Supporting Information

Biomolecule-derived supported cobalt nanoparticles for hydrogenation of industrial olefins, natural oils and more in water

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Content

S1. General Information, materials and methods

All catalyst preparation reactions were performed in dried glassware under atmosphere of dry argon unless otherwise noted. All hydrogenation reactions were performed in 8-mL glass vials, which were placed inside the 300mL autoclave series P4560 made of stainless steel by

Parr Instrument Company. All chemicals were purchased from Aldrich, abcr GmbH, Acros, Alfa Asar, TCI Europe or Strem and used as received without further purification unless otherwise noted. Solvents were additionally purified, degased or distilled under argon atmosphere. For hydrogenation reactions deionized water was used as solvent. Diisobutene and octenes were dried and distilled prior to use. Chemicals used for the catalyst preparation: Cobalt (II) acetate tetrahydrate, 98% (Alfa Aesar); Carbon powder, Vulcan XC72R (Cabot Corporation Prod., LOT 4173260); Aluminum oxide (activated acidic), Brockmann Grade, 60 mesh powder (Alfa Aesar), Aluminum oxide (activated, basic), 70-230 mesh (Merck). **Apricot kernel oil** was purchased from “Vom Fass” AG from Rostock (main components are: palmitic acid (saturated, $C_{15}H_{31}$) 5.9%; stearic acid (saturated, $C_{17}H_{35}$) 1.6%; oleic acid (mono unsaturated, $C_{17}H_{33}$) 66,1%; linoleic acid (doubly unsaturated, $C_{17}H_{31}$) 25.3%). Organic **linseed oil** was purchased from REWE GmbH Market (main components are: palmitic acid (saturated, $C_{15}H_{31}$) 7%; stearic acid (saturated, $C_{17}H_{35}$) 3.4–4.6%; oleic acid (monounsaturated, $C_{17}H_{33}$) 18.5–22.6%; linoleic acid (doubly unsaturated, $C_{17}H_{31}$) 14.2–17%; alpha-linolenic acid (triply unsaturated, $C_{17}H_{29}$) 51.9–55.2%). Refined **castor oil** was purchased from pharmacy, product of Henry Lamotte Oils GmbH (main components are: ricinoleic acid (monounsaturated, $C_{17}H_{33}O$) 85–95%; oleic acid (monounsaturated, $C_{17}H_{33}$) 2–6%; linoleic acid (doubly unsaturated, $C_{17}H_{31}$) 1–5%).

All compounds were characterized by ^{1}H NMR, ^{13}C NMR, and GC-MS or HRMS.

^{1}H **NMR** spectra were recorded on Bruker AV 300, Bruker Fourier 300 and AV 400 spectrometers spectrometers (300 or 400 MHz). ^{13}C NMR spectra were recorded at 75.5 or 101 MHz. Chemical shifts are reported in ppm relative to the centre of solvent resonance. Spectra were referenced to residual $CHCl_3$ (7.27 ppm ^{1}H; 77.00 ppm ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), hept (heptet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz.

Gas chromatography analysis was performed on an Agilent HP-7890A chromatograph with a FID instrument and HP-5 column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thicknesses) using argon as carrier gas. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Time-of-Flight LC/MS (Agilent) with electrospray ionization (ESI). The data are given as mass units per charge (m/z).

All yields reported refer to GC yield using hexadecane or NMR yield using mesitylene as internal standard. The reaction conditions were not optimized for every single compound.

The **pyrolysis** experiments were carried out in Nytech-Qex oven. Crucibles (height – 20 mm, top Ø – 40 mm, Ar. Nr. L219.1) and lids (Ø – 40 mm, Ar. Nr. L236.1) were purchased from Roth Industries GmbH & Co. KG.

Elemental analysis was carried out with a TruSpec micro by Leco. The substances were burned in pure oxygen in a flow of helium.

AAS was measured on contrAA 800D by Analytik Jena, using a flame atomizer and acetylene flame. Solid substances were mineralized with H_2SO_4-$KHSO_4$. Liquid samples in organic solvents were liberated of the volatiles in vacuum and the residue was mineralized with aqua regia (HCl : HNO_3 = 3:1) at 140 °C for 4 h.

XRD powder pattern were recorded either on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector used with automatic divergence slits and Cu kα1/α2 radiation (40 kV, 40 mA; λ= 0.015406 nm, 0.0154443 nm). Cu beta-radiation was excluded by using nickel filter foil. The measurements were performed in 0.0167° steps and 400 s of data collecting time per step. The samples were mounted on silicon zero background holders. The collected data were converted from automatic divergence slits to fixed divergence slits (0.25°) before data analysis to obtain the correct intensities. Peak positions and profile were fitted with Pseudo-Voigt function using the HighScore Plus software package (Panalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

The **XPS** (X-ray Photoelectron Spectroscopy) measurements were performed on an ESCALAB 220iXL (ThermoFisher Scientific) with monochromated AlKα radiation (E = 1486.6 eV) and a spot size of 400 µm. The electron binding energies were obtained with mild charge compensation using a flood electron source. Binding energies are referenced to the C1s peak of graphitic carbon assuming sp^2 hybridization as main component at 284.0 eV. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves, the peak areas were divided by the transmission function of the spectrometer and a sensitivity factor obtained from the element specific Scofield factor.

The **STEM** (Scanning Transmission Electron Microscopy) measurements were performed at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive x-ray-spectrometer (EDXS) and an Enfinum ER (GATAN) with Dual EELS for chemical analysis. Dual EELS was done at a camera length of 4 cm, an illumination semi angle of 27.8 mrad and an entrance aperture semi angle of 41.3 mrad. The solid samples were dry deposed without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope.

Nitrogen adsorption–desorption isotherms collected at 77 K on BELSORP-mini II (BEL Japan) were used to calculate the specific surface area (S_{BET}) of the pyrolized catalysts Co-Ura/C-600 and Co-Ura/C-1000 applying the Brunauer, Emmet and Teller (**BET**) equation for N_2 relative pressure in the range of $0.05 < P/P_0 < 0.30$. The pore size distribution was derived from the desorption branch using the BJH method.

S2. Experimental procedure for the catalyst preparation

S2.1 Preparation of 6 gr Co-Ura/C catalysts: 3 wt.% cobalt-based, uracil ligated and vulcan supported catalyst

In 500 mL two-neck round bottomed flask, equipped with a reflux condenser and a magnetic stir bar, $Co(OAc)_2 \cdot 4H_2O$ (762.2 mg, 3.06 mmol, 1.0 equiv.) and ligand uracil (692.9 mg, 6.12 mmol, 2.0 equiv.) were dissolved in ethanol (360 mL). The flask was immersed in an oil bath and heated at 70 °C. After 30 min to the reaction mixture 4.77 g of Vulcan powder was added and the resulting heterogeneous mixture was heated for 4 h at 80 °C. The solvent was removed at the rotary evaporator and the residue was dried overnight at 65 °C under high-vacuum. The dried sample was grinded in an agate mortar to a fine powder (5.9 g), from which a 0.5 g portion was transferred to a ceramic crucible and pyrolyzed at temperatures between 500-1000 °C (the oven was evacuated to ca. 5 mbar and then flushed with argon three times, heating rate was 25 °C per minute and held at pyrolysis temperature for 2 h under argon atmosphere). Pyrolyzed catalysts were grinded again in an agate mortar, stored in glass vials in the air, without special protection. The catalysts were labelled as Co-ligand\support-temperature (e.g. Co-Ura/C-600).

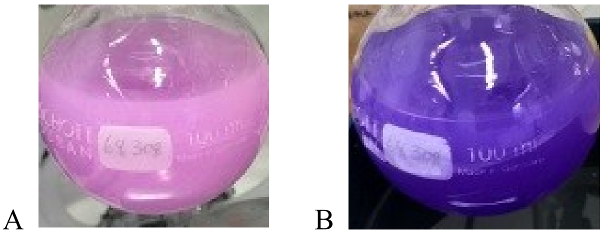


Figure S1. Cobalt-Uracil complex prior heating (A) and after heating at 70 °C for 30 min (B) before adding supporting material.

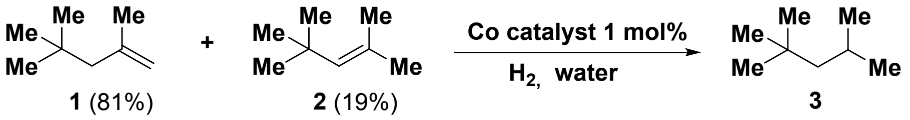
S2.2. The procedure S2.1 has been applied also for the preparation of catalysts based on ligands Tryptophan (Trp), Guanine (Gua) or Adenine (Ade) or/and supported on Vulcan, acidic or basic aluminum oxides. Also 15% Co-Ura/C-600 (before pyrolysis was 10 wt.% Co) as well as ligand free Co/C and Co/Al_2O_3(b) containing 3 wt.% cobalt were prepared according procedure S2.1.

S3. General procedures for hydrogenation reactions

A 4 mL screw-cap vial was charged with catalyst (30 mg, ~1 mol%), substrate (1.5 mmol), 1.5 mL of deionized water (or screened solvent) and Teflon-coated stirring bar. The vial was closed by phenolic cap with PTFE/white rubber septum (Wheaton 13 mm septa) and for the connection to the atmosphere septum was punctured with a syringe needle. The vial was fixed in an alloy plate and then transferred into a Parr 4560 series autoclave (300 mL). At room temperature, the autoclave was flushed with hydrogen for three times before it was pressurized at the required hydrogen pressure. The autoclave was placed into an aluminum block on a heating plate and heated up to required temperature. The heating was kept for 18 h under intensive stirring (1000 rpm). Afterwards, the autoclave was cooled in an ice bath to room temperature, the hydrogen was discharged and the vails containing reaction products were removed. In case of GC-analysis, to the crude reaction mixture internal standard n-hexadecane (100 µL) was added, the mixture was diluted with ethyl acetate and a GC sample was analyzed. For ^1H and ^{13}C NMR analysis, mesitylene (30 µL) was taken as internal standard. To the reaction mixture 2 mL $CDCl_3$ was added and the organic phase subjected to the NMR as well as GC analysis, after filtration through a 0.2 µm PTFE syringe filter. The obtained chromatograms and NMR spectra were compared with the reported ones in the literature.

S4. Screening of catalysts and reaction conditions

Catalysts and solvents were screened under standard conditions according to general hydrogenation procedure (S3).



Scheme S1. Diisobutene **1+2** (mixture of isomers) hydrogenation to isooctane **3**.

Table S1. Hydrogenation of diisobutene (Scheme 1) with different catalysts.[a]

Entry	Catalyst	Conversion 1+2 [%] [a]	Yield 3 [%] [a]
1	Co$_3$O$_4$	0	0
2	CoO$_4$W	2	traces
3	Co-Ura/C-dry	0	0
4	Co/C-600	5	0
5	Co-Ura/C-500	65	65
6	Co-Ura/C-600	100 (100[c])	>99 (>99 [c])
7	15%-Co-Ura/C-600	73	73
8	Co-Ura/C-700	100	>99
9	Co-Ura/C-800	96	94
10	Co-Ura/C-1000	37	35
11	Co-Trp/C-700	3	2
12	Co-Trp/Al$_2$O$_3$(a)-700	33	31
13	Co-Trp/Al$_2$O$_3$(a)-700-Air	10	9
14	Co-Trp/Al$_2$O$_3$(a)-800	12	11
15	Co-Trp/Al$_2$O$_3$(a)-800-Air	0	0
16	Co-Trp/Al$_2$O$_3$(a)-1000	23	22
17	Co-Trp/Al$_2$O$_3$(b)-700	40	38

18	Co-Trp/Al_2O_3(b)-700-Air	0	0
19	Co-Trp/Al_2O_3(b)-800	64	62
20	Co-Ade/C-700	18	17
21	Co-Ade/C-800	0	0
22	Co-Ade/Al_2O_3 (a)-800	34	25
23	Co-Gua/C-700	10	0
24	Co-Gua/C-800	0	0
25	Co-Ura/Al_2O_3(b)-dry	4	0
26	Co/Al_2O_3(b)-800	8	0
27	Co-Ura/Al_2O_3(b)-500	0	0
28	Co-Ura/Al_2O_3(b)-600	2	0
29	Co-Ura/Al_2O_3(b)-700	1	traces
30	Co-Ura/Al_2O_3(b)-800	6	5

[a] Reaction condition: 1.5 mmol substrate, 1.5 ml water, 1 mol% catalyst, 30 bar H_2, 60 °C, 18 h. [b] Yields were determined *via* GC, using hexadecane as internal standard.

Table S2. Hydrogenation of diisobutene (Scheme 1) with Co-Ura/C-600 in different solvents.[a]

Entry	Solvent	T (°C)	Conversion 1+2 [%][b]	Yield 3 [%][b]
1	**Water**	40	99	99
2	**Methanol**	40 100	5 25	0 0
3	**Acetonitrile**	40 100	0 12	0 0
4	**Propylene carbonate**	40 100	8 23	0 0
5	**Toluene**	40 100	0 9	0 0
6	**Hexane**	40	0	0
7	**Neat**	40	20	1

[a] Reaction condition: 1.5 mmol substrate, 1 mol% catalyst Co-Ura/C-600 , 30 bar H_2, 18 h. [b] Yields were determined *via* GC, using hexadecane as internal standard.

S5. Catalyst recycling procedure

The reaction was performed according to general procedure using Co-Ura/C-600 or Co-Ura/C-700 catalyst (30 mg, ~1 mol%) and diisobuthene (169 mg, 1.5 mmol) in 1.5 mL of deionized water. After 18 h to the crude reaction mixture internal standard n-hexadecane (100 μL) was added, the reaction mixture was diluted with ethyl acetate and a sample was analyzed by gas chromatography. Reported GC yields are the average of at least three runs. Afterwards, the reaction mixture was filtered off and obtained catalyst was washed with 10-15 ml acetone. The recycled catalyst was then dried at 60 °C under high vacuum for 4 h before using for the next run.

Table S3. Catalyst recycling tests by hydrogenation of diisobutene in water (Scheme S1)

Entry	Catalyst	Conversion **1+2** [%] [a]	Yield **3**[%] [a]
1st run	Co-Ura/C-600	100	>99
1st run	Co-Ura/C-700	100	>99
2nd run	Co-Ura/C-600-rec-1	92	91
2nd run	Co-Ura/C-700-rec-1	55	54
3rd run	Co-Ura/C-600-rec-2	28	27
3rd run	Co-Ura/C-700-rec-2	6	5
4th run	Co-Ura/C-600-rec-3	1	1
4th run	Co-Ura/C-700-rec-3	1	1
4th run	Co-Ura/C-600-rec-3-pyrolyzed	1	1

[a] Reaction condition: 1.5 mmol substrate, 1 mol% catalyst, 30 bar H_2, 60 °C, 18 h.
[b] Yields were determined *via* GC, using hexadecane as internal standard.

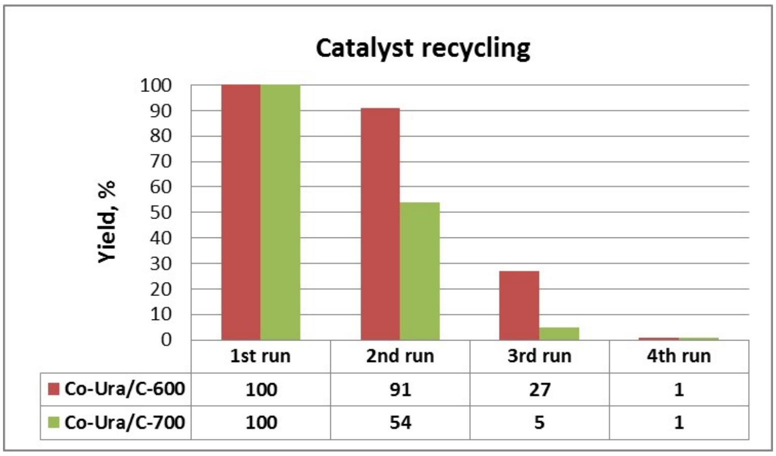


Figure S2. Recycling tests of Co-Ura/C-600 and Co-Ura/C-700 catalysts by hydrogenation of diisobutene in water.

S6. Kinetic investigation

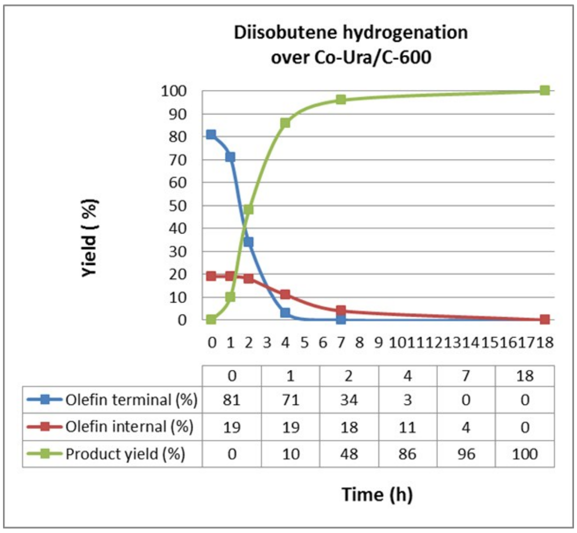
The kinetic experiments were performed under standard conditions (S3). The hydrogenation process of diisobutene (**1**+**2**) to isooctane **3** was stopped and the reaction mixture was analysed after 1 h, 2 h, 4 h, 7 h and 18 h reaction time.

Table S4. Hydrogenation of diisobutene in water (Scheme S1): kinetic investigation.[a]

Entry	Catalyst	t, h	Conversion 1+2 [%] [b]	Yield 3 [%] [b]
1	Co-Ura/C-600	1	10	10
2	Co-Ura/C-700	1	9	8
3	Co-Ura/C-600	2	48	48
4	Co-Ura/C-700	2	55	54
5	Co-Ura/C-600	4	86	86
6	Co-Ura/C-700	4	88	87
7	Co-Ura/C-600	7	96	96
8	Co-Ura/C-700	7	97	96
9	Co-Ura/C-600	18	100	>99
10	Co-Ura/C-700	18	100	>99

[a] Reaction condition: 1.5 mmol substrate, 1.5 ml water, 1 mol% catalyst, 30 bar H_2, 60 °C.

[b] Yields were determined *via* GC, using hexadecane as internal standard.

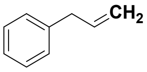
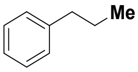
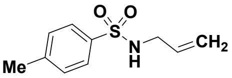
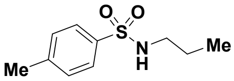
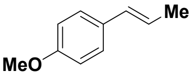
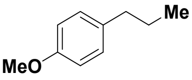
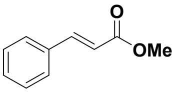
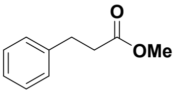
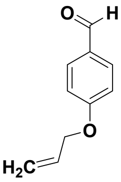
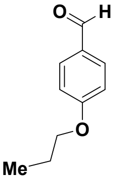
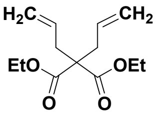
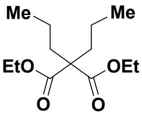
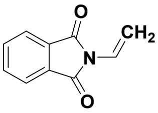
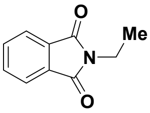
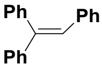
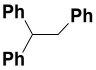
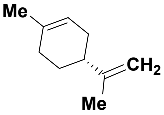
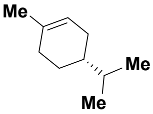
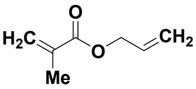
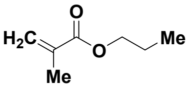
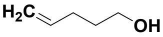
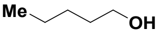
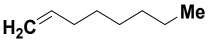
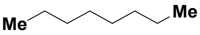
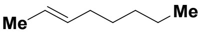
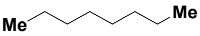
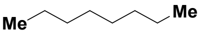
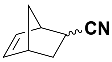
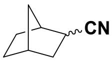


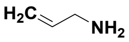
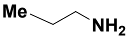
	0	1	2	4	7	18
Olefin terminal (%)	81	71	34	3	0	0
Olefin internal (%)	19	19	18	11	4	0
Product yield (%)	0	10	48	86	96	100

Figure S3. Reaction profile for the hydrogenation of diisobutene over Co-Ura\C-600 at 30 bar H_2, 60 °C, 1-18 h

S7. Substrate scope

Table S5. Co-Ura/C-600 catalyzed hydrogenations in water: Substrate scope [a]

Entry	Substrate	Product	T (°C)	Conversion [%] [b]	Yield [%] [b]
1		 **4**	60	100	>99
2		 **5**	60	100	>99
3		 **6**	60	100	>99
4		 **7**	60	99	99
5		 **8**	60	96	86
6		 **9**	60	100	98
7		 **10**	60 100	16 100	10 56
8		 **11**	60 120	0 21	0 21
9		 **12**	60 140	0 99	0 81
10		 **13**	60 80^{c} 100	52 52 80	43 36 8
11		 **14**	60	100	>99
12		 **15**	60	100	92
13		 **15**	60	83	72
14	1-Octene/2-Octene 4:1 1:4	 **15**	60 60	100 94	96 82
15		 **16**	60	50	48

16		 **17**	60	98	98

[a] Reaction condition: 1.5 mmol substrate, 1 mol% catalyst, 30 bar H_2, 1.5 ml water, 18 h. [b] Yields were determined *via* GC or NMR, using hexadecane or Mesitylene respectively as internal standard. [c] 50 bar H_2.

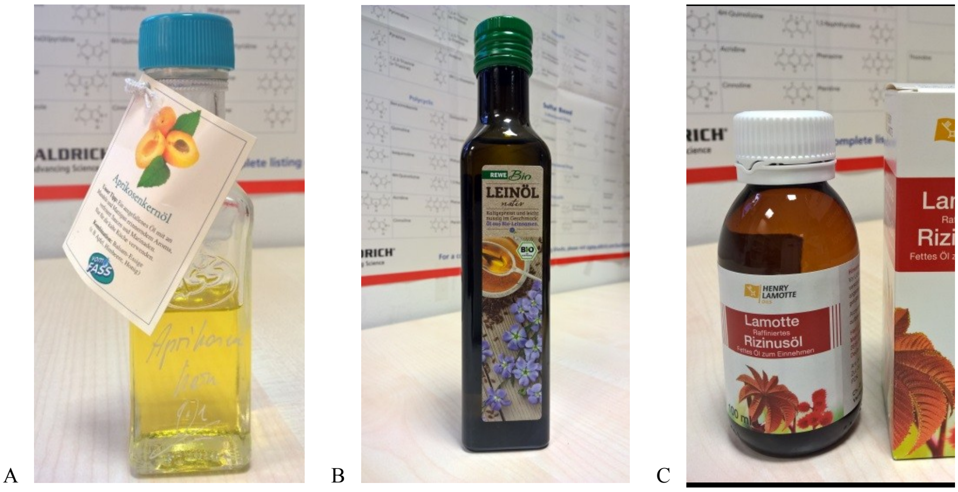
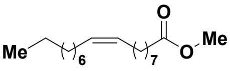
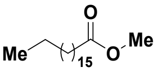
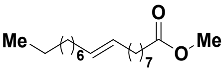
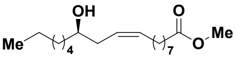
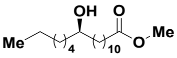
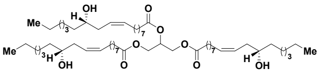
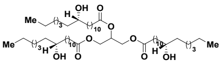
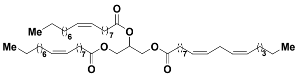
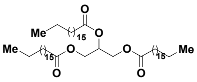
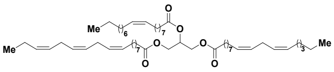
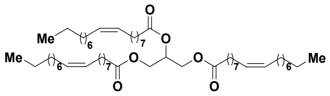
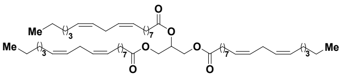


Figure S4. Natural apricot kernel (A), linseed (B) and castor oils (C).

Table S6. Co-Ura/C-600 catalyzed hydrogenations in water: Substrate scope – natural oils and fatty acid derivatives.[a]

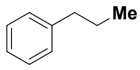
Entry	Substrate	Product	T (°C)	Conversion [%] [b]	Yield [%] [b]
1	 **Methyl oleate**	 **19**	**60** **100**	**90** **100**	**90** **>99**
2	 **Methyl elaidate**	**19**	**60** **100**	**55** **100**	**55** **>99**
3	 **Methyl ricinoleate**	 **20**	**60** **100**	**89** **100**	**89** **>99**
4	 **Castor oil**	 **21**	**60 (b)** **100 (b)**	**22** **100**	**22** **>99**
5	 **Apricot kernel oil**	 **22**	**60 (b)** **120 (c)** **140 (d)**	**0** **77** **87**	**0** **77** **87**
6	 **Linseed oil**	**22**	**100 (b)** **150 (e)**	**91** **100**	**91** **99**

7	 **Glycerine trioleate**	22	60 (b) 100 (b)	88 100	88 >99
8	 **Glycerine trilinoleate**	22	140 (d) 150 (e)	40 73	40 73

[a]Reaction condition: (a)1.5 mmol substrate, 1 mol% catalyst (30 mg), 1.5 ml water, 30 bar H_2, 60 or 100 °C, 18 h; (b) 300 mg substrate, 30 mg catalyst, 1.5 ml water, 30 bar H_2, 60 or 100 °C, 18 h; (c) like (b) at 120 °C; (d) like (b) at 140 °C; (e) like (b) at 150 °C, 50 bar H_2.
[b] Conversions were determined and yields were estimated *via* NMR, using mesitylene as internal standard.

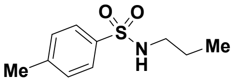
S8. Product characterization: yield, NMR shifts, GC-MS analysis

Propylbenzene 4



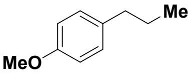
Yield: >99%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.32 – 7.14 (m, 5H), 2.65 – 2.52 (m, 2H), 1.73 – 1.58 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.66, 128.44, 128.18, 125.58, 38.07, 24.59, 13.83. **GC–MS** (EI, 70 eV): *m/z* (%) 120 (23) [M].

4-Methyl-*N*-propylbenzenesulfonamide 5



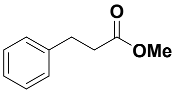
Yield: >99%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.82 – 7.71 (m, 2H), 7.33 – 7.28 (m, 2H), 5.01 (t, *J* = 6.2 Hz, 1H), 2.89 (td, *J* = 7.1, 6.2 Hz, 2H), 2.43 (s, 3H), 1.48 (h, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.18, 136.92, 129.58, 127.00, 44.86, 22.77, 21.41, 11.03. **GC–MS** (EI, 70 eV): *m/z* (%) 213 [M].

1-Methoxy-4-propylbenzene 6



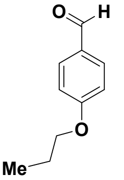
Yield: >99%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.21 – 7.12 (m, 2H), 6.95 – 6.86 (m, 2H), 3.85 (s, 3H), 2.67 – 2.54 (m, 2H), 1.76 – 1.62 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.60, 134.73, 129.25, 113.57, 55.13, 37.11, 24.77, 13.74. **GC–MS** (EI, 70 eV): *m/z* (%) 150 (26) [M].

Methyl 3-phenylpropanoate 7



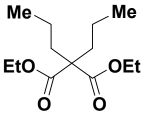
Yield: 99%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.31 – 7.13 (m, 5H), 3.64 (s, 3H), 2.93 (dd, *J* = 8.6, 7.1 Hz, 2H), 2.69 – 2.55 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.18, 140.40, 128.39, 128.16, 126.16, 51.46, 35.57, 30.83. **GC–MS** (EI, 70 eV): *m/z* (%) 164 (29) [M].

4-Propoxybenzaldehyde 8



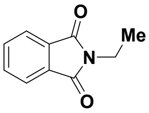
Yield: 86%. ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 9.86 (s, 1H), 7.84 – 7.78 (m, 2H), 7.01 – 6.95 (m, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.84 (dtd, *J* = 13.9, 7.4, 6.6 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 190.79, 164.19, 131.89, 129.56, 114.63, 69.74, 22.28, 10.32. **GC–MS** (EI, 70 eV): *m/z* (%) 164 [M].

Diethyl 2,2-dipropylmalonate <u>9</u>



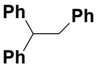
Yield: 98%. ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 4.15 (q, *J* = 7.1 Hz, 4H), 1.87 – 1.78 (m, 4H), 1.25 – 1.09 (m, 10H), 0.90 (t, *J* = 7.2 Hz, 6H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 171.86, 60.78, 57.47, 34.40, 17.28, 14.30, 13.98. **GC–MS** (EI, 70 eV): *m/z* (%) 245 [M+H].

2-Ethylisoindoline-1,3-dione <u>10</u>



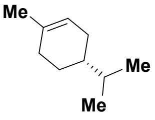
Yield: 56%. ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 7.89 – 7.76 (m, 2H), 7.76 – 7.63 (m, 2H), 3.73 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 168.15, 133.74, 132.17, 123.03, 32.81, 13.86. **GC–MS** (EI, 70 eV): *m/z* (%) 175 (43) [M].

Ethane-1,1,2-triyltribenzene[1, 2] <u>11</u>



Yield: 21%. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 6.94 (m, 15H), 4.22 (t, *J* = 7.8 Hz, 1H), 3.34 (d, *J* = 7.8 Hz, 2H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 144.40, 140.19, 129.02, 128.28, 128.00, 126.13, 125.83, 53.05, 42.05. **GC–MS** (EI, 70 eV): *m/z* (%) 258 (0.5) [M].

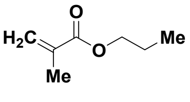
(R)-4-isopropyl-1-methylcyclohex-1-ene[3] <u>12</u>



Yield: 81%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.48 – 5.35 (m, 1H), 2.10 – 1.90 (m, 3H), 1.81 – 1.71 (m, 2H), 1.69 – 1.64 (m, 3H), 1.53 – 1.45 (m, 1H), 1.32 – 1.20 (m, 2H), 0.94 – 0.89 (m, 6H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 133.87, 121.02, 40.02, 32.29, 30.82, 28.96, 26.49, 23.45, 19.98, 19.67. **GC–MS** (EI, 70 eV): *m/z* (%) 138 (31) [M].

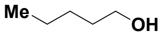
Analytical data are in agreement with literature data.[3-5]

Propyl methacrylate <u>13</u>



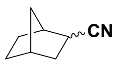
Yield: 43%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.12 – 6.07 (m, 1H), 5.56 – 5.51 (m, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 1.94 (t, *J* = 1.4 Hz, 3H), 1.70 (h, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.44, 136.47, 132.19, 125.03, 66.13, 21.92, 10.35. **GC–MS** (EI, 70 eV): *m/z* (%) 128 (0.3) [M].

Pentan-1-ol <u>14</u>



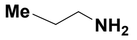
Yield: 100%. ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 3.62 (t, *J* = 6.7 Hz, 2H), 1.92 (s, 1H), 1.63 – 1.49 (m, 2H), 1.41 – 1.25 (m, 4H), 0.96 – 0.83 (m, 3H). ^{13}**C NMR** (75 MHz, CDCl$_3$) δ 62.87, 32.39, 27.86, 22.43, 13.97. **GC–MS** (EI, 70 eV): *m/z* (%) 87 (1) [M$^+$].

Norbornane-2-carbonitrile <u>16</u> (mixture of isomers)



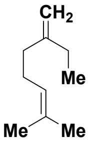
GC-yield: 48%. ^{1}H NMR – many signals of substrate and product isomers are overlaid for correct assignment. ^{13}C NMR (75 MHz, CDCl$_3$) δ 123.47, 122.68, 41.63, 39.68, 38.56, 37.00, 36.34, 35.91, 35.85, 35.19, 30.87, 29.91, 28.88, 28.31, 28.19, 24.76. **GC–MS** (EI, 70 eV): *m/z* (%) 120 (5) [M-H].

1-Aminopropane <u>17</u>



GC-yield: 98%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.62 (t, 2H), 1.46 (br. s, 2H), 1.42 (hept, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 43.99, 26.71, 11.17. **GC–MS** (EI, 70 eV): *m/z* (%) 59 (21.6) [M].

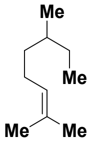
2-Methyl-6-methyleneoct-2-ene <u>18a</u>



Yield: ~ 20%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.30 – 5.20 (m, 1H), 4.75 (m, 2H), 2.21 – 1.91 (m, 6H), 1.72 (s, 3H), 1.64 (s, 3H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 151.39, 131.43, 124.39, 107.50, 36.27, 28.87, 26.77, 25.66, 17.63, 12.35. GC–MS (EI, 70 eV): m/z (%) 138 [M].

Analytical data were in agreement with literature data.[6, 7]

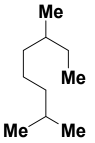
2,6-Dimethyloct-2-ene <u>18c</u>



Yield: 49-61%. ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 5.15 (tdq, *J* = 7.1, 2.9, 1.4 Hz, 1H), 2.14 – 1.93 (m, 2H), 1.73 (s, 3H), 1.64 (s, 3H), 1.46 – 1.28 (m, 3H), 1.24 – 1.09 (m, 2H), 0.93 – 0.84 (m, 6H). ^{13}**C NMR** (75 MHz, CDCl$_3$) δ 130.89, 125.13, 36.77, 34.08, 29.45, 25.70, 25.63, 19.09, 17.58, 11.35. **GC–MS** (EI, 70 eV): *m/z* (%) 140 (27) [M].

Analytical data were in agreement with literature data.[6, 7]

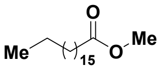
2,6-Dimethyloctane <u>18d</u>



Yield: 98%. ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 1.64 – 1.50 (m, 1H), 1.46 – 1.03 (m, 9H), 0.92, 0.90, 0.88 (3s, 12H). ^{13}**C NMR** (75 MHz, CDCl$_3$) δ 39.43, 36.94, 34.48, 29.57, 28.04, 24.89, 22.73, 22.64, 19.24, 11.43. **GC–MS** (EI, 70 eV): *m/z* (%) 142 [M].

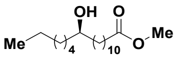
Analytical data were in agreement with literature data.[5-7]

Methyl stearate <u>19</u> obtained from methyl oleate and methyl elaidate



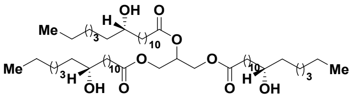
Yield: 100%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.65 (s, 3H), 2.30 (d, *J* = 7.5 Hz, 2H), 1.68 – 1.55 (m, 2H), 1.31 (d, *J* = 10.0 Hz, 28H), 0.93 – 0.82 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.14, 51.26, 34.02, 31.90, 29.67, 29.64, 29.57, 29.43, 29.34, 29.23, 29.12, 24.91, 22.65, 14.03. **GC–MS** (EI, 70 eV): *m/z* (%) 298 (22) [M].

Methyl (R)-12-hydroxyoctadecanoate 20



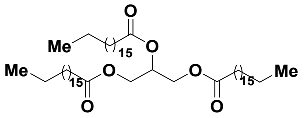
Yield: 100%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.64 (s, 3H), 3.60 – 3.46 (m, 1H), 2.32 – 2.26 (m, 2H), 1.91 (s, 1H), 1.66 – 1.54 (m, 2H), 1.47 – 1.19 (m, 26H), 0.92 – 0.81 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.23, 71.81, 51.31, 37.40, 37.38, 33.98, 31.77, 29.61, 29.50, 29.42, 29.31, 29.14, 29.03, 25.56, 25.54, 24.84, 22.53, 13.97. **GC–MS** (EI, 70 eV): *m/z* (%) 313 [M-H].

Hydrogenated castor oil: 2-(((S)-12-hydroxyoctadecanoyl)oxy)propane-1,3-diyl (12R,12'R)-bis(12-hydroxyoctadecanoate) 21



Conversion: 100%. ^{1}H NMR (300 MHz, Chloroform-d) δ 5.27 (m, 1H), 4.30 (dd, *J* = 11.9, 4.3 Hz, 2H), 4.15 (dd, *J* = 11.9, 5.9 Hz, 2H), 3.57 (m, 4.2 Hz, 3H), 2.32 (m, 6H), 1.70 – 1.20 (m, 87H), 0.93 – 0.83 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.25, 172.83, 71.90, 68.81, 62.04, 37.45, 34.15, 33.99, 31.88, 31.81, 29.67, 29.62, 29.56, 29.49, 29.42, 29.39, 29.35, 29.32, 29.22, 29.20, 29.04, 29.01, 25.62, 25.59, 24.84, 24.79, 22.64, 22.58, 14.07, 14.04

Propane-1,2,3-triyl tristearate 22 from glycerine trioleate and trilinoleate



Yield: 100%. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 4.39 – 4.24 (m, 2H), 4.22 – 4.08 (m, 2H), 2.33 (td, *J* = 7.5, 1.8 Hz, 6H), 1.63 (qd, *J* = 9.9, 9.3, 6.7 Hz, 6H), 1.27 (s, 84H), 0.94 – 0.85 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.22, 172.81, 68.84, 62.06, 34.19, 34.02, 31.92, 29.70, 29.66, 29.62, 29.50, 29.48, 29.36, 29.29, 29.27, 29.10, 29.07, 24.89, 24.84, 22.68, 14.09.

Glycerin trilinoleate hydrogenation to propane-1,2,3-triyl tristearate 22 as a main product

Glycerin trilinoleate was hydrogenated similar to standard conditions (S3) at 150 °C, 50 bar hydrogen with 73% conversion.

Linseed oil hydrogenation to propane-1,2,3-triyl tristearate 22 as a main product

Linseed oil was hydrogenated similar to standard conditions (S3) at 100 °C, 30 bar hydrogen or 150 °C, 50 bar hydrogen with 91% or 99% conversion respectively.

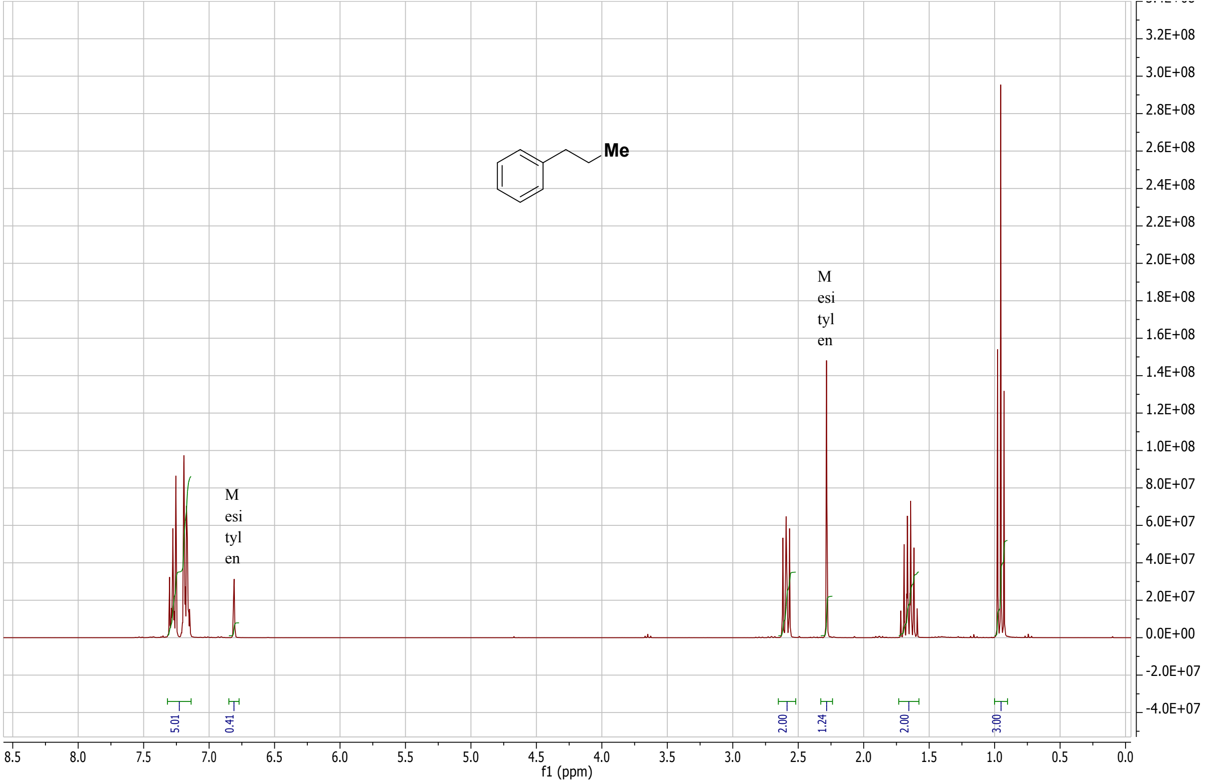
Apricot kernel oil hydrogenation to propane-1,2,3-triyl tristearate 22 as a main product

Apricot kernel oil was hydrogenated similar to standard conditions (S3) at 120 °C, 30 bar hydrogen or 140 °C, 30 bar hydrogen with 77% or 87% conversion respectively.

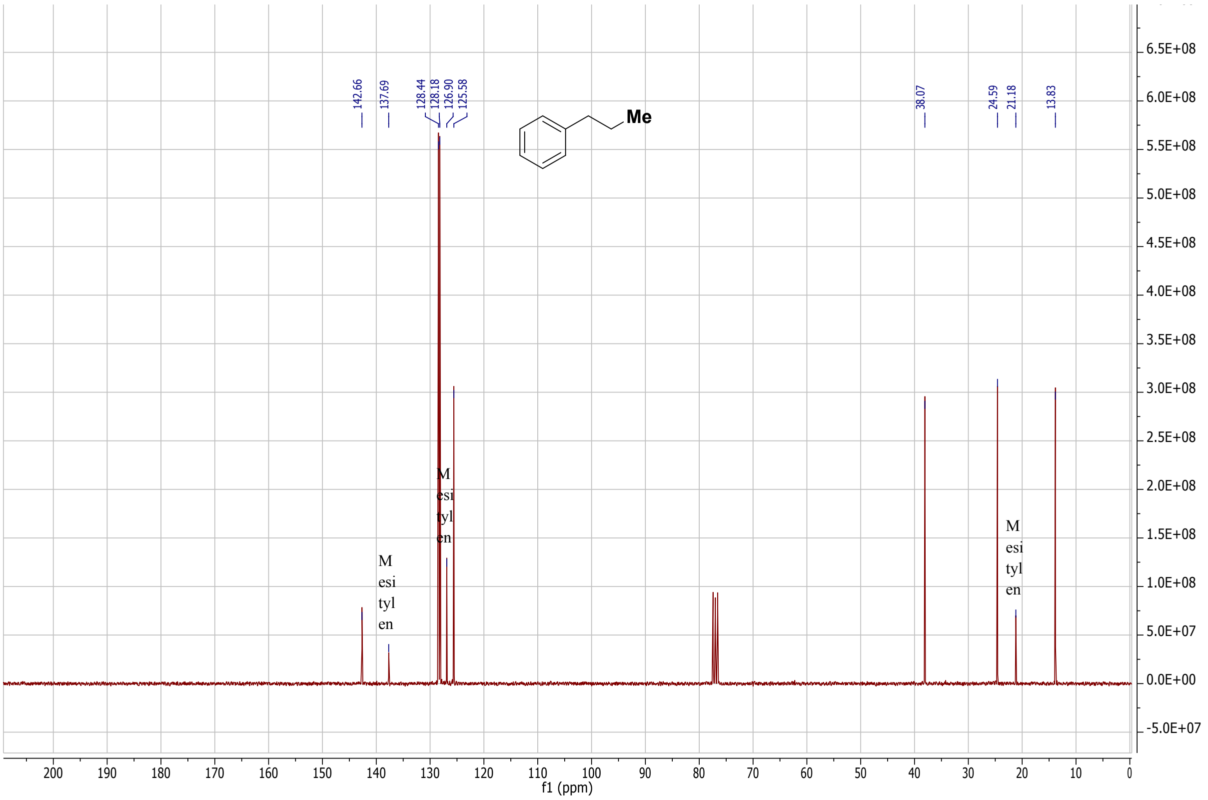
S9. Scans of products ^{1}H and ^{13}C NMR spectra with internal standard mesitylene

Propylbenzene 4

^{1}H-NMR in CDCl$_3$

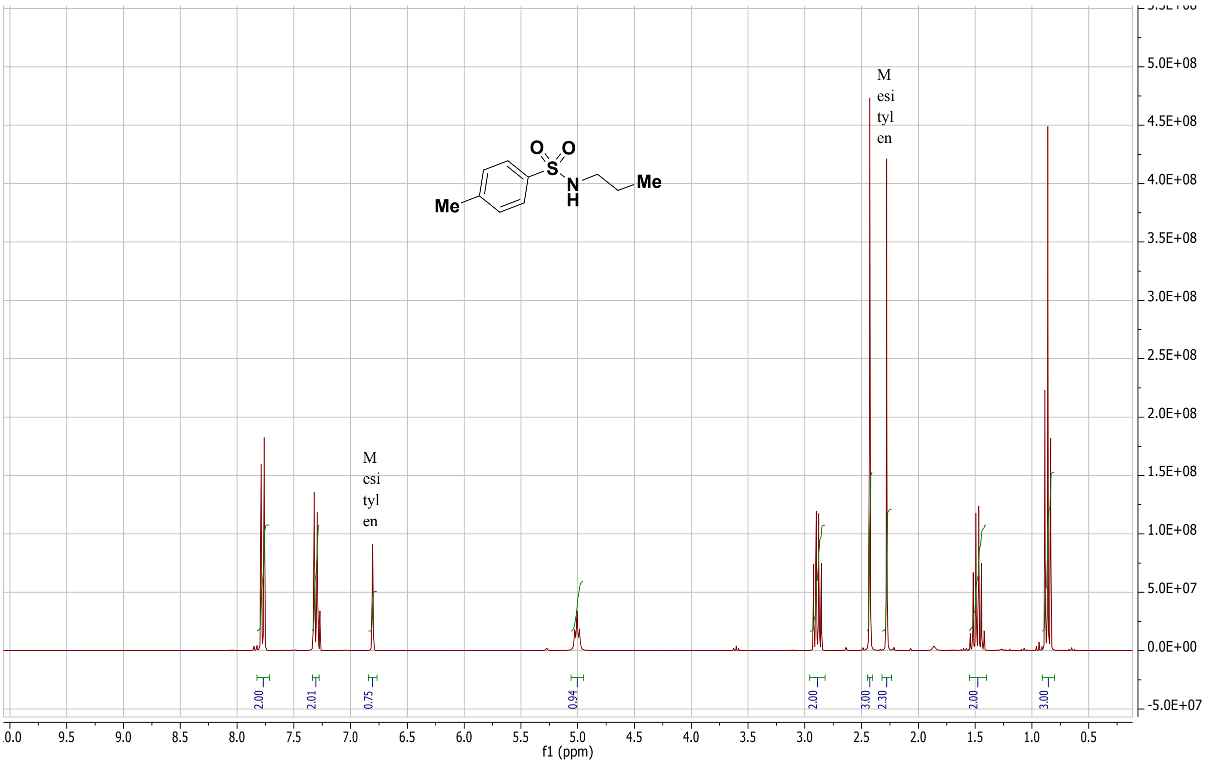


^{13}C-NMR in CDCl$_3$

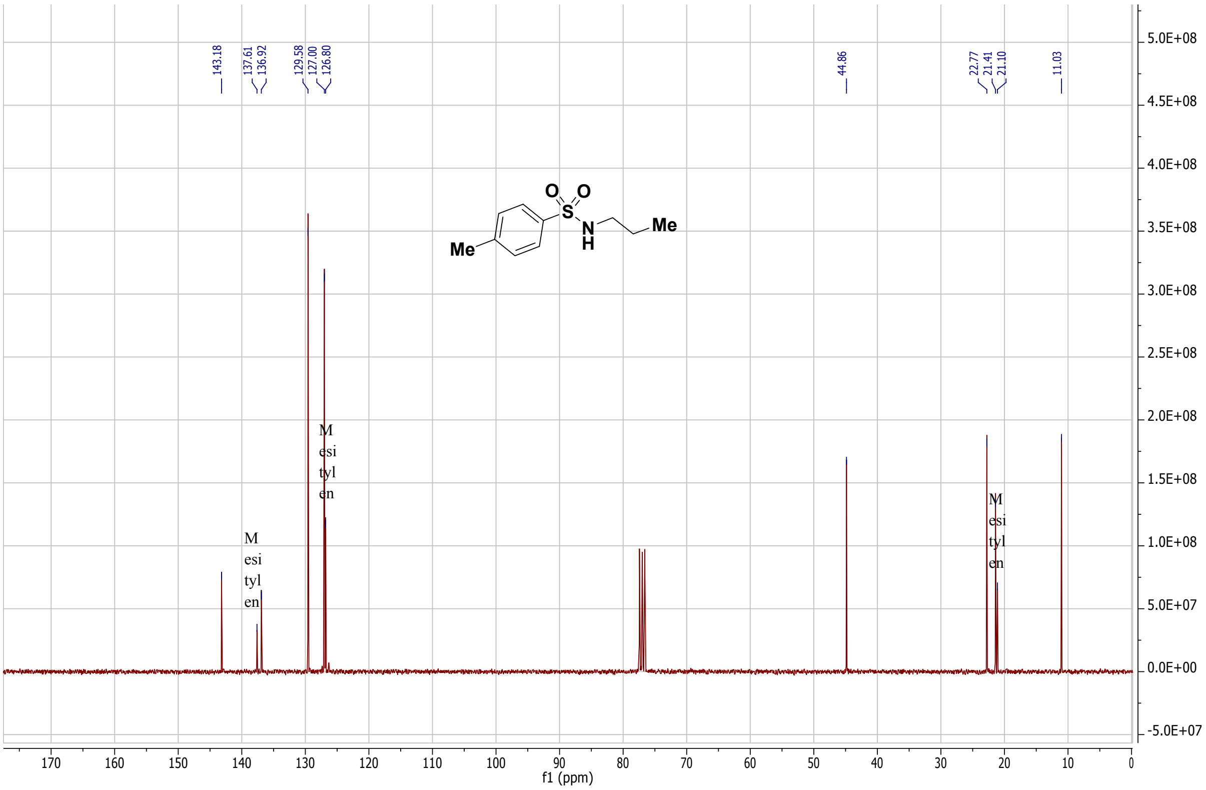


4-Methyl-*N*-propylbenzenesulfonamide <u>5</u>

^{1}H-NMR in CDCl$_3$

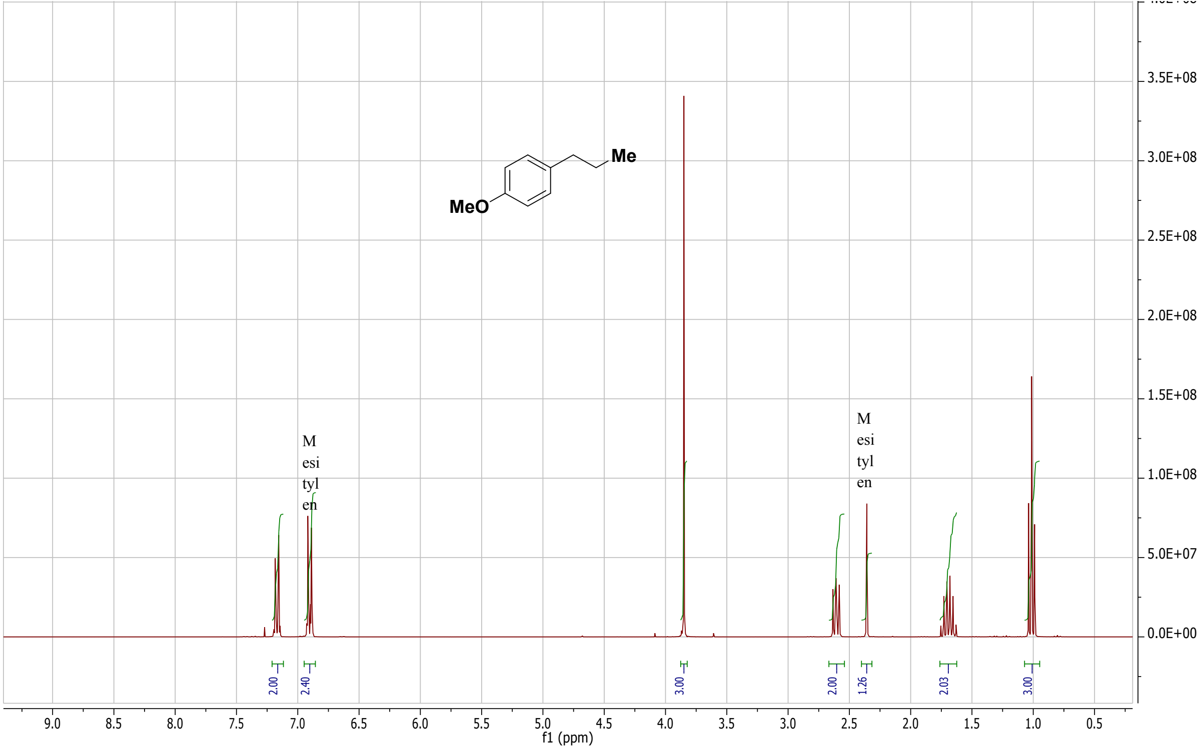


^{13}C-NMR in CDCl$_3$

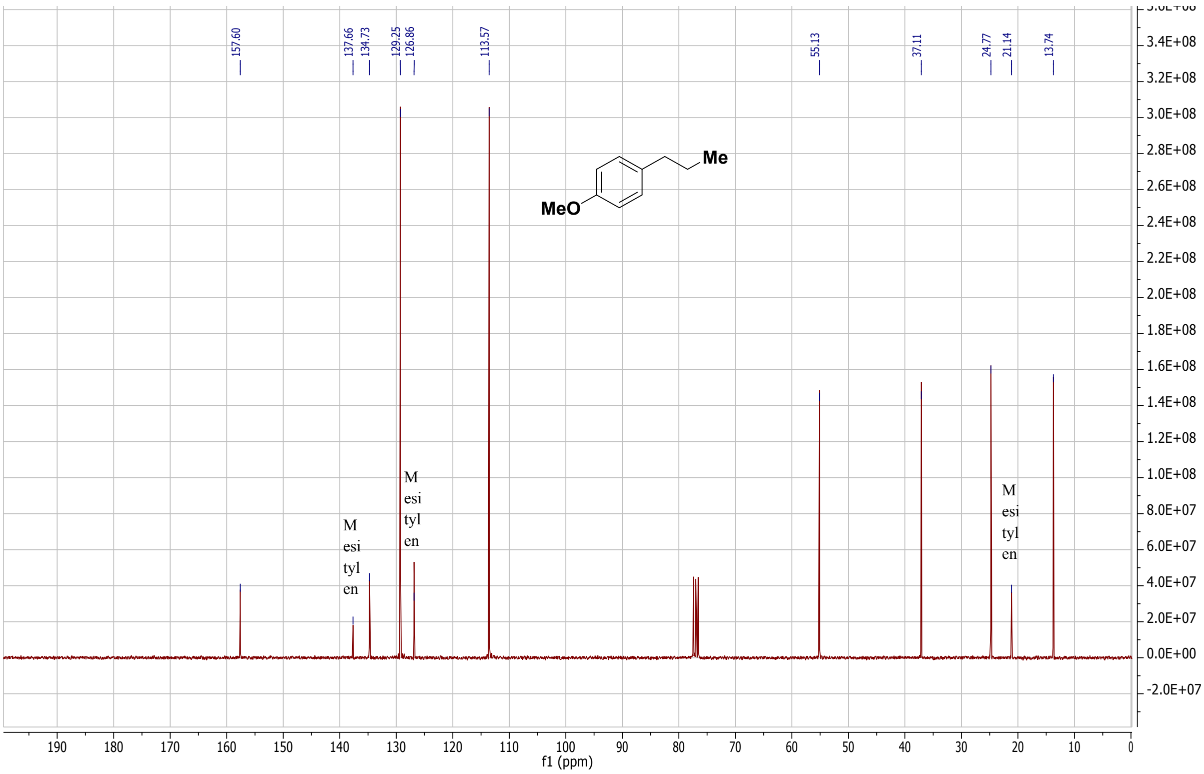


1-Methoxy-4-propylbenzene 6

^{1}H-NMR in CDCl$_3$

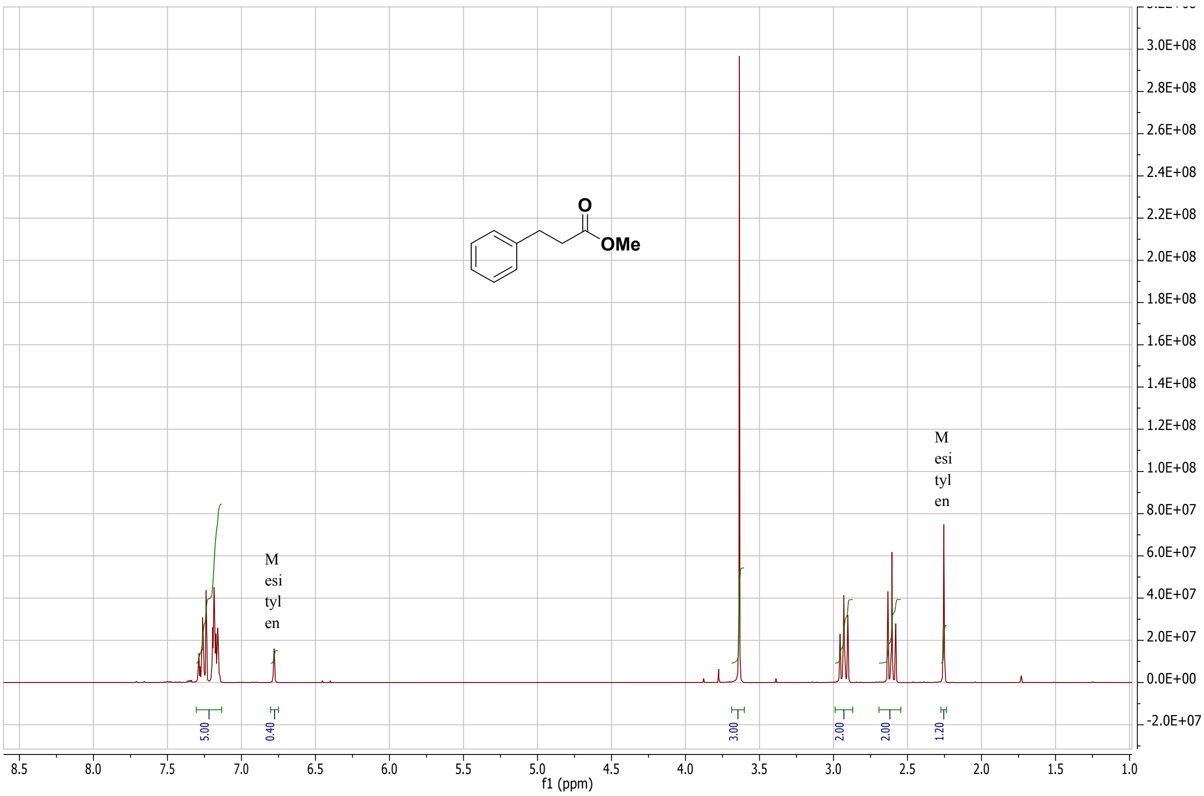


^{13}C-NMR in CDCl$_3$

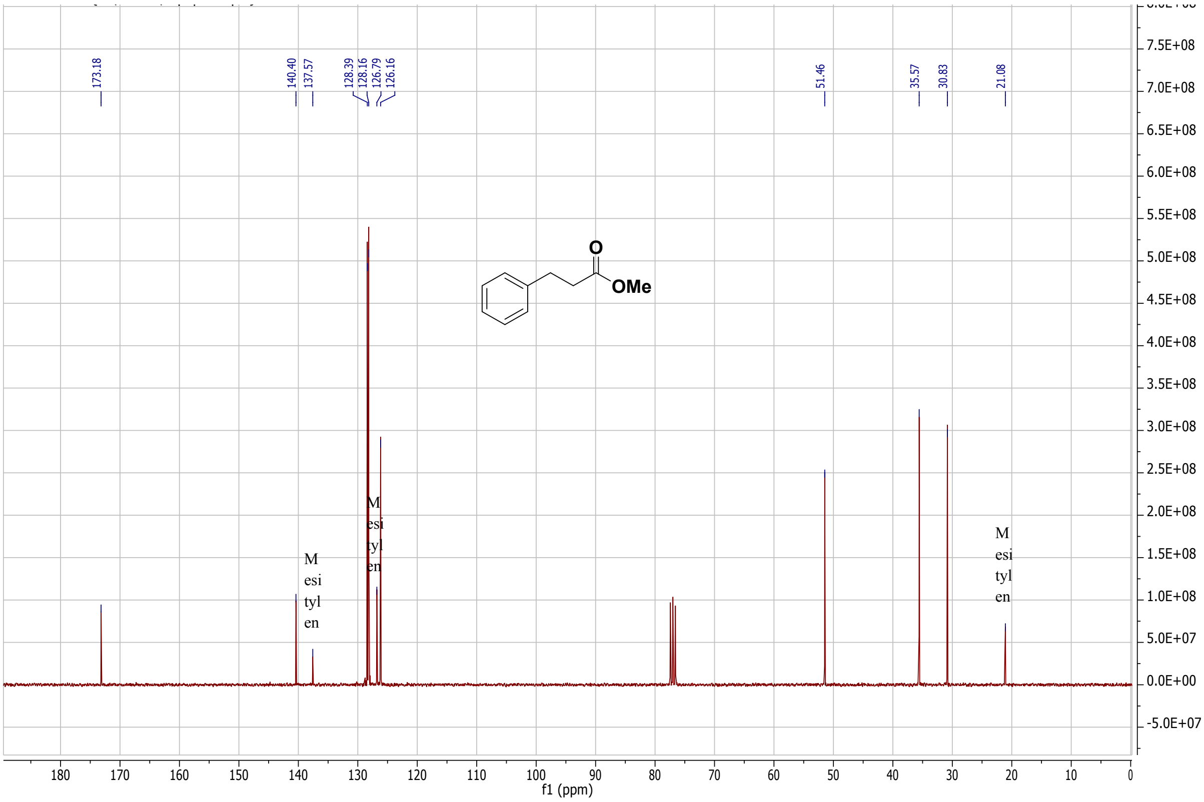


Methyl 3-phenylpropanoate 7

^{1}H-NMR in CDCl$_3$

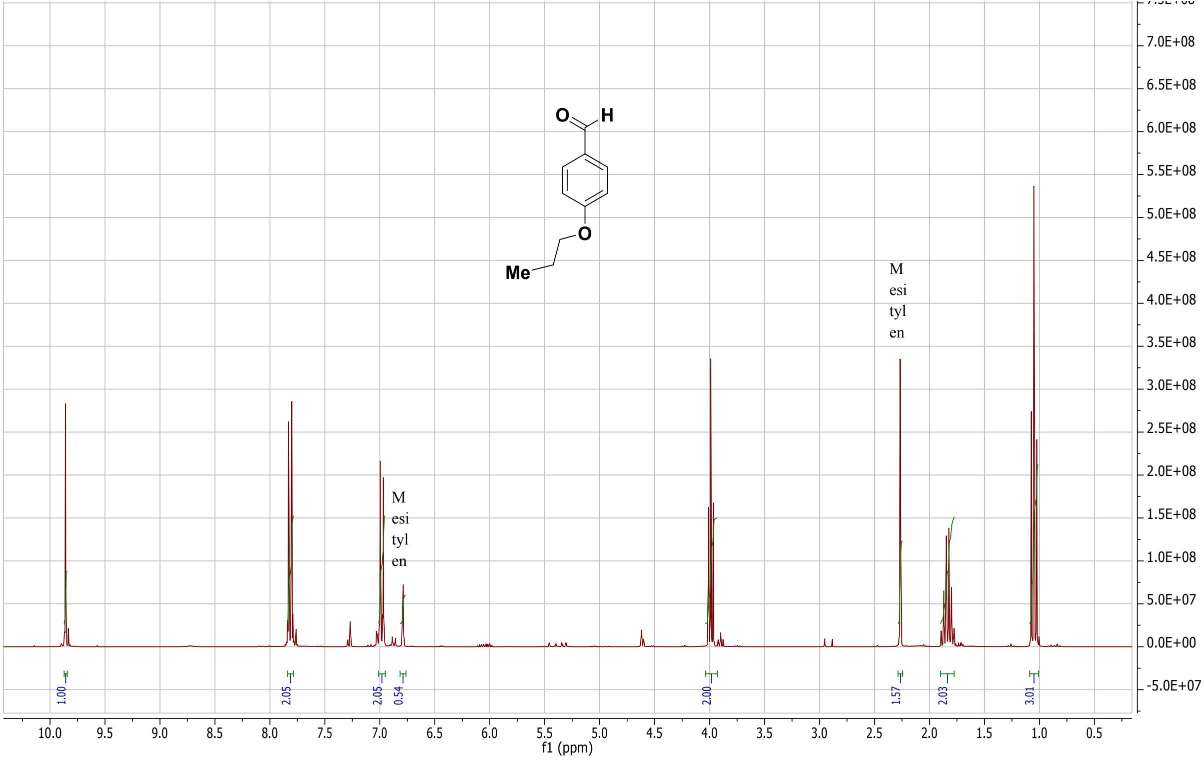


^{13}C-NMR in CDCl$_3$

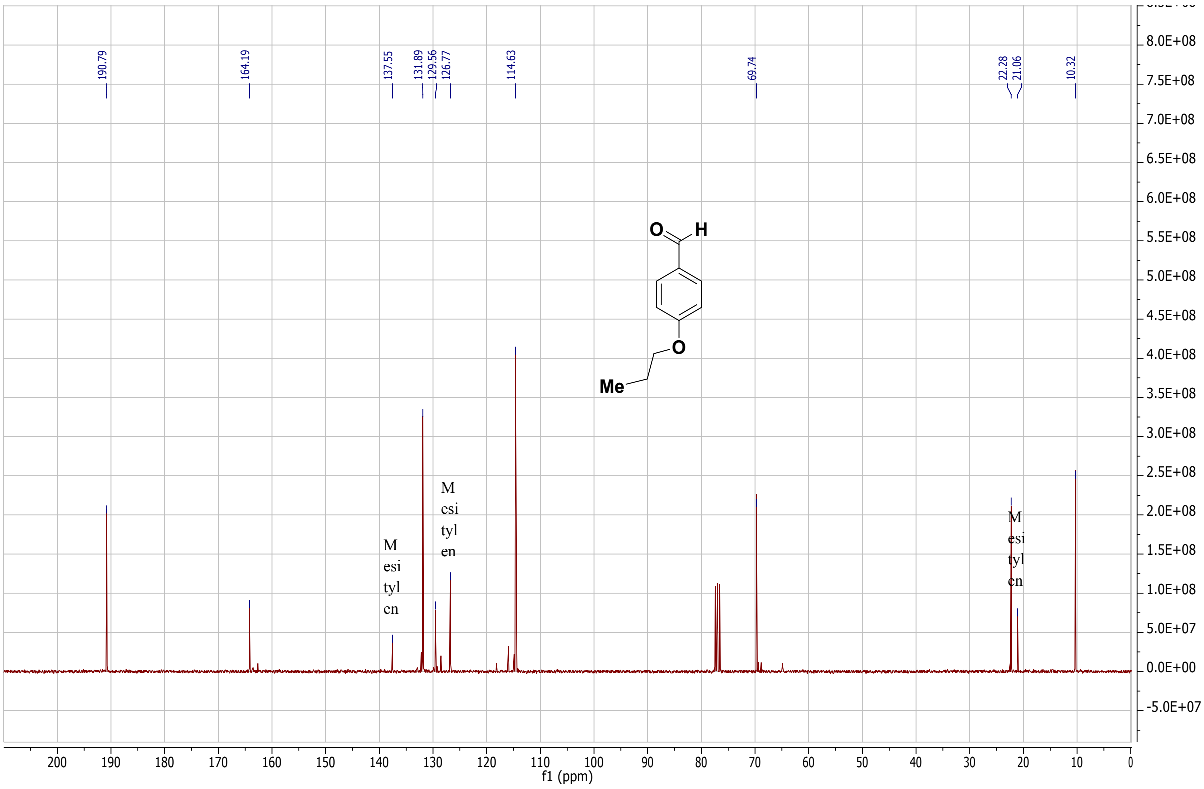


4-Propoxybenzaldehyde 8

^{1}H-NMR in CDCl$_3$

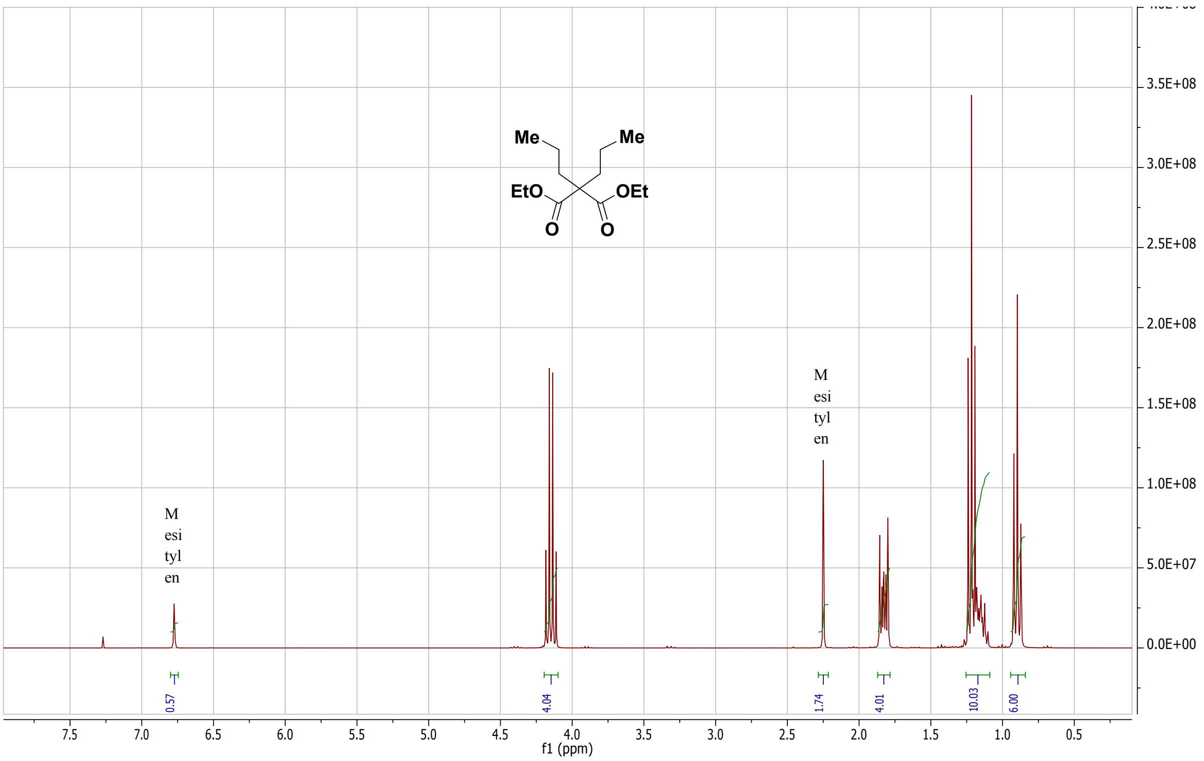


^{13}C-NMR in CDCl$_3$

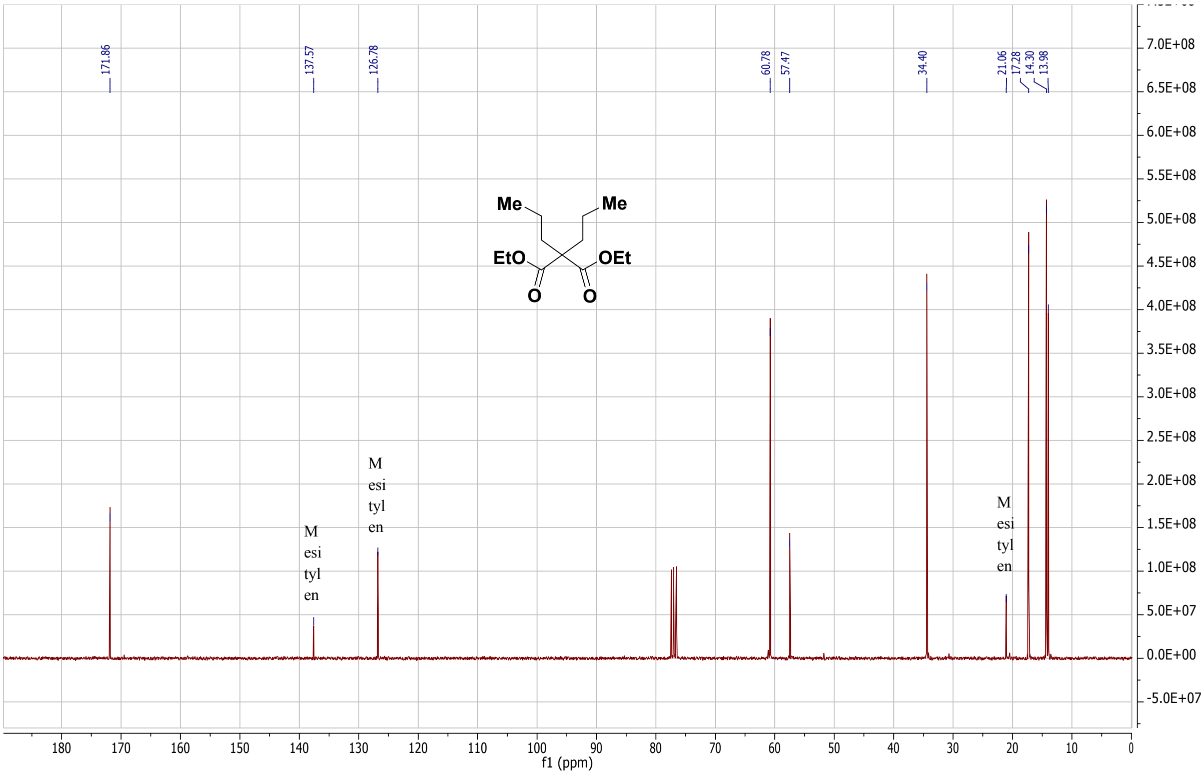


Diethyl 2,2-dipropylmalonate 9

^{1}H-NMR in CDCl$_3$

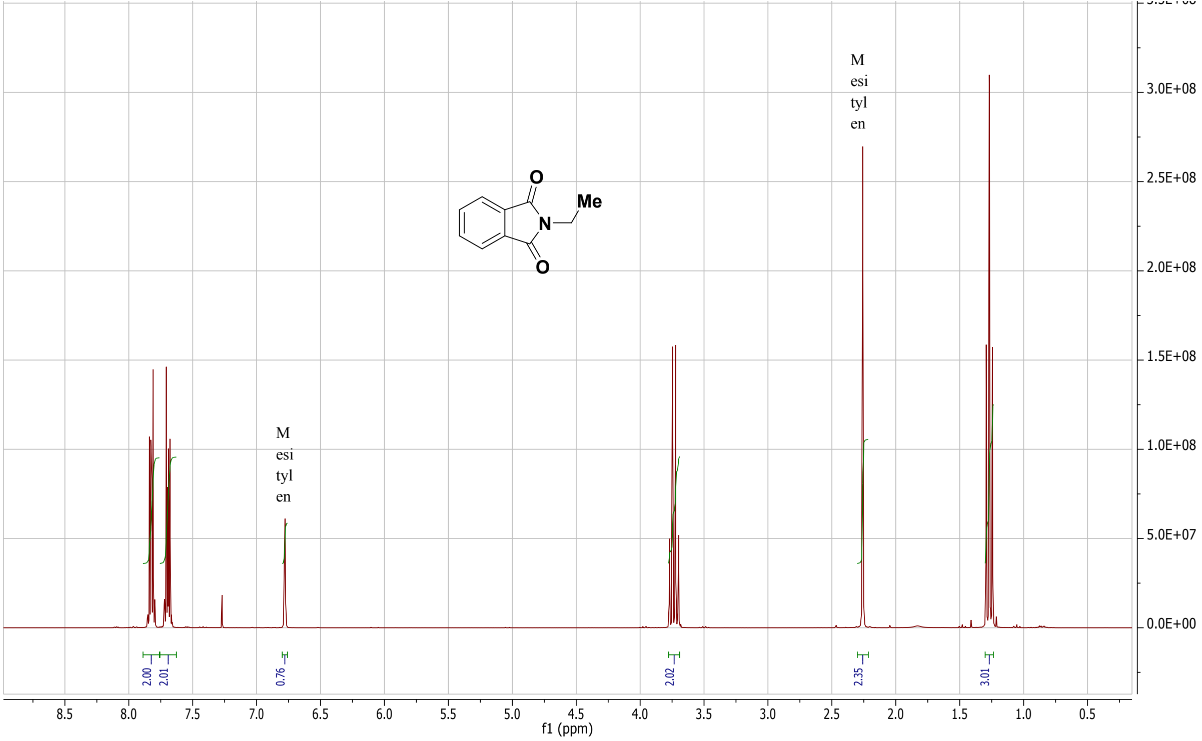


^{13}C-NMR in CDCl$_3$

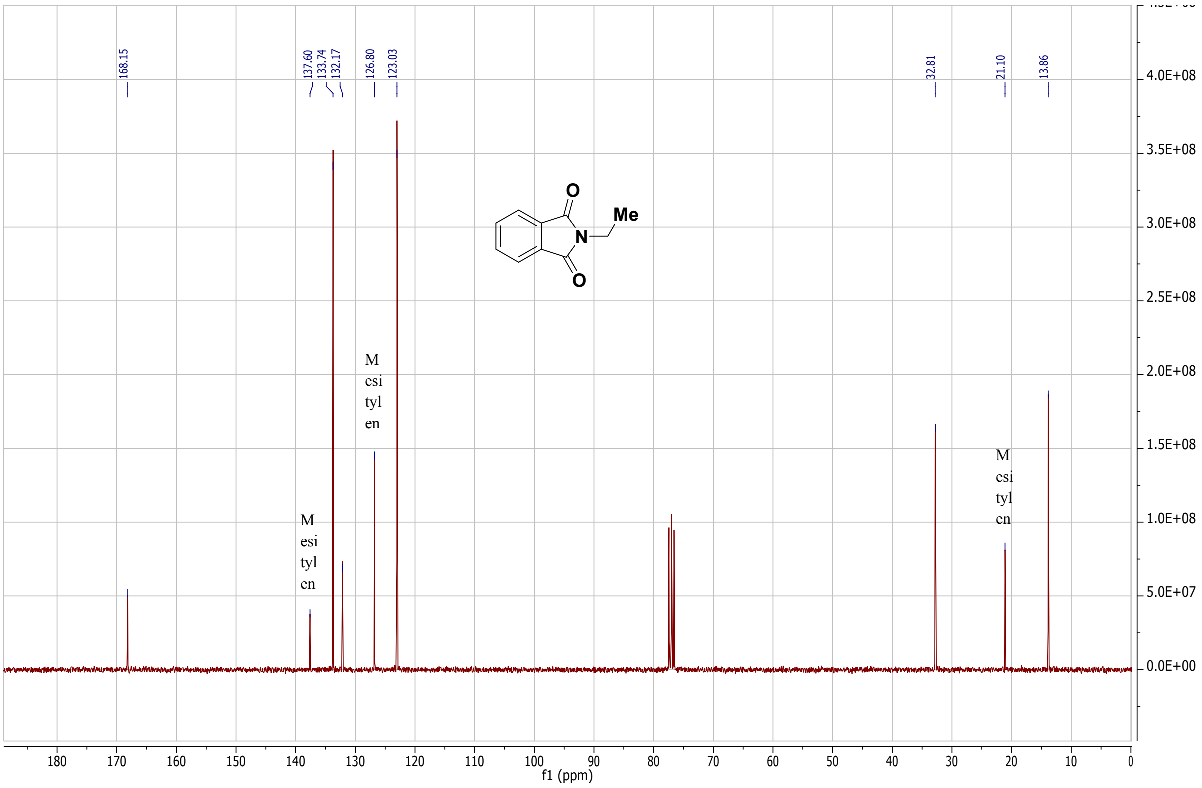


2-Ethylisoindoline-1,3-dione <u>10</u>

^{1}H-NMR in CDCl$_3$

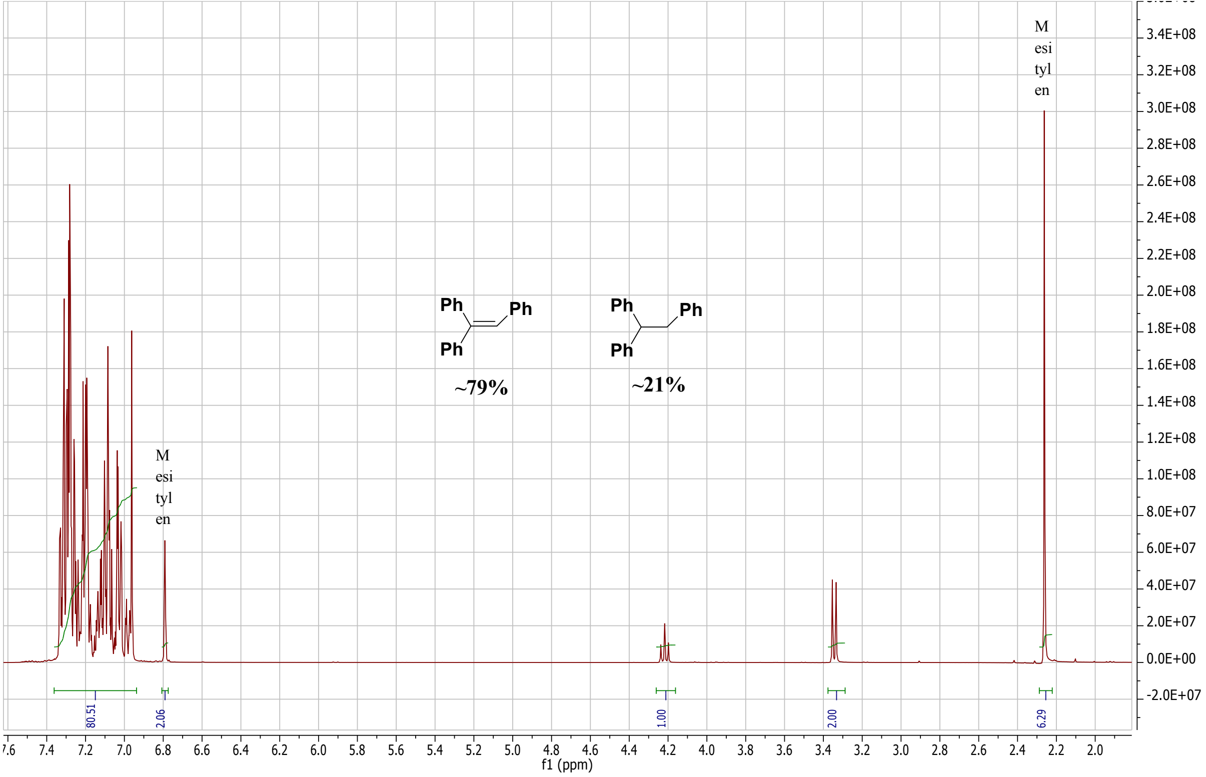


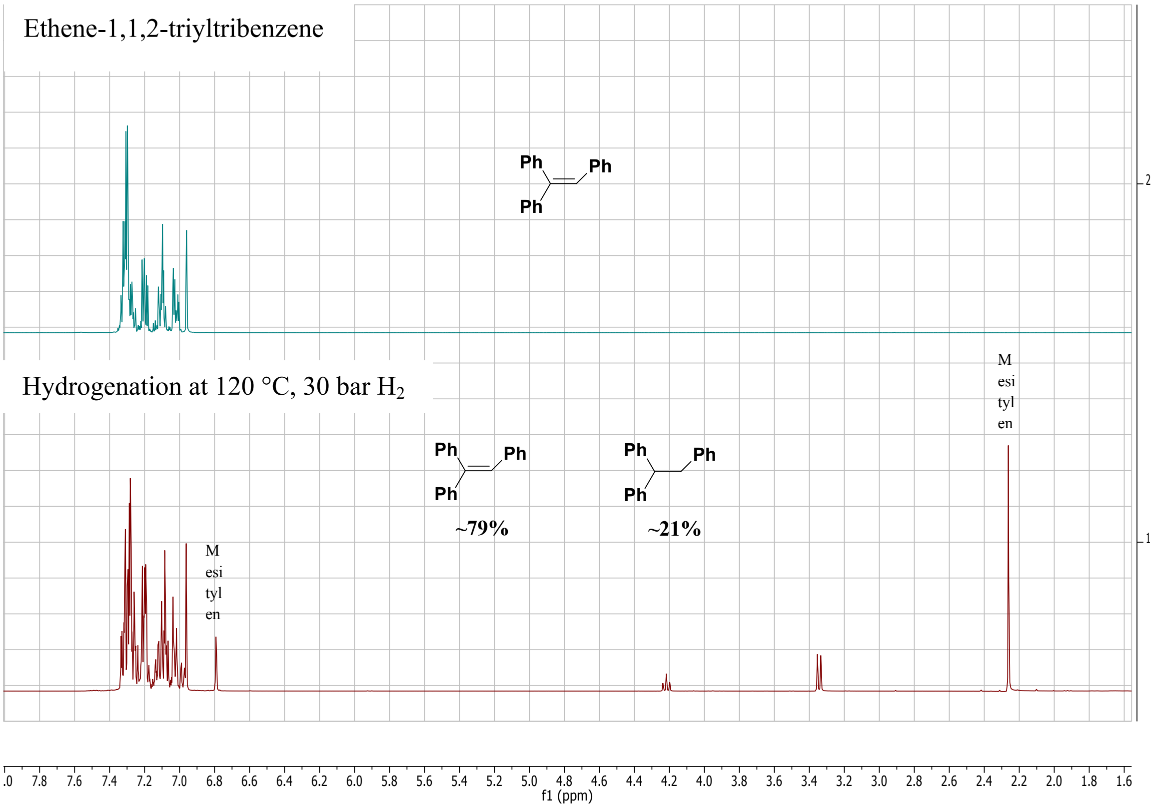
^{13}C-NMR in CDCl$_3$



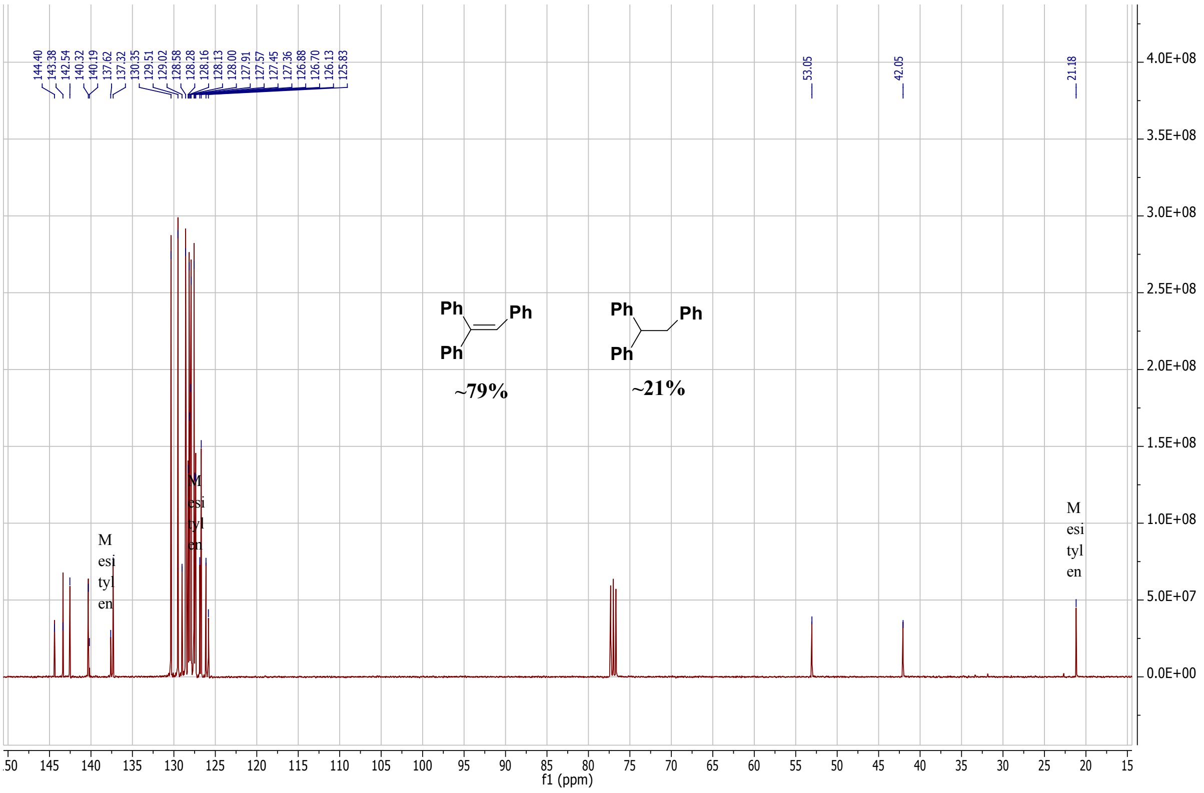
Ethane-1,1,2-triyltribenzene 11

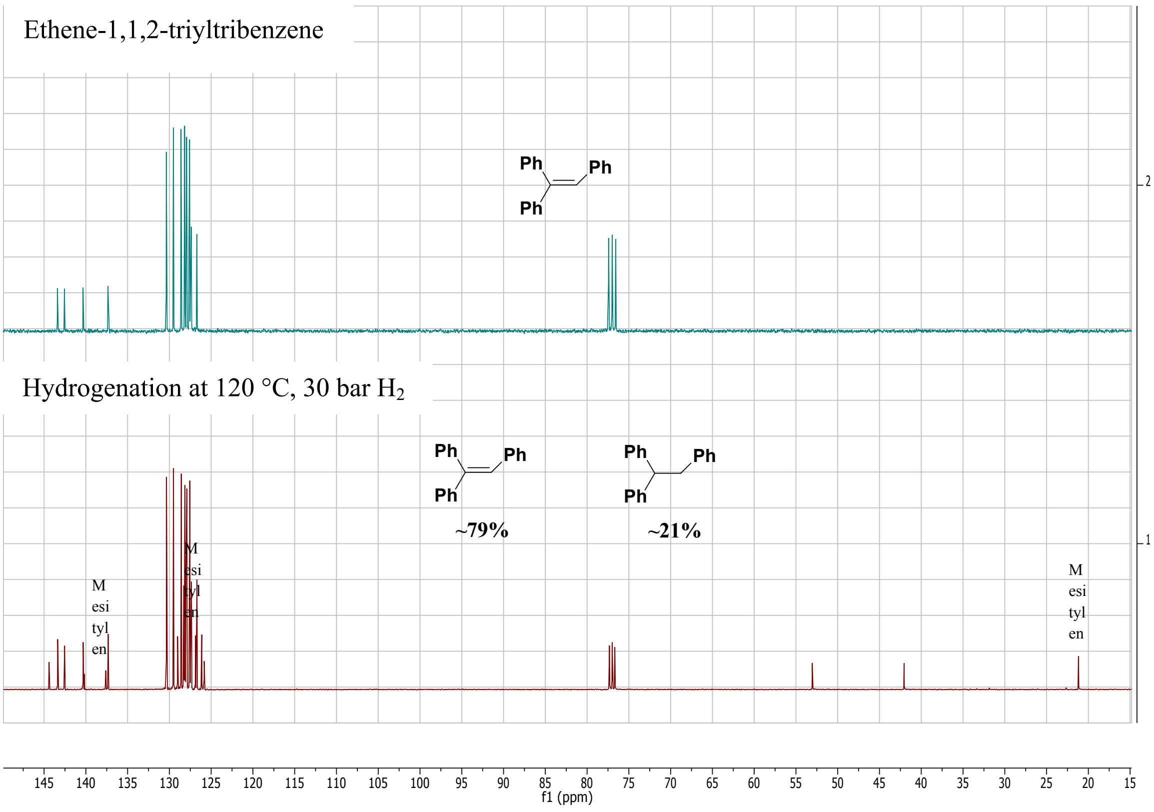
^{1}H-NMR in $CDCl_3$





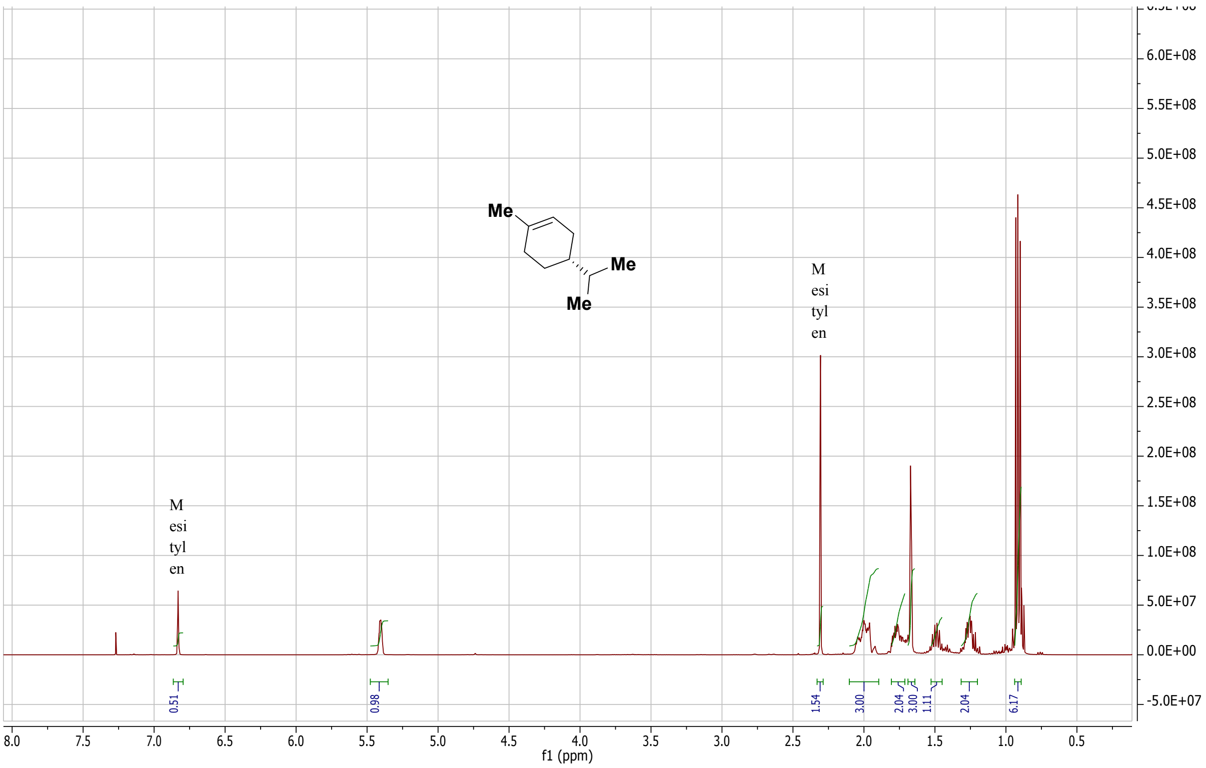
^{13}C-NMR in CDCl$_3$



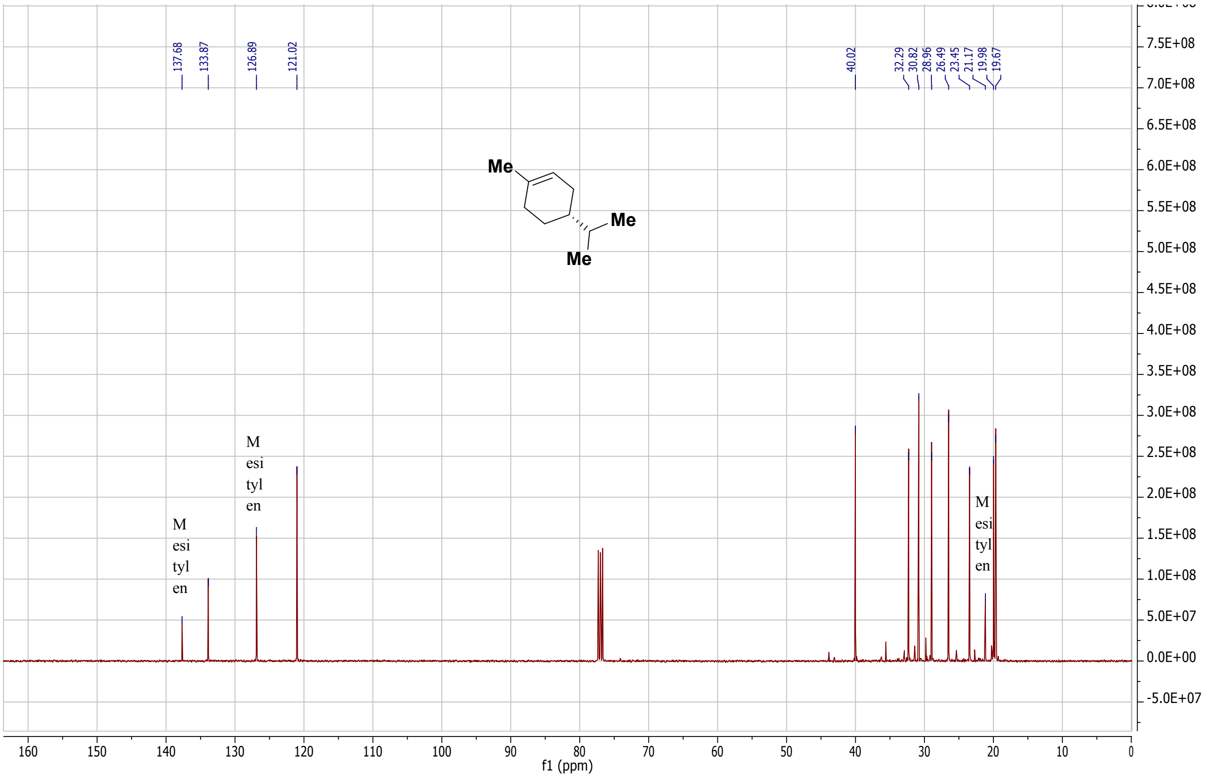


(R)-4-Isopropyl-1-methylcyclohex-1-ene 12

^{1}H-NMR in CDCl$_3$

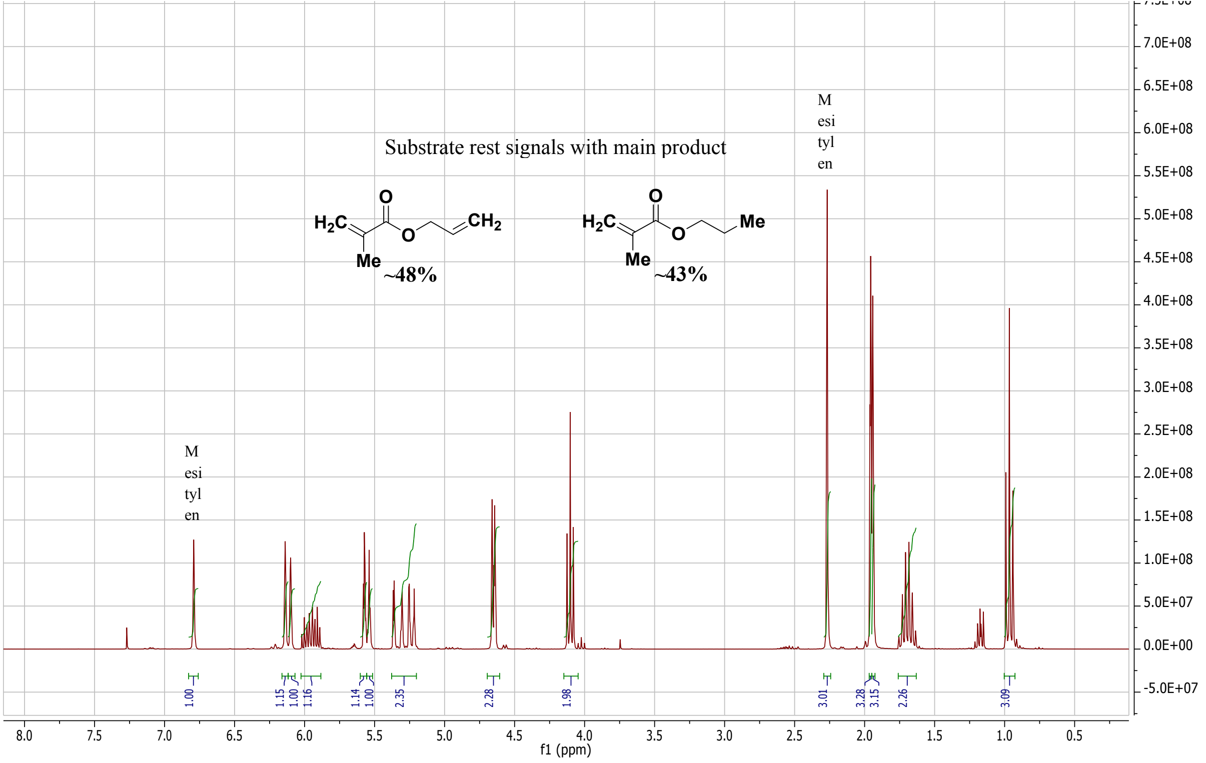


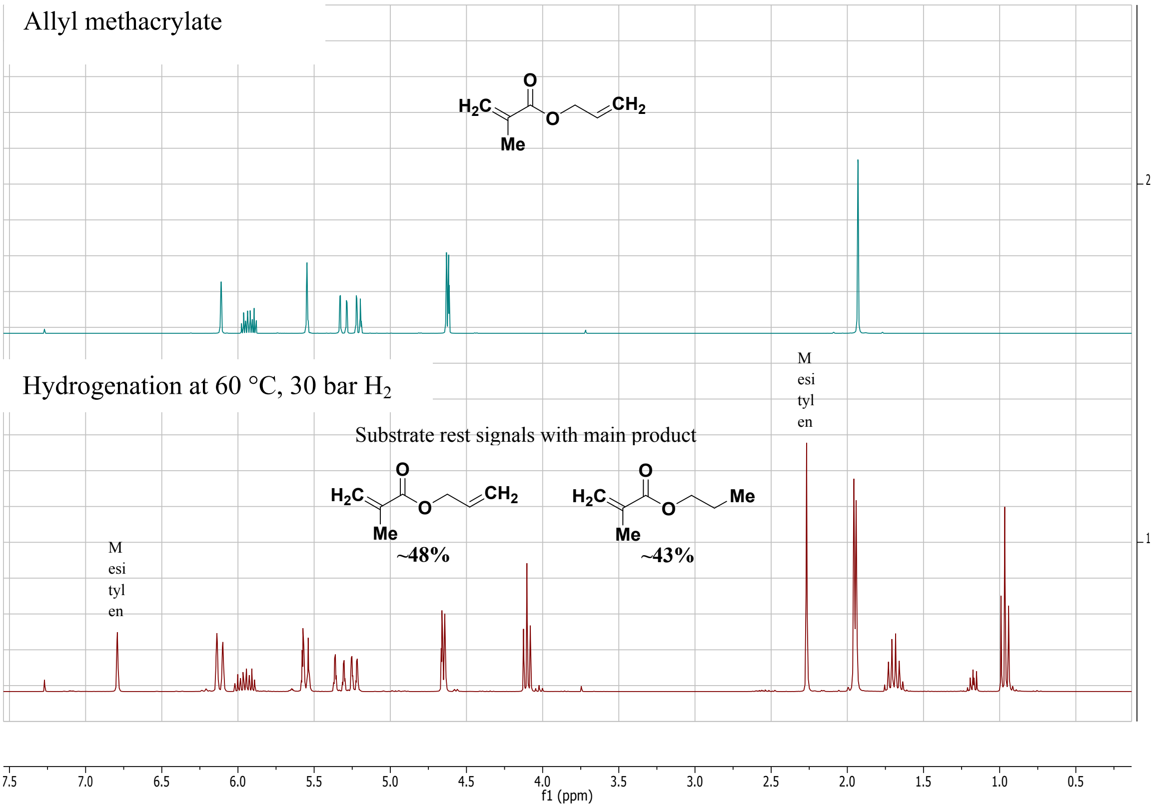
^{13}C-NMR in CDCl$_3$



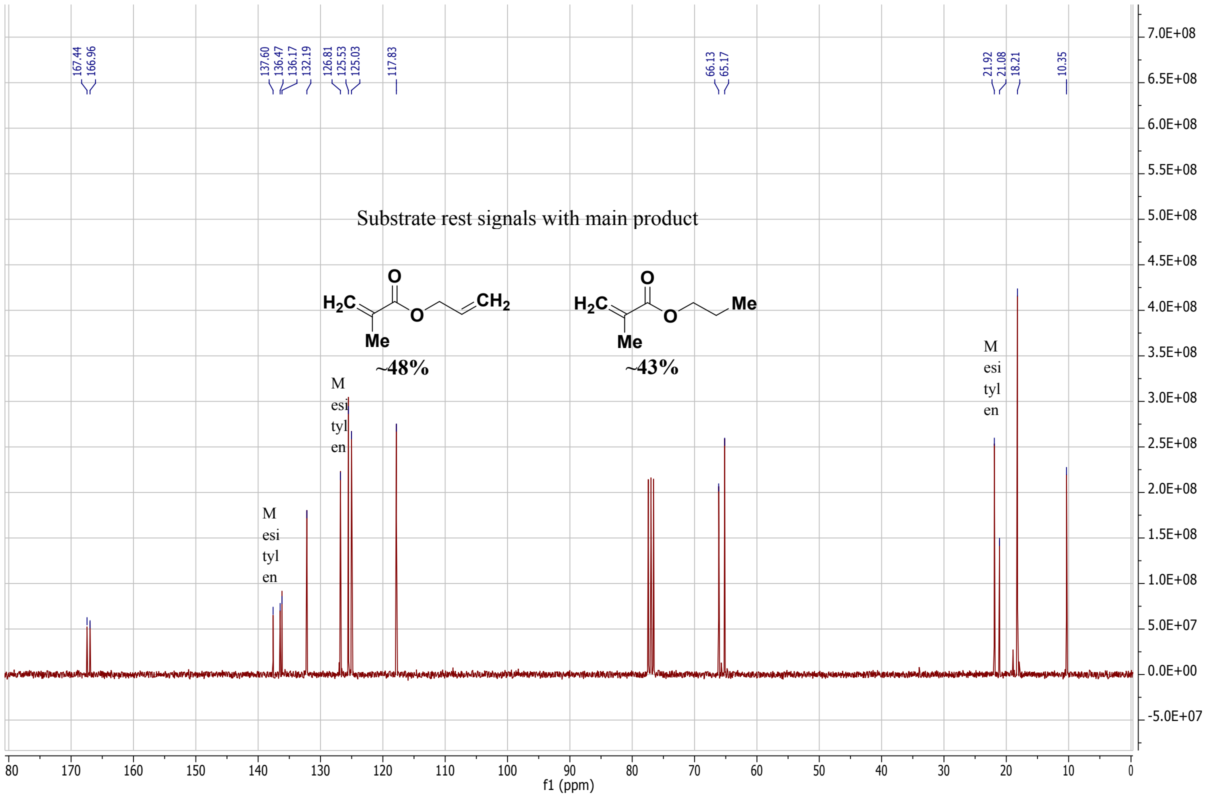
Propyl methacrylate 13

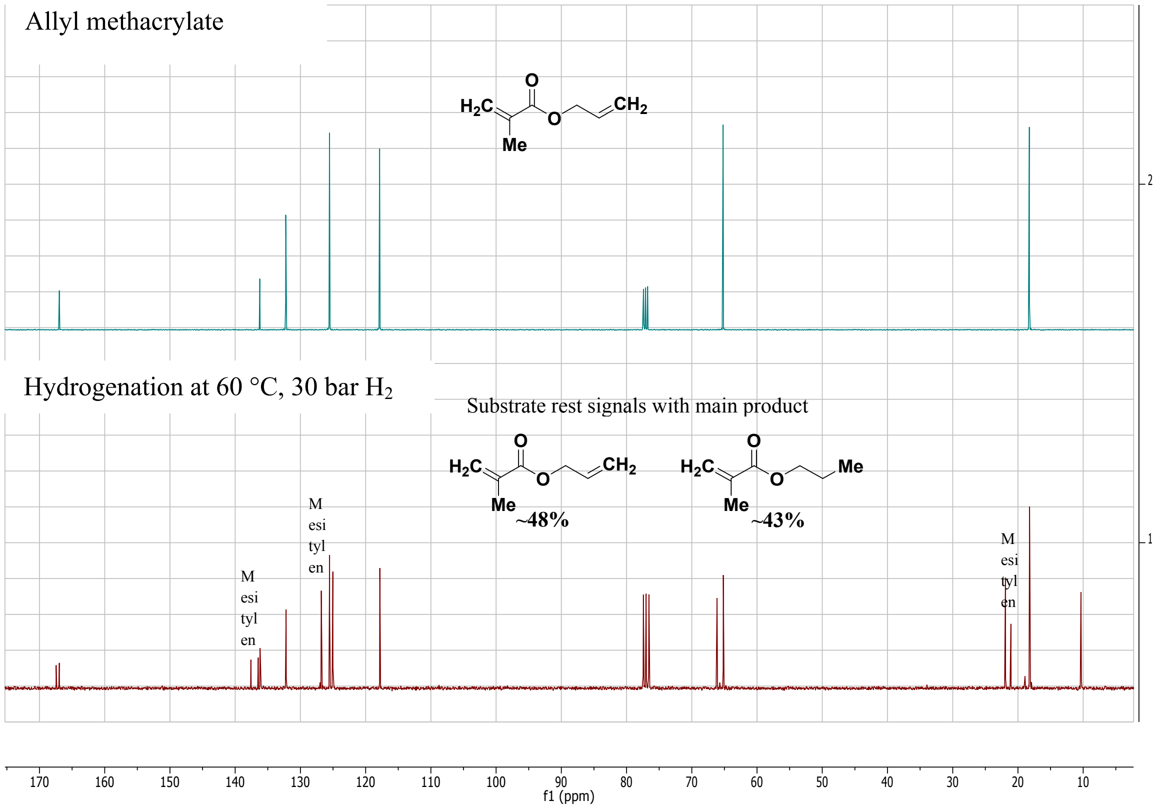
^{1}H-NMR in CDCl$_3$





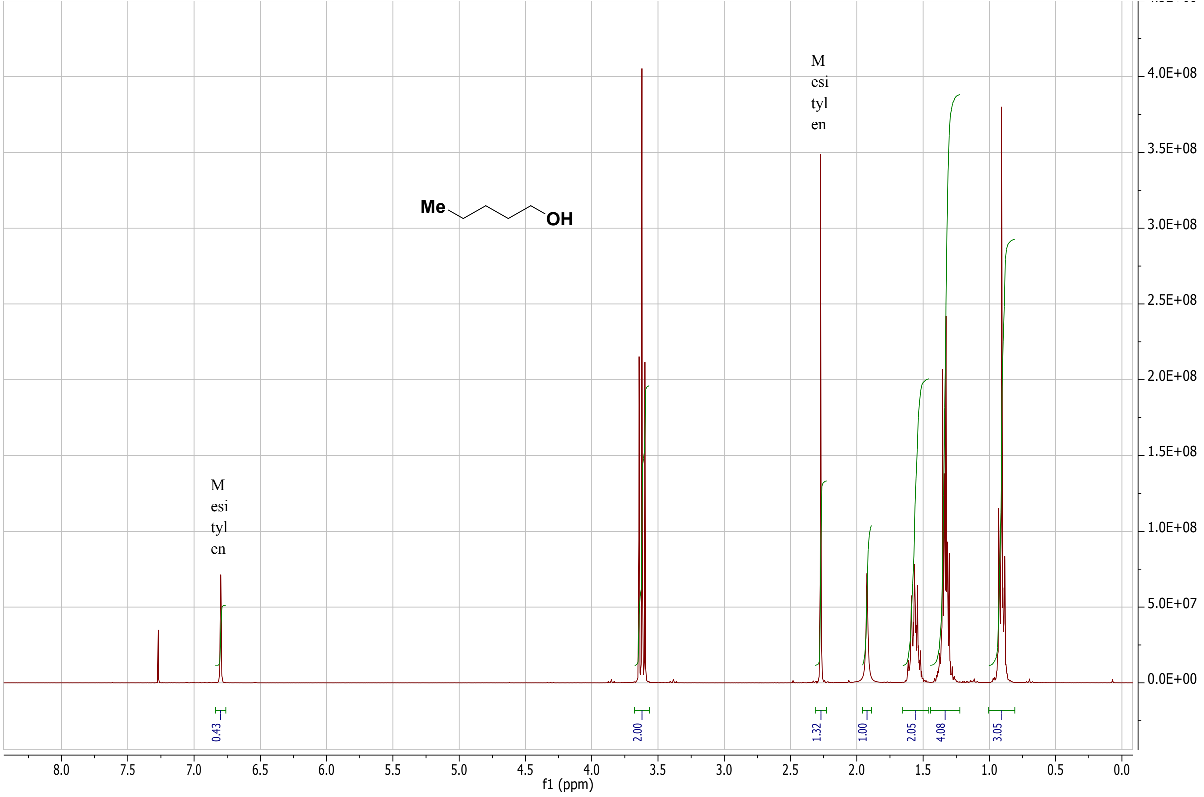
^{13}C-NMR in $CDCl_3$



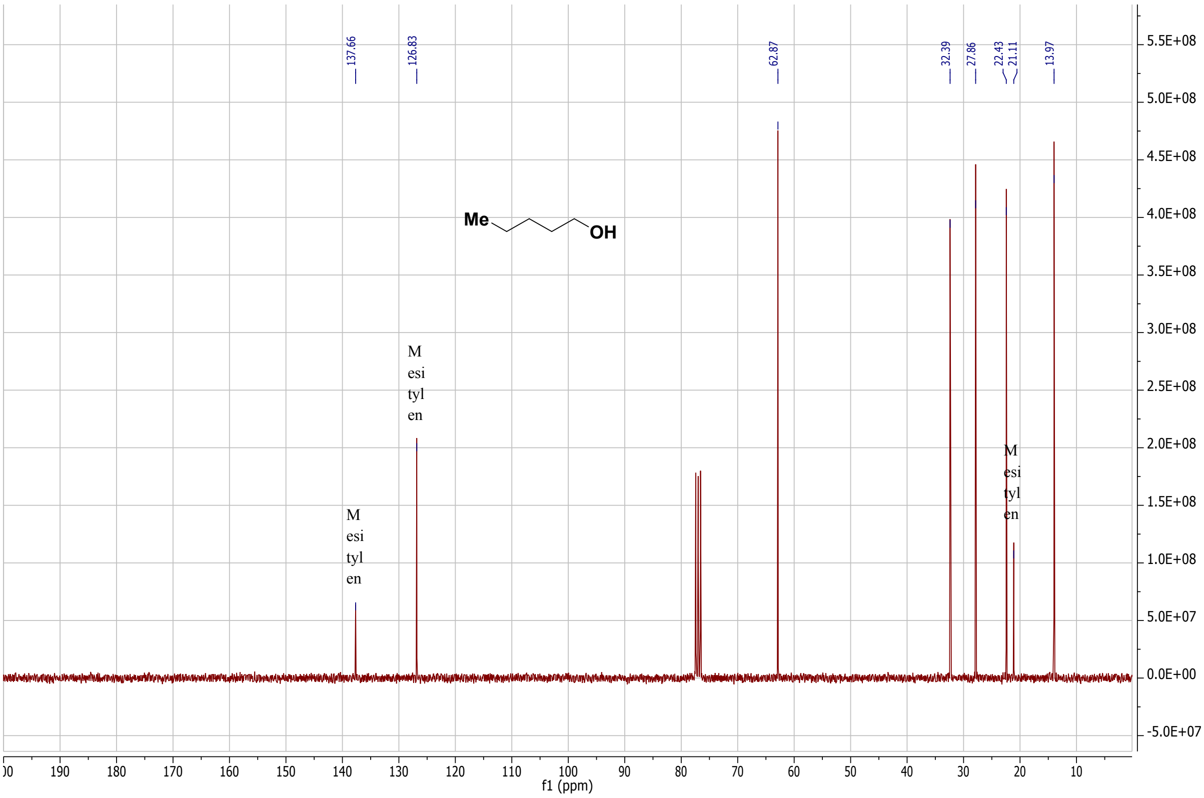


Pentan-1-ol 14

^{1}H-NMR in CDCl$_3$

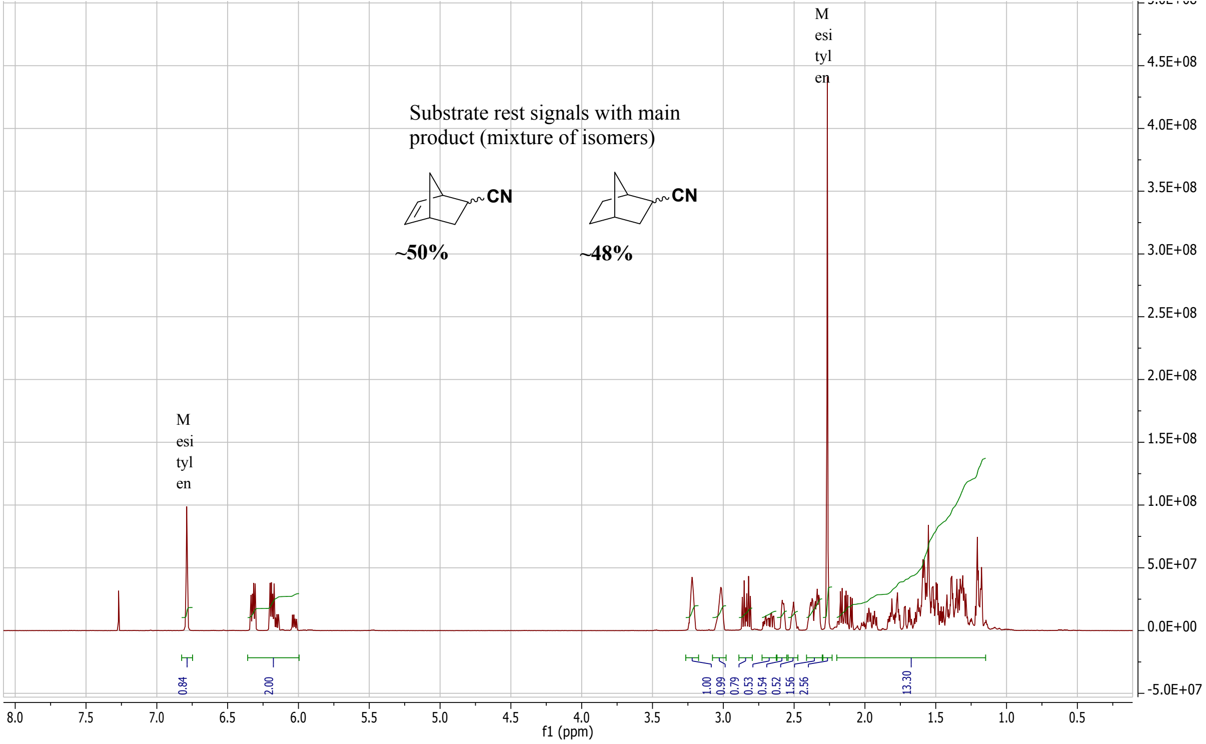


^{13}C-NMR in CDCl$_3$

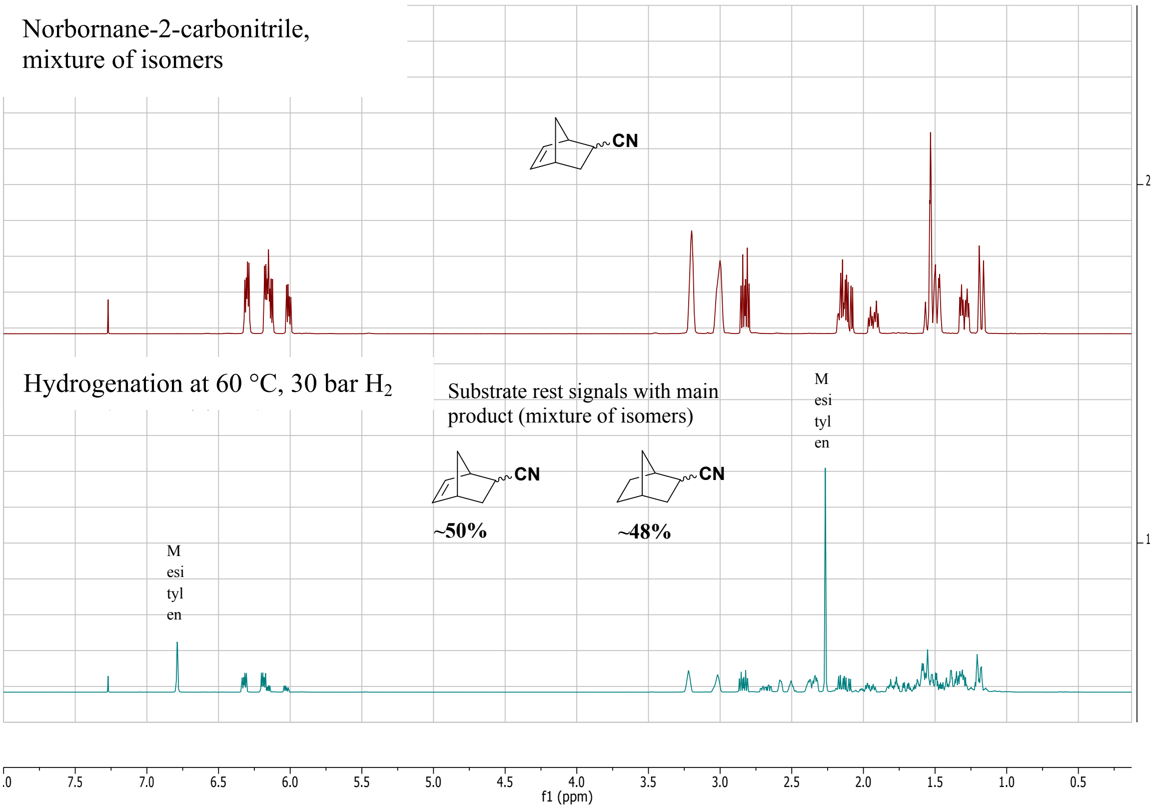


Norbornane-2-carbonitrile 16

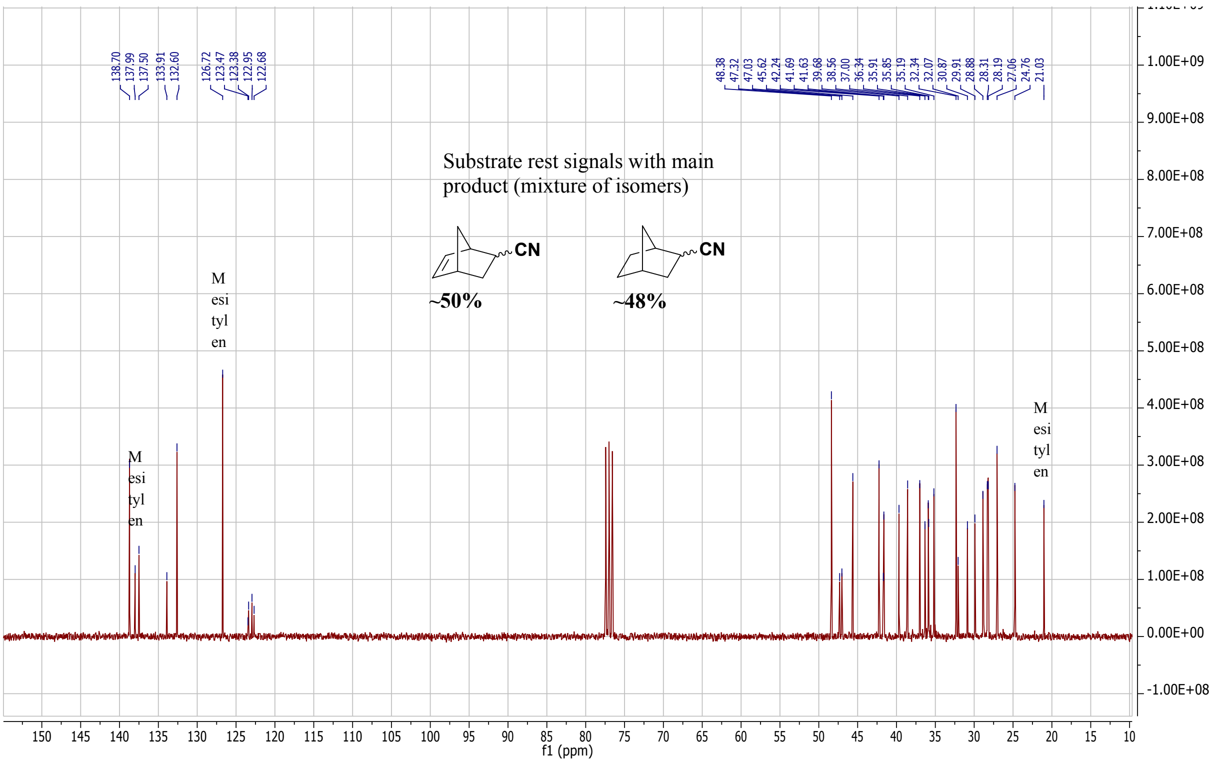
^{1}H-NMR in $CDCl_3$



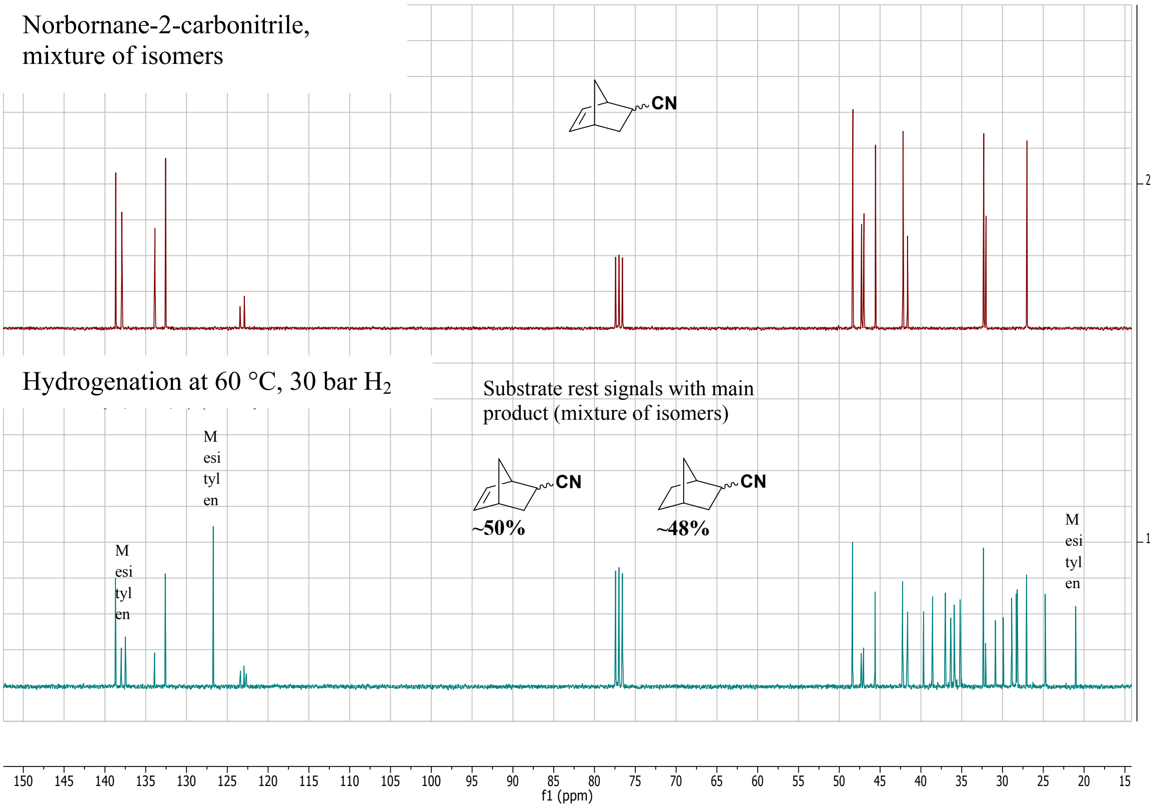
^{1}H-NMR in $CDCl_3$



^{13}C-NMR in $CDCl_3$

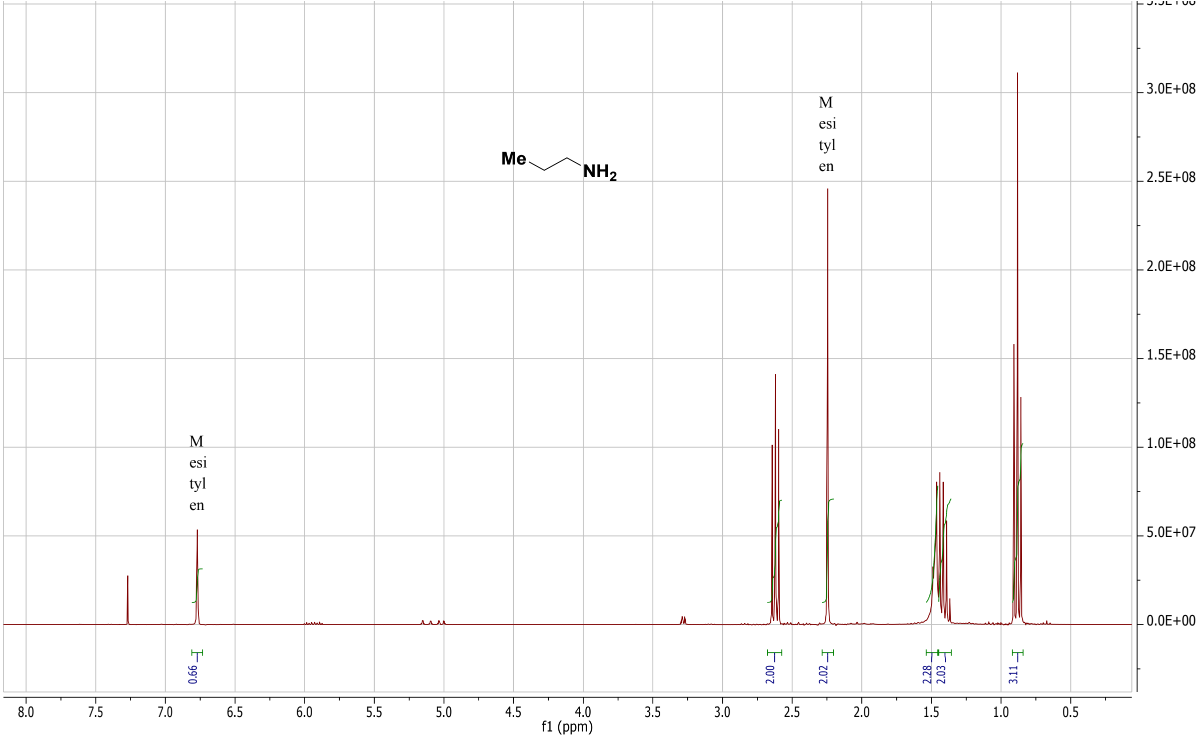


^{13}C-NMR in $CDCl_3$

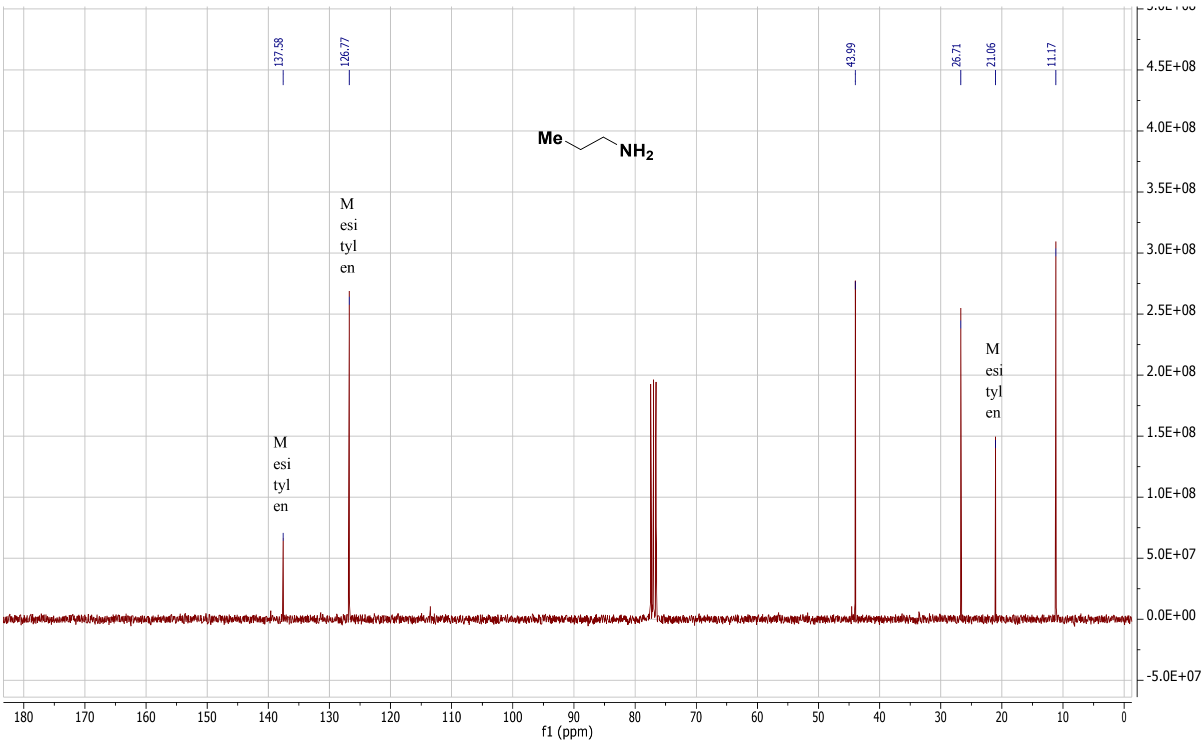


1-Aminopropane 17

^{1}H-NMR in CDCl$_3$

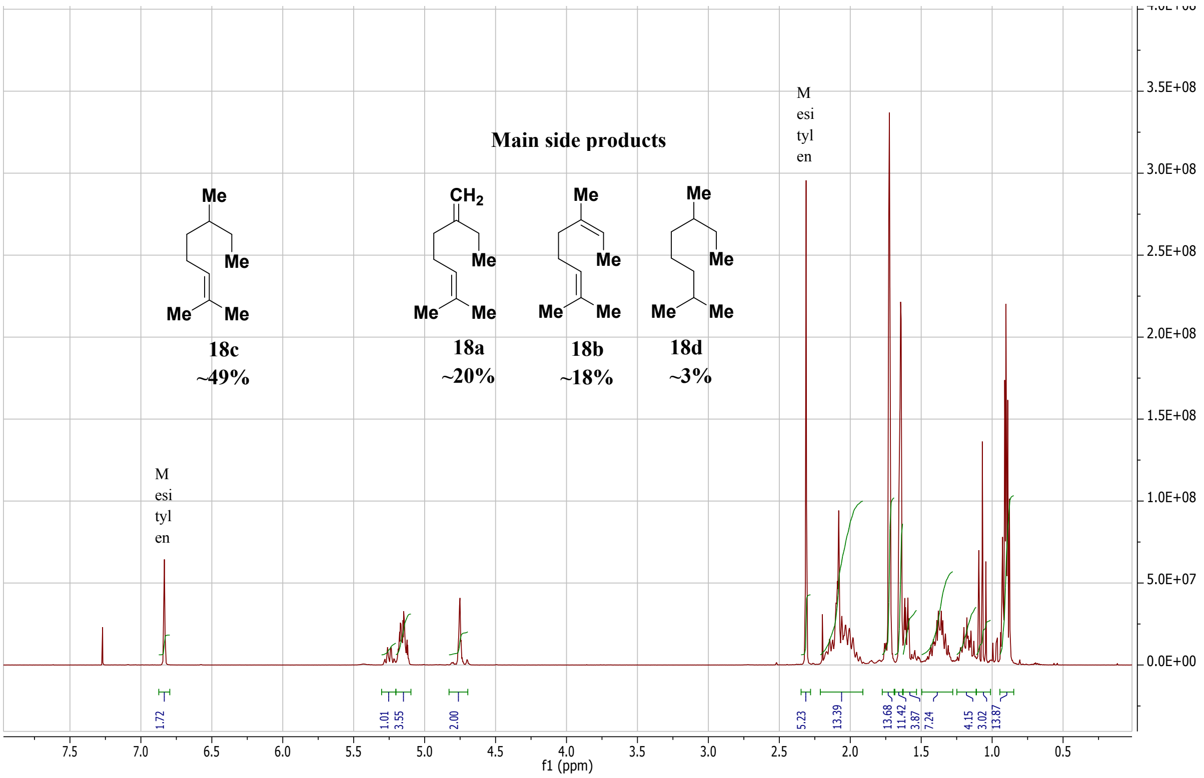


^{13}C-NMR in CDCl$_3$

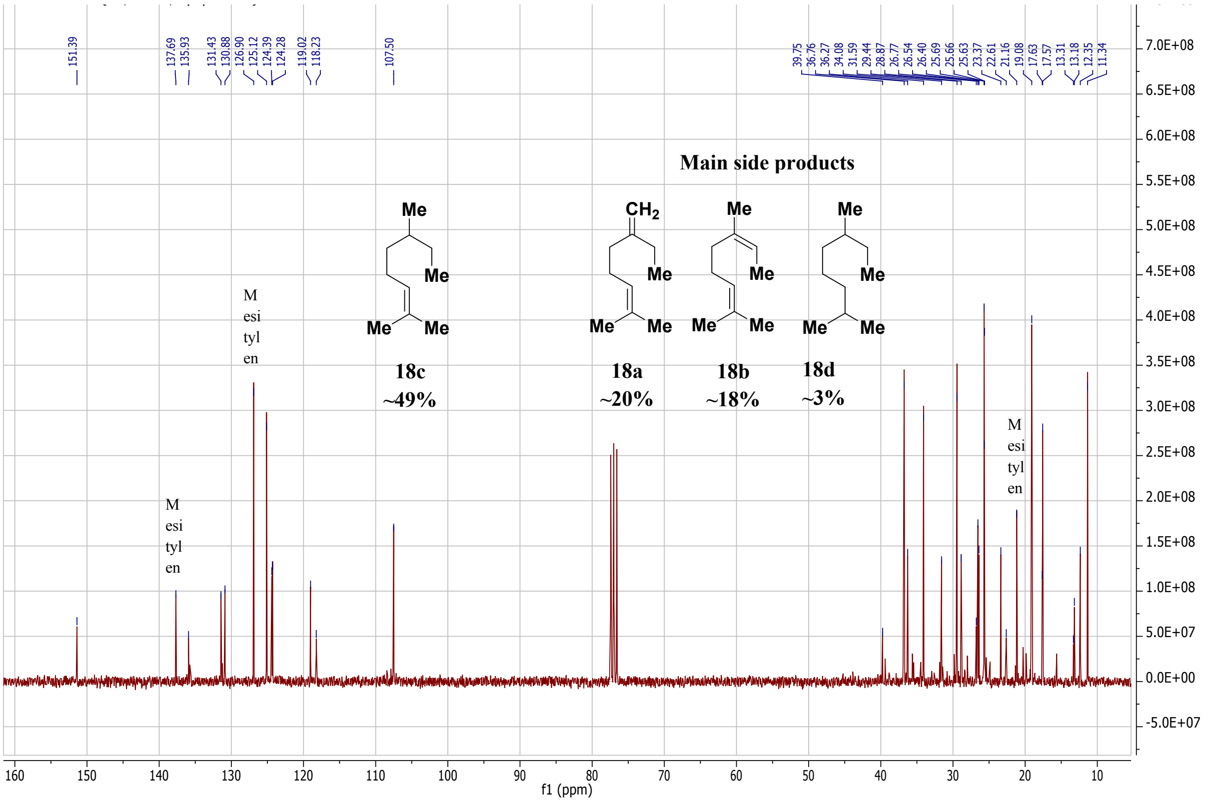


Myrcene hydrogenation at 40 °C, 30 bar H_2
2-Methyl-6-methyleneoct-2-ene <u>18c</u> as main product

^{1}H-NMR in $CDCl_3$

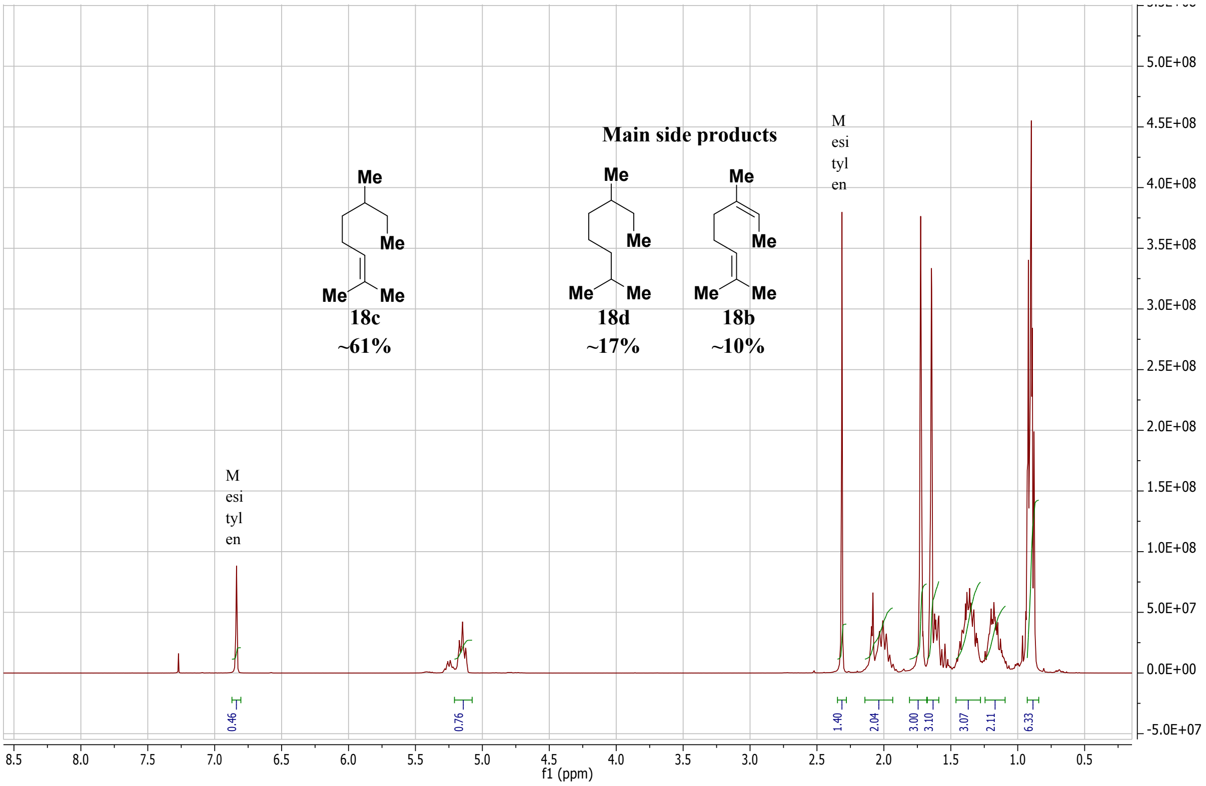


^{13}C-NMR in $CDCl_3$

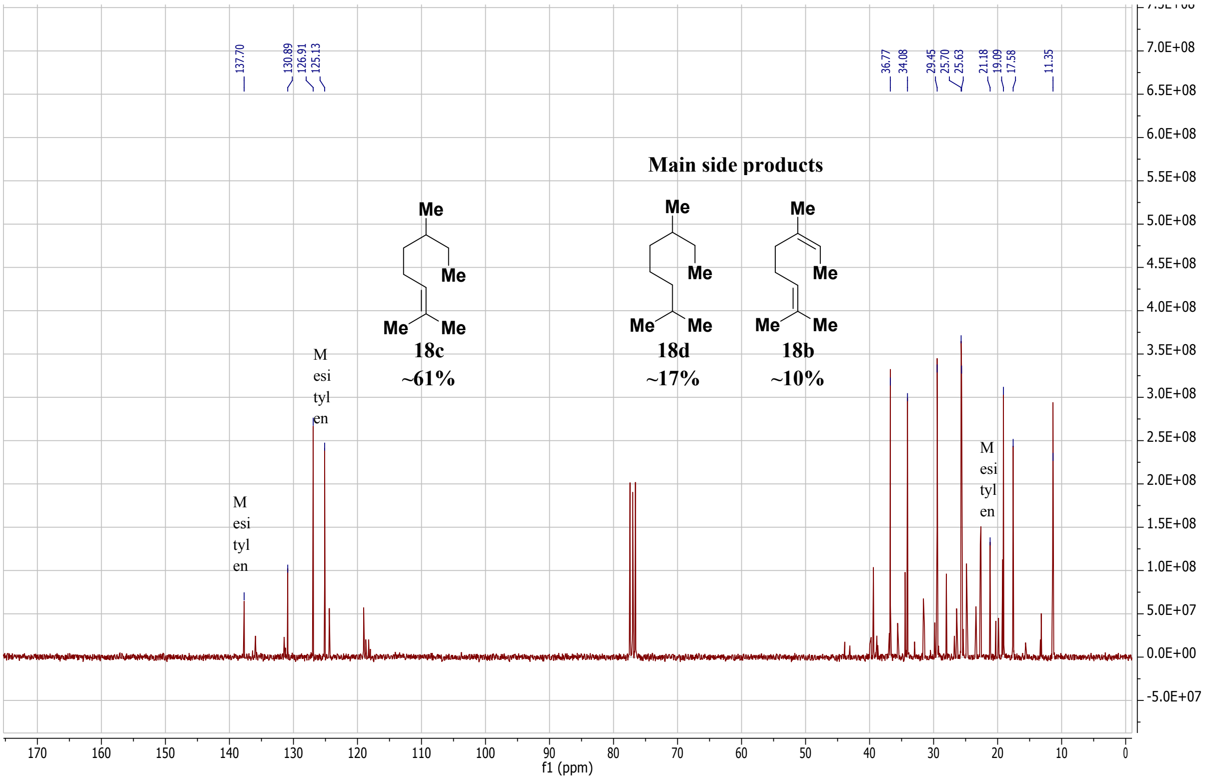


Myrcene hydrogenation at 60 °C, 30 bar H_2
2-Methyl-6-methyleneoct-2-ene <u>18c</u> as main product

^{1}H-NMR in $CDCl_3$

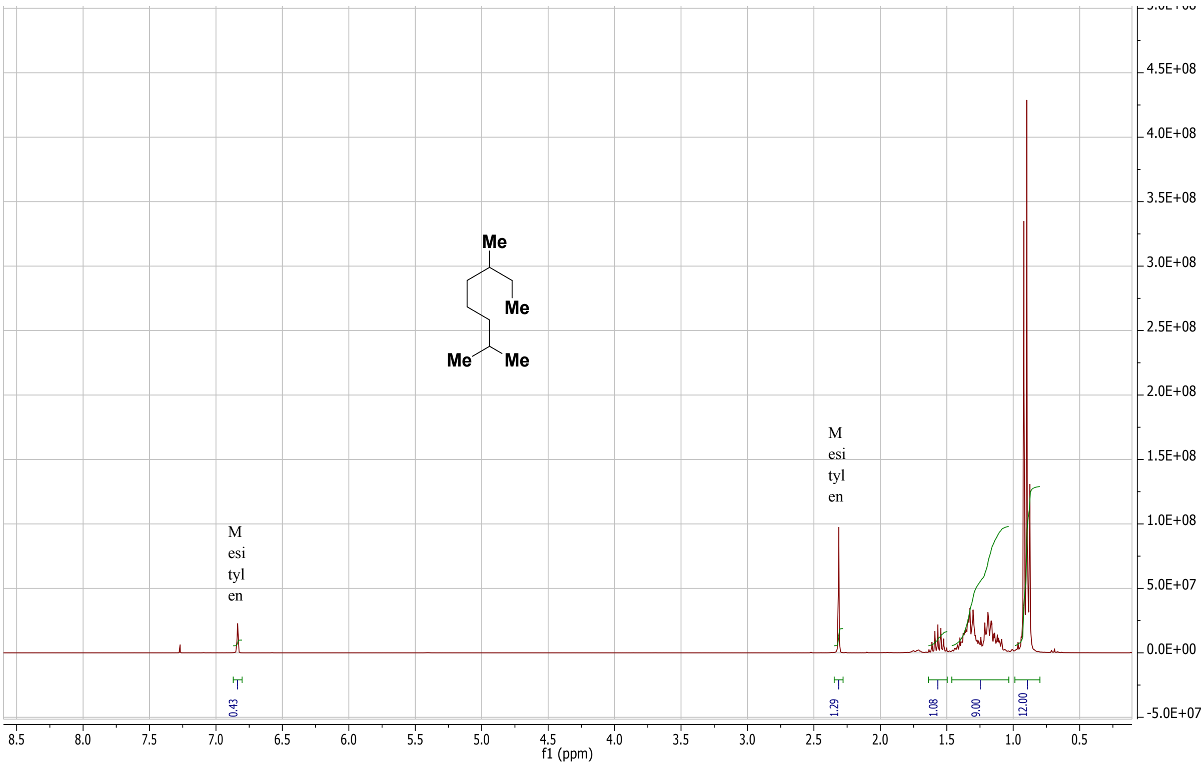


^{13}C-NMR in $CDCl_3$

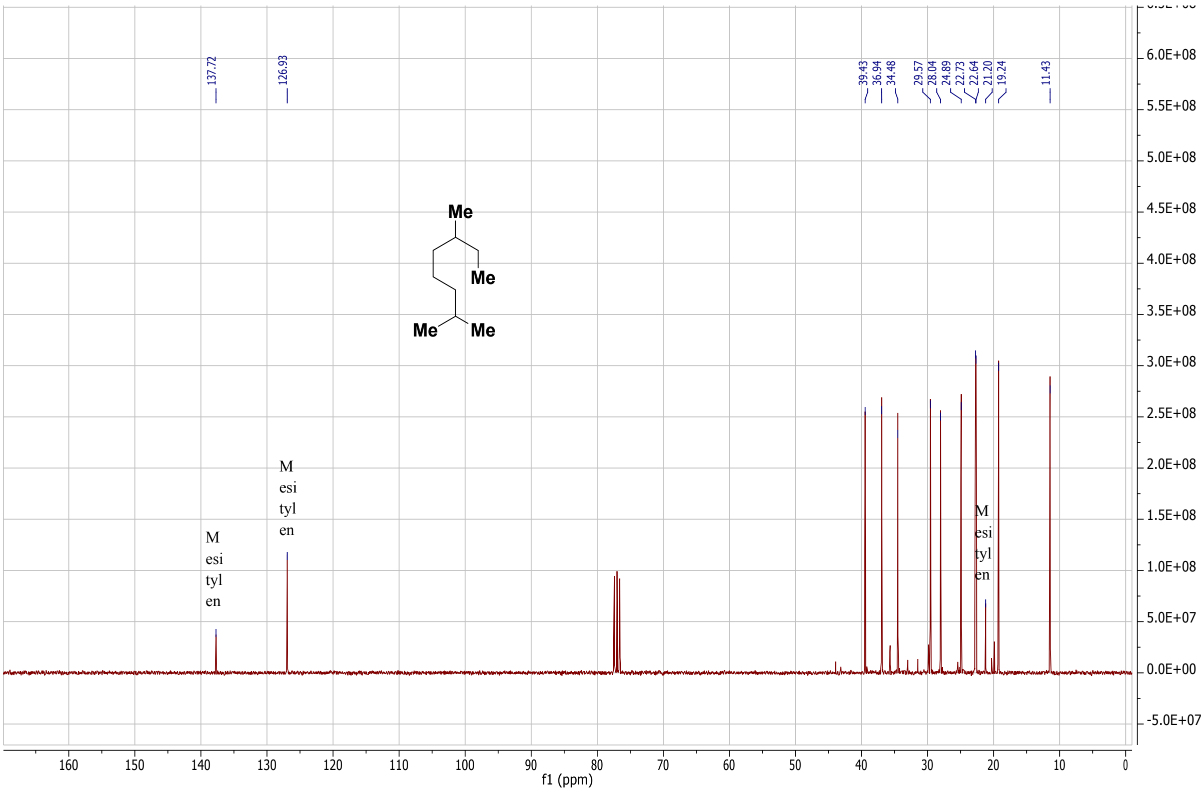


Myrcene hydrogenation at 100 °C, 30 bar H_2
2,6-Dimethyloctane <u>18d</u>

^{1}H-NMR in $CDCl_3$

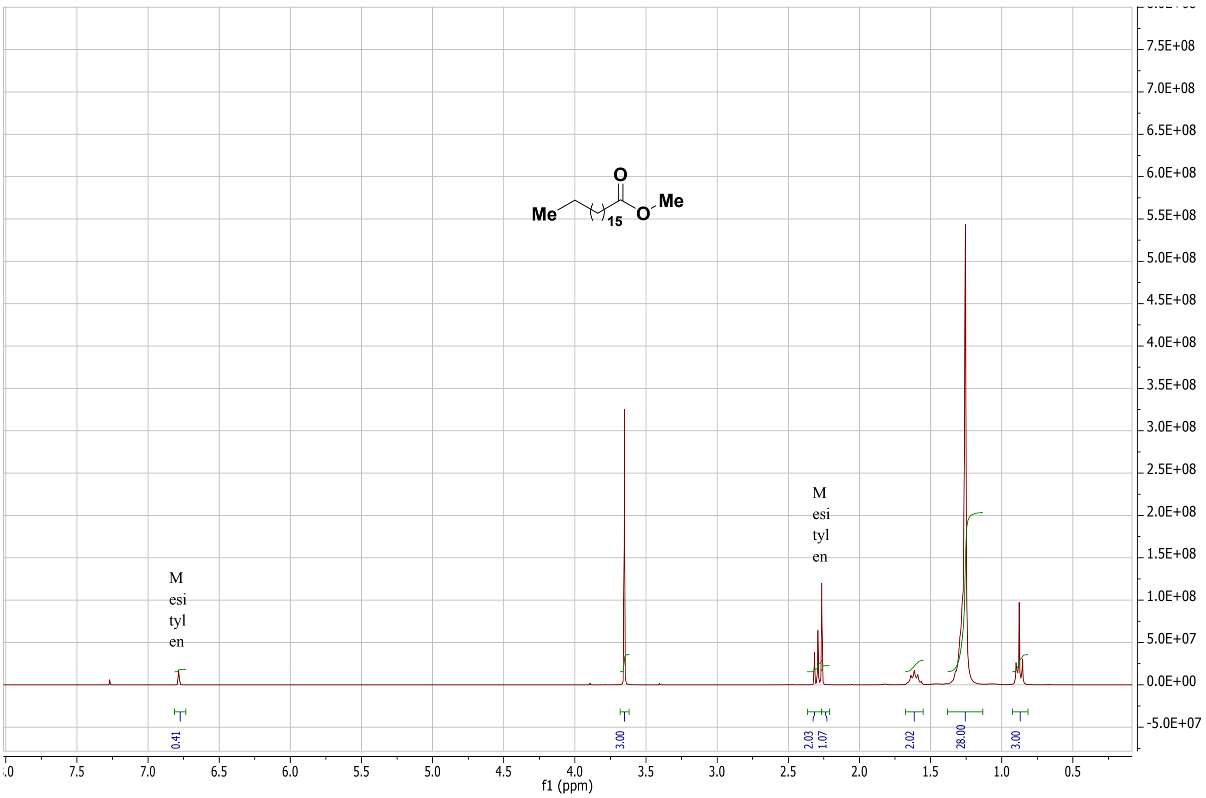


^{13}C-NMR in $CDCl_3$

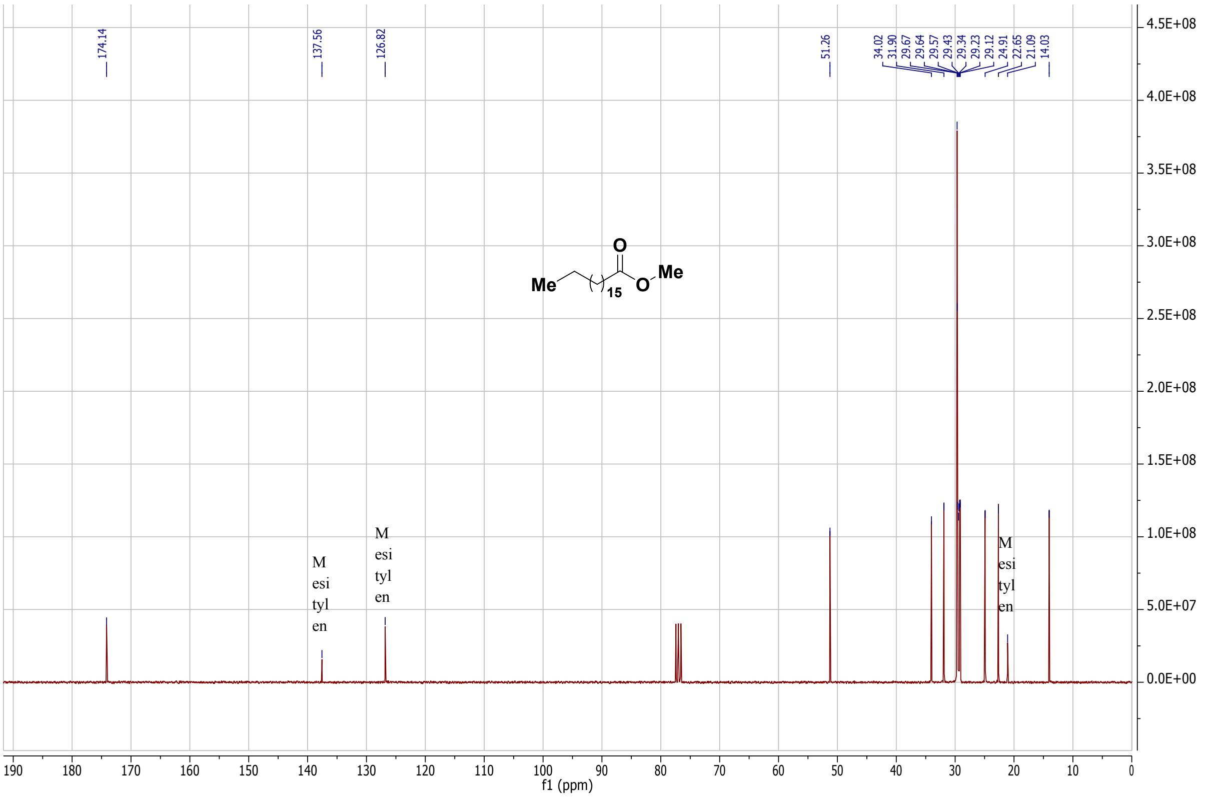


Methyl stearate 19 obtained from methyl oleate and methyl elaidate

^{1}H-NMR in CDCl$_3$

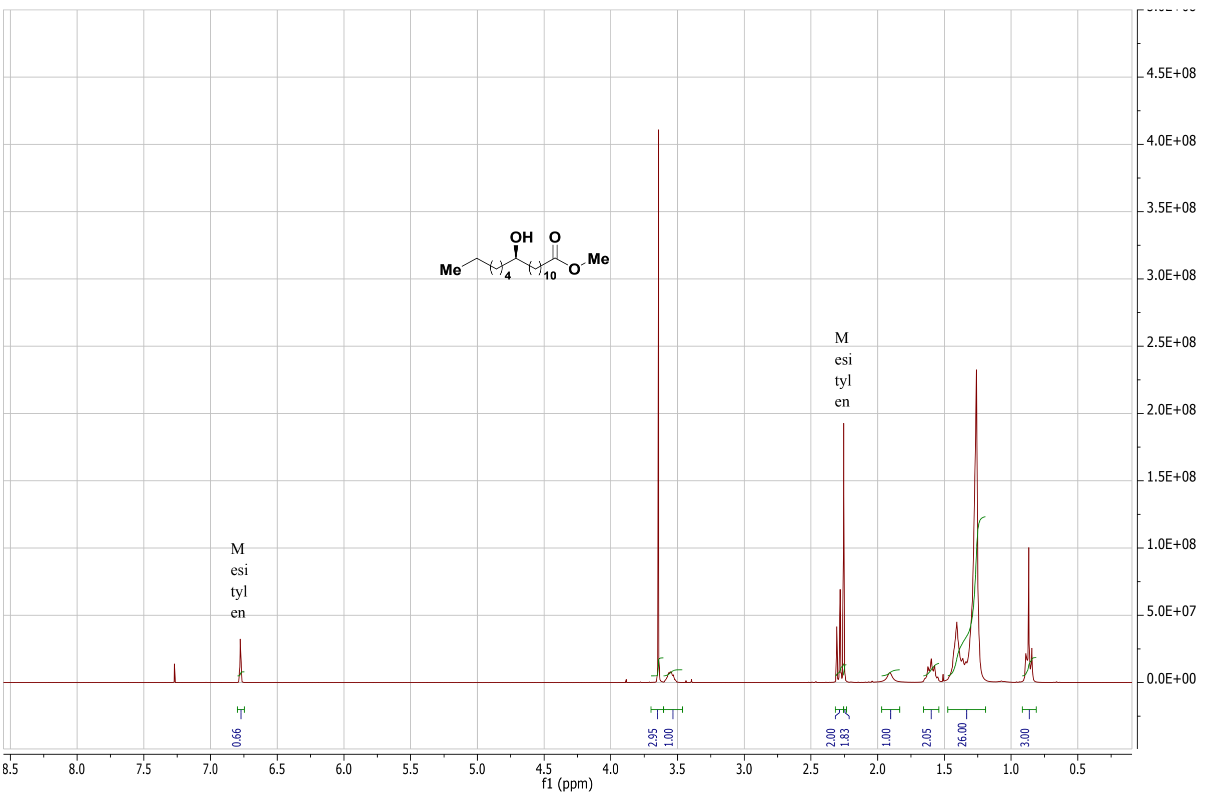


^{13}C-NMR in CDCl$_3$

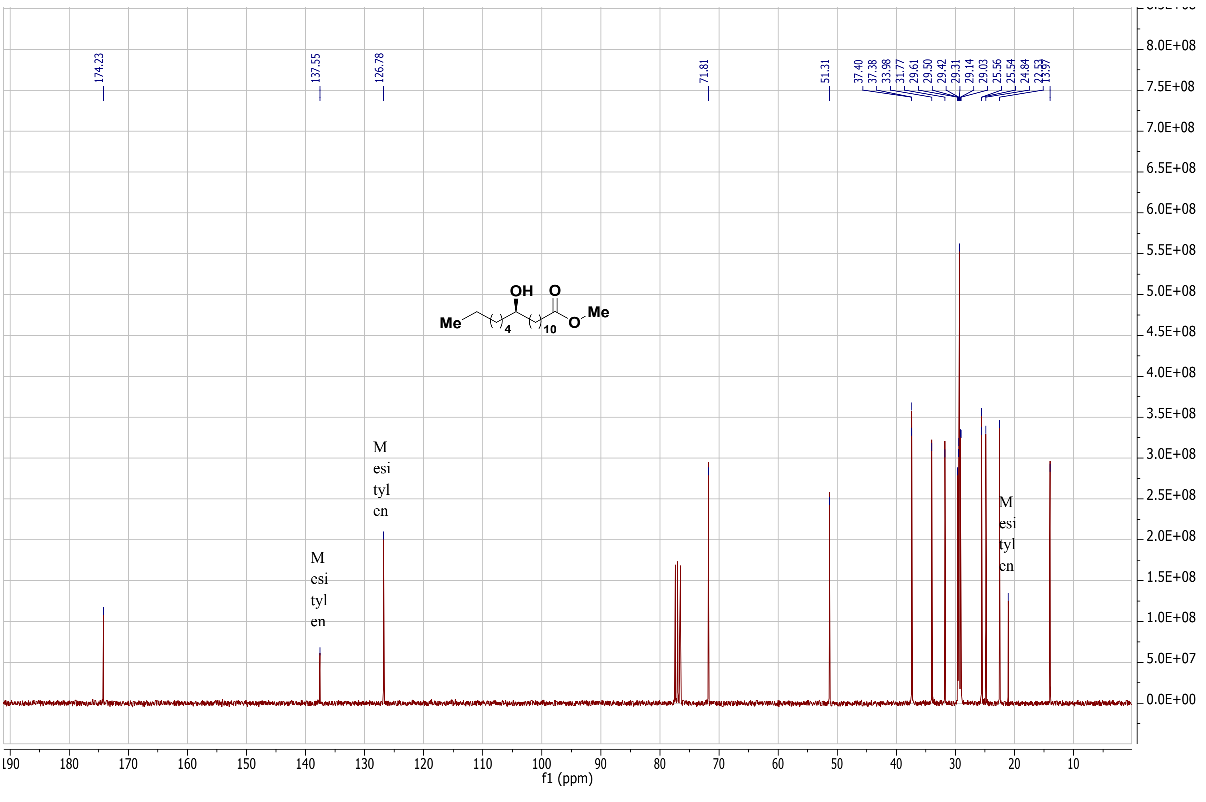


Methyl (R)-12-hydroxyoctadecanoate 20

^{1}H-NMR in CDCl$_3$

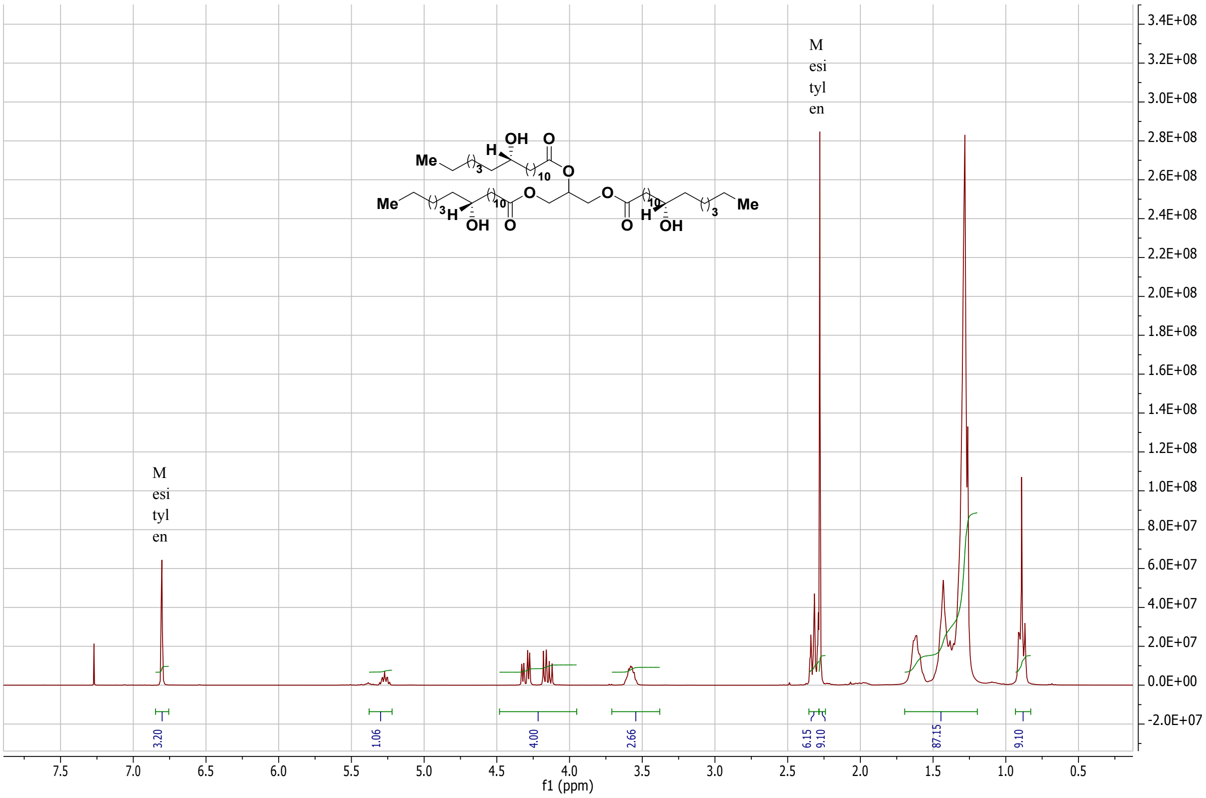


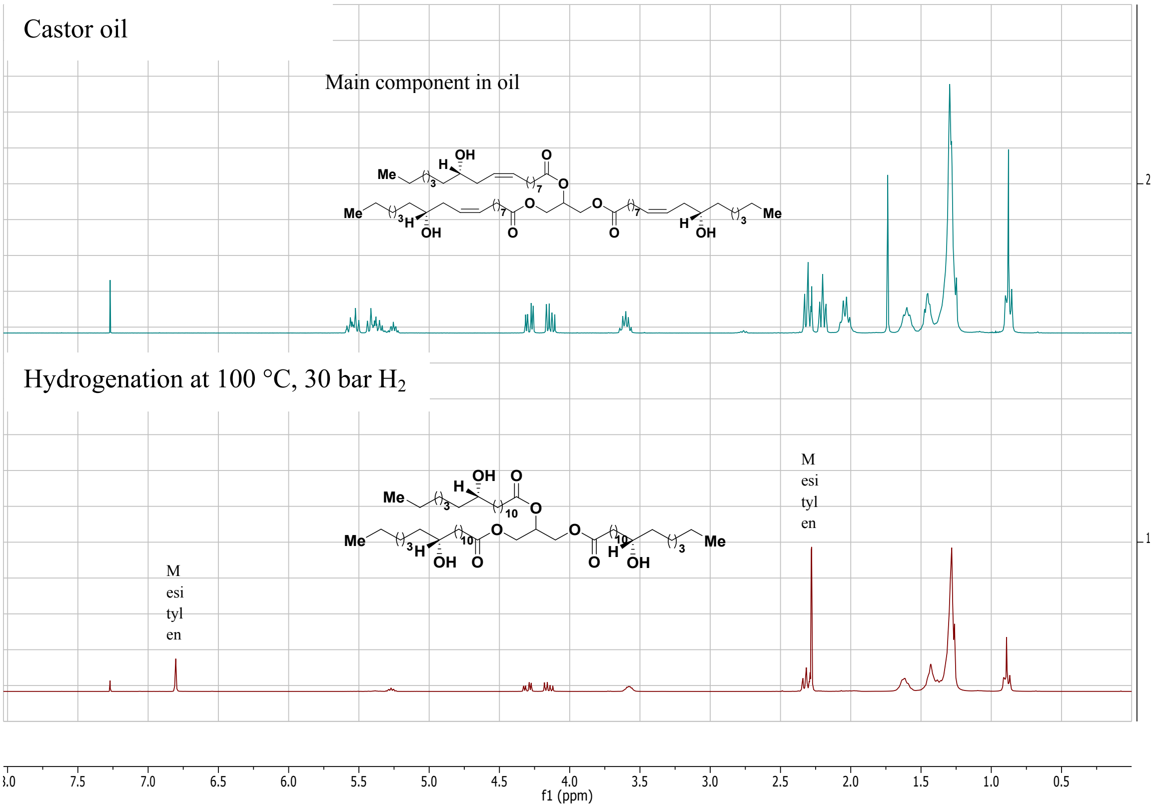
^{13}C-NMR in CDCl$_3$



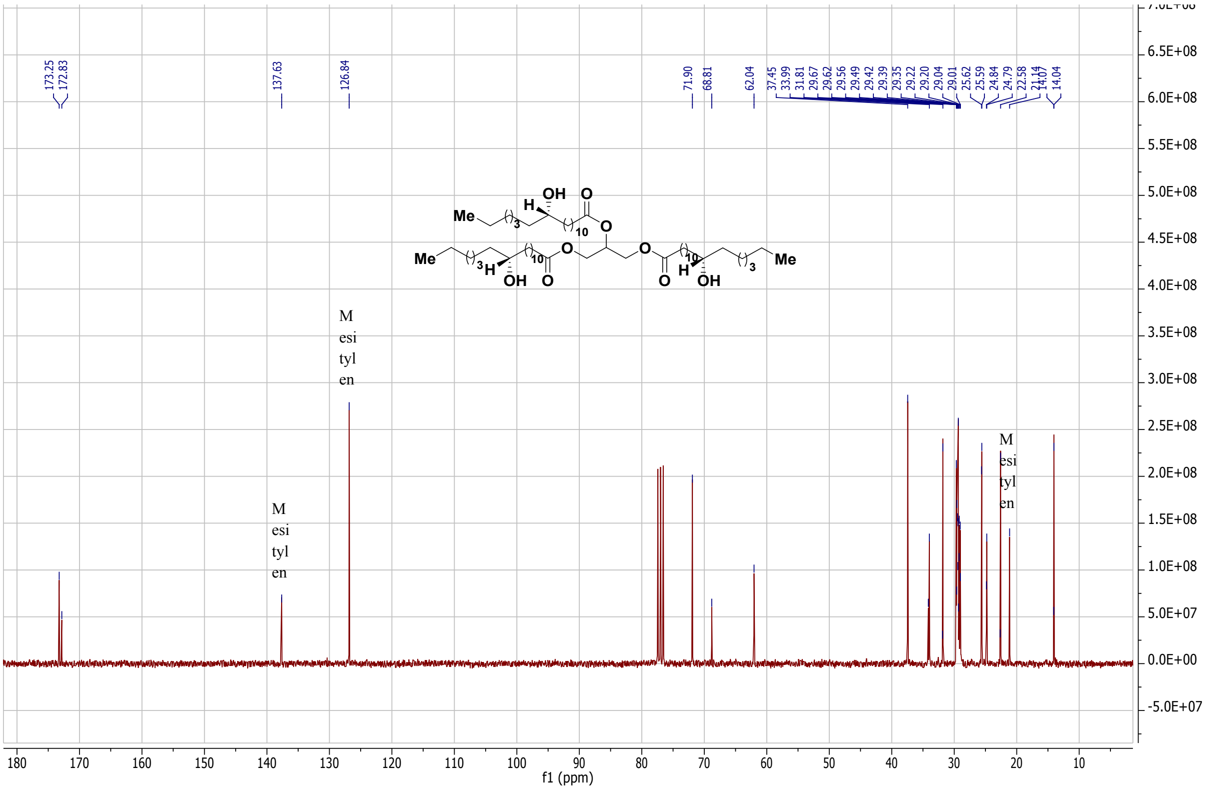
Hydrogenated castor oil: 2-(((S)-12-hydroxyoctadecanoyl)oxy)propane-1,3-diyl (12R,12'R)-bis(12-hydroxyoctadecanoate) 21

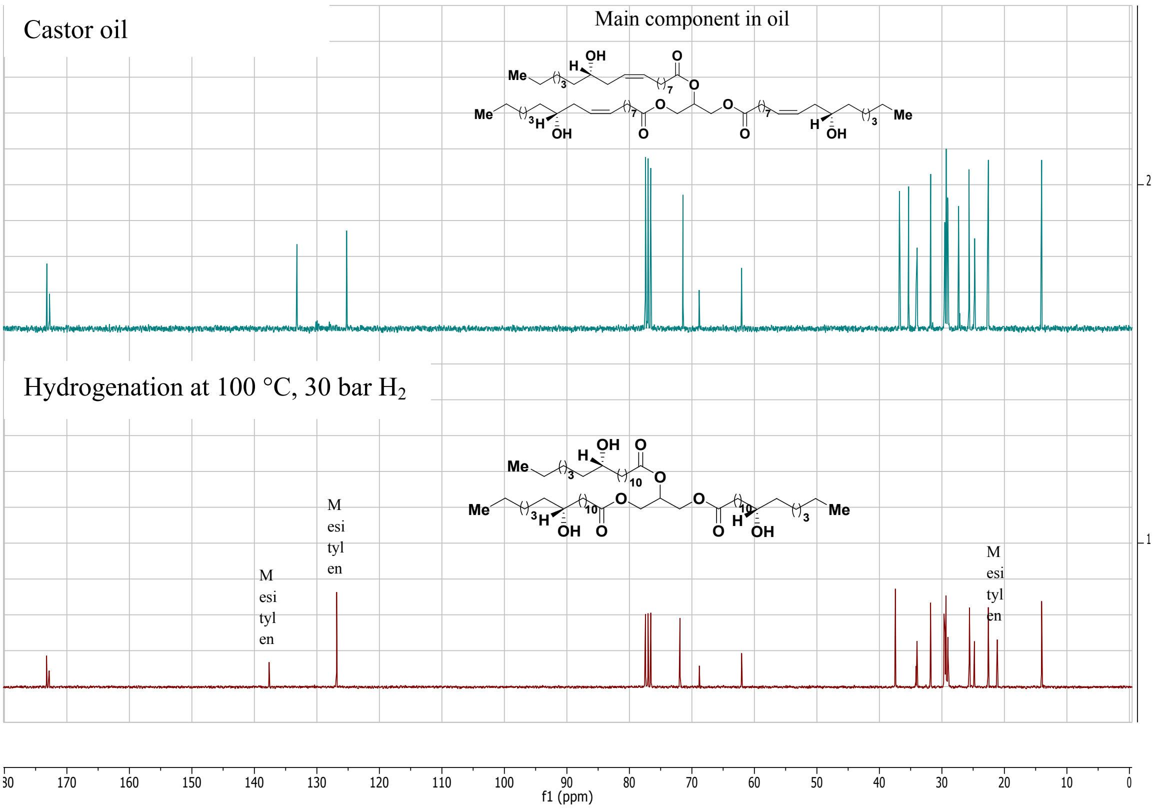
^{1}H-NMR in $CDCl_3$





^{13}C-NMR in $CDCl_3$



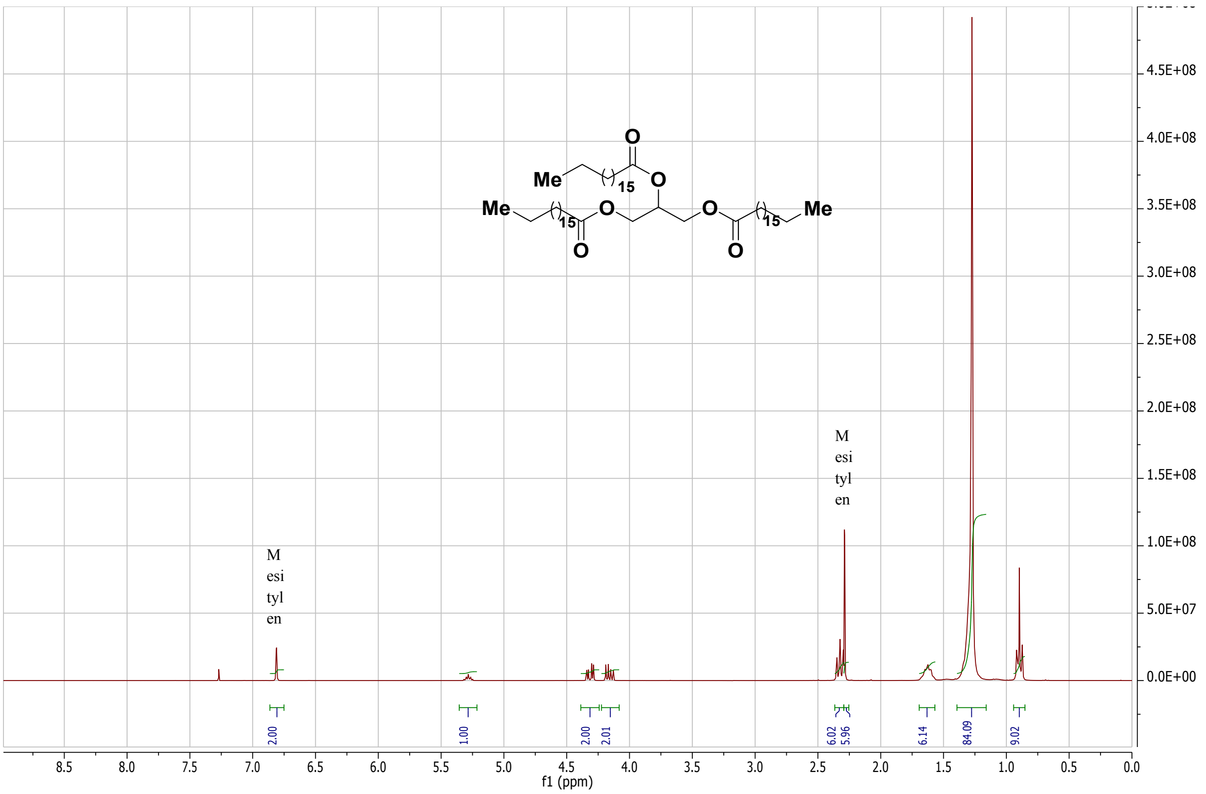

Castor oil

Main component in oil

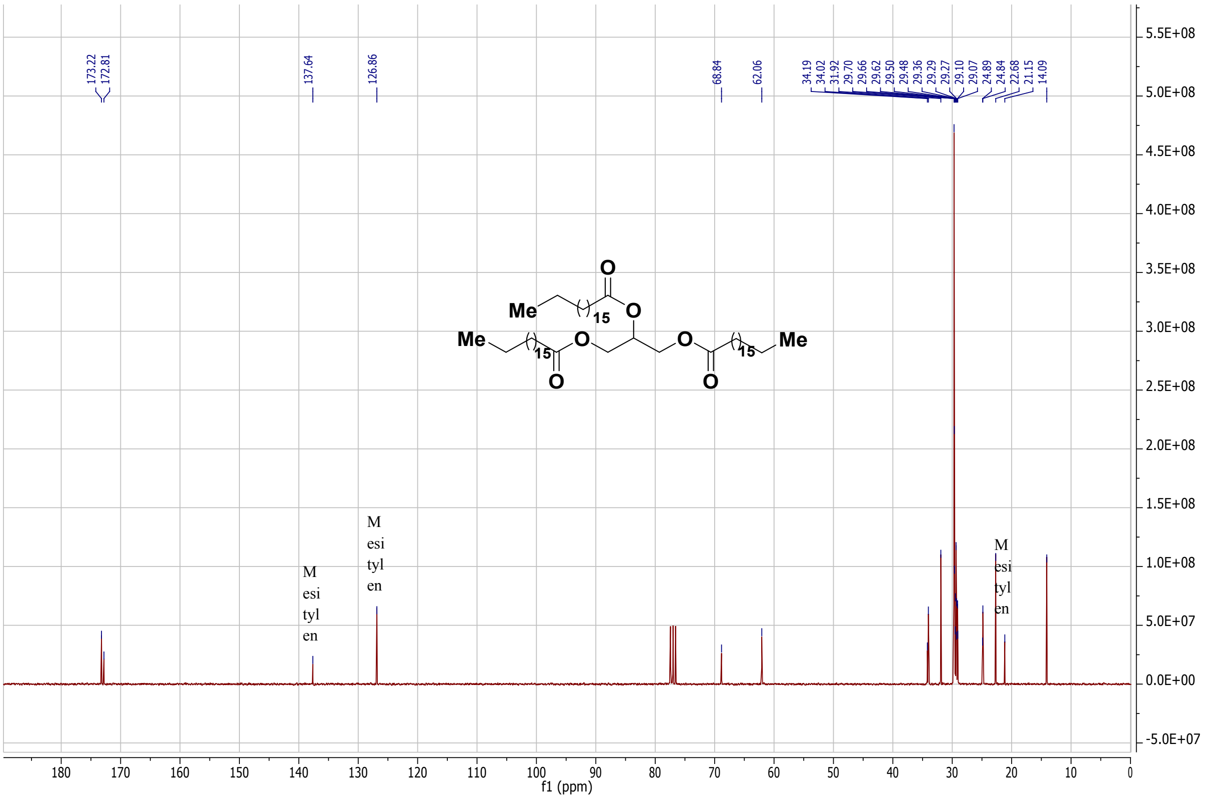
Hydrogenation at 100 °C, 30 bar H_2

Propane-1,2,3-triyl tristearate 22 from glycerine trioleate

^{1}H-NMR in CDCl$_3$

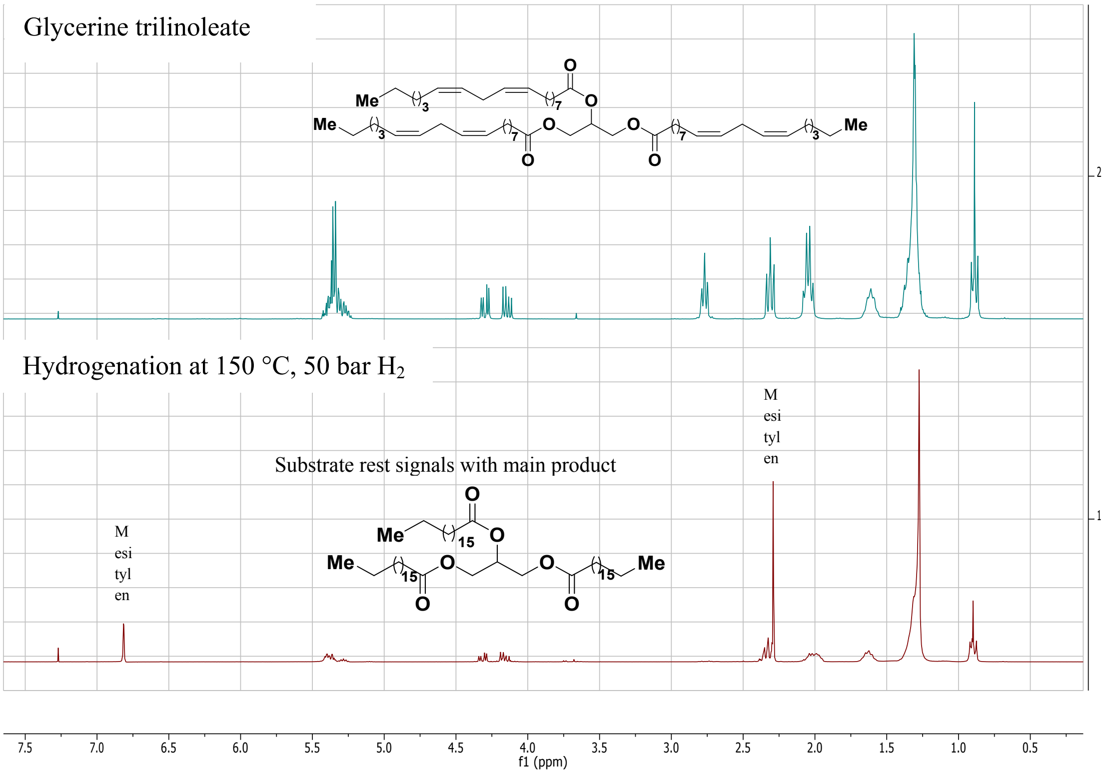


^{13}C-NMR in CDCl$_3$

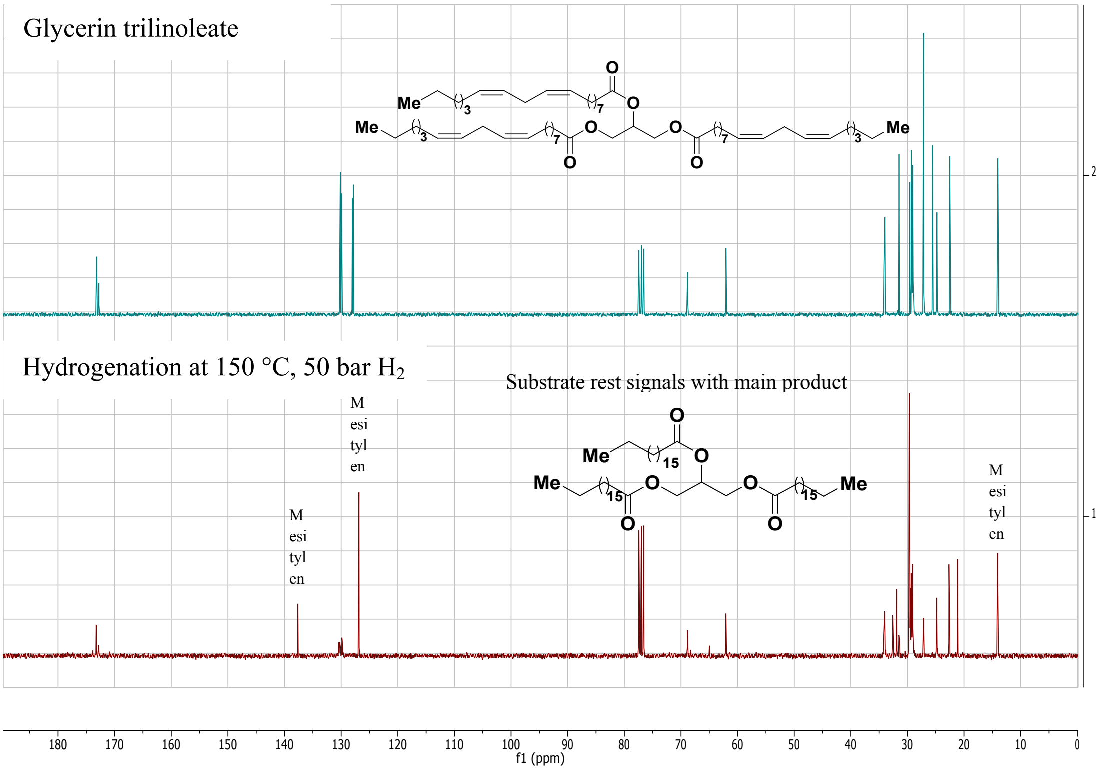


Glycerine trilinoleate hydrogenation to propane-1,2,3-triyl tristearate 22 as a main product

^{1}H-NMR in CDCl$_3$

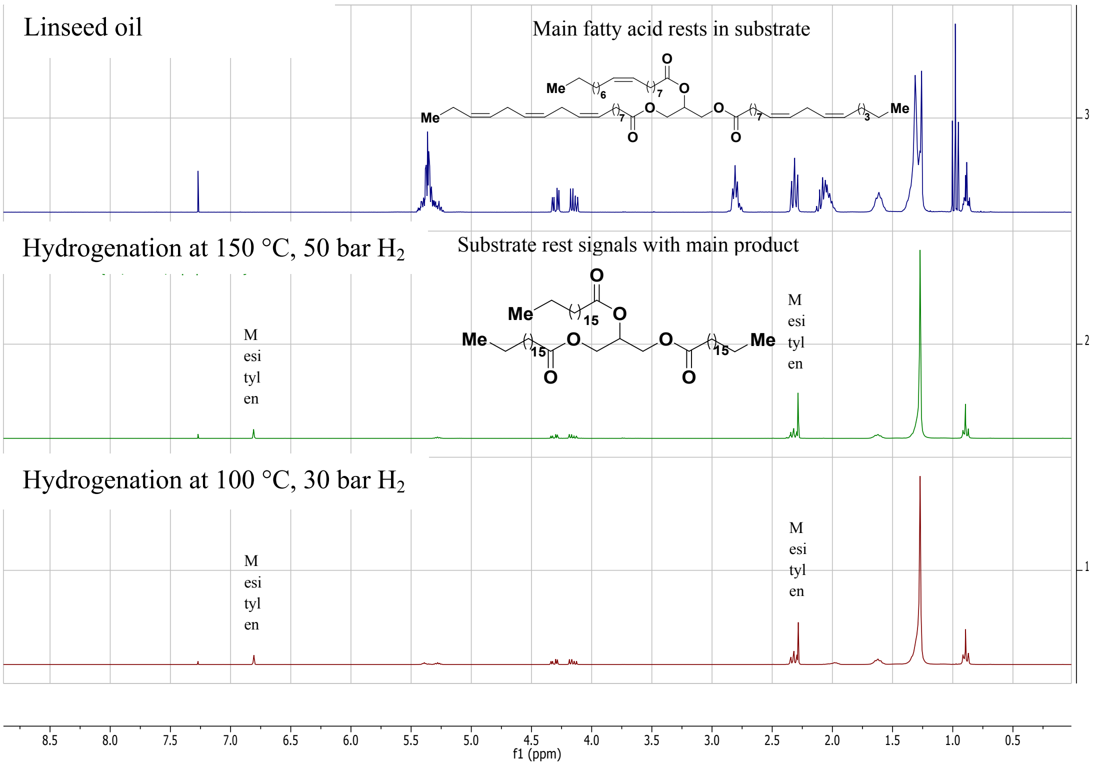


^{13}C-NMR in CDCl$_3$

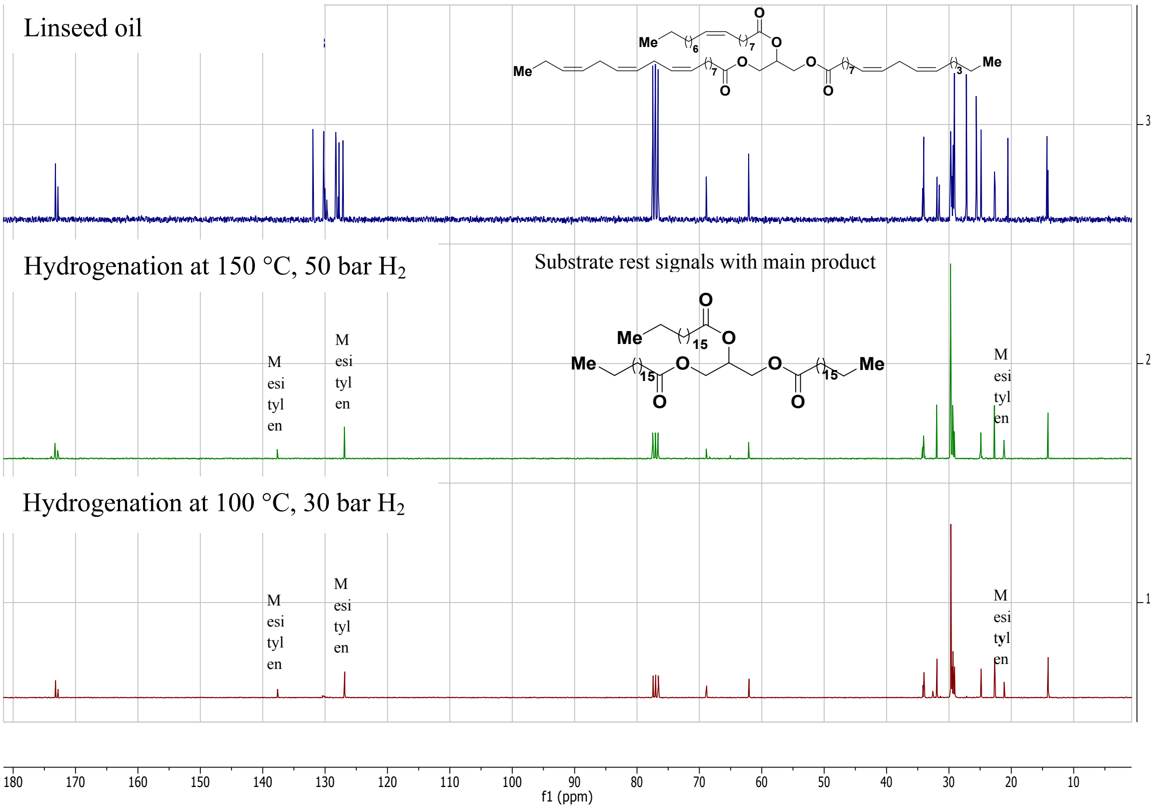


Linseed oil hydrogenation to propane-1,2,3-triyl tristearate 22 as a main product

^{1}H-NMR in $CDCl_3$

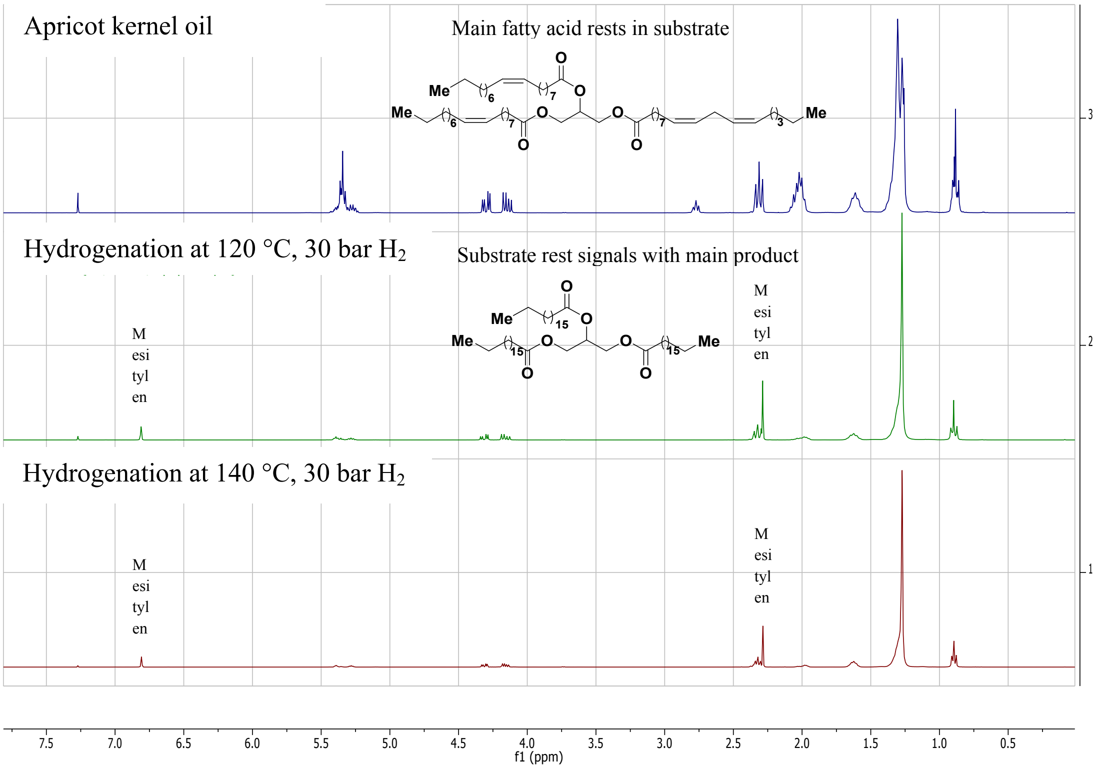


^{13}C-NMR in $CDCl_3$

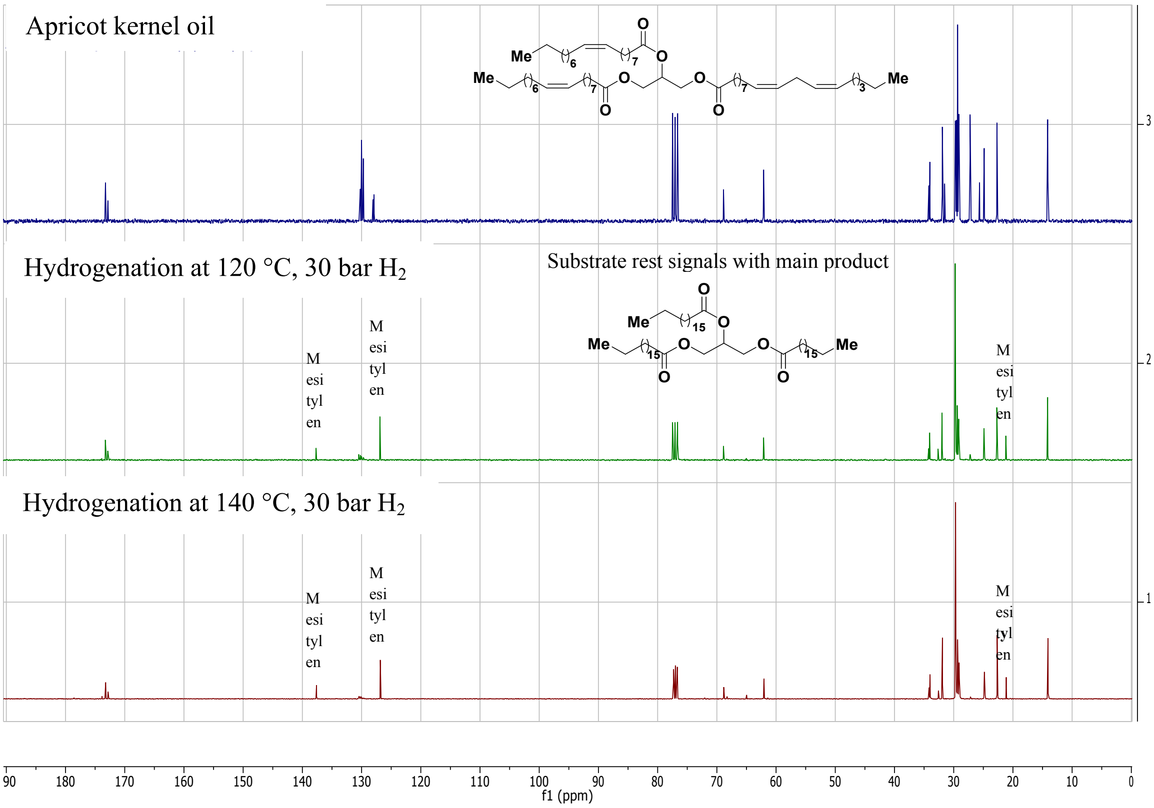


Apricot kernel oil hydrogenation to propane-1,2,3-triyl tristearate 22 as a main product

^{1}H-NMR in $CDCl_3$



^{13}C-NMR in $CDCl_3$



S10. Catalyst characterization

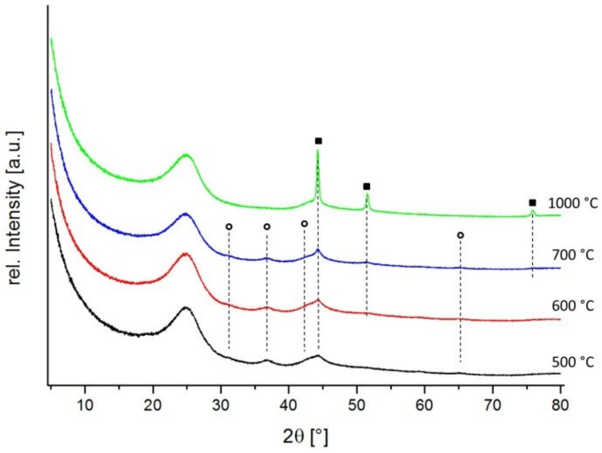
A) Elemental analysis

Table S6. Elemental analysis of the selected catalysts

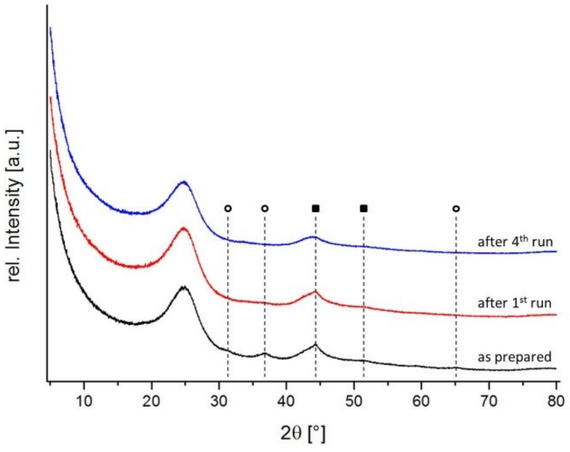
Catalyst	Co, %	C, %	N, %	H, %
Co-Ura/C, 3% Co, dry	3.03	80.38	2.89	0.62
Co-Ura/C-500	3.05	89.09	1.59	0.34
Co-Ura/C-600	**3.31**	**86.64**	**1.05**	**0.24**
Co-Ura/C-700	**2.80**	**90.71**	**0.94**	**0.75**
Co-Ura/C-1000	2.79	91.53	0.50	0.29
Co-Ura/C, 10% Co, dry	10.31	51.10	9.78	0.92
Co-Ura/C-600-10%	15.74	68.57	1.91	0.45

B) **Powder X-ray diffraction** (PXRD) patterns and data

B-1) Powder X-ray pattern of as-prepared Co-Ura/C catalysts. Phases are labelled as squares (Co) and circles (Co_3O_4).



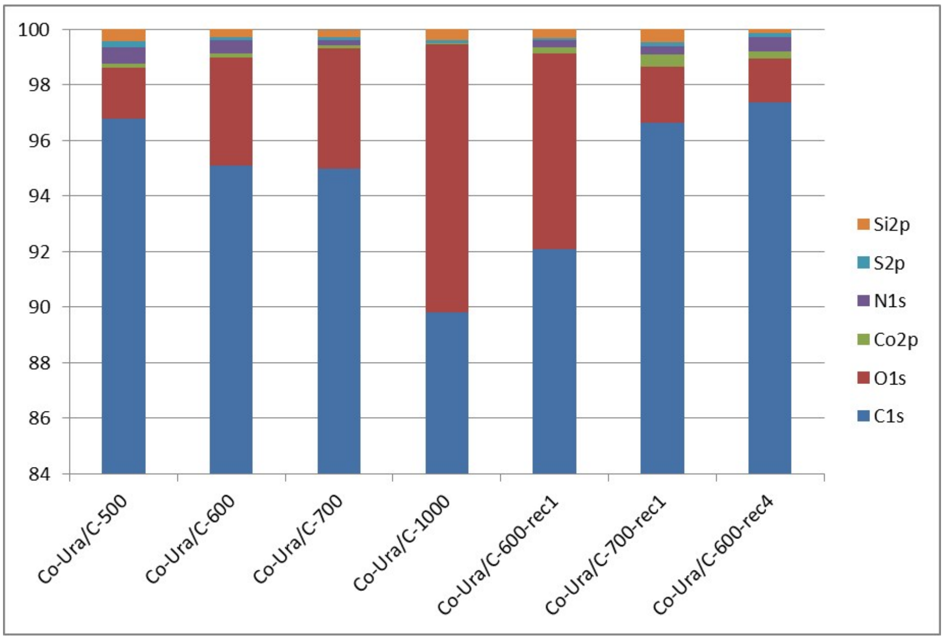
B-2) Powder X-ray diffraction pattern of as-prepared and recycled catalyst Co-Ura/C-600.



C) **XPS** spectra and data

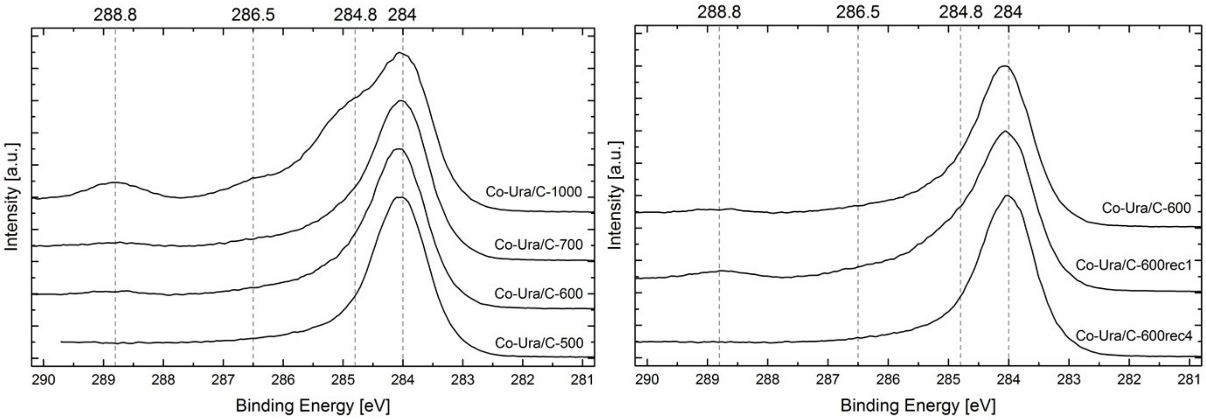
C-1) Quantitative surface analysis of selected catalysts (as table and diagram).

Catalyst	**C**, at.%	**O**, at.%	**Co**, at.%	**N**, at.%	**S**, at.%	**Si**, at.%
Co-Ura/C-500	96.77	1.83	0.16	0.59	0.20	0.45
Co-Ura/C-600	95.09	3.87	0.16	0.47	0.13	0.29
Co-Ura/C-700	94.98	4.33	0.12	0.17	0.11	0.26
Co-Ura/C-1000	89.82	9.65	0.02	0	0.11	0.39
Co-Ura/C-600-rec1	92.08	7.04	0.22	0.26	0.08	0.32
Co-Ura/C-700-rec1	96.62	2.03	0.44	0.29	0.13	0.49
Co-Ura/C-600-rec4	97.37	1.56	0.26	0.51	0.16	0.16
Vulcan XC72R	98.31	0.99	0	0	0.24	0.46

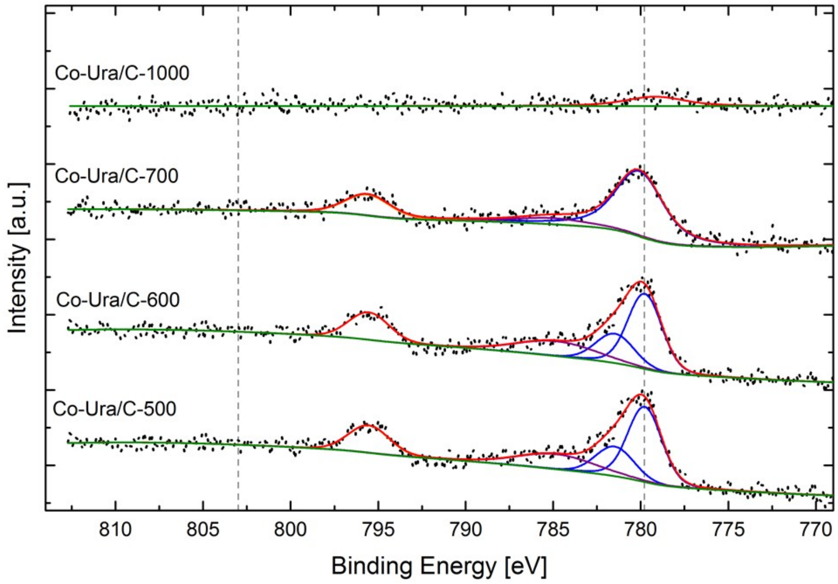


The detected silicon and sulfur can be found in similar concentration already on the pure Vulcan XC72R as purchased.

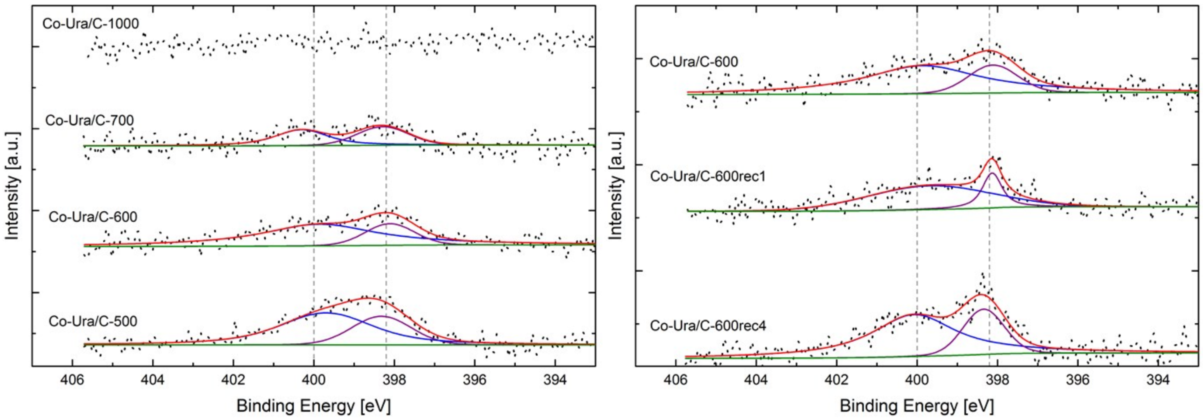
C-2) C1s spectra of fresh Co-Ura/C-500, Co-Ura/C-600, Co-Ura/C-700, and Co-Ura/C-1000 (left) and fresh and recycled Co-Ura/C-600, Co-Ura/C-600rec1, and Co-Ura/C-600rec4 (right) catalyst. The dashed lines mark characteristic binding energies of carbon sp^2 (284.0 eV), carbon sp3 (284.8 eV), C–OH and C–O–C (~286.5 eV), and O–C=O (288.8 eV). Especially at high pyrolysis temperatures oxygen species at higher binding energies become more pronounced. This is in agreement with increasing oxygen concentration on the surface, compare table C-1. For the recycled catalyst only minor changes in the C1s spectra can be observed.



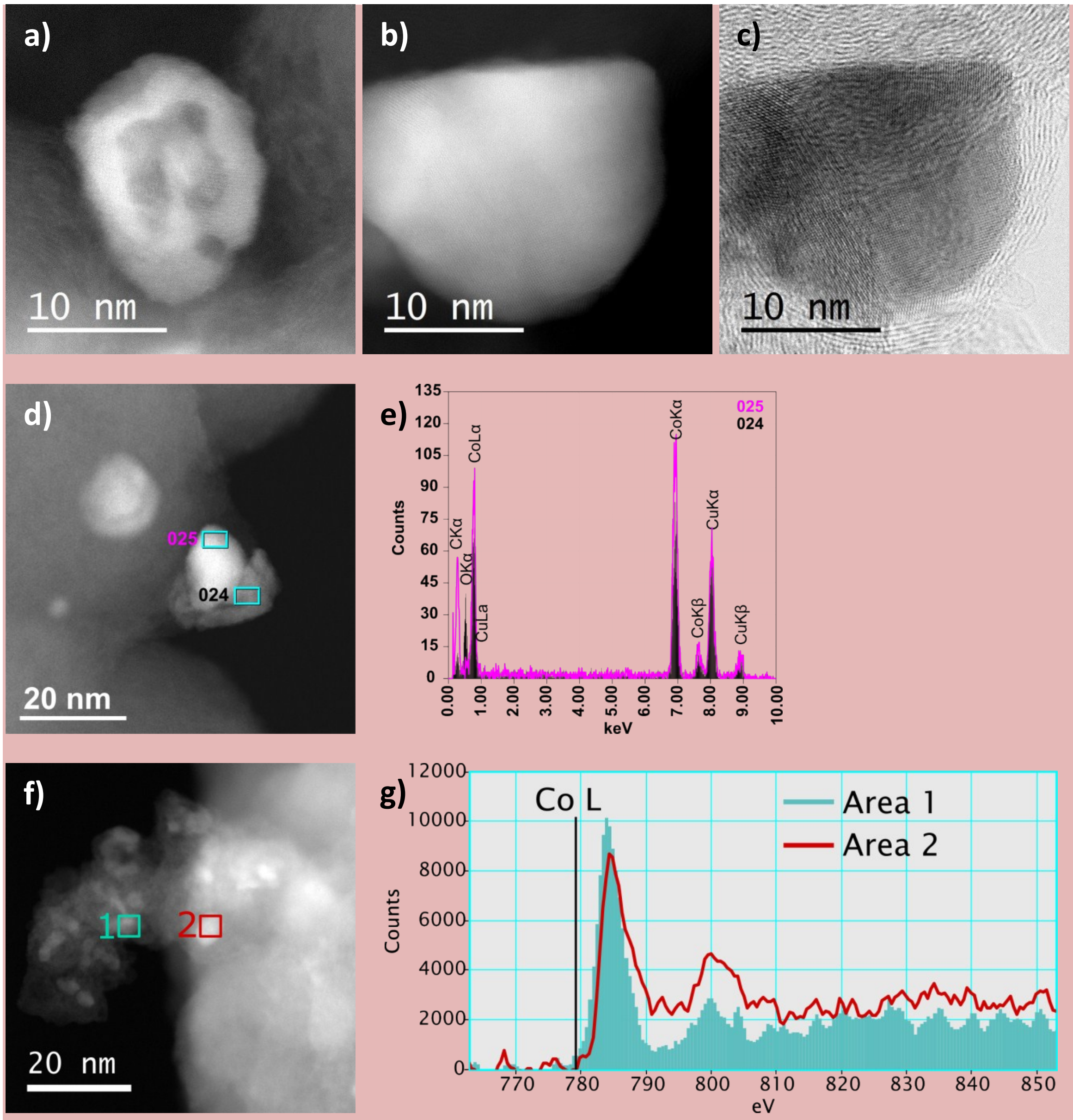
C-3) Co2p spectra of fresh Co-Ura/C-500, Co-Ura/C-600, Co-Ura/C-700, and Co-Ura/C-1000 catalyst. The dashed lines at 779.8 eV and 803 eV mark characteristic binding energies of Co_3O_4 and a satellite feature of CoO or $Co(OH)_2$.[8] Spectra for pyrolysis temperatures up to 700 °C are quite similar and indicate mainly Co_3O_4. For the highest temperature 1000 °C almost no cobalt can be detected at the surface.



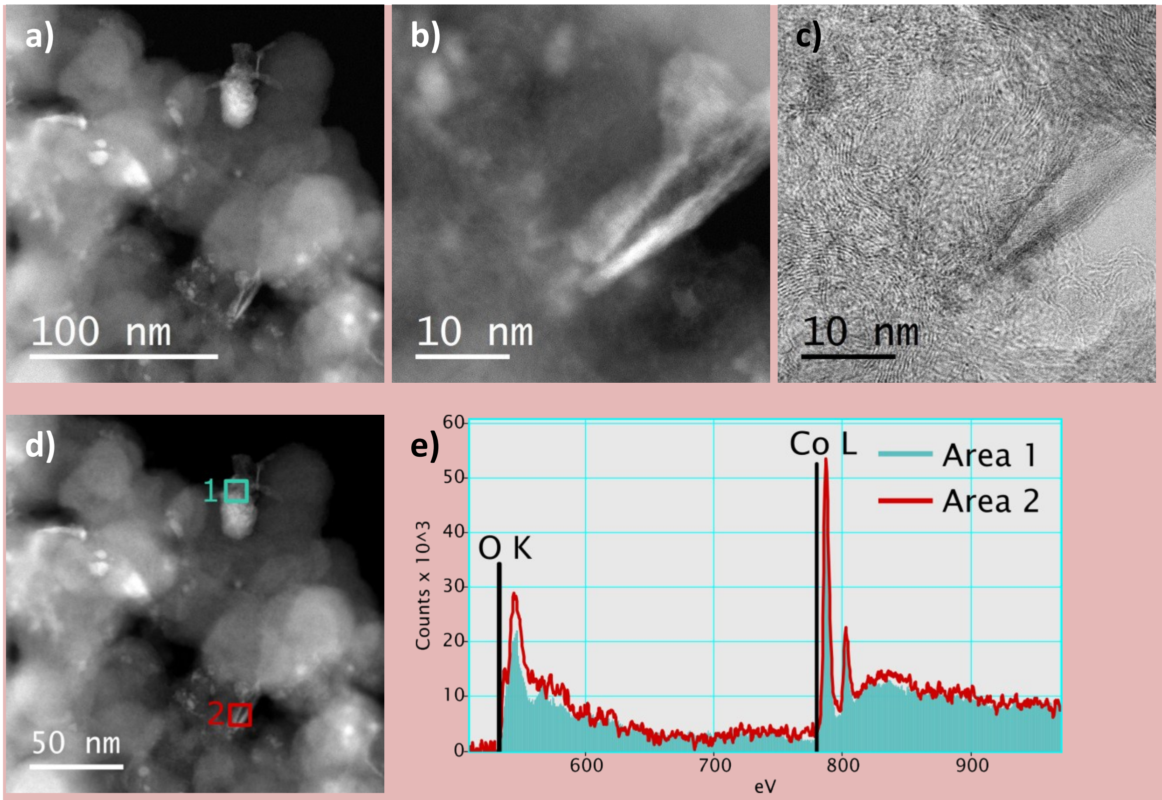
C-4) N1s spectra of fresh Co-Ura/C-500, Co-Ura/C-600, Co-Ura/C-700, and Co-Ura/C-1000 (left) and fresh and recycled Co-Ura/C-600, Co-Ura/C-600rec1, and Co-Ura/C-600rec4 (right) catalyst. The dashed lines at 398.2 eV and 400 eV indicate the binding energies for pyridinic and pyrrolic nitrogen[9] which can be found in all spectra. Only for 1000 °C pyrolysis temperature no nitrogen can be detected. During the recycling of the catalyst the pyridinic nitrogen peak becomes more pronounced.



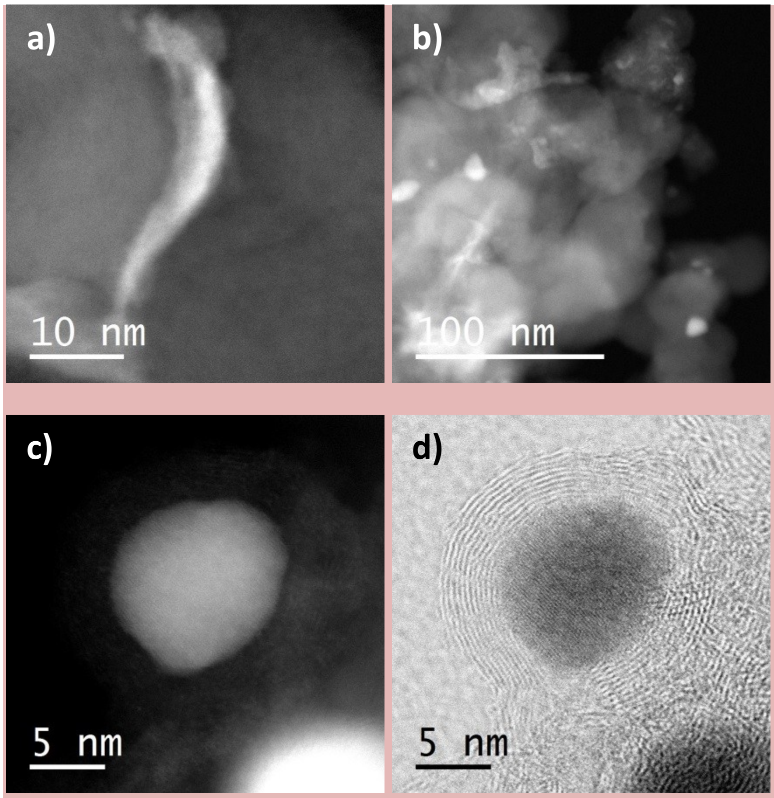
D) Scanning Transmission Electron Microscopy (STEM) and EDX data



D-1) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of fresh Co-Ura/C-600 catalyst showing a pure Co oxide particle a) and a metal Co particle b). The corresponding annular bright field (ABF) image c) shows the carbon covering the surface of the metal Co particle. The HAADF image d) marked with the areas used for acquisition of energy dispersive x-ray (EDX) spectra e) confirms the metal core and oxide shell description of this type of particle by way of the difference in oxygen signal. Further confirmation of the metal/oxide interpretation of the image contrast can be deduced from annular dark field (ADF) image f) marked with two areas for electron energy loss spectroscopy (EELS). The spectra shown in g) show the typical difference in fine structure for Co oxide in area 1 and Co metal in area 2.[10] The EEL spectra have been background subtracted and deconvolved.



D-2) HAADF images of one time used Co-Ura/C-600rec1 showing an additional overview a) with mostly oxygen containing Co particles and some veil-like structures. A higher resolution image b) of this Co phase reveals its layered structure especially visible in the corresponding ABF image c). The ADF image d) is marked with the areas used for EELS analysis e) where both areas show the typical fine structure of the Co-L edge for Co oxide, but the fine structure of the O-Kedge is slightly different indicating differences in electronic structure. The EEL spectra have been background subtracted, deconvolved and scaled to matching Co-L edge intensities.



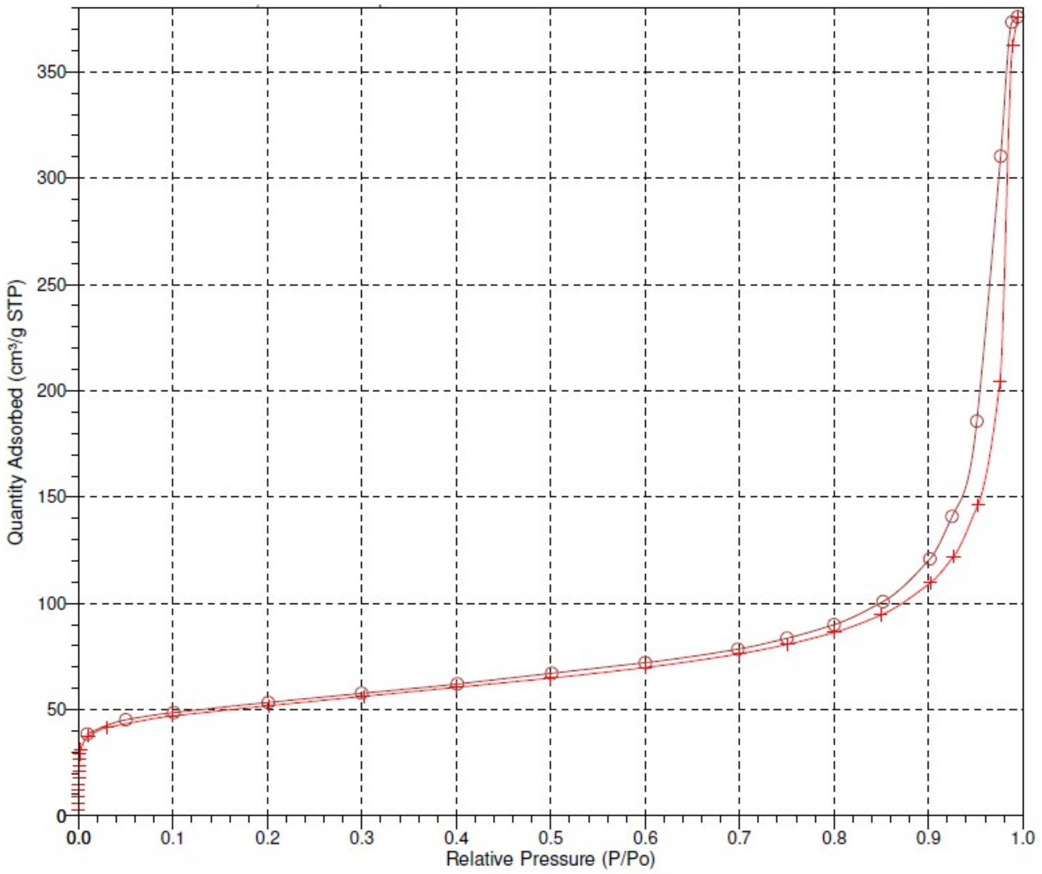
D-3) The higher magnified HAADF image a) of a veil type structure in four times recovered Co-Ura/C-600rec4 shows its adherence to the Vulcan spport particle. An additional HAADF overview image b) shows mostly veil type structure in different orientation (plan-view and edge view) but also a few remaining particles of oxide and metal type. Notably, the metal type particles are still tightly surrounded by graphitic carbon as shown in the high resolution HAADF c) and ABF d) image pair indicating a possible isolation from any catalytic reaction.

E) **BET** data

E-1) **Summary Report for Co-Ura/C-600**

Surface Area
Single point surface area at P/Po = 0.010188154: 161.5743 m^2/g
BET Surface Area: 166.3158 m^2/g
t-Plot Micropore Area: 82.3238 m^2/g
t-Plot External Surface Area: 83.9920 m^2/g
Pore Volume
t-Plot micropore volume: 0.045884 cm^3/g
BJH Desorption cumulative volume of pores between 2.0000 nm and 100.0000 nm width: 0.559683 cm^3/g

E-2) Isotherm linear plot for catalyst Co-Ura/C-600: + - Adsorption, **o** - Desorption

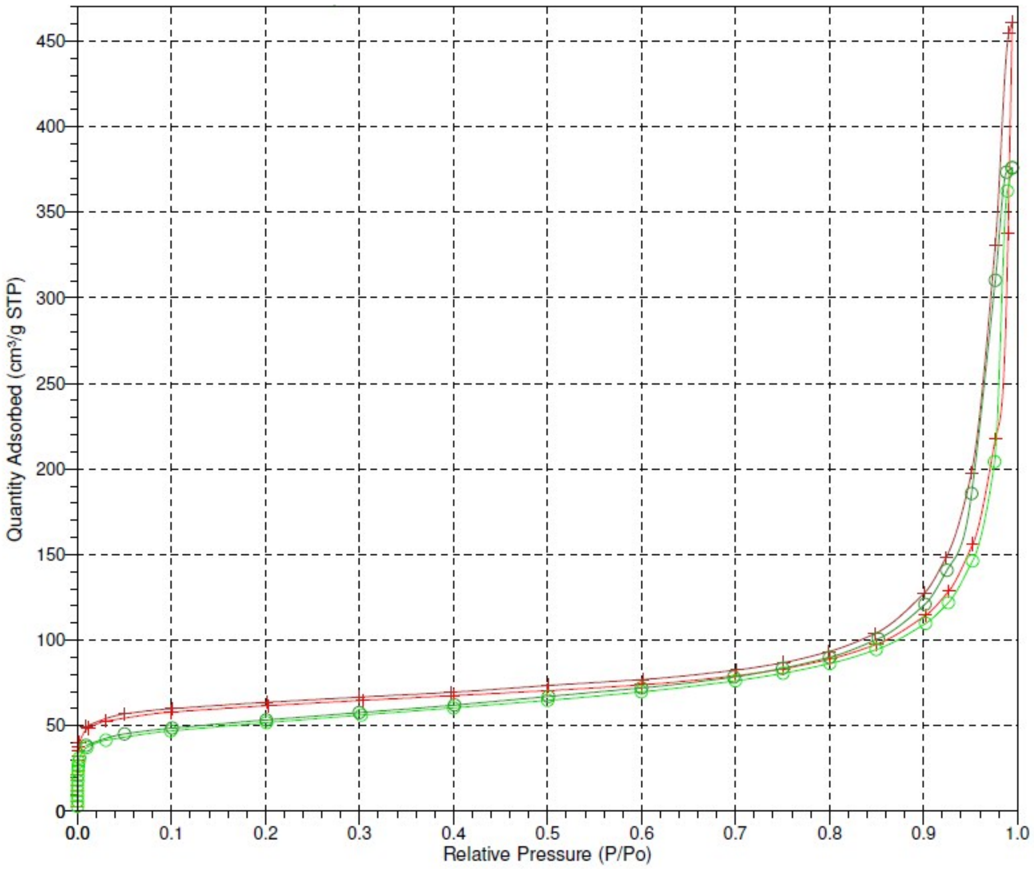


E-3) **Summary Report for Co-Ura/C-1000**

Summary Report
Surface Area
Single point surface area at P/Po = 0.011533393: 209.4023 m^2/g
BET Surface Area: 214.4480 m^2/g
t-Plot Micropore Area: 149.5431 m^2/g
t-Plot External Surface Area: 64.9049 m^2/g
Pore Volume

t-Plot micropore volume: 0.067155 cm³/g
BJH Desorption cumulative volume of pores
between 2.0000 nm and 100.0000 nm width: 0.438310 cm³/g

E-4) Isotherm linear plots: + – Adsorption, **o** – Desorption for catalysts Co-Ura/C-600 (red) and Co-Ura/C-1000 (green)



1. F. D. King and S. Caddick, *Organic & Biomolecular Chemistry*, 2011, **9**, 4361-4366.
2. T. C. Fessard, H. Motoyoshi and E. M. Carreira, *Angew. Chem. Int. Ed.*, 2007, **46**, 2078-2081.
3. G. Rubulotta, K. L. Luska, C. A. Urbina-Blanco, T. Eifert, R. Palkovits, E. A. Quadrelli, C. Thieuleux and W. Leitner, *ACS Sustain. Chem. Eng.*, 2017, **5**, 3762-3767.
4. G. Villa, G. Povie and P. Renaud, *J. Am. Chem. Soc.*, 2011, **133**, 5913-5920.
5. P. Büschelberger, E. Reyes-Rodriguez, C. Schöttle, J. Treptow, C. Feldmann, A. Jacobi von Wangelin and R. Wolf, *Catal. Sci. Technol.*, 2018, **8**, 2648-2653.
6. P. A. Robles-Dutenhefner, M. G. Speziali, E. M. B. Sousa, E. N. dos Santos and E. V. Gusevskaya, *Appl. Catal., A*, 2005, **295**, 52-58.
7. M. G. Speziali, F. C. C. Moura, P. A. Robles-Dutenhefner, M. H. Araujo, E. V. Gusevskaya and E. N. dos Santos, *J. Mol. Catal. A: Chem.*, 2005, **239**, 10-14.
8. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717.
9. B. J. Matsoso, K. Ranganathan, B. K. Mutuma, T. Lerotholi, G. Jones and N. J. Coville, *RSC Adv.*, 2016, **6**, 106914-106920.
10. Z. Zhang, *Ultramicroscopy*, 2007, **107**, 598-603.