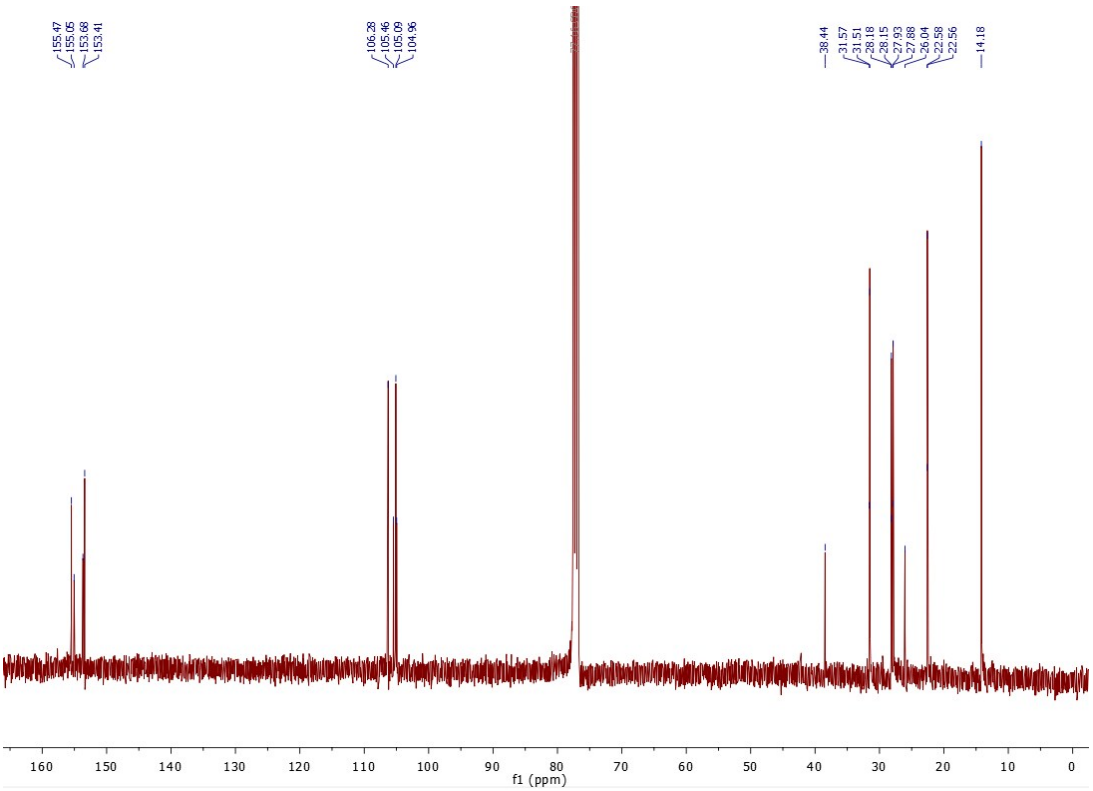


HR-MS-LIFDI: $C_{31}H_{46}O_3$ Calc. mass 466.3460; found mass 466.3447.

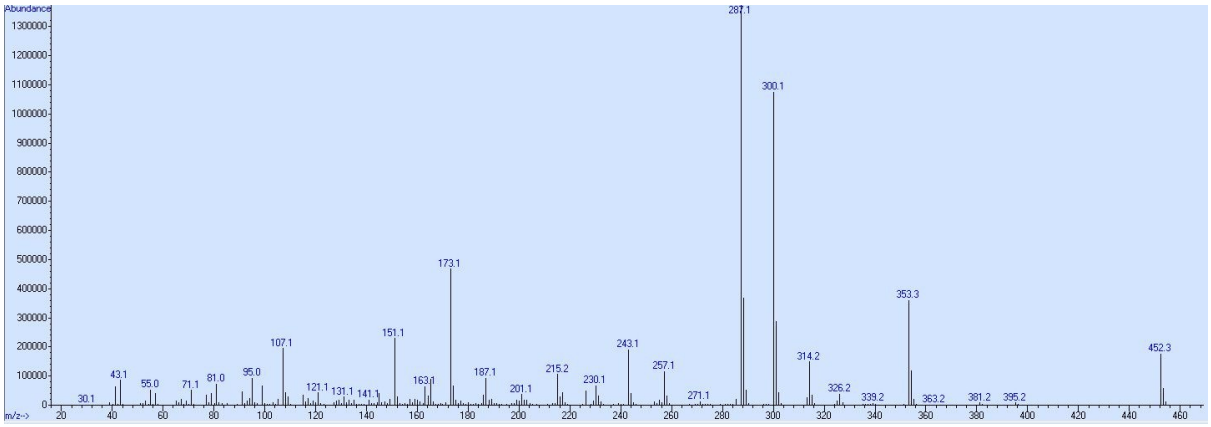
C_{30} condensed furan: CA-HAA of 2-pentylfuran + acrolein

^{1}H and ^{13}C-NMR spectra





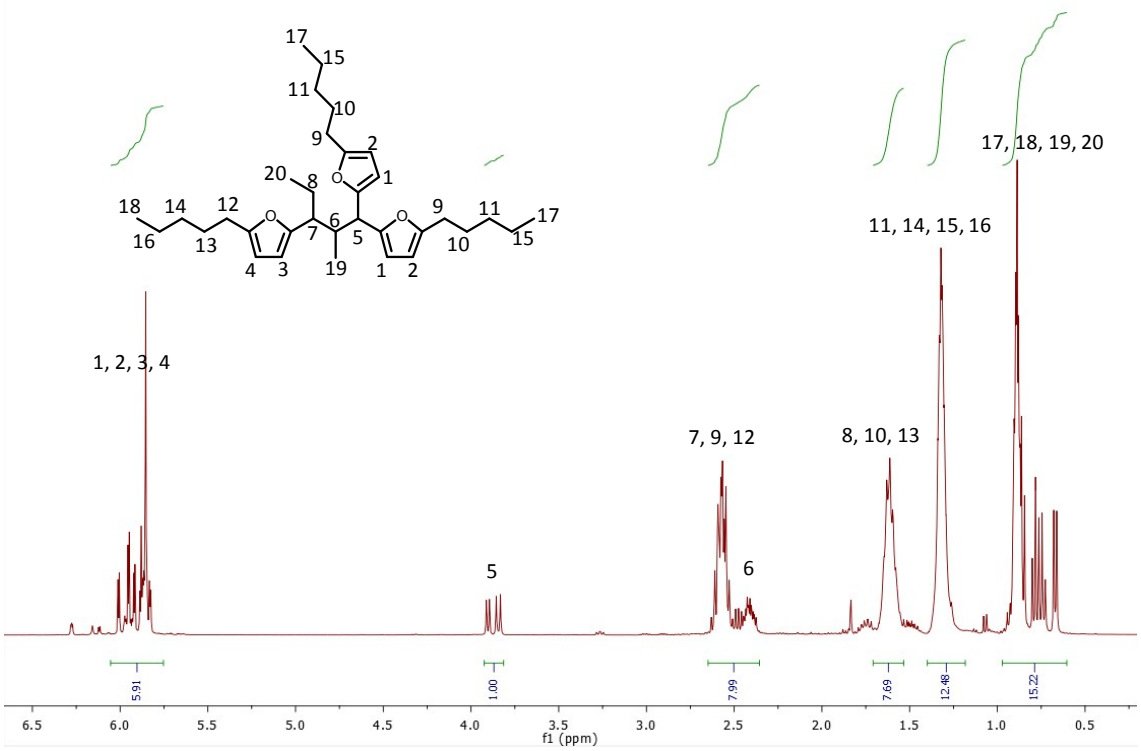
GC-MS (MS spectrum)

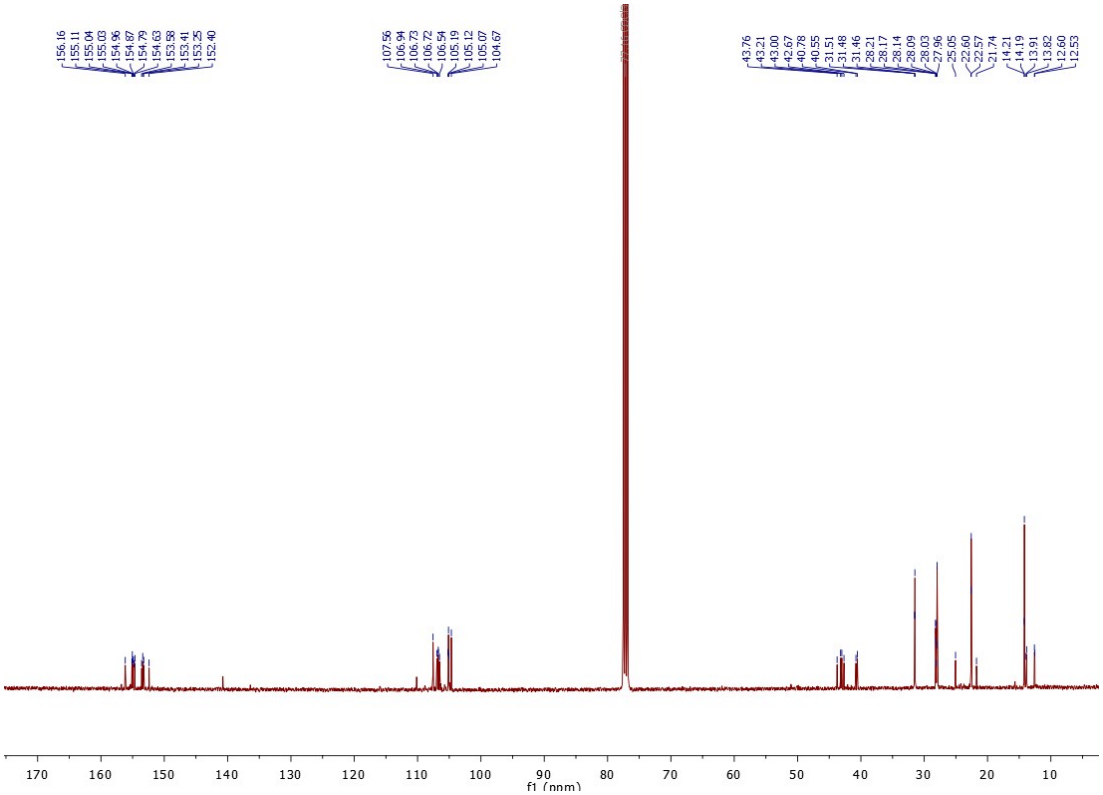


HR-MS-LIFDI: $C_{30}H_{44}O_3$ Calc. mass 452.3290; found mass 452.3285.

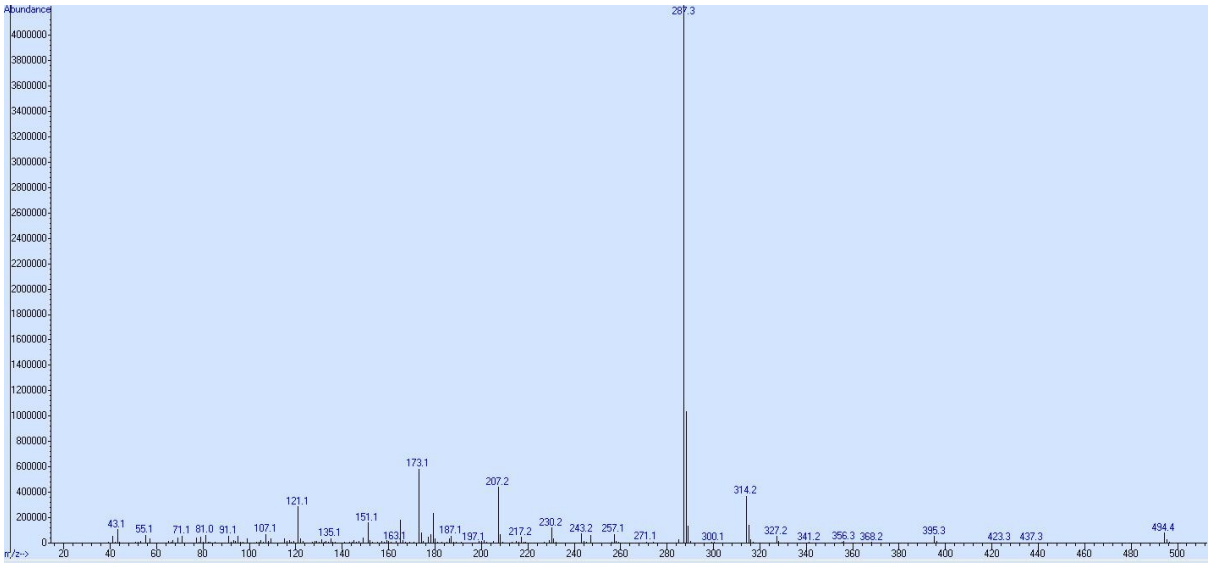
C_{33} condensed furan: CA-HAA of 2-pentylfuran + 2-methyl-2-pentenal

^{1}H and ^{13}C-NMR spectra





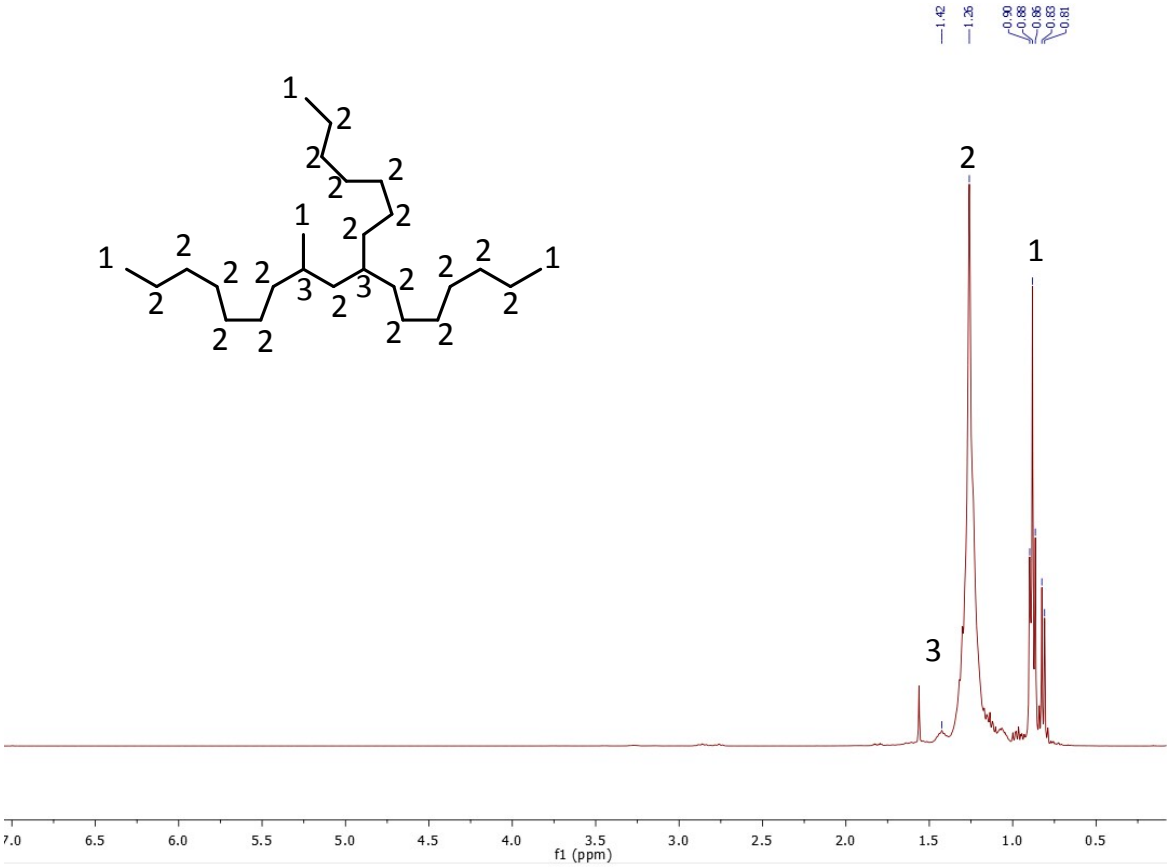
GC-MS (MS spectrum)

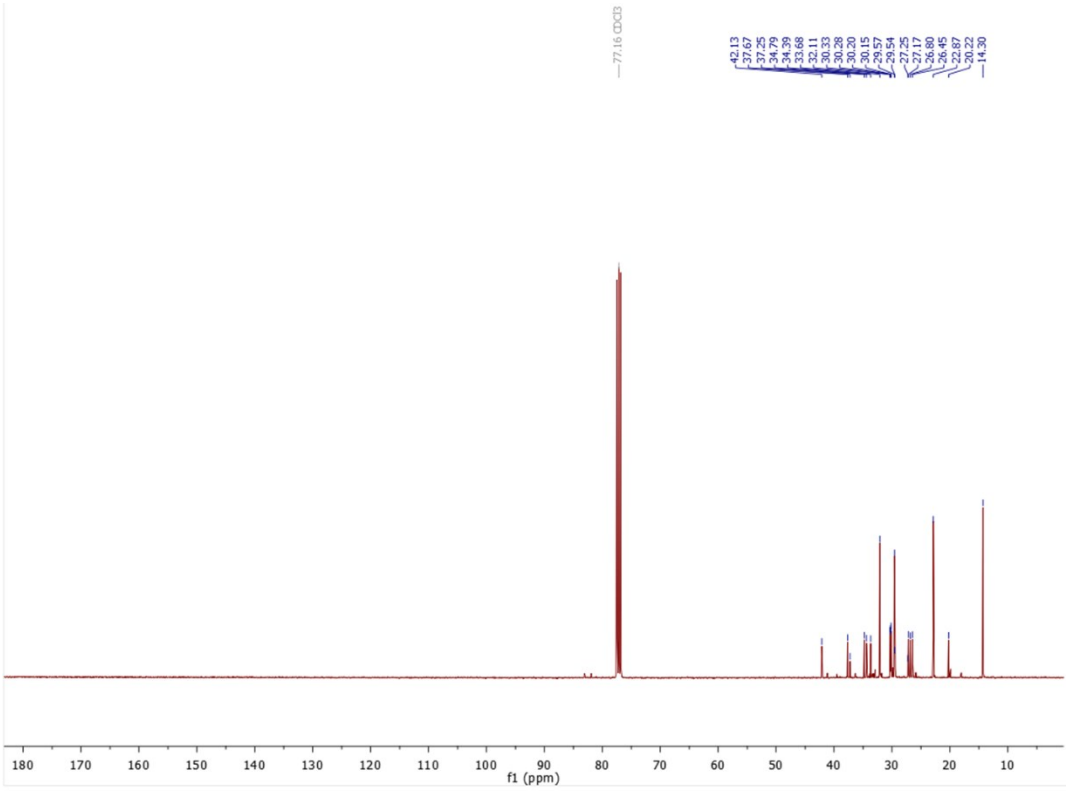


HR-MS-LIFDI: $C_{33}H_{50}O_3$ Calc. mass 494.3760; found mass 494.3793.

Base oil from HDO of C_{25} condensed furan

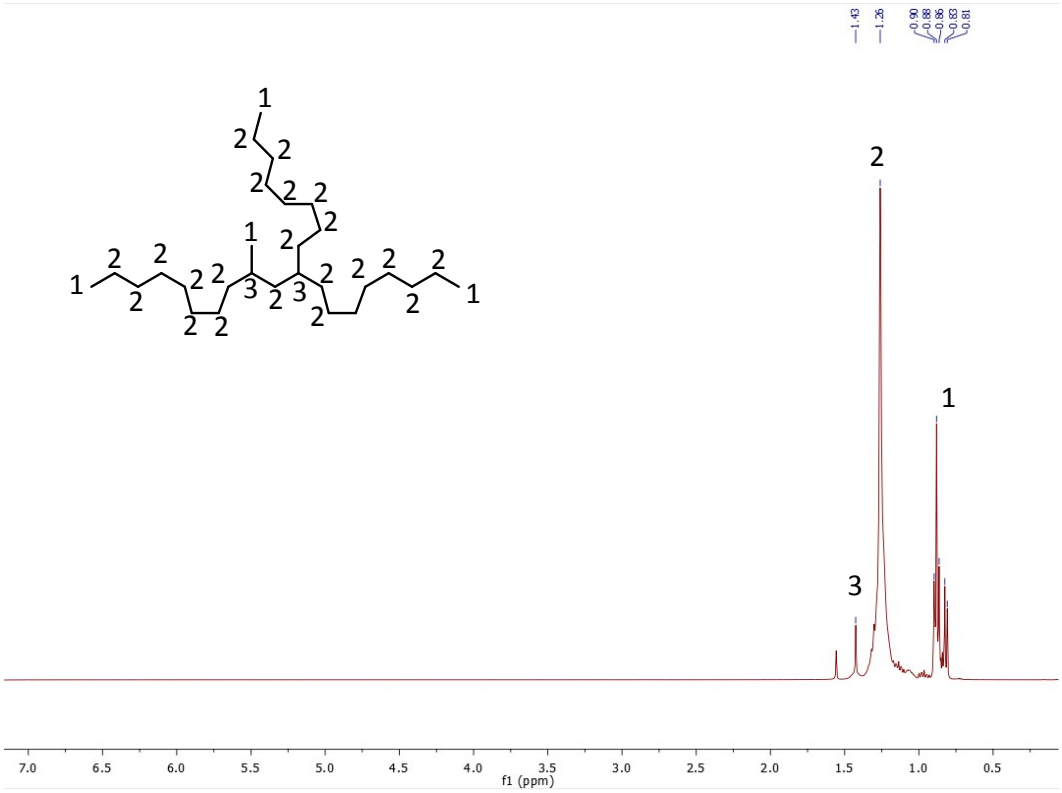
^{1}H and ^{13}C-NMR spectra

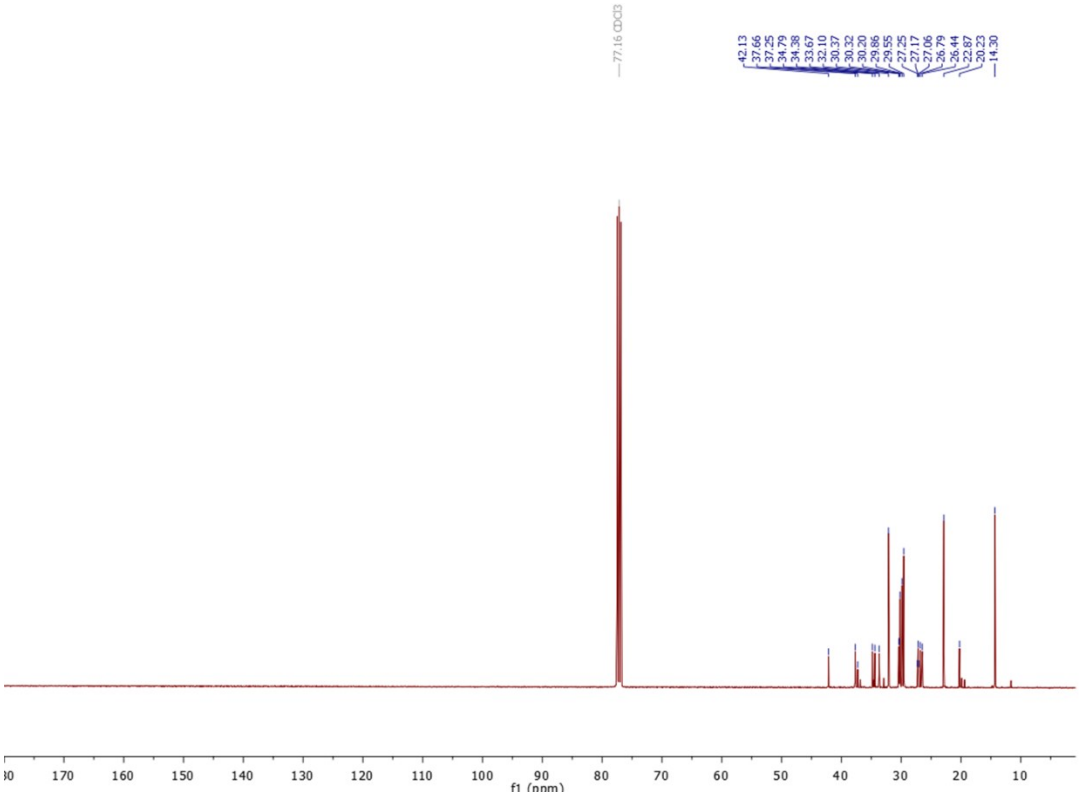




Base oil from HDO of C_{28} condensed furan

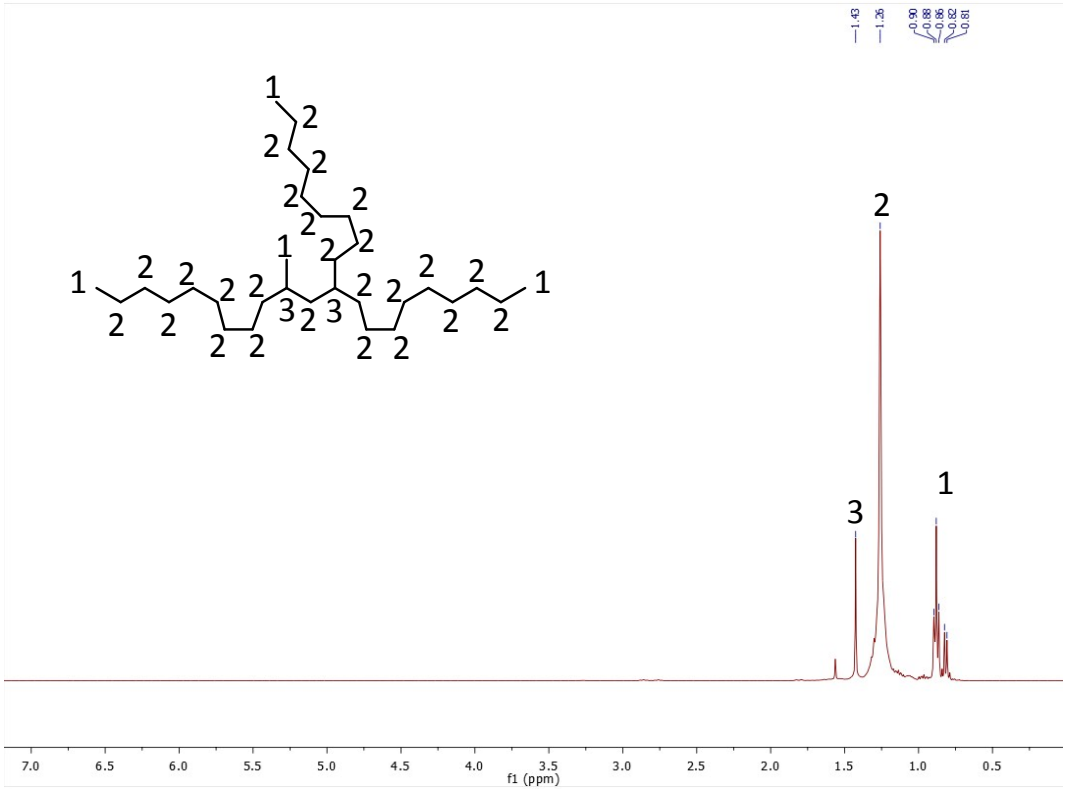
^{1}H and ^{13}C-NMR spectra

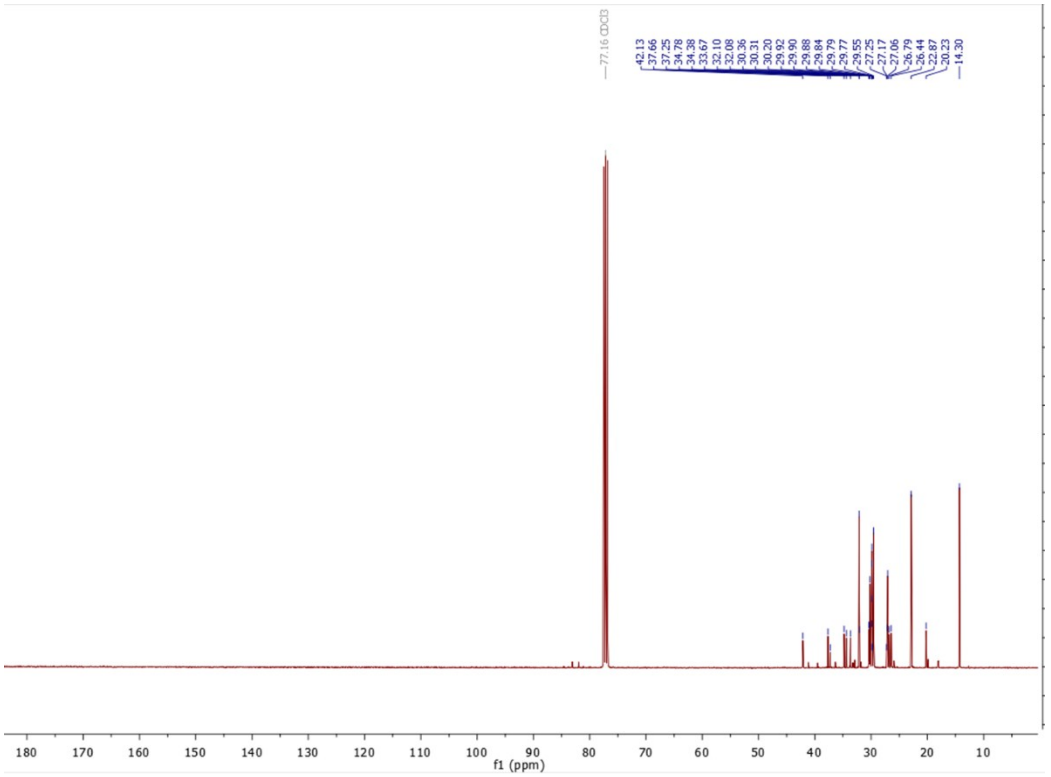




Base oil from HDO of C_{31} condensed furan

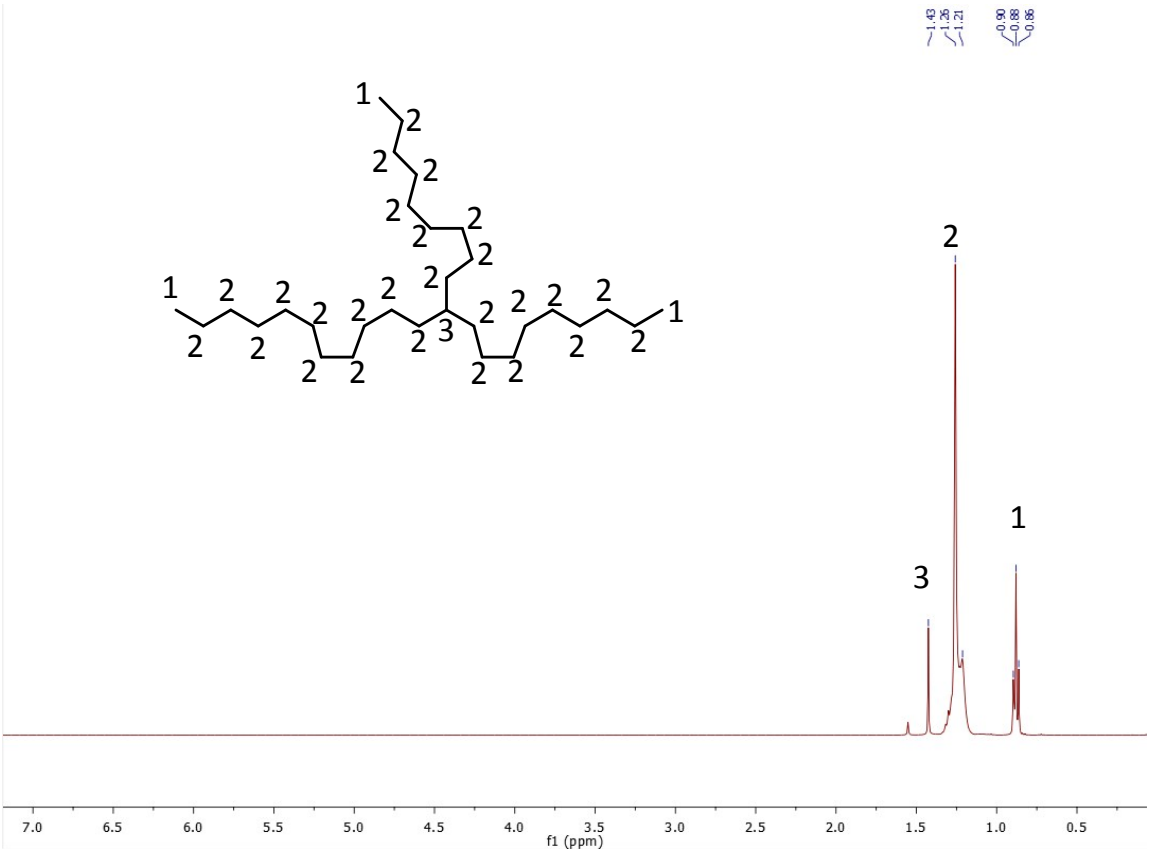
^{1}H and ^{13}C-NMR spectra

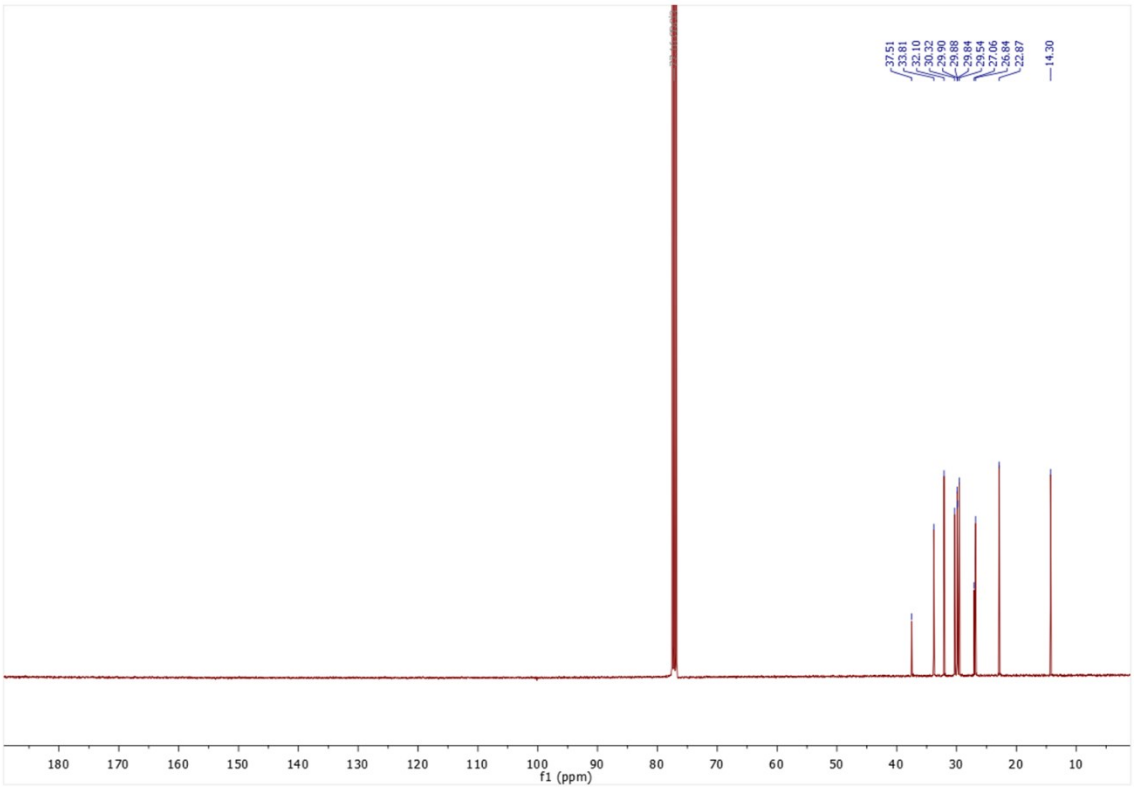




Base oil from HDO of C_{30} condensed furan

^{1}H and ^{13}C-NMR spectra





Base oil from HDO of C_{33} condensed furan

^{1}H and ^{13}C-NMR spectra