Electronic Supplementary Material (ESI) for Energy & Environmental Science

Electronic Supplementary Information

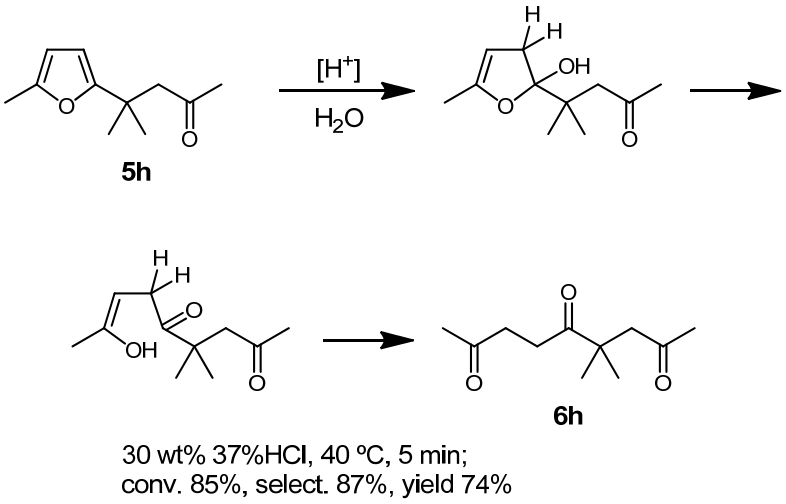
Table S1. Catalytic activity of different Faujasite (USY) and Beta zeolites synthesized in F^- medium (Beta (F^-)) and in alkaline medium (Beta (OH^-)) for the hydroxyalkylation/alkylation of Sylvan (**1**) with butanal (**2a**).

Reaction conditions: Sylvan (3.00 g) and butanal (1.30g; molar ratio 2 : 1) were mixed, a 50-mg sample of the catalyst was added and the reaction mixture stirred magnetically and heated to 50 ºC for 8 h.

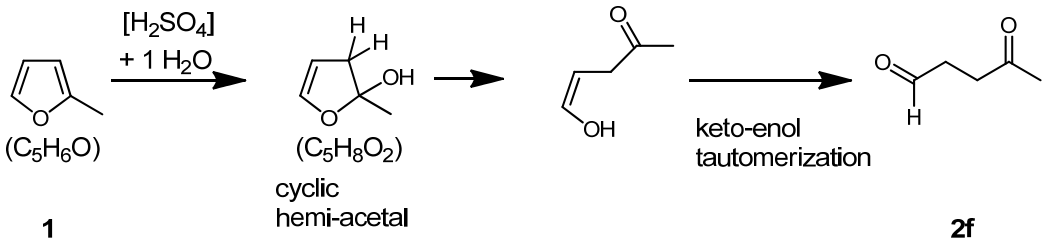
Entry	Catalyst	Si/Al ratio[a] [mol/mol]	BET[b] [m^2g^{-1}]	V_0[c] [cm^3g^{-1}]	Initial activity[d] [mmol g^{-1} h^{-1}]	Yield[e] [%]	TON[f] [mol/mol]
1	USY	2.5	554	0.240	14	4	3
2	USY	6.0	562	0.213	65	9	14
3	USY	15.0	641	0.233	115	18	69
4	USY	20.0	673	0.229	331	53	241
5	USY	27.5	551	0.180	144	36	230
6	Beta (F^-)	13	517	0.24	29	16	49
7	Beta (F^-)	27	519	0.23	39	33	197
8	Beta (F^-)	47	486	0.22	37	18	191
9	Beta (F^-)	103	471	0.22	35	11	246
10	Beta (F^-)	∞	457	0.22	0	0	0
11	Beta (comm.)[g]	13	607	0.18	101	67	202
12	Beta (nano)[h]	15	590	0.24	111	59	199
13	Beta (OH^-)	13	580	0.24	72	34	102
14	Beta (OH^-)	26	576	0.26	10	9	50
15	Beta (OH^-)	∞			0	0	0

[a] Silicon to aluminum ratio in the zeolite. [b] BET surface area. [c] Microporous volume. [d] Initial activity in mmol of product/g of catalyst/h; measured after 15 min reaction time. [e] Yield of 2,2'-butylidenebis[5-methylfuran] (**3a**) with a purity of at least 93% after 8 h reaction time. [f] mol of product obtained per mol of Al. [g] Commercial sample from Zeolyst. [h] Nanocrystalline sample.

Scheme S1. Transformation of ketone **5h** into triketone **6h** by hydrolysis of the furan ring. Alternatively, the initial water attack may also occur to the other furan double bond.



Scheme S2. Proposed mechanism for the hydrolysis of Sylvan (**1**) to 4-oxopentanal (**2f**).



Scheme S3. Possible pathways for the by-product formation in the hydrodeoxygenation (hdo) of difuran **3a**.

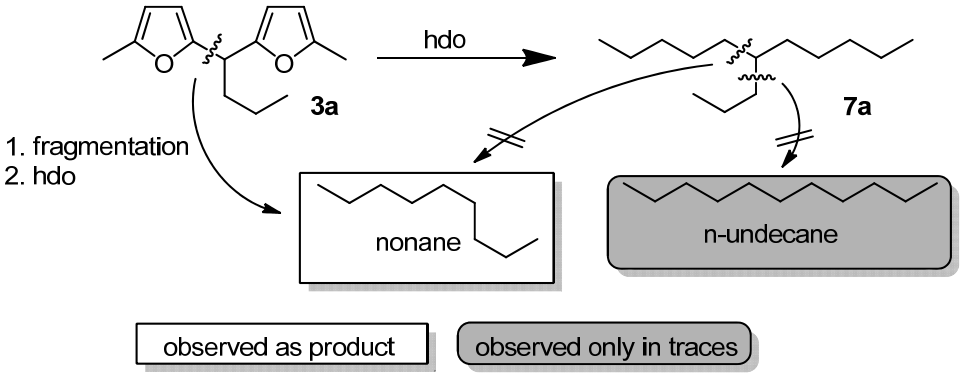


Figure S1. Yield of difuran **3a** when synthesized in the presence of USY and H-Beta (F^-) zeolite sample with different Si/Al ratios.

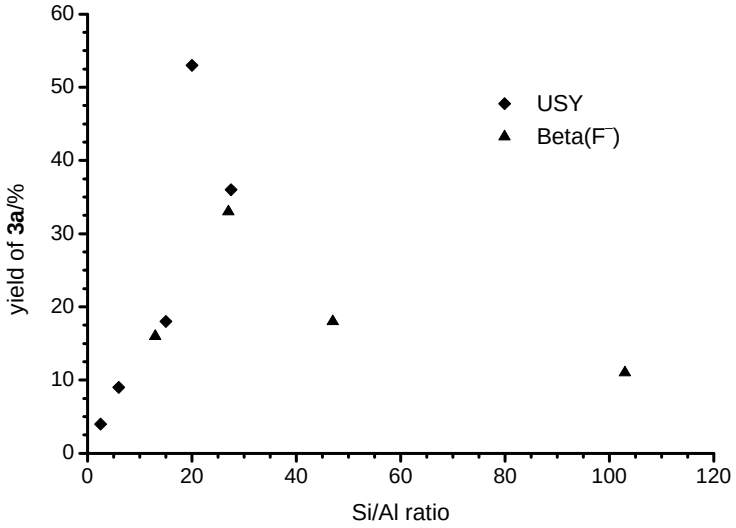


Figure S2. Molecular dimensions of diesel precursor **3a** (left hand side) and the pore diameter of Beta zeolite (right hand side).

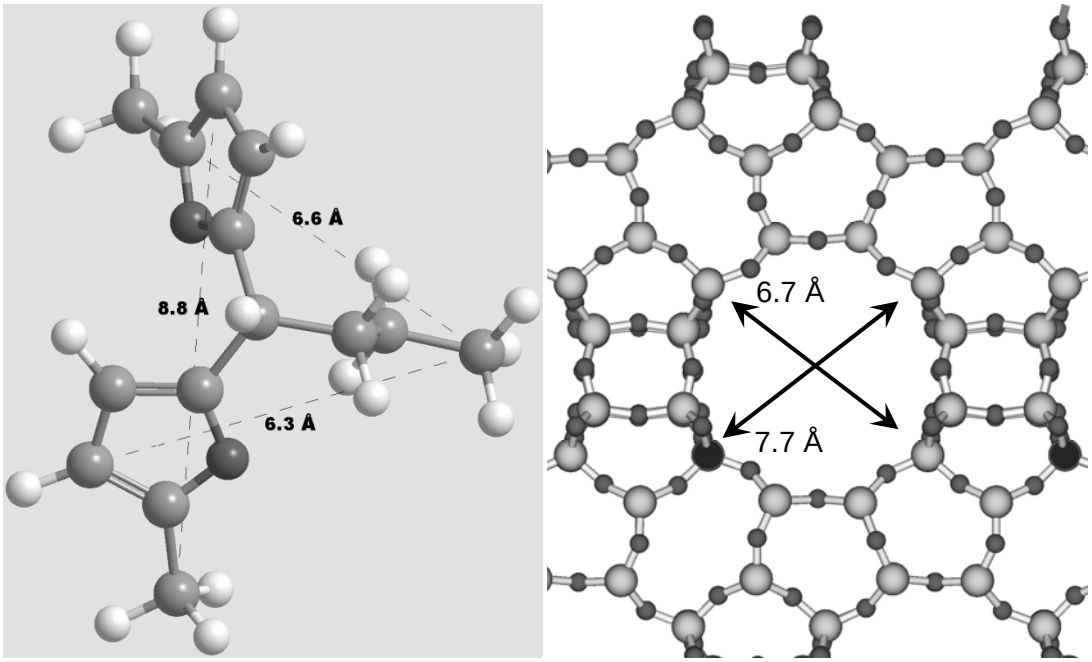


Figure S3. TEM image of catalyst Beta (Zeolyst) with ratio of Si/Al = 13.

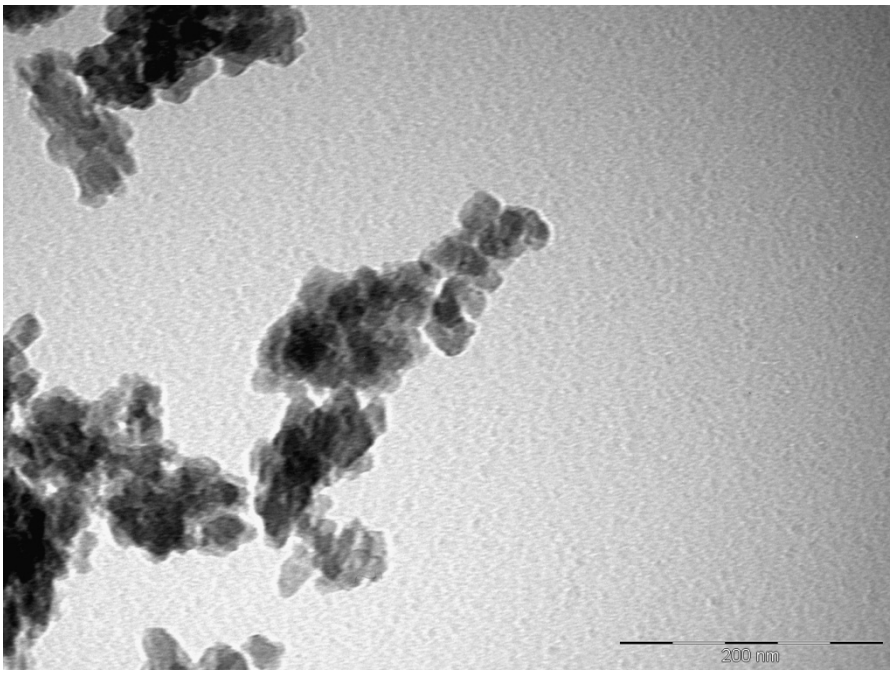


Figure S4. TEM image of catalyst Beta nanocrystalline with ratio of Si/Al = 15.

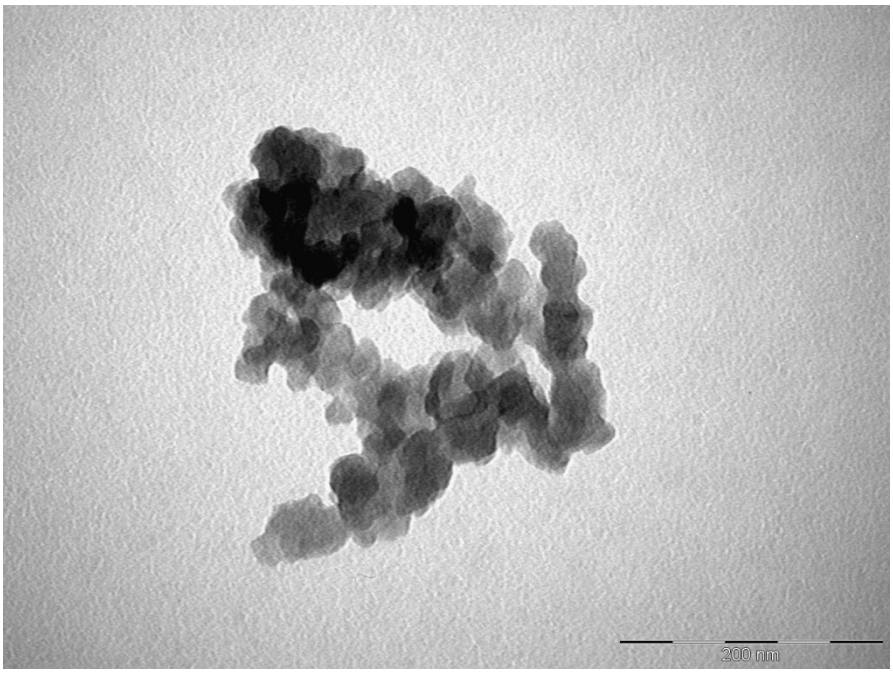


Figure S5. SEM image of catalyst Beta (OH^-) with ratio of Si/Al = 13.

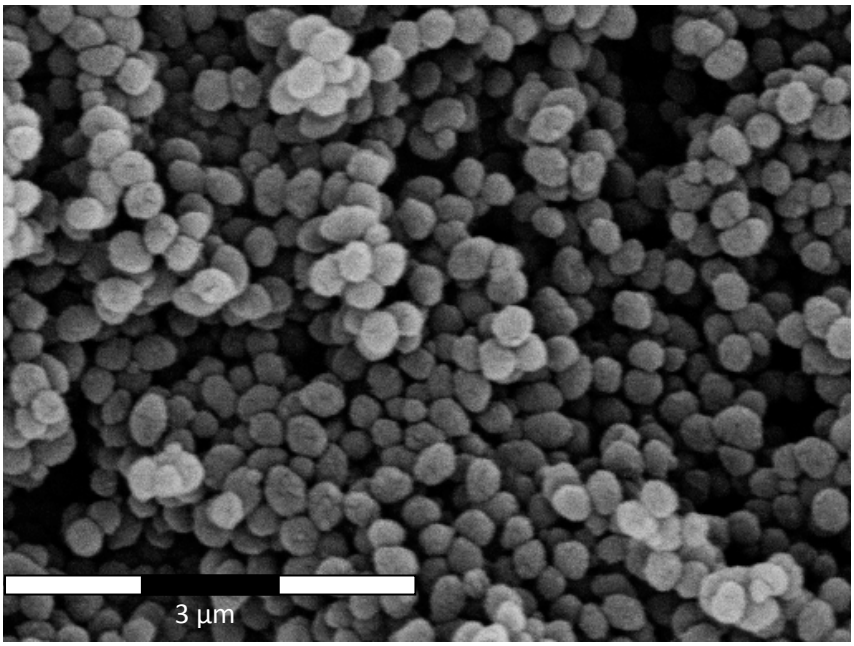


Figure S6. SEM image of catalyst Beta (F^-) with ratio of Si/Al = 13.

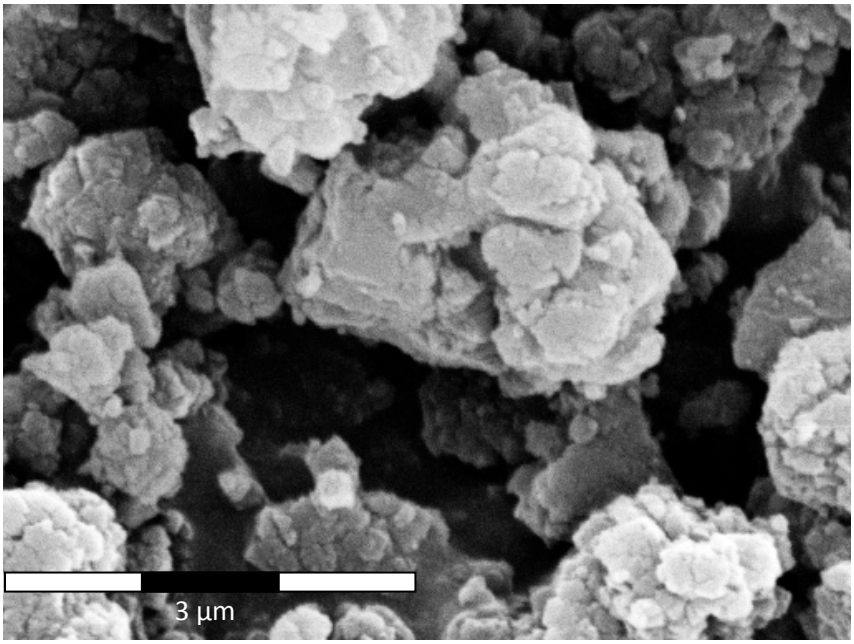


Figure S7. Yields (wt%) of aqueous and organic phase in the recycling reactions of the aqueous acidic phase in the trimerization of Sylvan. After each cycle the aqueous phase is recovered by decantation, lost liquid replaced and submitted to the next cycle with fresh Sylvan.

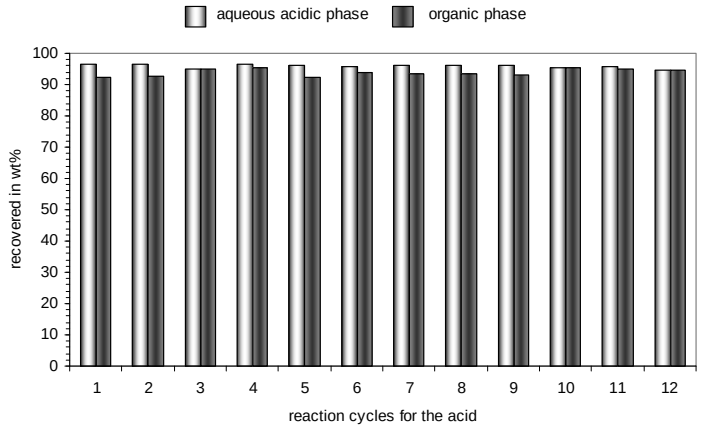


Figure S8. Product distribution of the organic liquid phase obtained by catalytic hydrodeoxygenation of difuran **3a** during 140 h time on stream.

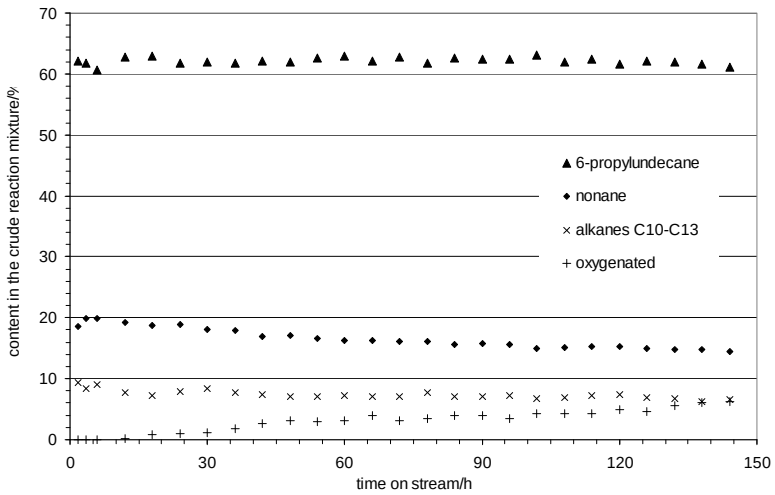


Figure S9. Conversion and product yield for the hydrogenation of 2-methyltetrahydrofuran in the liquid phase carried out at 350ºC in a fixed-bed continuous-flow reactor equipped with a Pt/C catalyst. In the liquid phase 35 wt% to 50 wt% of the feed were recovered.

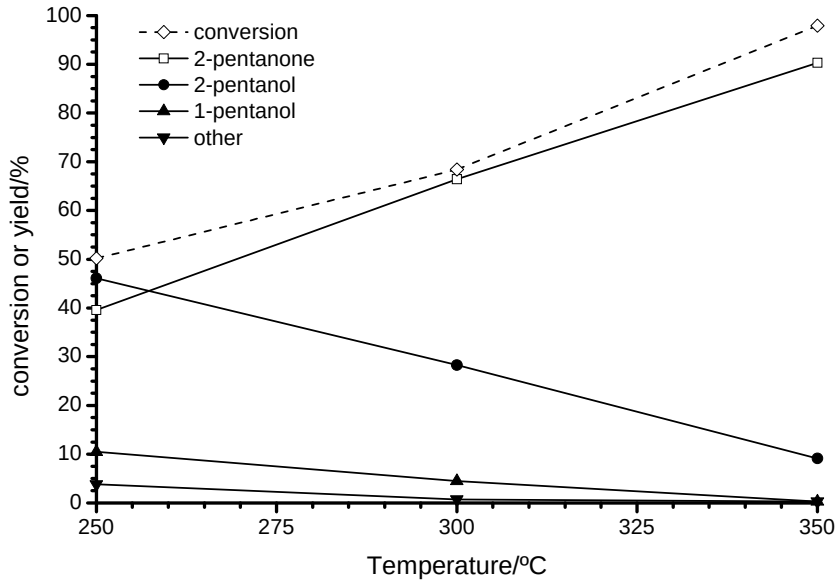


Figure S10. ^{1}H NMR spectrum of 6-(5-methyl-2-furanyl)-6-methyl-2,5-nonadione (**4g**).

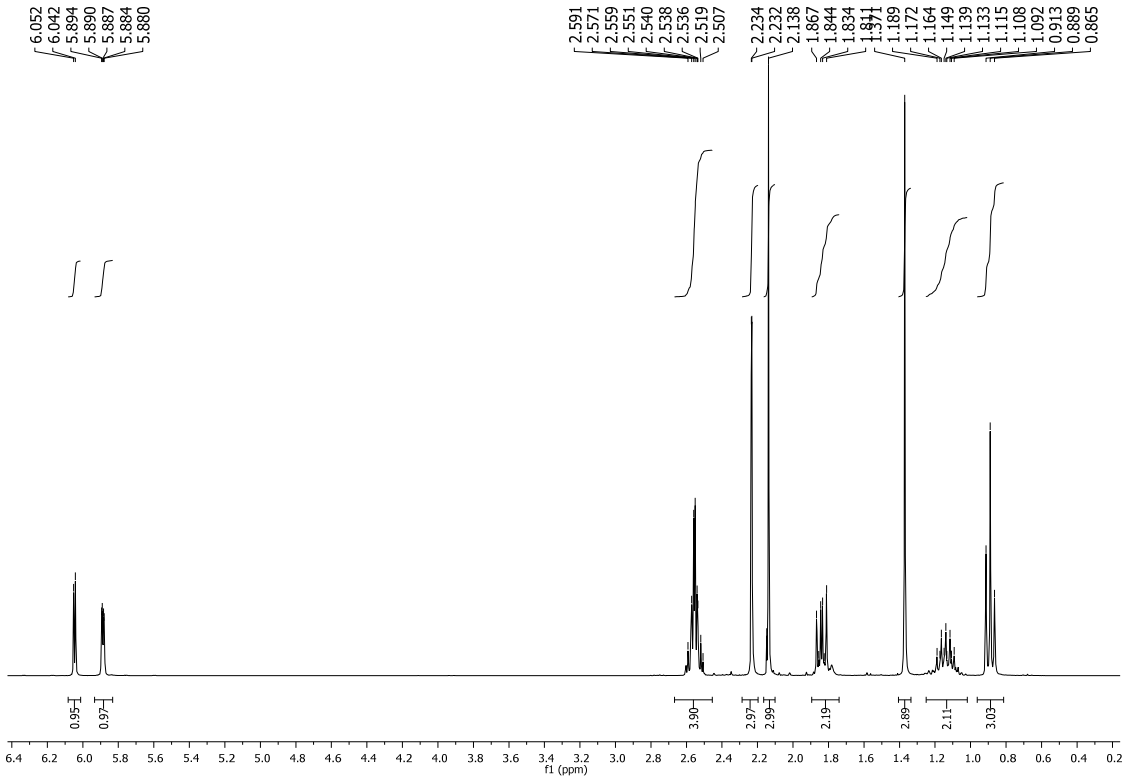


Figure S11. ^{13}C NMR spectrum of 6-(5-methyl-2-furanyl)-6-methyl-2,5-nonadione (**4g**).

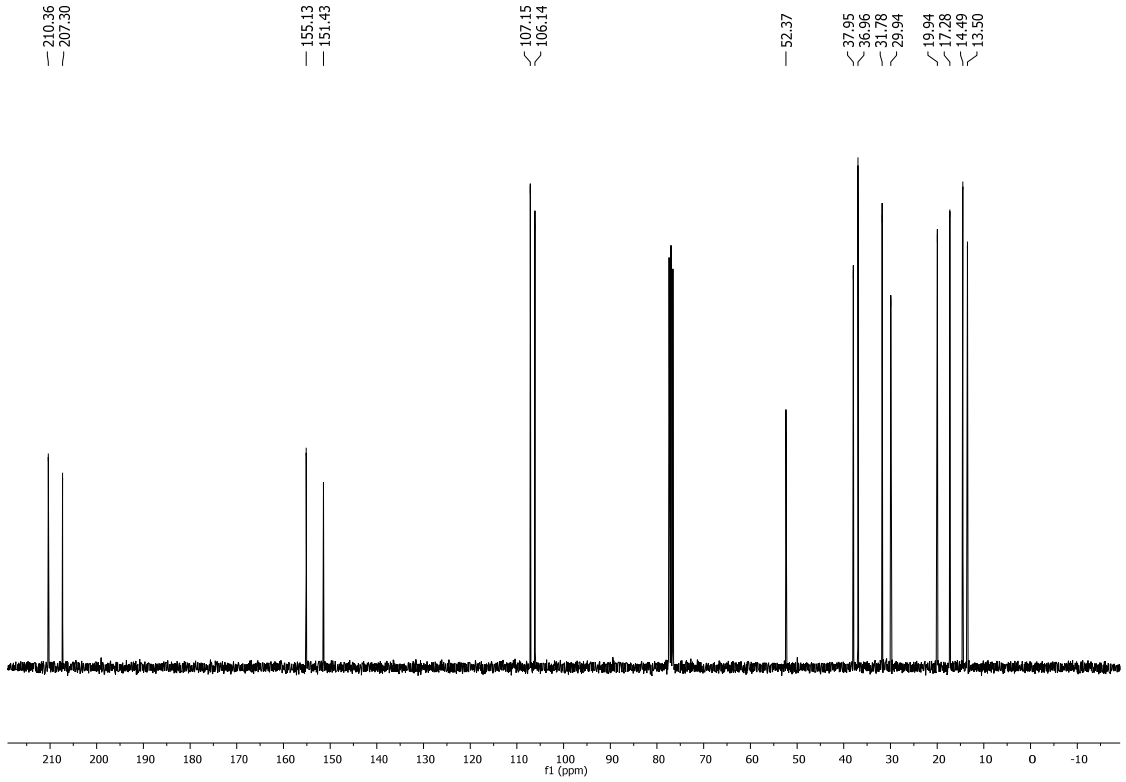


Figure S12. ^{13}C NMR and DEPT (upper line) spectra of 6-propylundecane (**7a**).

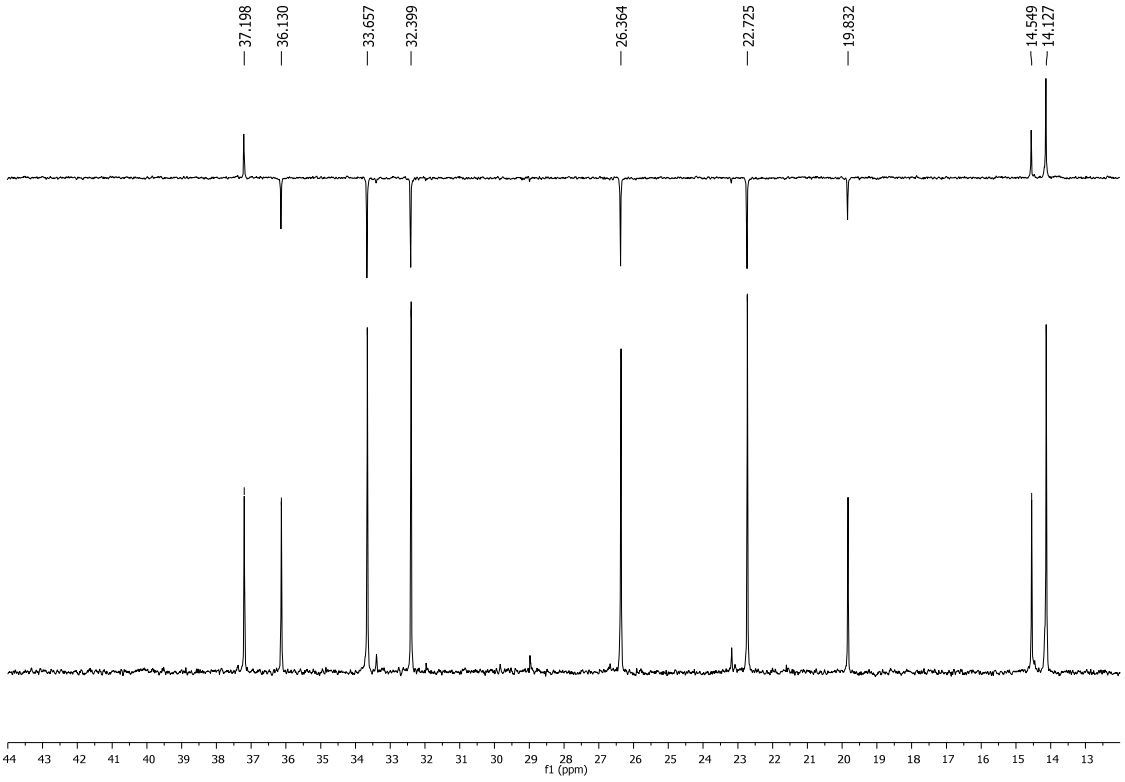


Figure S13. ^{1}H NMR spectrum of 6-propyl-2,10-undecanedione (**9a**).

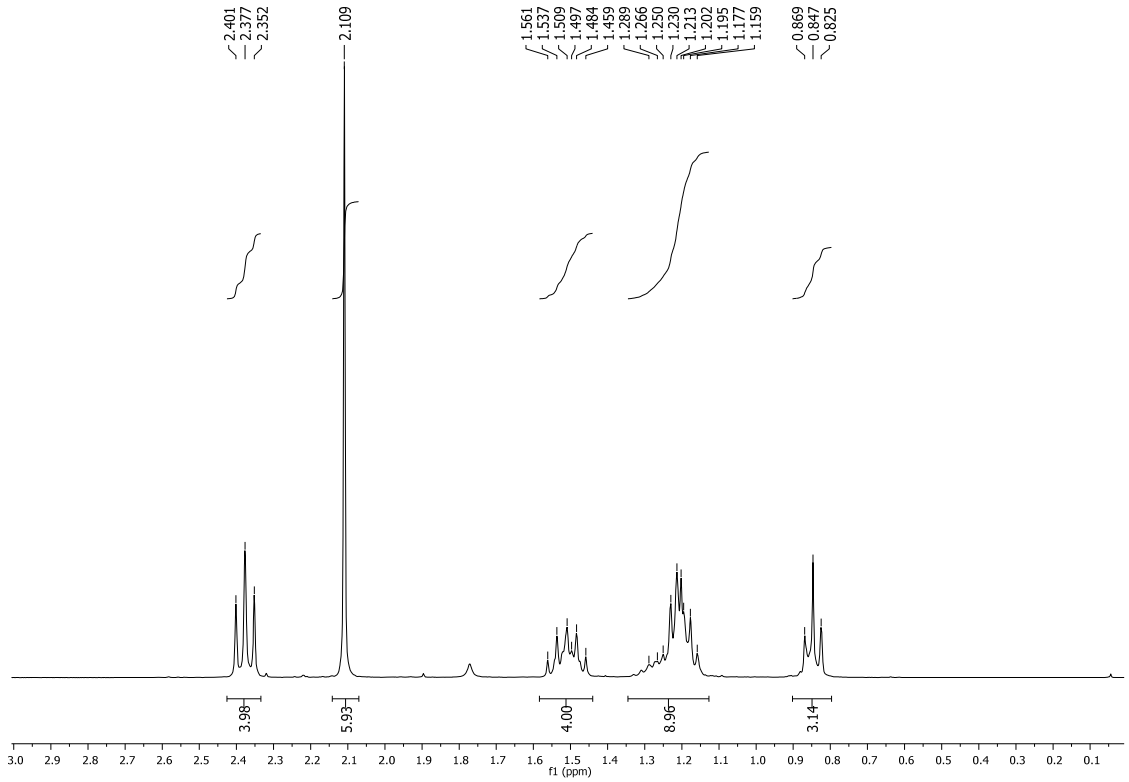


Figure S14. ^{13}C NMR and DEPT (upper line) spectra of 6-propyl-2,10-undecanedione (**9a**).

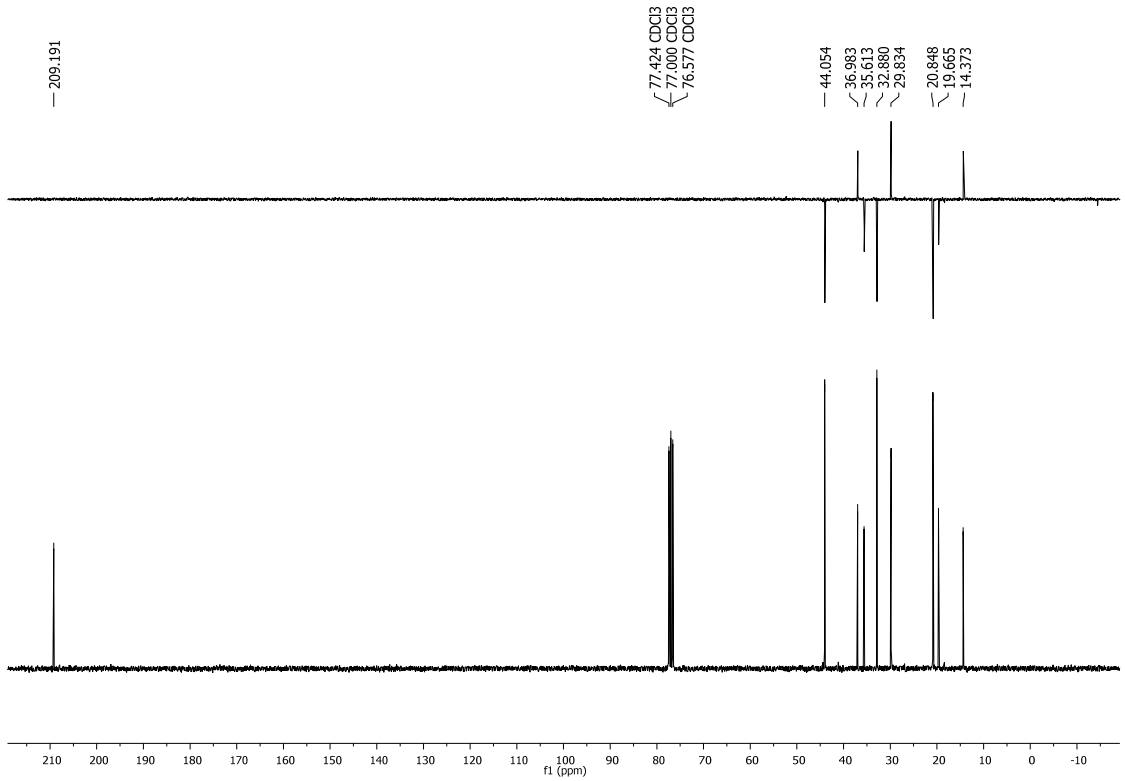


Figure S15. ^{1}H NMR spectrum of 6-propyl-2,7-undecanedione (**10a**).

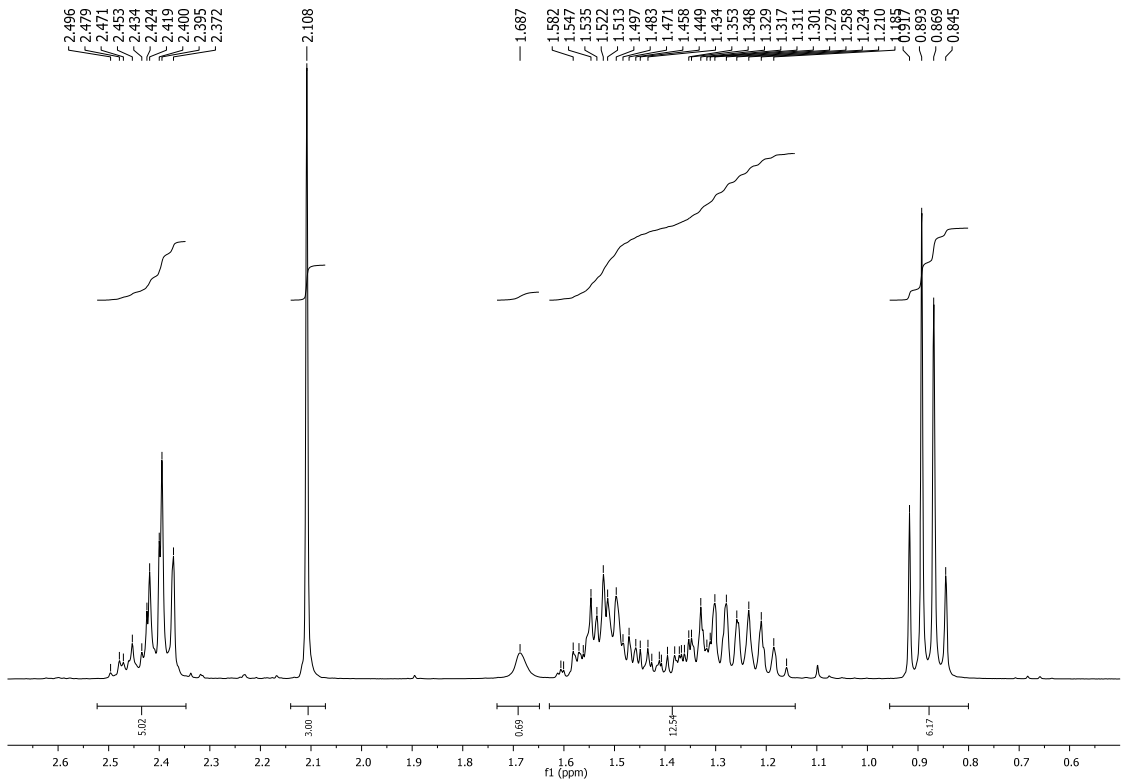


Figure S16. ^{13}C NMR and DEPT (upper line) spectra of 6-propyl-2,7-undecanedione (**10a**).

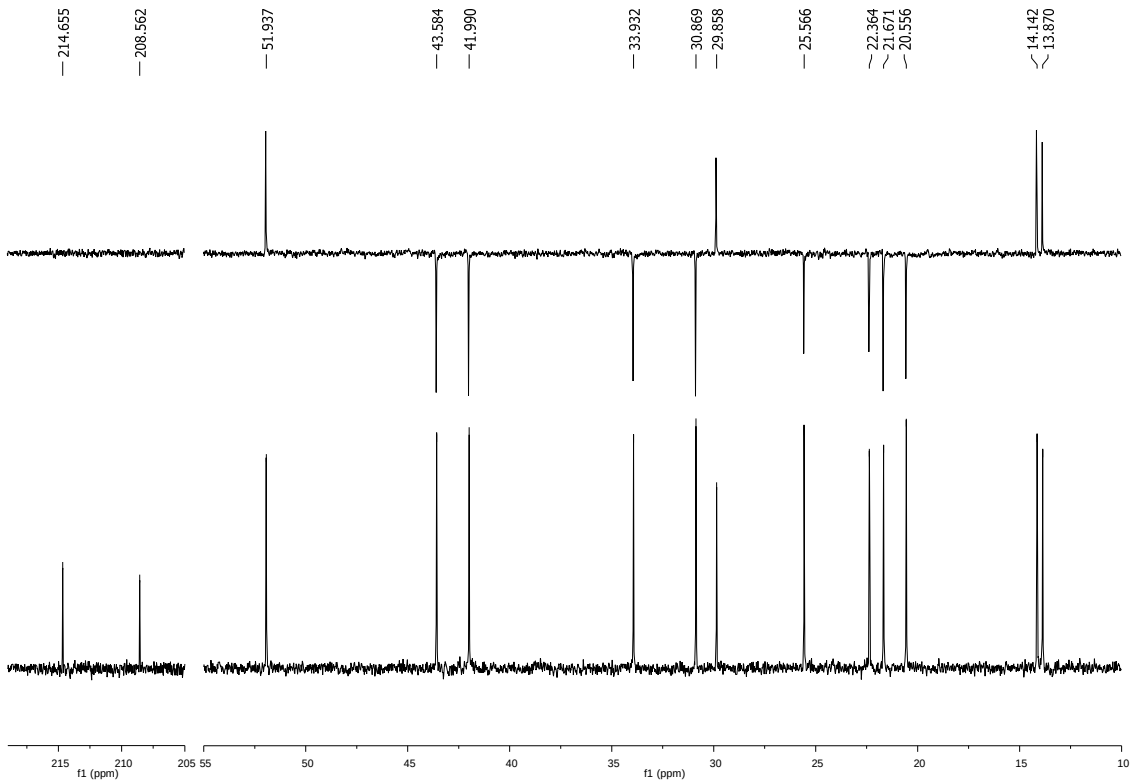


Figure S17. ^{13}C NMR spectrum of 6-propyl-5-undecanone (**8a**).