

Supplementary Materials for

Hydrogenation of terminal and internal olefins using a biowaste-derived heterogeneous cobalt catalyst

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Published 21 September 2018, *Sci. Adv.* **4**, eaau1248 (2018)
DOI: 10.1126/sciadv.aau1248

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General remarks

All chemicals were purchased from Sigma-Aldrich, abcr, TCI or Alfa Aesar. Sunflower oil was purchased from Kaufland Dienstleistung GmbH & Co. KG (composition: palmitic acid (saturated, C₁₅H₃₁): 5%; stearic acid (saturated, C₁₇H₃₅): 6%; oleic acid (mono unsaturated, C₁₇H₃₃): 30%; linoleic acid (double unsaturated, C₁₇H₃₁): 59%). 2,3-Dimethyl-2-butene, 1-methylstyrene, 2-methyl-3-butene-2-ol, allylbutylether, allyl acetate, 1*H*,1*H*,2*H*-perfluoro-1-decene, safrol, allylcinnamate, 4-allylanisole, 4-vinylianisole, 2-allylphenol, allylphenylether, allylbenzylether, *N*-methyl-*N*-vinylacetamide, allylglycidylether, 4-chloro- α -methylstyrene, 4-fluoro- α -methylstyrene, and 1,1-diphenylethylene were filtered over a plug (3-4 cm) of basic Al₂O₃, prior to reaction. Diisobutene was dried over Na and distilled prior to use. Citronellol was filter over a plug (3-4 cm) of basic Al₂O₃ and distilled freshly. Solvents were used as received. Chitosan (low viscosity) was purchased from Sigma-Aldrich. Reactions were performed in P4560 series 300mL autoclave or 25mL autoclave made of stainless steel by Parr Instrument Company.

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

NMR spectra were recorded on Bruker AV-300, Bruker Fourier 300 or Bruker AV-400 spectrometers. Chemical shifts (δ) are reported in ppm downfield of tetramethylsilane.

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*).

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 μ m film thickness) using argon as carrier gas.

AAS was measured on contraAA 800D by Analytik Jena, using a flame atomizer and acetylene flame. Solid substances were mineralized with H₂SO₄-KHSO₄. Liquid samples in organic solvents were liberated of the volatiles in vacuum and the residue was mineralized with aqua regia (HCl : HNO₃ = 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 system. The measurements were done with automatic divergence slits and Cu α 1/ α 2 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 25 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 TEM measurements were performed at 200kV with a probe aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive x-ray-spectrometer (EDXS) and an Enfinium ER (Gatan, USA) electron energy loss spectrometer (EELS) for chemical analysis. High angle annular dark field (HAADF) and annular bright field (ABF) images were recorded in parallel.

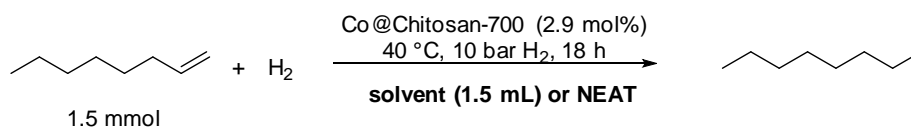
The sample was deposited on a Cu-grid (mesh 300) with a holey carbon film without any pre-treatment and transferred to the microscope.

Screening of catalysts and conditions

Table S1. Screening of different supports, substrates, solvents, conditions, and temperatures of pyrolysis.

Entry	Catalyst	Substrate	Solvent	T [°C]	p [bar]	Yield [%]
1	Co/Chitosan@SiO ₂ -800	Neohexene	Heptane	100	10	98
2	Co/Chitosan@SiO ₂ -1000	Neohexene	Heptane	100	10	94
3	Co/Chitosan@TiO ₂ -700	Neohexene	Heptane	100	10	93
4	Co/Chitosan@CeO ₂ -1000	Neohexene	Heptane	100	10	99
5	Co/Chitosan@Al ₂ O ₃ -800	Neohexene	Heptane	100	10	96
6	Co/Chitosan@BN-1000	Neohexene	Heptane	100	10	62
7	Co/Chitosan@SiO ₂ -700	1-Octene	Heptane	100	30	4
8	Co/Chitosan@SiO ₂ -800	1-Octene	Heptane	100	30	87
9	Co/Chitosan@SiO ₂ -1000	1-Octene	Heptane	100	30	2
10	Co/Chitosan@TiO ₂ -700	1-Octene	Heptane	100	30	6
11	Co/Chitosan@CeO ₂ -1000	1-Octene	Heptane	100	30	4
12	Co/Chitosan@Al ₂ O ₃ -800	1-Octene	Heptane	100	30	86
13	Co/Chitosan@Al ₂ O ₃ -1000	1-Octene	Heptane	100	30	95
14	Co/Chitosan@Al ₂ O ₃ -700	1-Octene	Heptane	80	10	4
15	Co/Chitosan@Al ₂ O ₃ -800	1-Octene	Heptane	80	10	84
16	Co/Chitosan@Al ₂ O ₃ -1000	1-Octene	Heptane	80	10	85
17	Co/Chitosan@SiO ₂ -700	1-Octene	Heptane	80	10	1
18	Co/Chitosan@SiO ₂ -800	1-Octene	Heptane	80	10	1
19	Co/Chitosan@Al ₂ O ₃ -800	1-Octene	Heptane	40	10	90
20	Co/Chitosan@Al ₂ O ₃ -1000	1-Octene	Heptane	40	10	traces
21 ^a	Co@Chitosan-700	1-Octene	Heptane	40	10	88
22	Co/Chitosan@Al ₂ O ₃ -800	1-Octene	H₂O	40	10	86
23 ^a	Co@Chitosan-700	1-Octene	H₂O	40	10	99
24 ^a	Co@Chitosan-800	1-Octene	H₂O	40	10	94
25 ^a	Co@Chitosan-1000	1-Octene	H₂O	40	10	86
26 ^b	Co@Chitosan-700	1-Octene	H₂O	40	10	92
27 ^c	Co@Chitosan-700	1-Octene	H₂O	40	10	84
28	Co@Chitosan	1-Octene	H₂O	40	10	0

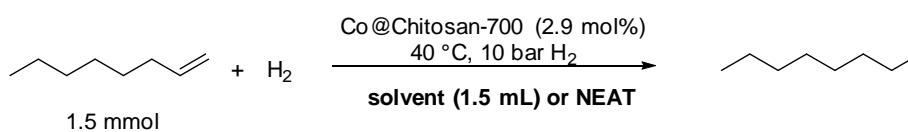
Reaction conditions: 1.5 mmol substrate, 1.0 mol% catalyst, 1.5 mL solvent, 18 h, yields were determined *via* GC, using hexadecane as internal standard. ^a 2.9 mol% catalyst was used. ^b 0.3 mol% catalyst was used. ^c 0.03 mol% catalyst was used.

Table S2. Solvent screening for the hydrogenation of 1-octene.

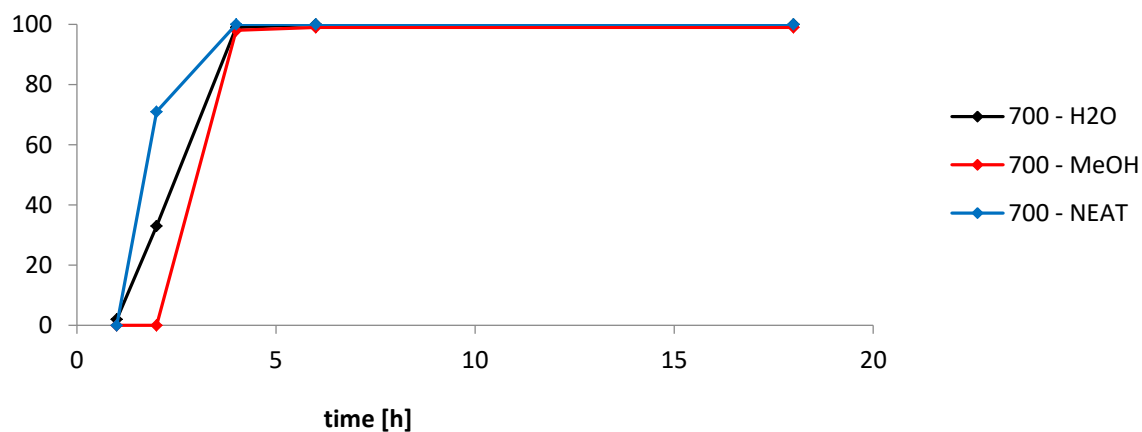
Entry	Solvent	Conv. [%] ^a	Yield [%] ^a
1	Heptane	98	88
2 ^b	Heptane	58	53
3	PC	45	35
4	MeCN	10	1
5	MeOH	99	95
6 ^b	MeOH	99	95
7	THF	13	13
8	H₂O/PEG (1:1)	37	21
9	H₂O/Heptane (1:1)	99	94
10 ^b	H₂O/Heptane (1:1)	98	93
11	H₂O/MeOH (1:1)	99	90
12 ^b	H₂O/MeOH (1:1)	98	90
13	H₂O	>99	99
14 ^b	H₂O	97	96
15	Neat	>99	>99
16 ^b	Neat	>99	>99

General conditions: 1.5 mmol (237 μ L, 168.3 mg) 1-Octene, 2.9 mol% (8.8 mg) catalyst, 1.5 mL solvent, 40 °C, 10 bar H₂, 18 h ^a Yields were determined *via* GC, using Hexadecane as internal standard ^b Reaction was conducted for 6 h

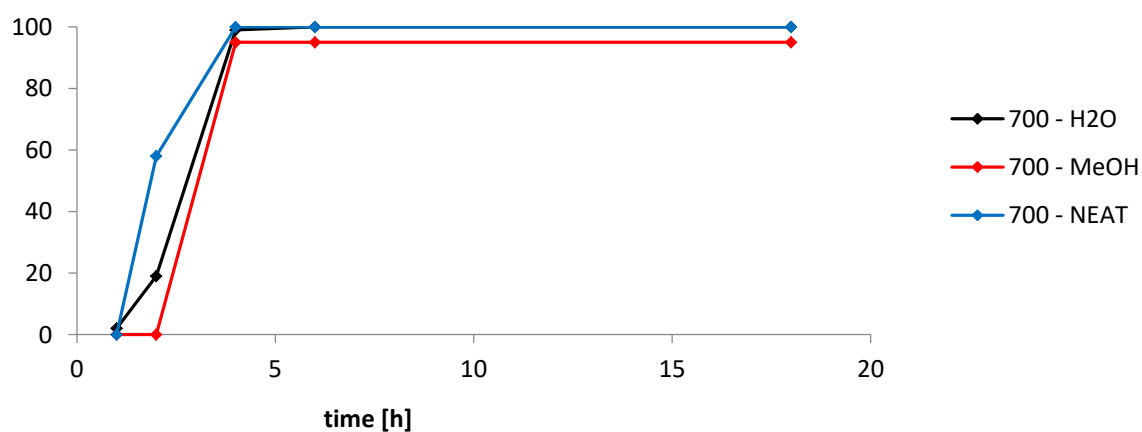
Kinetic investigation



Conversions



Yields



Scheme S1. Plot of conversions (top) and yields (bottom) against time in different solvent conditions of Co@Chitosan-700.

Recycling procedure

A 4 mL screw-cap vial was charged with Co@Chitosan-700 (8.8 mg, 2.9 mol%), 1-octene (1.5 mmol, 168.3 mg, 237 μL), 1.5 mL H_2O and a glass coated stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was fixed in an alloy plate and put into a Parr 4560 series autoclave (300 mL). At room temperature, the autoclave was flushed with H_2 for three times and 10 bar H_2 was charged. The autoclave was placed in an aluminum block on a heating plate equipped with magnetic stirring. The reaction was heated at 60 $^\circ\text{C}$ for 18 hours. Afterwards, the autoclave was cooled with an ice bath and the pressure was carefully released. For GC-analysis, hexadecane (32 μL) was added into the reaction mixture as an internal standard. The mixture was diluted with ethyl acetate, stirred properly and the organic fraction analyzed by gas chromatography. Then, a magnet was placed at the outer wall of the vial, in a way that as much catalyst as possible was attracted by it. The liquids were decanted off, and the catalyst was washed with acetone three times, and once with deionized water. Then, new substrate was added, along with 1.5 mL H_2O and the vial was closed by new PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a fresh needle. The next reaction was started analogously to the first one.



Fig. S1. Recycling of Co@Chitosan-700. Left: Vial containing the reaction mixture with catalyst. Right: The catalyst is attracted by a magnet. Photo Credit: Florian K. Scharnagl, Leibniz-Institut für Katalyse e.V. an der Universität Rostock

Catalyst characterisation

Scanning Transmission Electron Microscopy

Fresh catalyst:

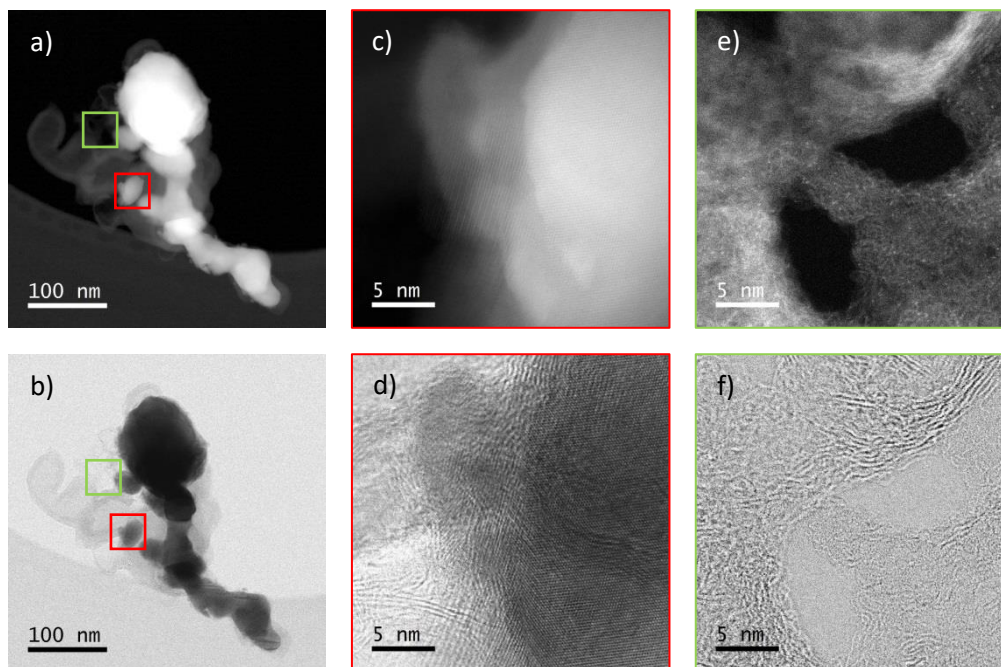


Fig. S2. High-resolution (HR)-STEM images of Co@Chitosan-700. a) HAADF image of Co@Chitosan-700; b) ABF image of Co@Chitosan-700; c&d) metallic cobalt particle (bright contrast) with smaller Co oxide particles on the surface; e&f) bright spots on carbon, probably indicating Co single atoms.

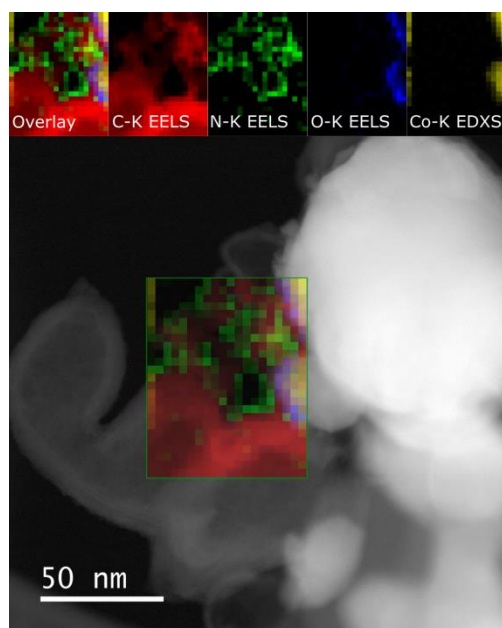


Fig. S3. EELS and energy-dispersive x-ray spectroscopy (EDXS) elemental distributions of carbon, nitrogen, oxygen and cobalt, along with the overlay put onto the annular dark field (ADF) survey image of Co@Chitosan-700. Nitrogen can be partially observed in an amorphous carbon structure, and oxygen in forms of small cobalt oxide crystallites as a partial shell for metallic cobalt.

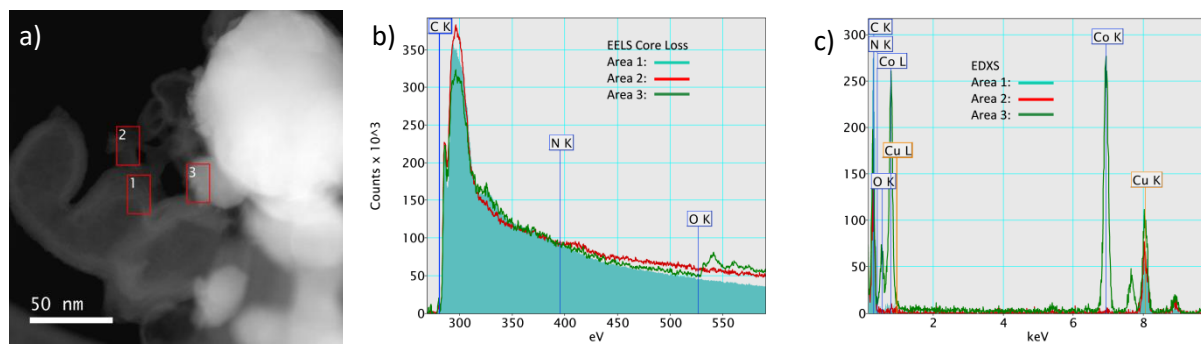


Fig. S4. ADF survey image, EELS, and EDX spectra of fresh Co@Chitosan-700. (a), Electron energy loss spectra (b) and EDX spectra (c) from the areas marked in (a), same data set as used for elemental distributions in S3. Nitrogen can be identified in area 2 in the EELS data where amorphous carbon is present (see also S2 e and f)), whereas the oxygen of area 3 corresponds well with the Co oxide crystallites. The EELS data have been background subtracted, deconvolved and scaled to matching intensities in front of the nitrogen K-edge.

Recycled catalyst:

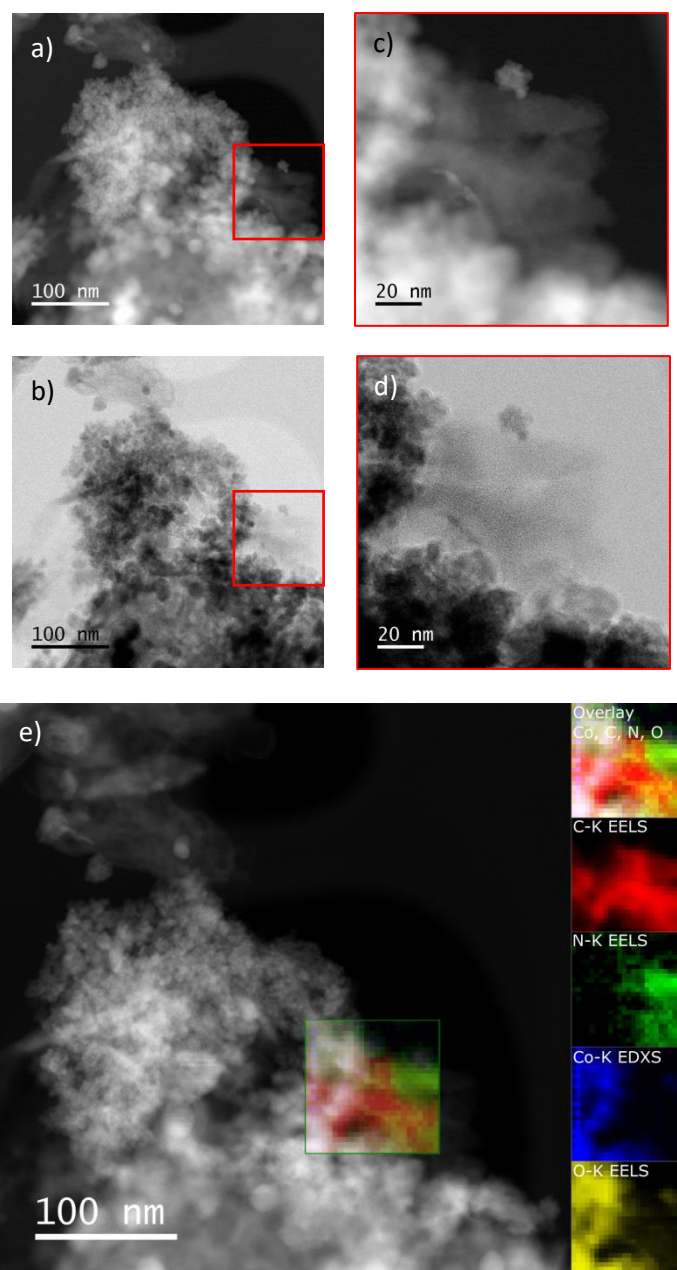


Fig. S5. HR-STEM images of nine-times-used Co@Chitosan-700. a) HAADF image of nine times used Co@Chitosan-700; b) ABF image of nine times used Co@Chitosan-700; c&d) close up of carbon phase with Co oxide particles attached; e) EELS and EDXS elemental maps of carbon, oxygen and cobalt, and the overlay on the corresponding ADF survey image. In contrast to the fresh catalyst, cobalt oxide can be recognized but still the carbon and nitrogen containing phase remains.

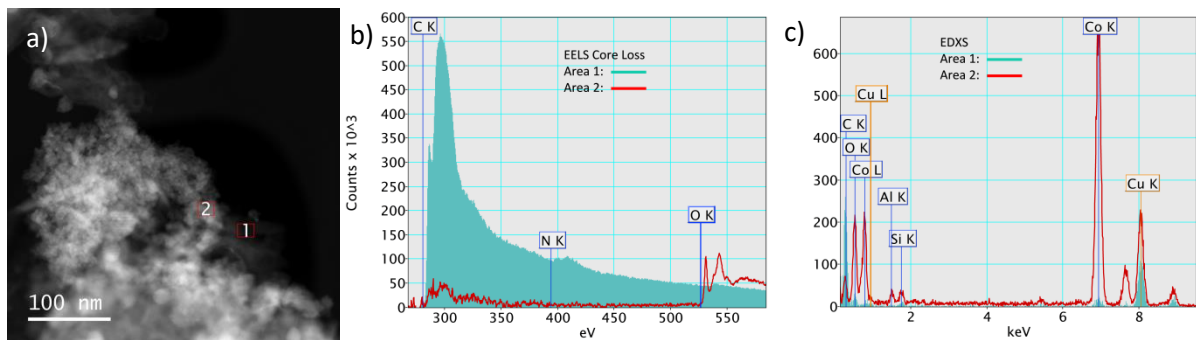


Fig. S6. ADF survey image, EELS, and EDX spectra of recycled Co@Chitosan-700. (a), electron energy loss spectra (b) and EDX spectra (c) from the areas marked in (a), same data set as used for elemental distributions in S5. The nitrogen in area 1 can be clearly identified in the EEL spectrum and in the corresponding EDX spectrum also some Co signal is present. Area 2 shows little carbon signal, however the form of the strong O-K edge in the EEL spectrum is comparable to Co_3O_4 spectra from literature.^[41] The EELS data have been background subtracted, deconvolved and scaled to matching intensities in front of the nitrogen K-edge.

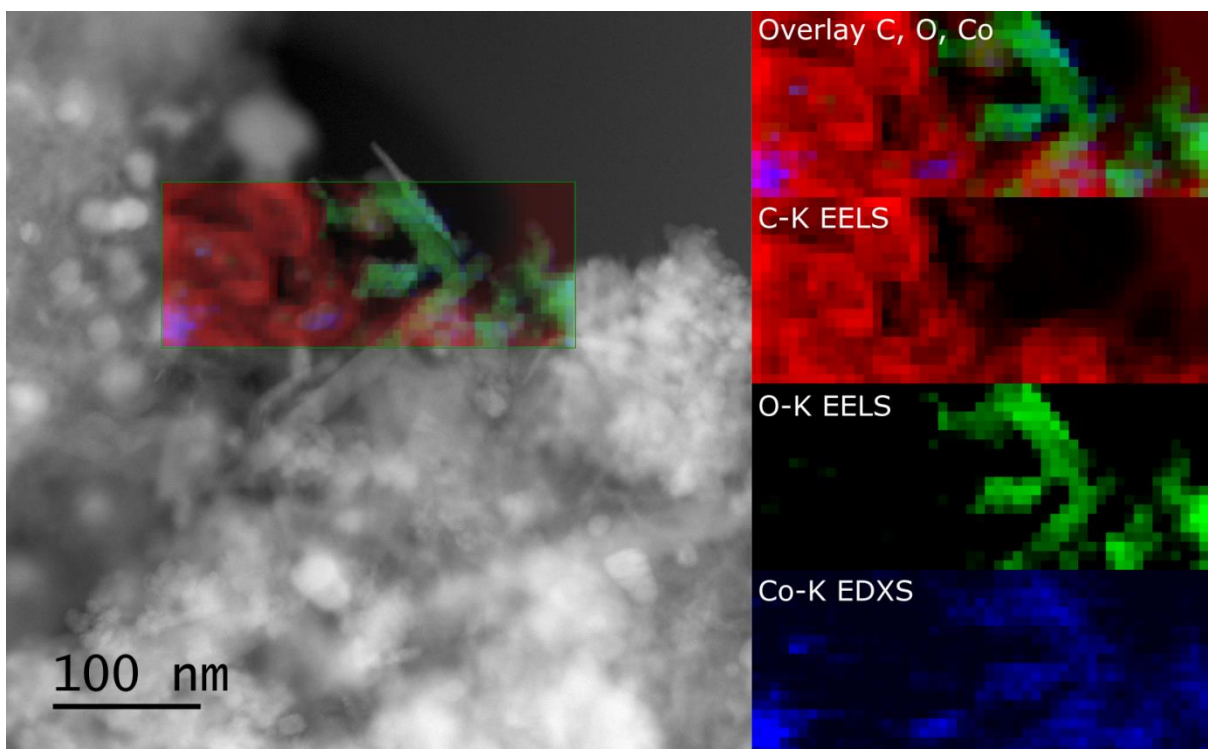


Fig. S7. EELS and EDXS elemental maps of carbon, oxygen, and cobalt, and the overlay on the corresponding ADF survey image of nine-times-used Co@Chitosan-700. In contrast to the fresh catalyst, cobalt oxide can be easily recognized by their oxygen content in addition to metal Co particles surrounded by graphitic carbon.

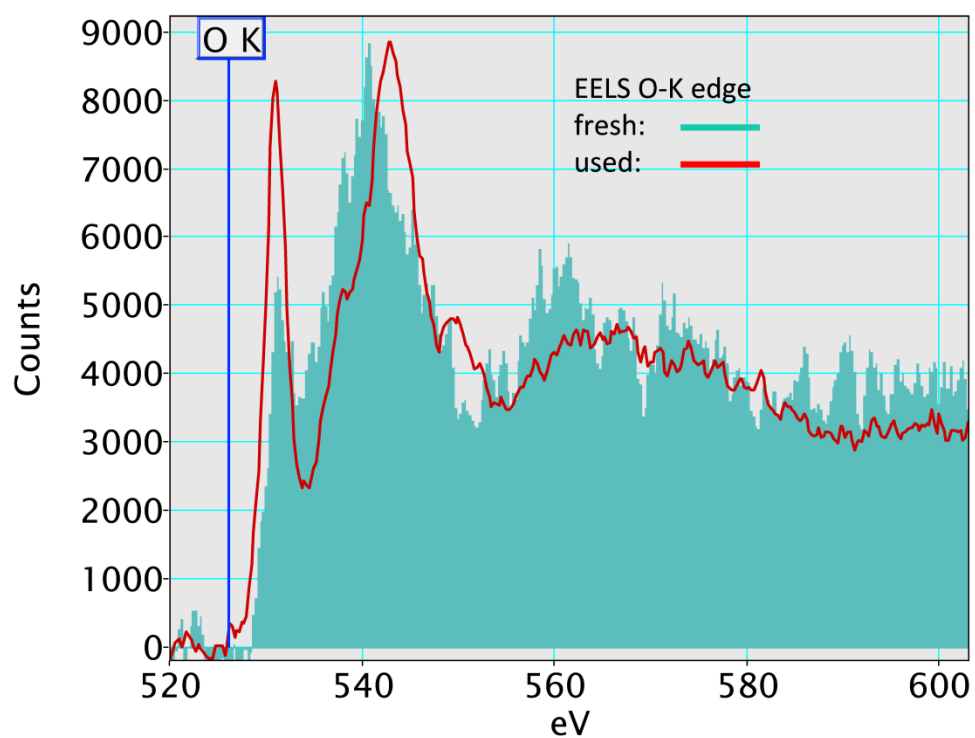


Fig. S8. Comparison of O-K edge from Co oxide particles of fresh and nine-times-used Co@Chitosan-700 showing the difference in edge fine structure. The fine structure of the used catalyst is similar to Co_3O_4 as in the literature^[41] and therefore fits well with XRD analysis, while the fine structure of the fresh catalyst is quite different. The EELS data have been background subtracted, deconvolved and scaled to matching maximum intensities.

Powder X-ray diffraction

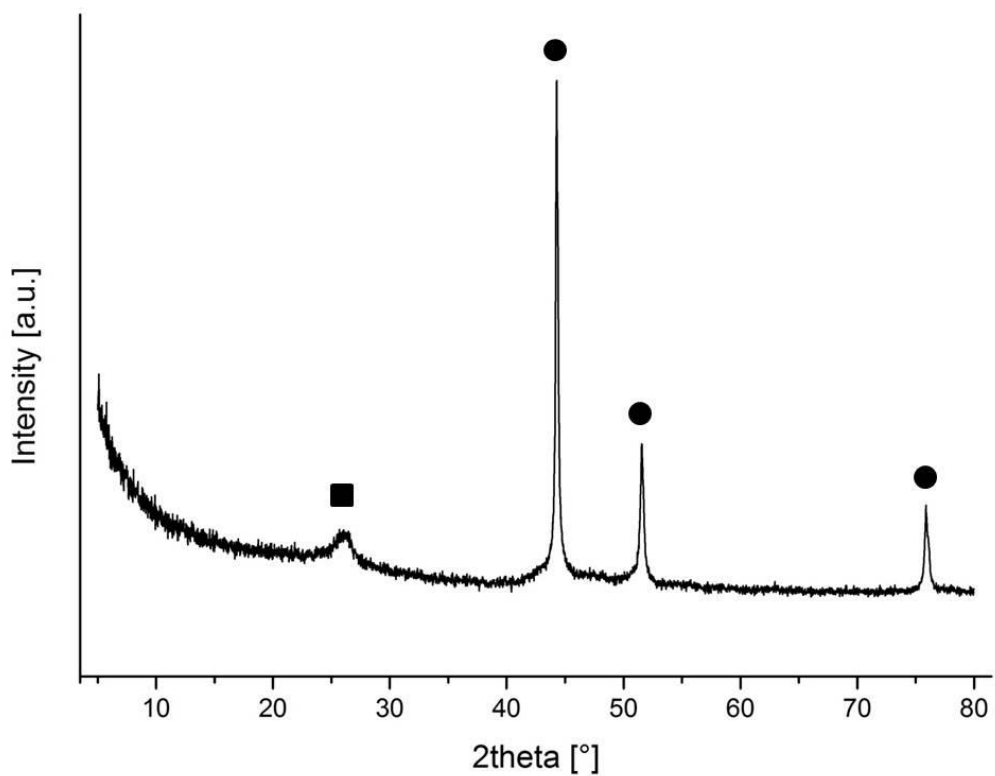


Fig. S9. Powder pattern of fresh Co@Chitosan-700. Phases are labelled as squares (Carbon, ICDD 01-071-4630) and circles (Co, 00-015-0806).

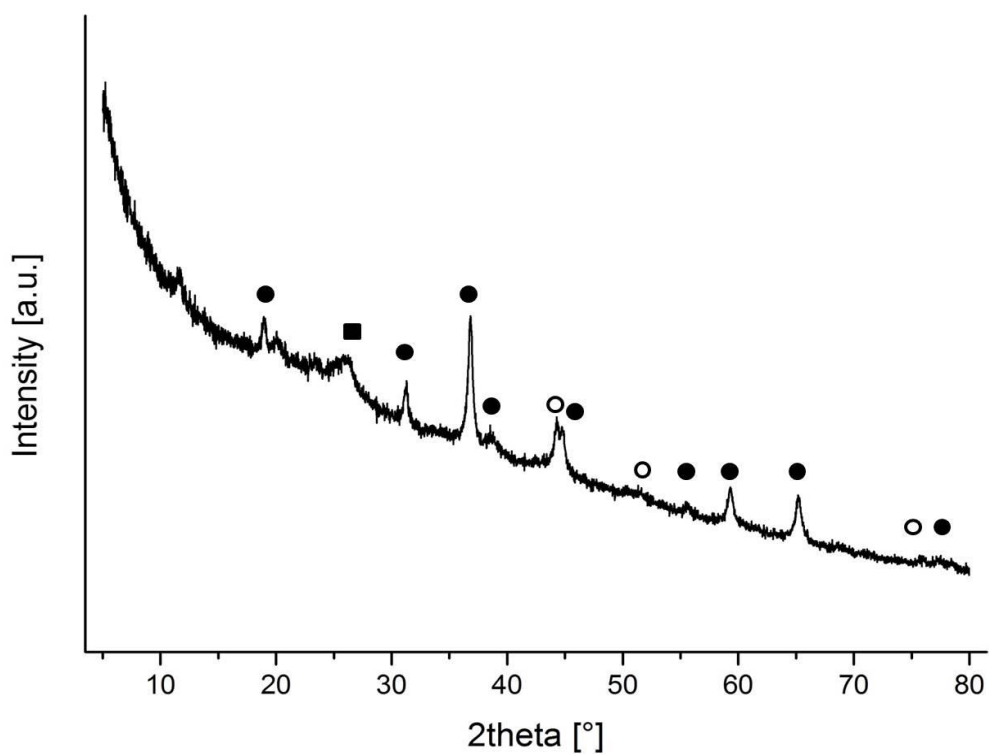


Fig. S10. Powder pattern of nine-times-used Co@Chitosan-700. Phases are labelled as squares (Carbon, ICDD 01-071-4630), black circles (Co, 00-015-0806), and white circles (Co_3O_4 , 01-078-5614).

Elemental analysis

Table S3. Content of C, H, N, and Co before and after pyrolysis.

Co@Chitosan -700	Before pyrolysis [%]	After pyrolysis [%]
C	33.6	58.94
H	6.4	0.14
N	4.9	2.53
Co	10.3	29.31

NMR shifts

Yields were calculated by comparison of product with mesitylene as internal standard. In the following, chemical shifts of the products are given.

Undecanoic acid, 2a

^1H (300 MHz, CDCl_3) δ 0.89 (t, $J = 6.9$ Hz, 3H, CH_3), 1.27 (bs, 14H, CH_2), 1.69 (m, 2H, $\text{CH}_2\text{CH}_2\text{COOH}$), 2.56 (bs, 2H, $\text{CH}_2\text{CH}_2\text{COOH}$), 9.43 ppm (bs, 1H, COOH).

2-Hexanone, 2b

^1H (300 MHz, CDCl_3) δ 0.88 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.22-1.35 (m, 2H, CH_2CH_3), 1.47-1.58 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.11 (t, $J = 0.4$ Hz, 3H, $\text{CH}_3\text{C}(\text{O})\text{CH}_2$), 2.40 ppm (t, $J = 7.6$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

1-Pentanol, 2c

^1H (300 MHz, CDCl_3) δ 0.84-0.94 (m, 3H, CH_3), 1.23-1.37 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.47-1.61 (m, 2H, $\text{CH}_2\text{CH}_2\text{OH}$), 2.13 (bs, 1H, OH), 3.60 ppm (t, $J = 6.7$ Hz, 2H, CH_2OH).

1-Chlorohexane, 2d

^1H (300 MHz, CDCl_3) δ 0.90 (t, $J = 6.7$ Hz, 3H, CH_2CH_3), 1.19-1.51 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.71-1.83 (m, 2H, $\text{CH}_2\text{CH}_2\text{Cl}$), 3.53 ppm (t, $J = 6.7$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{Cl}$).

6-Methyl-2-heptanol, 2f

^1H (300 MHz, CDCl_3) δ 0.86 (d, $J = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.16 (d, $J = 6.2$ Hz, 3H, $\text{C}(\text{OH})\text{CH}_3$), overlaps with 1.13-1.45 (m, 7H, CH_2), 1.53 (quint, $J = 6.6$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 1.97 (bs, 1H, OH), 3.72-3.82 ppm (m, 1H, CHOH).

3,7-Dimethyl-1-octanol, 2g

^1H (400 MHz, CDCl_3) δ 0.84-0.91 (m, 9H, CH_3), 1.01-1.20 (m, 3H), 1.20-1.43 (m, 5H), 1.51 (hept, $J = 6.6$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$) overlaps with 1.53-1.64 (m, 2H), 3.58-3.70 ppm (m, 2H, CH_2OH).

^{13}C (100 MHz, CDCl_3) δ 19.5, 22.5, 22.6, 24.6, 27.9, 29.4, 37.3, 39.2, 39.8, 61.0 ppm.

4-Propoxybenzaldehyde, 2h

^1H (300 MHz, CDCl_3) δ 1.00 (t, $J = 7.5$ Hz, 3H, CH_3), 1.71-1.84 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.91 (t, $J = 6.5$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 6.88-6.95 (m, 2H, ArH), 7.71-7.79 (m, 2H, ArH), 9.79 ppm (bs, 1H, $\text{C}(\text{O})\text{H}$).

4-Propylanisol, 2i and 2ae

^1H (300 MHz, CDCl_3) δ 1.36 (t, $J = 7.4$ Hz, 3H, CH_3), 2.03 (sext, $J = 7.5$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.94 (t, $J = 7.5$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.16 (s, 3H, OCH_3), 7.18-7.28 (m, 2H, ArH), 7.45-7.54 ppm (m, 2H, ArH).

2-Propylphenol, 2j

^1H (300 MHz, CDCl_3) δ 1.05 (t, $J = 7.3$ Hz, 3H, CH_3), 1.65-1.79 (m, 2H, CH_2CH_3), 2.66 (t, $J = 7.6$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 5.23 (bs, 1H, OH), 6.81 (dd, $J = 7.9$, 1.1 Hz, 1H, ArH), 6.94 (dt, $J = 7.4$, 1.2 Hz, 1H, ArH), 7.14 (dt, $J = 7.7$, 1.7 Hz, 1H, ArH), 7.19 ppm (dd, $J = 7.5$, 1.7 Hz, 1H, ArH).

n-Propylphenylether, 2k

^1H (300 MHz, CDCl_3) δ 1.12 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.82-1.95 (m, 2H, CH_2CH_3), 3.98 (t, $J = 6.6$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 6.95-7.04 (m, 3H, ArH), 7.31-7.39 ppm (m, 2H, ArH).

Benzyl-*n*-propylether, 2l

^1H (300 MHz, CDCl_3) δ 1.02 (t, $J = 7.5$ Hz, 3H, CH_2CH_3), 1.71 (sext, 2H, CH_2CH_3), 3.50 (t, $J = 6.7$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.57 (s, 2H, PhCH_2O), 7.30-7.42 ppm (m, 5H, ArH).

N-Ethylcaprolactam, 2m

^1H (300 MHz, CDCl_3) δ 0.93 (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 1.40-1.61 (m, 6H, CH_2), 2.82-2.37 (m, 2H, $\text{CH}_2\text{C}(\text{O})\text{N}$), 3.12-3.19 (m, 2H, NCH_2CH_2), 3.24 ppm (q, $J = 7.2$ Hz, 2H, NCH_2CH_3).

Glycidylpropylether, 2n

^1H (300 MHz, CDCl_3) δ 0.91 (t, $J = 7.4$ Hz, 3H, CH_3), 1.53-1.66 (m, 2H, CH_2CH_3), 2.57-2.62 (m, 1H, $\text{CH}_2(\text{O})\text{CHCH}_2\text{O}$), 2.76-2.80 (m, 1H, $\text{CH}_2(\text{O})\text{CHCH}_2\text{O}$), 3.10-3.17 (m, 1H, $\text{CH}_2(\text{O})\text{CHCH}_2\text{O}$), 3.32-3.49 (m, 3H), 3.66-3.73 ppm (m, 1H).

***N*-Ethyl-*N*-methylethanamide, 2o** (mixture of syn and anti)

^1H (300 MHz, CDCl_3) δ 0.98 (t, $J = 7.1$ Hz, 3H, CH_2CH_3 (syn)), 1.06 (t, $J = 7.1$ Hz, 3H, CH_2CH_3 (anti)), 1.93 (s, 3H, $\text{C}(\text{O})\text{CH}_3$ (anti)), 1.96 (s, 3H, $\text{C}(\text{O})\text{CH}_3$ (syn)), 2.80 (s, 3H, NCH_3 (syn)), 2.88 (s, 3H, NCH_3 (anti)), 3.23 (q, $J = 7.1$ Hz, 2H, CH_2CH_3 (syn)) overlaps with 3.30 ppm (q, $J = 7.1$ Hz, 2H, CH_2CH_3 (anti)).

Dihydroquinine, 2p

^1H (400 MHz, CDCl_3) δ 0.75 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.07-1.25 (m, 2H, CH_2CH_3), 1.28-1.44 (m, 3H), 1.63-1.78 (m, 3H), 2.23-2.34 (m, 1H), 2.48-2.63 (m, 1H), 2.89-3.07 (m, 2H), 3.37-3.53 (m, 1H), 3.85 (s, 3H), 5.48 (d, $J = 3.4$ Hz, 1H, CH_2OH), 5.84 (bs, 1H, OH), 7.19-7.25 (m, 2H, ArH), 7.43 (d, $J = 4.6$ Hz, 1H, ArH), 7.81-7.85 (m, 1H, ArH), 8.38 ppm (d, $J = 4.5$ Hz, 1H, ArH).

^{13}C (100 MHz, CDCl_3) δ 12.0, 21.1, 25.4, 27.6, 28.2, 37.4, 43.3, 55.6, 58.5, 59.7, 71.6, 101.4, 118.4, 121.2, 126.5, 131.1, 143.8, 147.2, 148.6, 157.5 ppm.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$ (M^+) 326.19888, found 326.19863

Butylpropylether, 2q

^1H (400 MHz, CDCl_3) δ 0.87-0.95 (m, 6H, CH_2CH_3), 1.29-1.43 (m, 2H, CH_2), 1.49-1.65 (m, 4H, CH_2), 3.35 (t, $J = 6.8$ Hz, 2H, OCH_2) overlaps with 3.40 ppm (t, $J = 6.6$ Hz, 2H, OCH_2).

2-Methyl-2-butanol, 2r

^1H (300 MHz, CDCl_3) δ 0.90 (t, $J = 7.5$ Hz, 3H, CH_2CH_3), 1.18 (s, 6H, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$), 1.49 ppm (q, $J = 7.5$ Hz, 2H, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$), OH was not detected.

***n*-Propylacetate, 2s**

^1H (300 MHz, CDCl_3) δ 0.89 (t, $J = 7.5$ Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.59 (sext, $J = 7.5$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.99 (s, 3H, $\text{CH}_3\text{C}(\text{O})\text{OCH}_2$), 3.96 ppm (t, 2H, $J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$).

1*H*,1*H*,2*H*-Perfluorodecane, 2t

^1H (300 MHz, CDCl_3) δ 1.04 (t, $J = 7.5$ Hz, 3H, CH_2CH_3), 1.88-2.11 ppm (m, 2H, CH_2CH_3).

Dihydrosafrole, 2u

^1H (300 MHz, CDCl_3) δ 0.96 (t, $J = 7.4$ Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.63 (sext, $J = 7.4$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.54 (t, $J = 7.6$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 5.93 (s, 2H, O- CH_2 -O), 6.61-6.80 ppm (m, 3H, ArH).

2,4,6-Tribromophenyl propyl ether, 2v

^1H (300 MHz, CDCl_3) δ 1.10 (t, $J = 7.4$ Hz, 3H, CH_3), 1.90 (sext, $J = 7.1$ Hz, 2H, CH_2CH_3), 3.95 (t, $J = 6.5$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 7.64 ppm (s, 2H, ArH).

^{13}C (75 MHz, CDCl_3) δ 10.4, 23.3, 75.1, 117.0, 119.1, 134.9, 153.0 ppm

Cinnamic acid propyl ester, 2w

^1H (300 MHz, CDCl_3) δ 1.00 (t, $J = 7.5$ Hz, 3H, CH_3), 1.74 (sext, $J = 7.4$ Hz, 2H, CH_2CH_3), 4.17 (t, $J = 6.7$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 6.45 (d, $J = 16.1$, 1H, $\text{CHCHC}(\text{O})\text{OCH}_2$), 7.36-7.41 (m, 3H, ArH), 7.50-7.57 (m, 2H, ArH), 7.69 ppm (d, $J = 16.0$, 1H, $\text{CHCHC}(\text{O})\text{OCH}_2$).

N-Propyl-4-methylbenzenesulfonamide, 2x

^1H (300 MHz, CDCl_3) δ 0.85 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.46 (sext, $J = 7.2$ Hz, 2H, CH_2CH_3), 2.41 (s, 3H, Ar- CH_3), 2.88 (t, $J = 7.1$ Hz, 2H, $\text{NHCH}_2\text{CH}_2\text{CH}_3$), 4.84 (bs, 1H, NH), 7.26-7.33 (m, 2H, ArH), 7.71-7.78 ppm (m, 2H, ArH).

^{13}C (75 MHz, CDCl_3) δ 11.0, 21.4, 22.8, 44.9, 127.0, 137.0, 143.2 ppm.

N-Ethylimidazol, 2y

^1H (400 MHz, CDCl_3) δ 1.39 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 3.93 (q, $J = 7.4$ Hz, 2H, CH_2CH_3), 6.87 (t, $J = 1.2$ Hz, 1H, ArH), 6.99 (t, $J = 0.9$ Hz, 1H, ArH), 7.42 ppm (s, 1H, ArH).

^{13}C (75 MHz, CDCl_3) δ 16.2, 41.6, 118.2, 129.2, 136.4 ppm.

Heptanenitrile, 2z

^1H (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 1.26-1.46 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) overlaps with unreacted starting material, 1.60-1.68 (m, 2H, $(\text{NC})\text{CH}_2\text{CH}_2$), 2.32 ppm (t, $J = 7.2$ Hz, 2H, $(\text{NC})\text{CH}_2\text{CH}_2$) overlaps with unreacted starting material.

Butyronitrile, 2aa

^1H (300 MHz, CDCl_3) δ 1.10 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.71 (sext, $J = 7.3$ Hz, 2H, CH_2CH_3), 2.27-2.30 ppm (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$) overlaps with CH_3 of the internal standard mesitylene.

Ethylbenzene, 2ab

^1H (400 MHz, CDCl_3) δ 1.35 (t, $J = 7.6$ Hz, 3H, CH_3), 2.76 (q, $J = 7.6$ Hz, 2H, CH_2CH_3), 7.25-7.44 ppm (m, 5H, ArH).

1-Ethyl-4-fluorobenzene, 2ac

^1H (400 MHz, CDCl_3) δ 1.12-1.37 (m, 3H, CH_3), 2.53-2.77 (m, 2H, CH_2CH_3), 6.90-7.31 ppm (m, 4H, ArH).

^{19}F (282 MHz, CDCl_3) δ -118.17 ppm.

^{13}C (75 MHz, CDCl_3) δ 15.7, 28.1, 114.9 (d, $J = 21.0$ Hz), 129.1 (d, $J = 7.7$ Hz), 139.8 (d, $J = 3.1$ Hz), 161.2 ppm (d, $J = 242.9$ Hz).

1-Chloro-4-ethylbenzene, 2ad

^1H (400 MHz, CDCl_3) δ 1.27 (t, $J = 7.3$ Hz, 3H, CH_3), 2.66 (q, $J = 7.5$ Hz, 2H, CH_2CH_3), 7.12-7.33 ppm (m, 4H, ArH).

4-Ethyltoluene, 2ae

^1H (300 MHz, CDCl_3) δ 1.33 (t, $J = 7.6$ Hz, 3H, CH_2CH_3), 2.42 (s, 3H, Ar CH_3), 2.71 (q, $J = 7.6$ Hz, 2H, CH_2CH_3), 7.19 ppm (s, 4H, ArH).

4-Ethylanisol, 2af

^1H (300 MHz, CDCl_3) δ 1.29 (t, $J = 7.6$ Hz, 3H, CH_2CH_3), 2.67 (q, $J = 7.6$ Hz, 2H, CH_2CH_3), 3.84 (s, 3H, O CH_3), 6.89-6.93 (m, 2H, ArH), 7.17-7.21 ppm (m, 2H, ArH).

2-Ethyltoluene, 2ag

^1H (300 MHz, CDCl_3) δ 1.31 (t, $J = 7.6$ Hz, 3H, CH_2CH_3), 2.38-2.41 (m, 3H, Ar CH_3), 2.72 (q, $J = 7.5$ Hz, 2H, CH_2CH_3), 7.15-7.26 ppm (m, 4H, ArH).

4-Ethylaniline, 2ah

^1H (300 MHz, CDCl_3) δ 1.22 (t, $J = 7.6$ Hz, 3H, CH_2CH_3), 2.58 (q, $J = 7.6$ Hz, 2H, CH_2CH_3), 3.39 (bs, 2H, NH_2), 6.63-6.69 (m, 2H, ArH), 6.99-7.06 ppm (m, 2H, ArH).

Propylbenzene, 2aj

^1H (400 MHz, CDCl_3) δ 0.86 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.50-1.61 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.49 (t, $J = 7.6$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 7.05-7.11 (m, 3H, ArH), 7.15-7.21 ppm (m, 2H, ArH).

1,2-Diphenylethane, 2ak

^1H (300 MHz, CDCl_3) δ 3.07 (s, 4H, CH_2), 7.29-7.37 (m, 6H, ArH), 7.39-7.46 ppm (m, 4H, ArH).

1-Fluoro-4-isopropylbenzene, 2al

^1H (400 MHz, CDCl_3) δ 1.12 (d, $J = 6.9$ Hz, 6H, CH_3), 2.77 (hept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 6.81-6.88 (m, 2H, ArH), 7.02-7.08 ppm (m, 2H, ArH).

1-Chloro-4-isopropylbenzene, 2am

^1H (400 MHz, CDCl_3) δ 1.12 (d, $J = 6.9$ Hz, 6H, CH_3), 2.76 (hept, $J = 7.0$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 7.00-7.05 (m, 2H, ArH), 7.11-7.15 ppm (m, 2H, ArH).

2-Isopropylnaphthalene, 2an

^1H (400 MHz, CDCl_3) δ 1.55 (d, $J = 6.9$ Hz, 6H, CH_3), 3.26 (hept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 7.58-7.66 (m, 3H, ArH), 7.84-7.85 (m, 1H, ArH), 7.95-8.01 ppm (m, 3H, ArH).

1,1-Diphenylethane, 2ao

^1H (400 MHz, CDCl_3) δ 1.70 (dd, $J = 7.2, 0.9$ Hz, 3H, CH_3), 4.21 (q, $J = 7.2$ Hz, 1H, CHCH_3), 7.20-7.38 ppm (m, 10H, ArH).

^{13}C (75 MHz, CDCl_3) δ 21.8, 44.8, 126.0, 127.6, 128.3, 146.3 ppm.

2,2,4-Trimethylpentane, 2ap

^1H (300 MHz, CDCl_3) δ 0.93-0.99 (m, 15H, CH_3), 1.18 (d, $J = 5.4$ Hz, 2H, CH_2), 1.63-1.81 ppm (m, 1H, CH).

Cyclooctane, 2aq and 2ar

^1H (300 MHz, CDCl_3) δ 1.54 ppm (s, 16H, CH_2).

1,2,4-Triethylcyclohexane, 2ax

^1H (300 MHz, CDCl_3) δ 0.73-1.93 ppm (m, 24H).

Norbornane, 2ay

^1H (300 MHz, CDCl_3) δ 1.13-1.22 (m, 6H), 1.43-1.54 (m, 4H), 2.18-2.24 ppm (m, 2H).

2,3-Dimethylbutane, 2az

^1H (300 MHz, CDCl_3) δ 0.85-0.94 (m, 12H, CH_3), 1.38-1.55 ppm (m, 2H, CH).

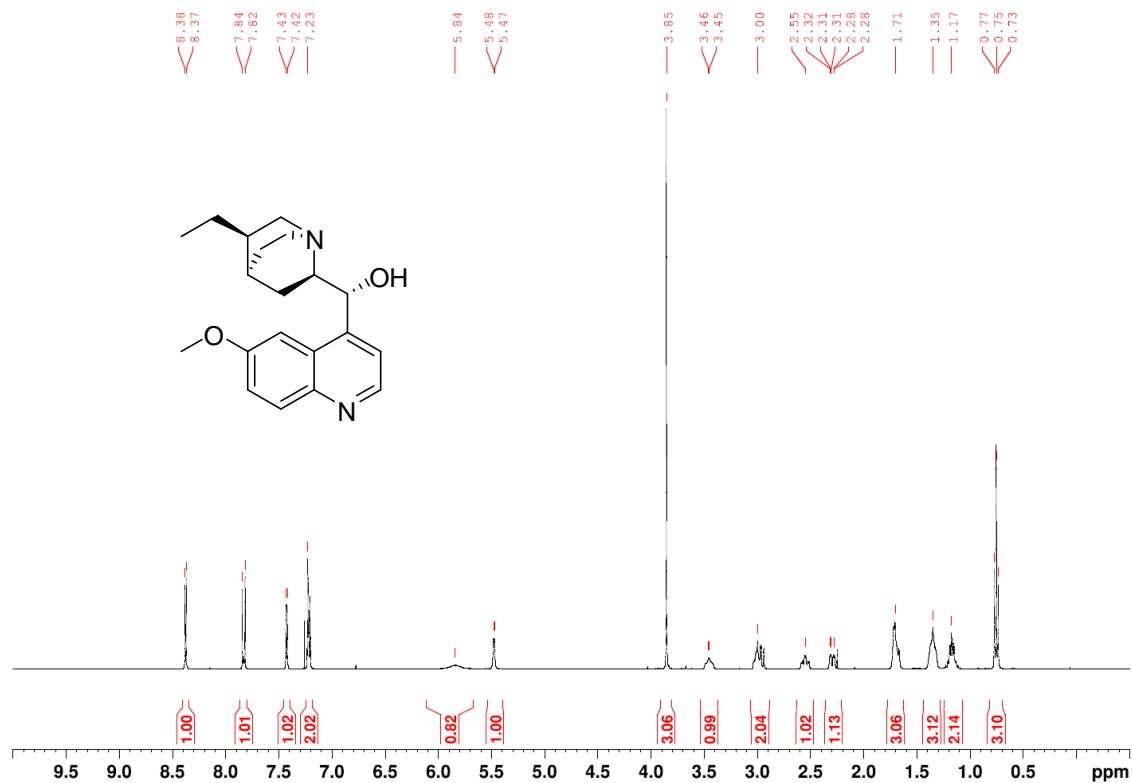
Stearic acid, 2ba

^1H (300 MHz, CDCl_3) δ 0.93 (t, $J = 6.5$ Hz, 3H, CH_3), 1.22-1.48 (m, 28H, CH_2), 1.60-1.84 (m, 2H, CH_2), 2.28-2.34 (m, 2H, CH_2), 9.4 ppm (bs, 1H, COOH).

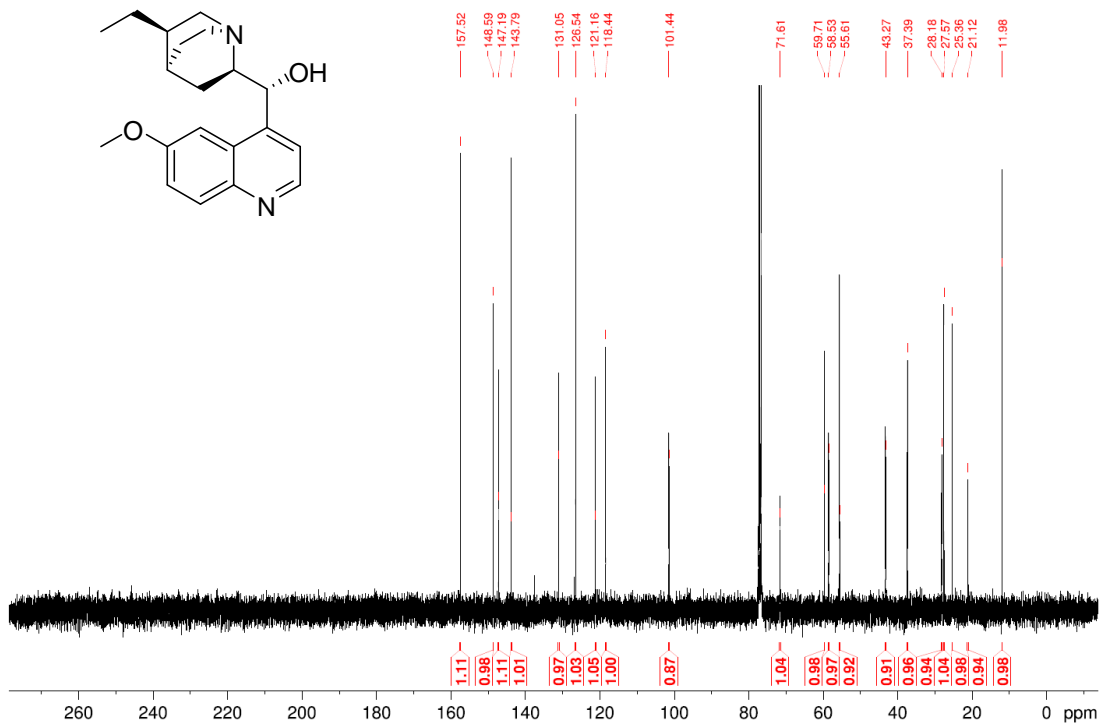
Tristearin, 2bb

^1H (300 MHz, CDCl_3) δ 0.78 (t, $J = 6.6$ Hz, 9H, CH_3), 1.12-1.25 (m, 84H, CH_2), 1.44-1.59 (m, 6H, $\text{CH}_2\text{CH}_2\text{COO}$), 2.16-2.26 (m, 6H, CH_2COO), 4.05 (dd, $J = 11.9, 6.0$ Hz, 2H, CH_2CHCH_2), 4.20 (dd, $J = 11.9, 4.3$ Hz, 2H, CH_2CHCH_2), 5.12-5.21 ppm (m, 1H, CH_2CHCH_2).

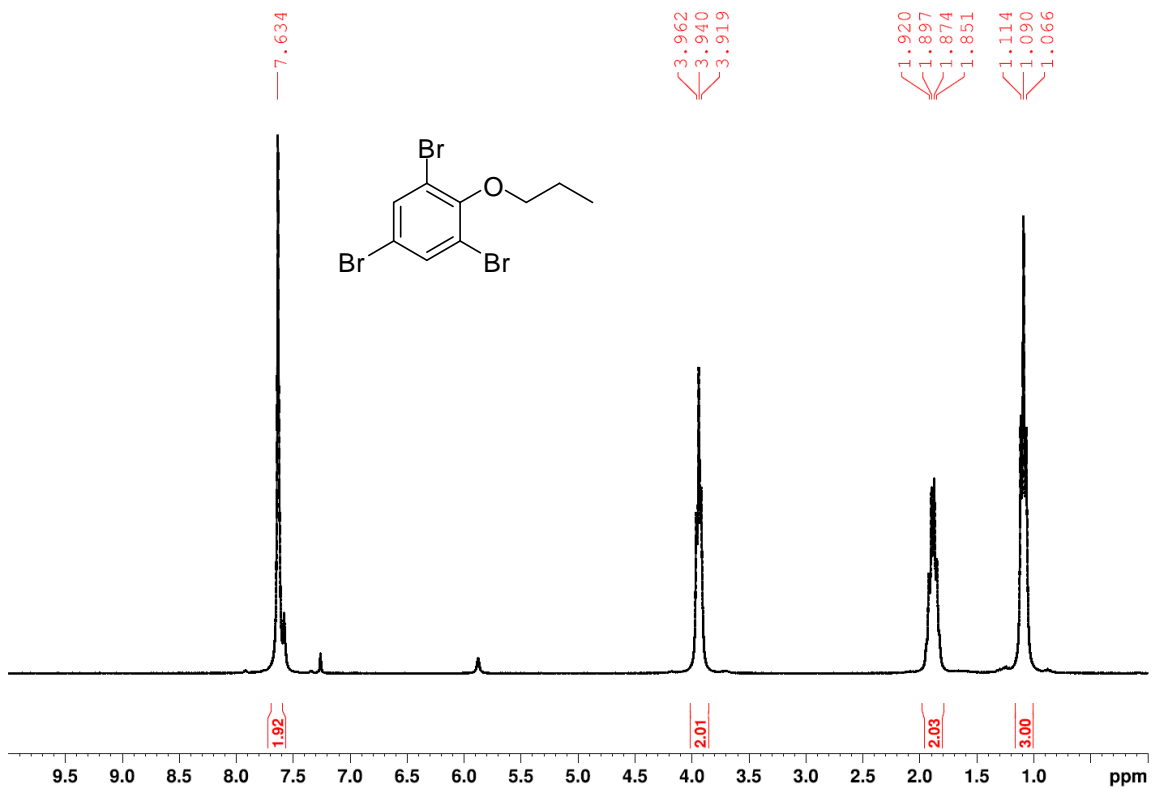
NMR spectra



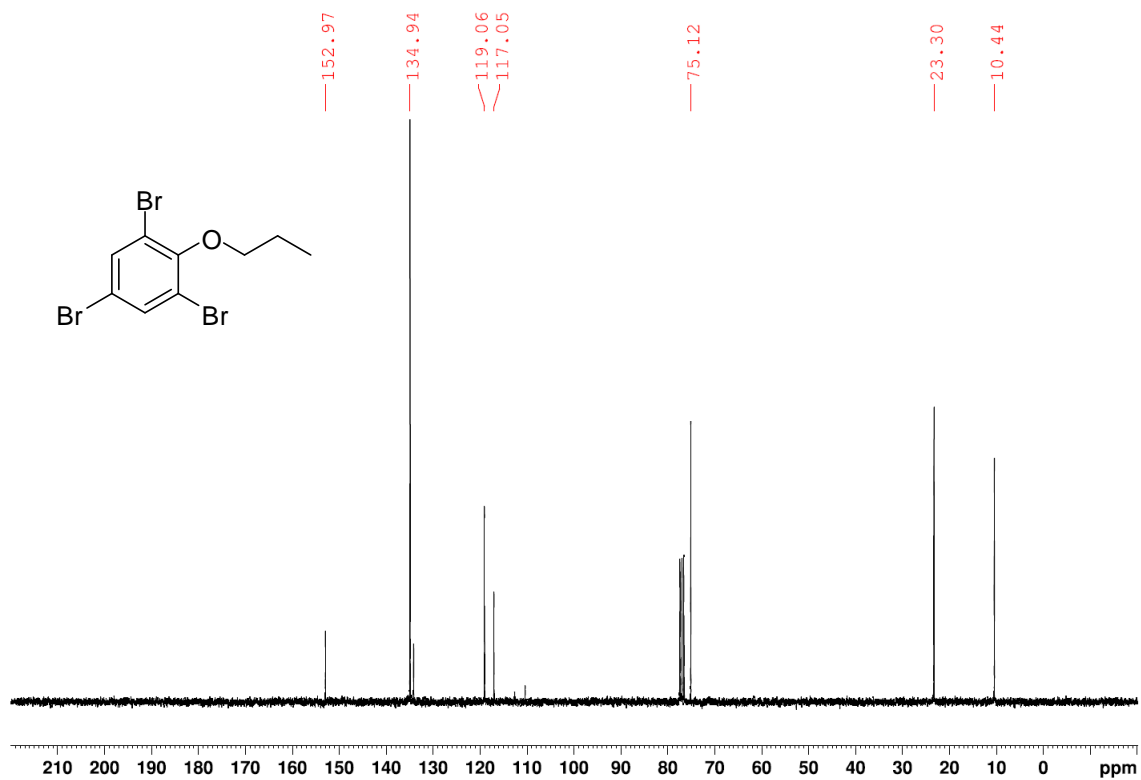
^1H spectrum (CDCl_3 , 400 MHz) of dihydroquinine **2p**.



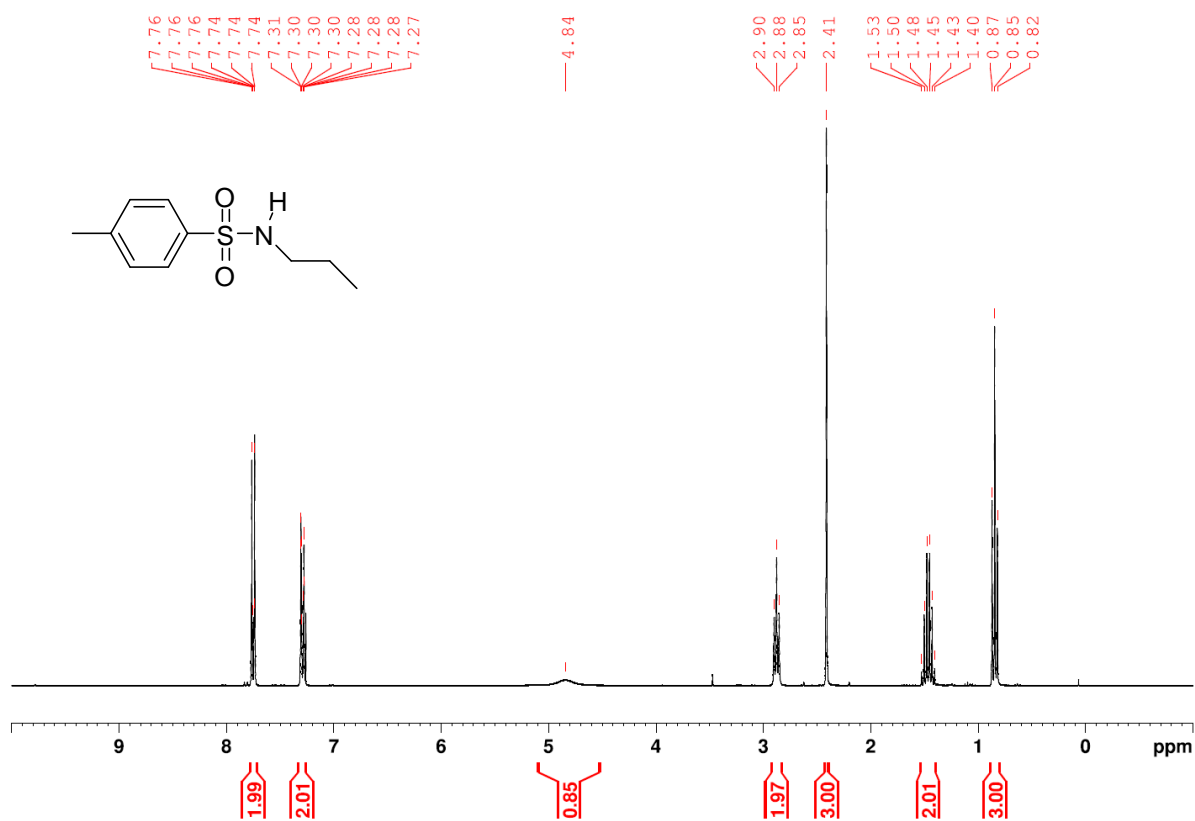
$^{13}\text{C}_{\text{quant}}$ spectrum (CDCl_3 , 100 MHz) of dihydroquinine **2p**.



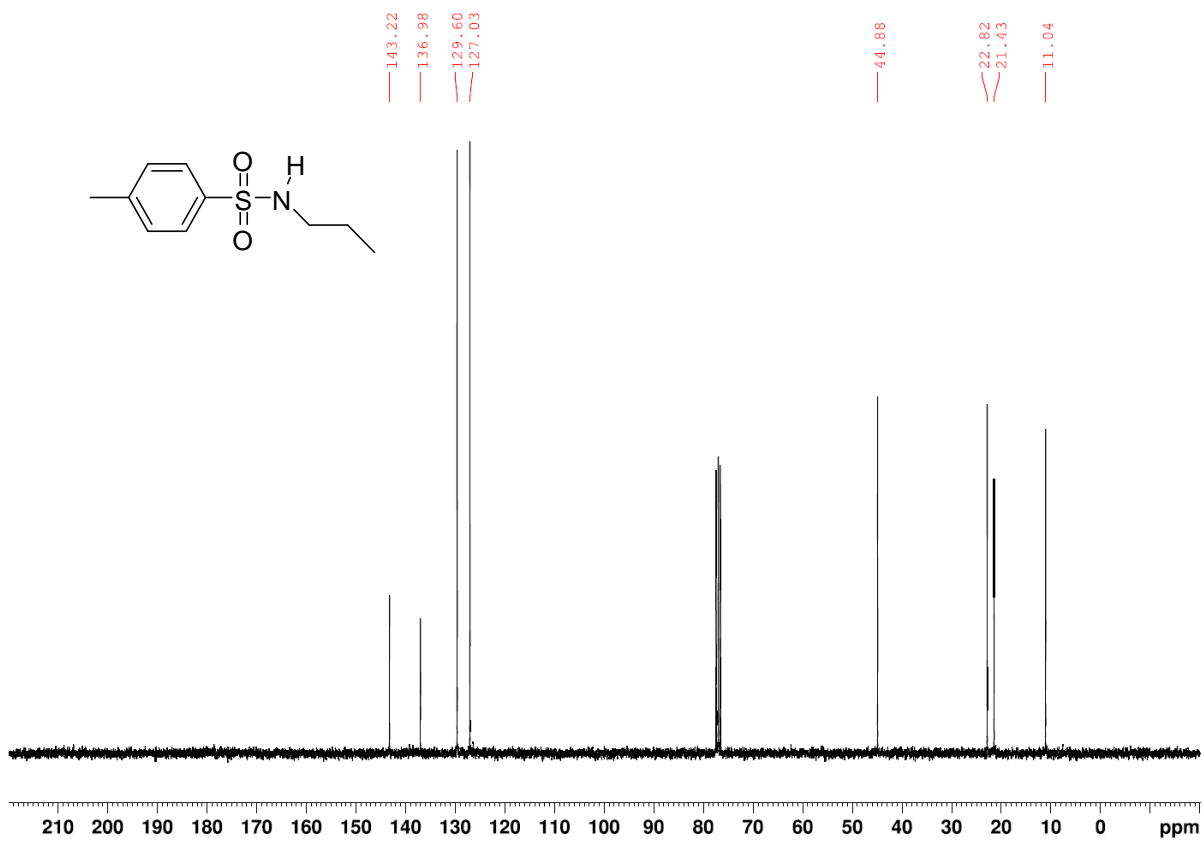
^1H spectrum (CDCl_3 , 300 MHz) of 2,4,6-tribromophenyl propyl ether **2v**.



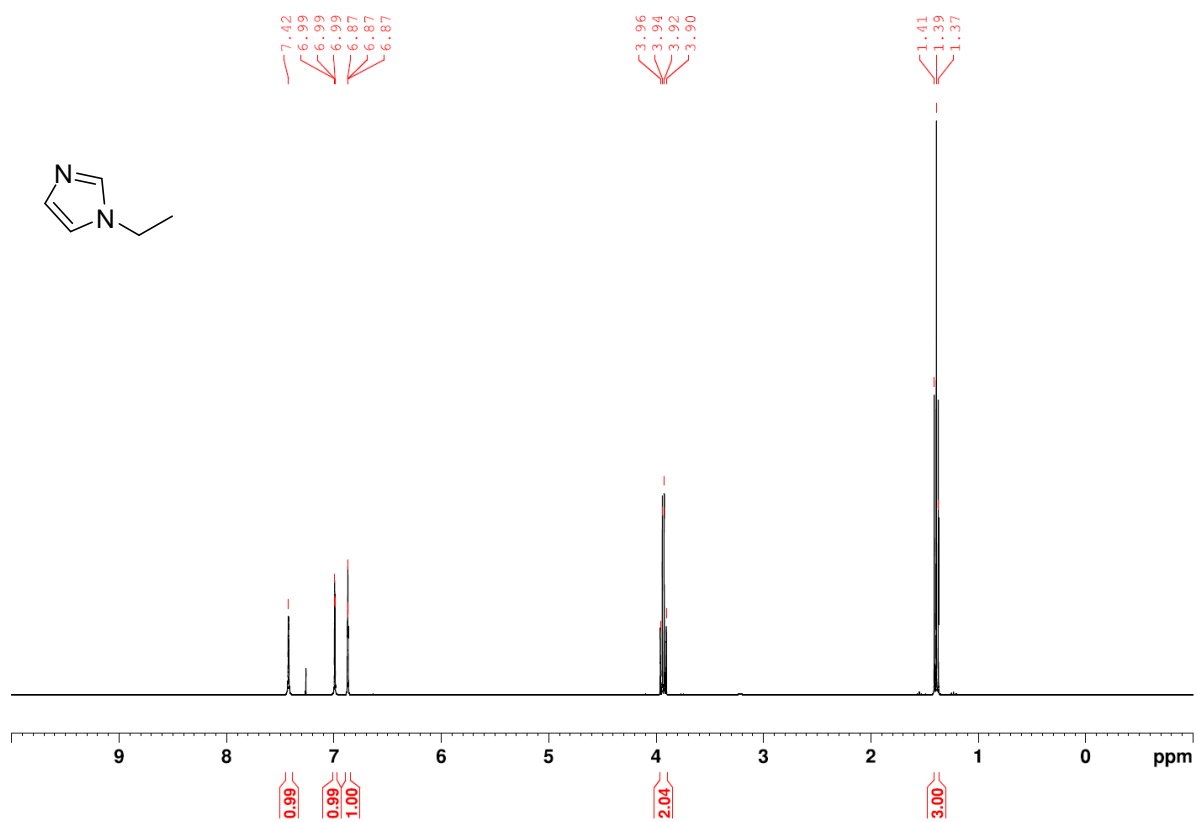
¹³C spectrum (CDCl₃, 75 MHz) of 2,4,6-tribromophenyl propyl ether **2v**.



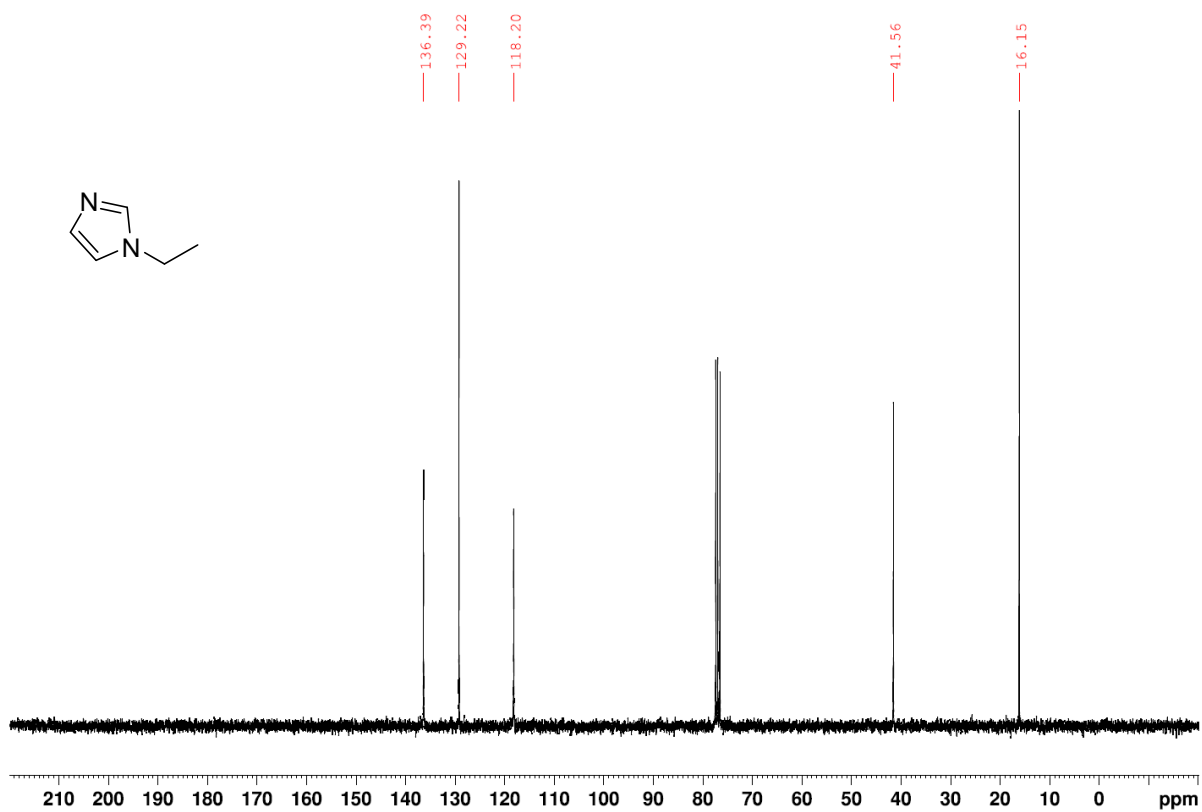
¹H spectrum (CDCl₃, 300 MHz) of N-Propyl-4-methylbenzenesulfonamide, **2x**.



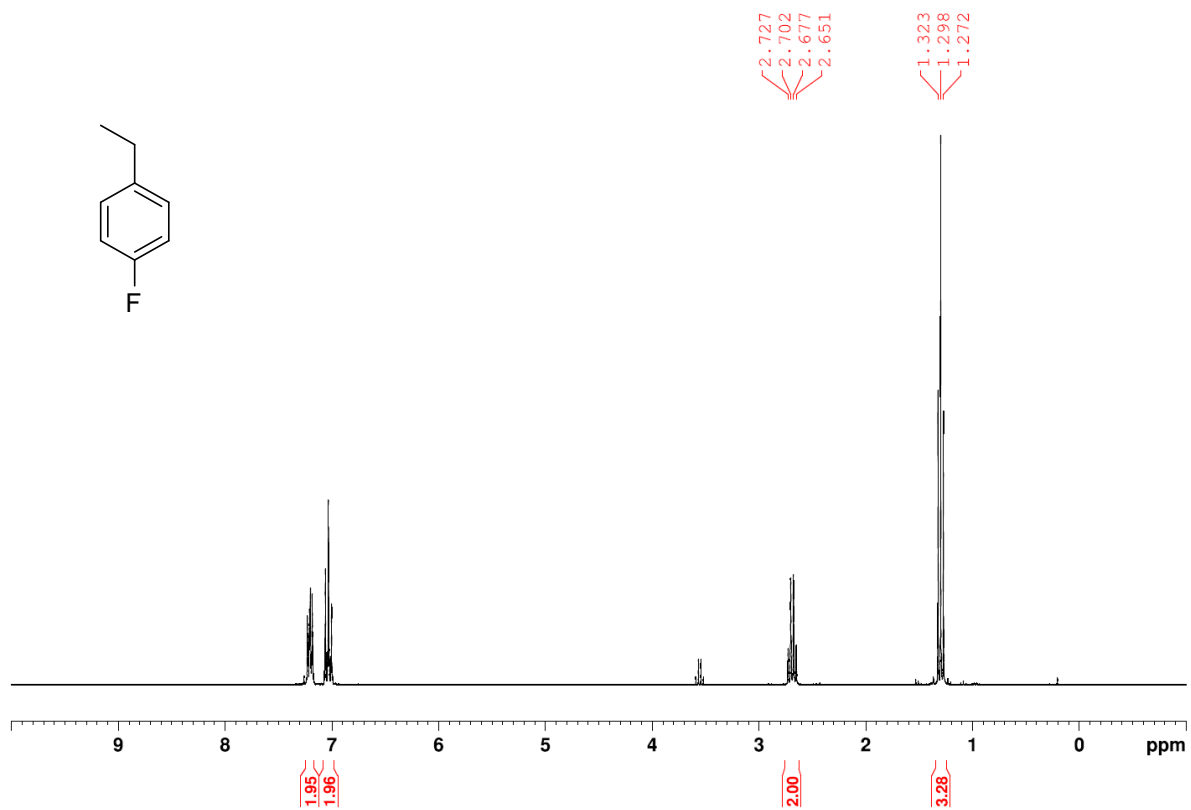
¹³C spectrum (CDCl₃, 75 MHz) of *N*-Propyl-4-methylbenzenesulfonamide, **2x**.



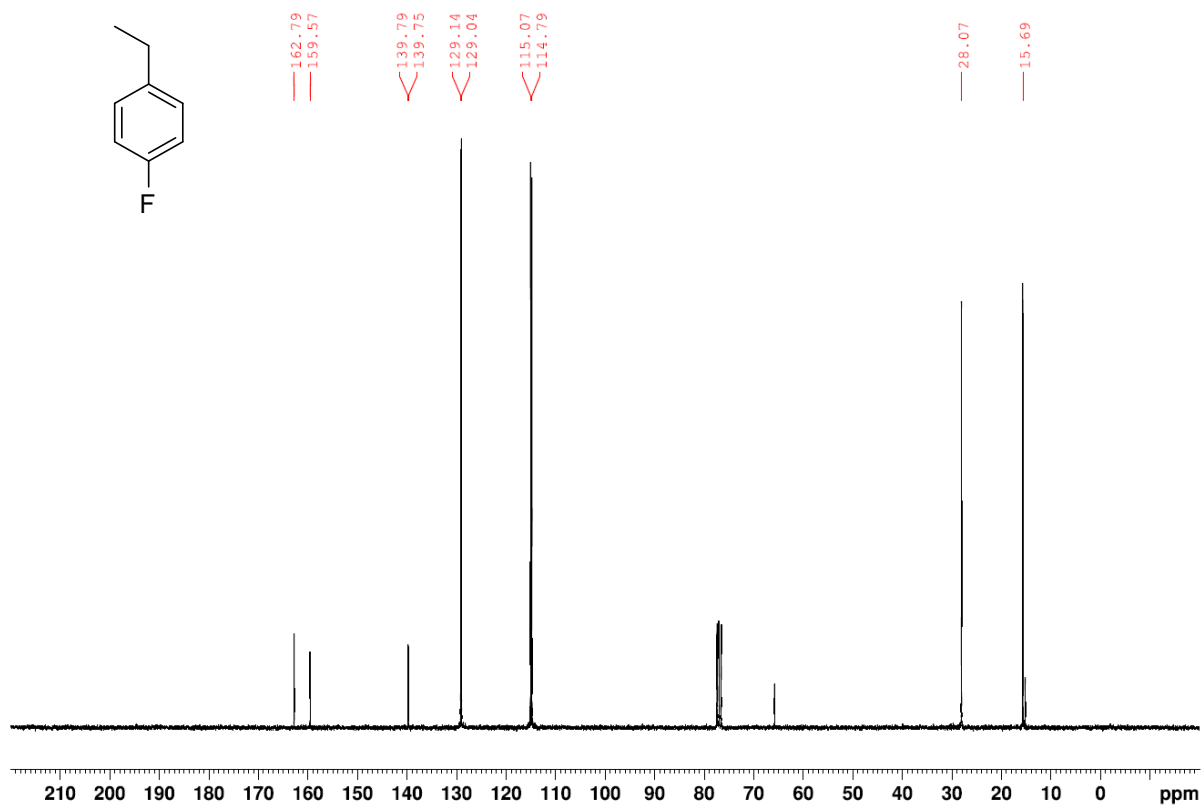
¹H spectrum (CDCl₃, 400 MHz) of *N*-Ethylimidazol, **2y**.



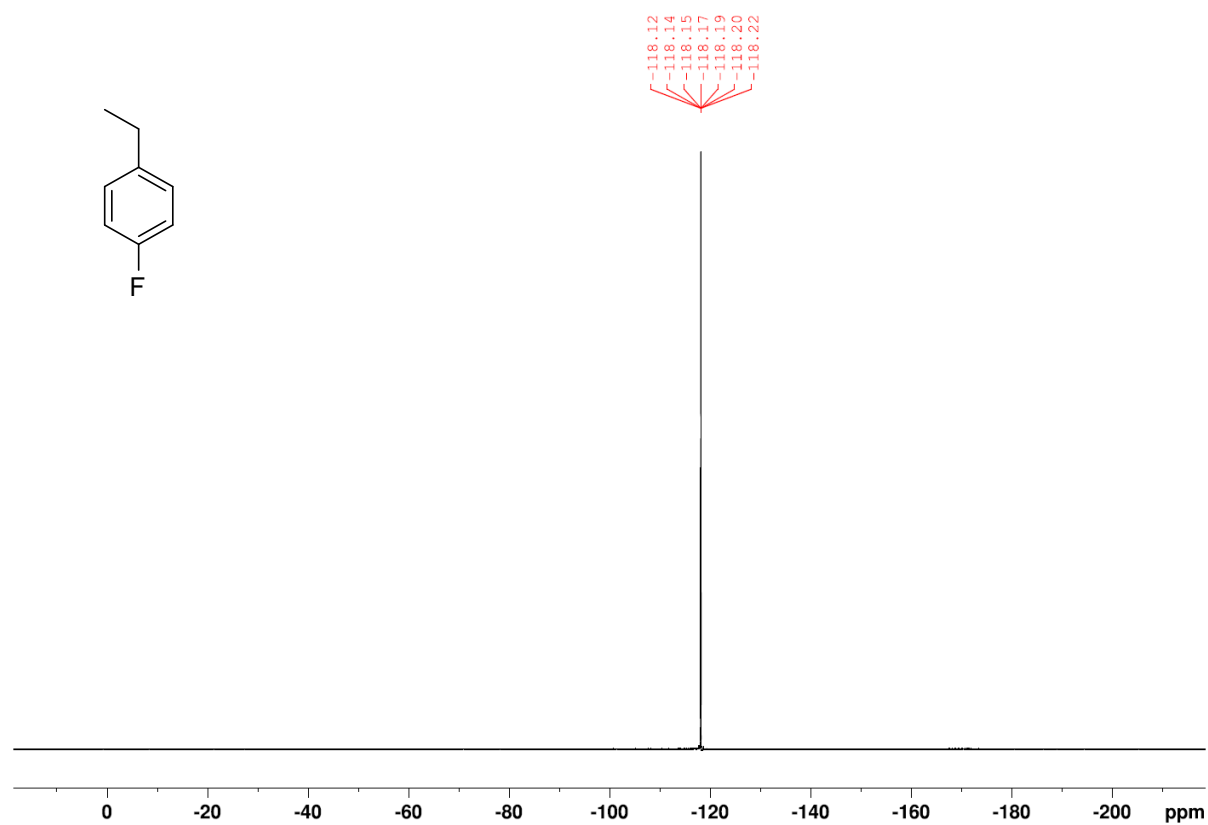
¹³C spectrum (CDCl₃, 75 MHz) of *N*-Ethylimidazol, **2y**.



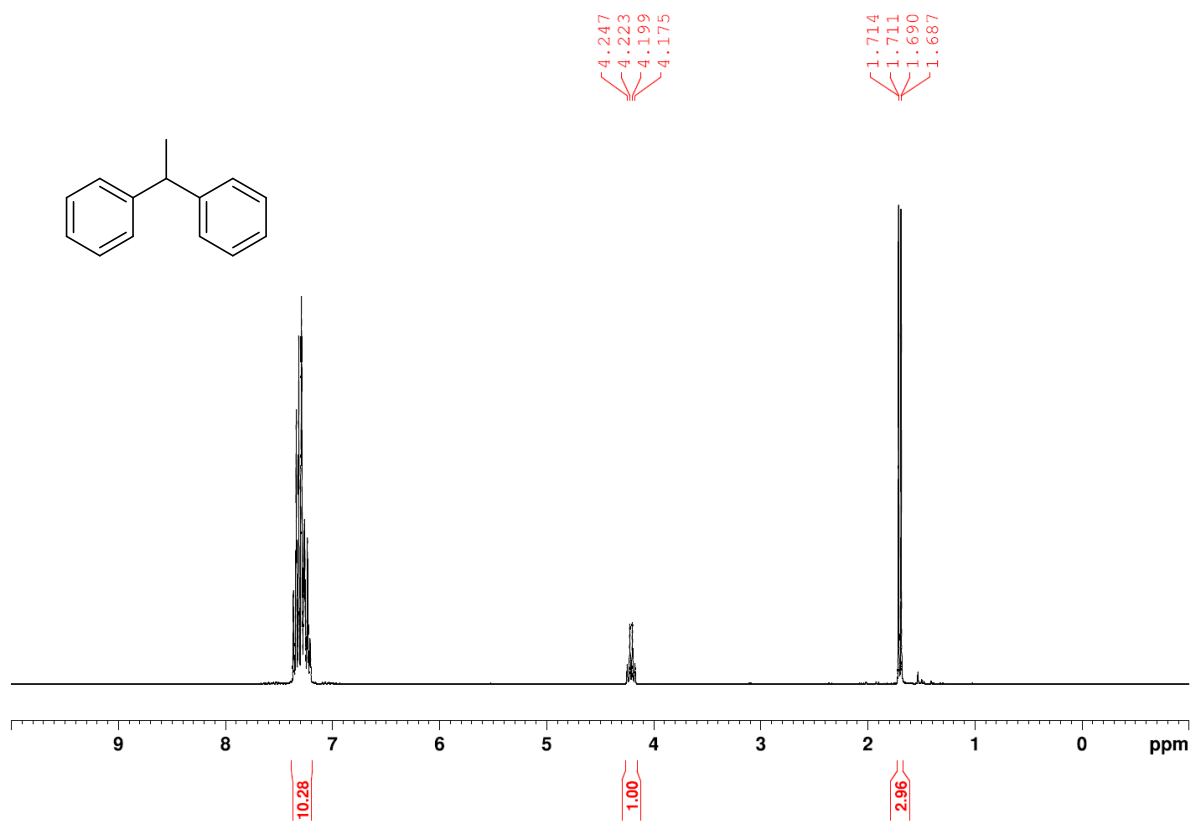
¹H spectrum (CDCl₃, 300 MHz) of 1-Ethyl-4-fluorobenzene, **2ac**.



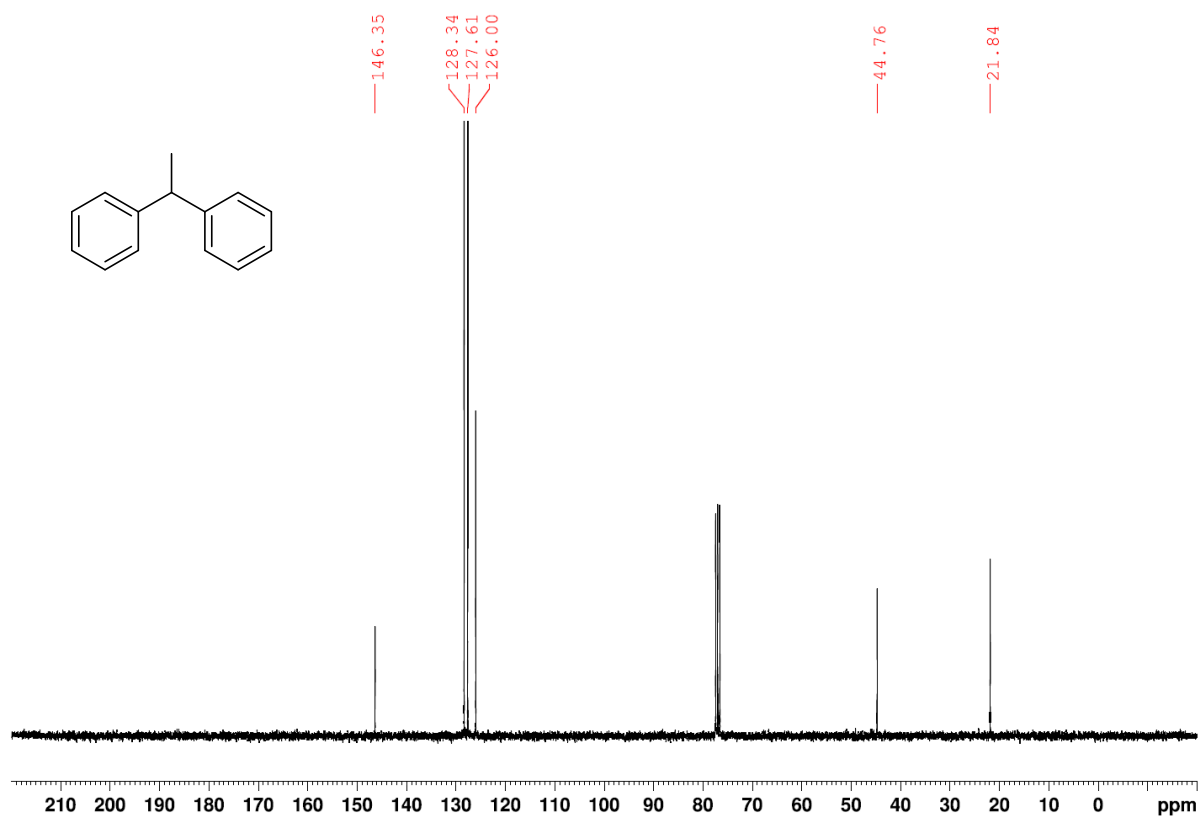
^{13}C spectrum (CDCl₃, 75 MHz) of 1-Ethyl-4-fluorobenzene, **2ac**.



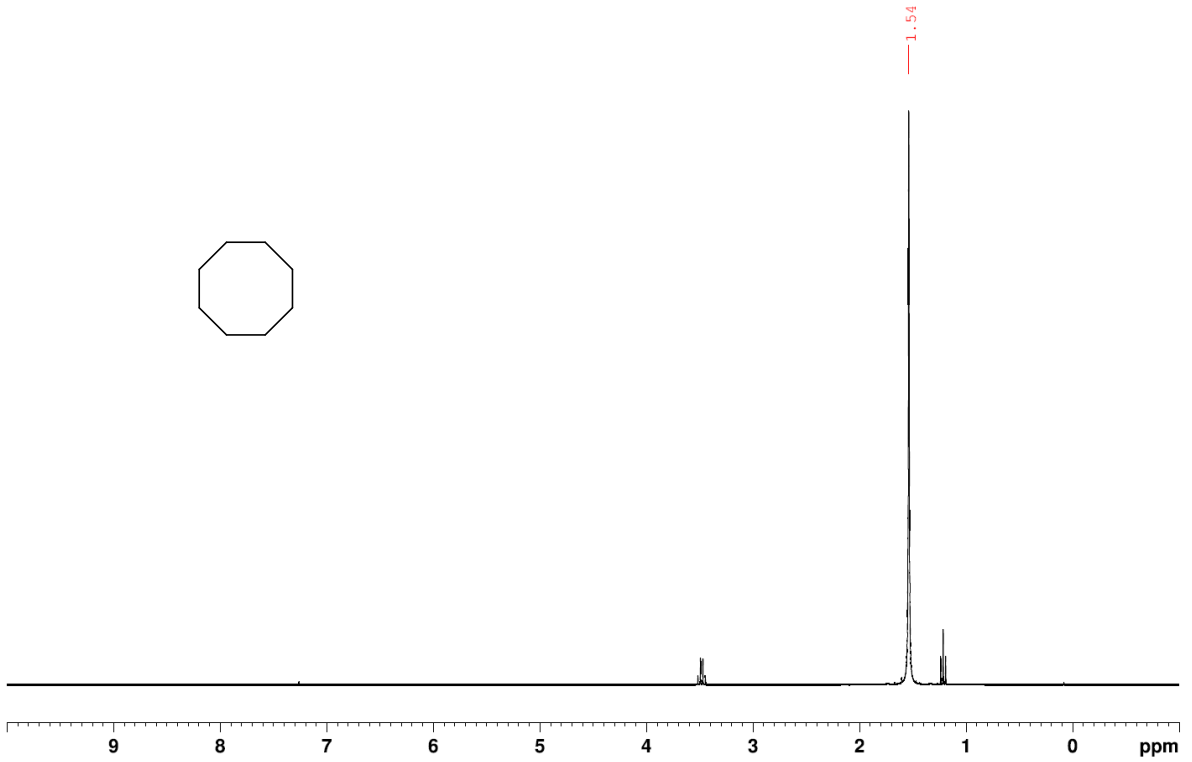
^{19}F spectrum (CDCl₃, 282 MHz) of 1-Ethyl-4-fluorobenzene, **2ac**.



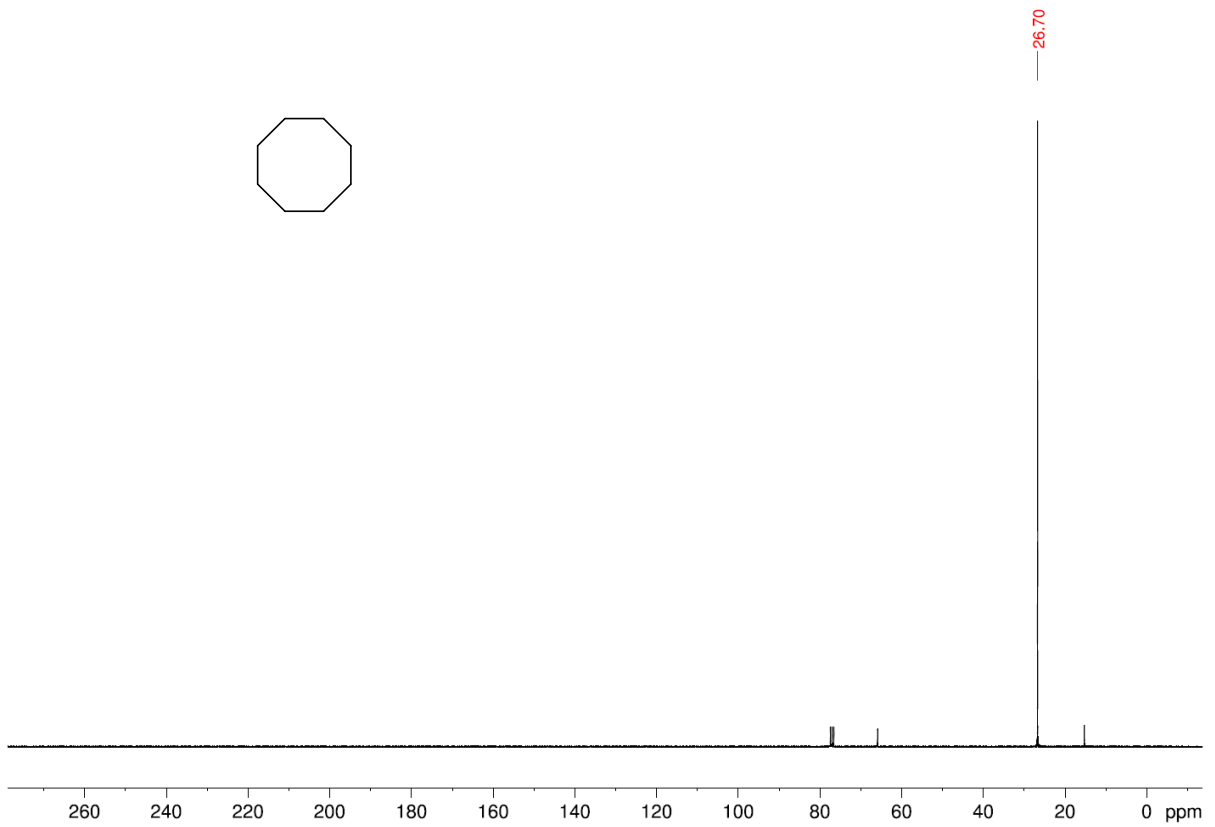
¹H spectrum (CDCl₃, 300 MHz) of 1,1-Diphenylethane, **2ao**.



¹³C spectrum (CDCl₃, 75 MHz) of 1,1-Diphenylethane, **2ao**.

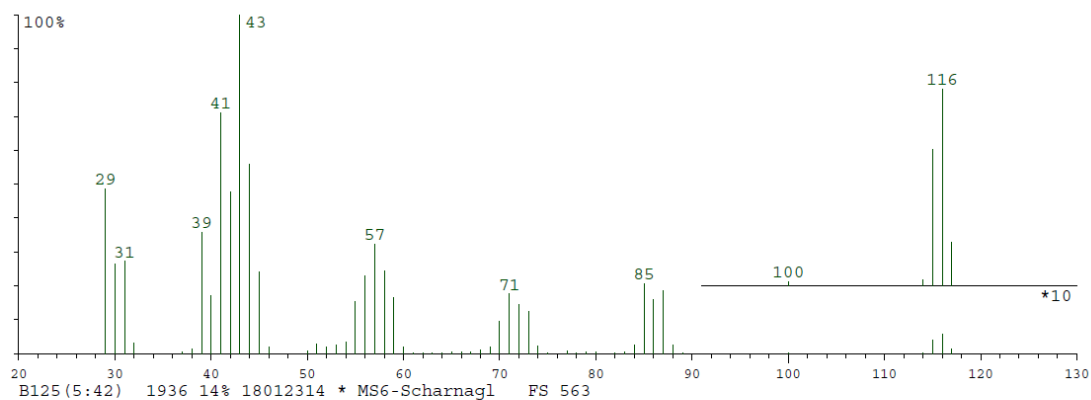
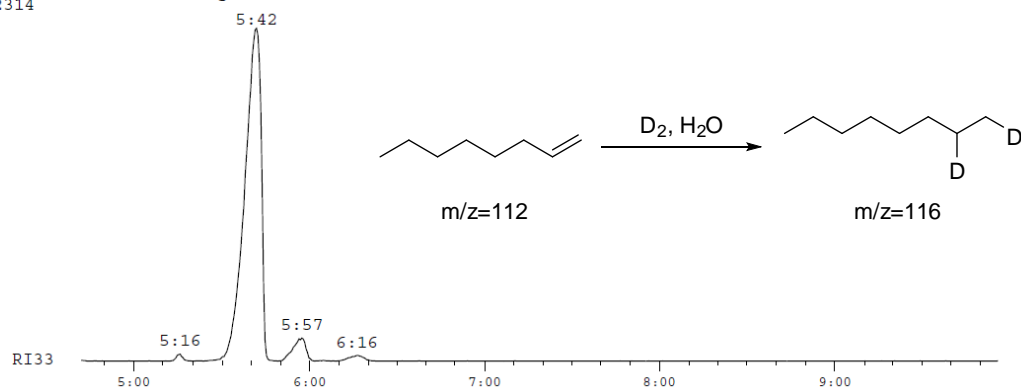
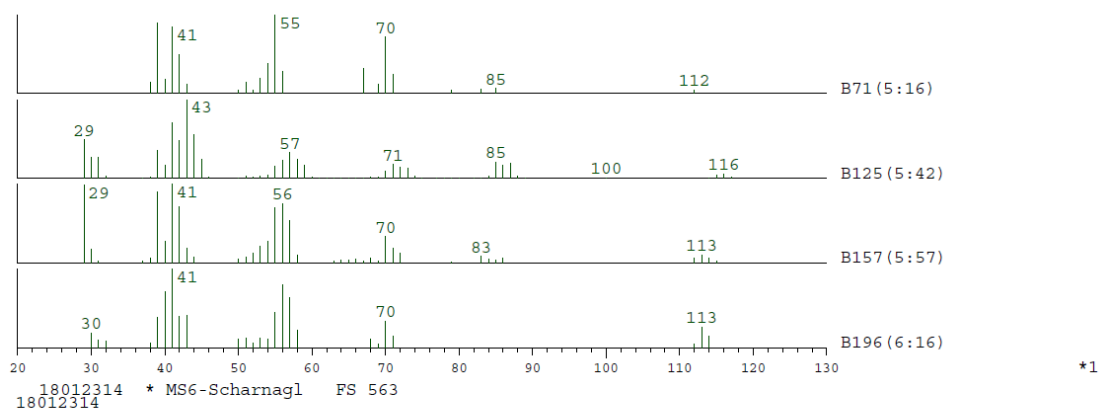


¹H spectrum (CDCl₃, 300 MHz) of Cyclooctane, **2aq**.



¹³C spectrum (CDCl₃, 75 MHz) of Cyclooctane, **2aq**.

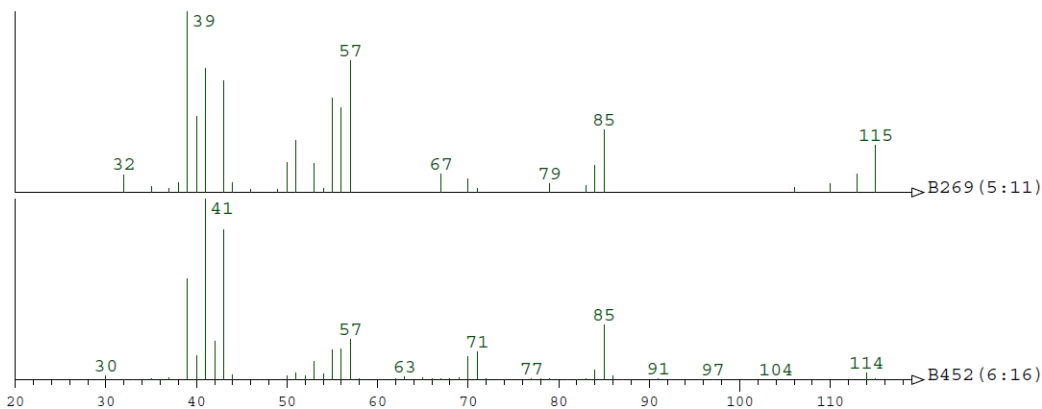
Investigations with D₂



m/z	Relative Intensity (%)	m/z	Relative Intensity (%)	m/z	Relative Intensity (%)
29	48.66	57	32.39	79	0.34
30	26.56	58	24.25	80	0.45
31	27.20	59	16.45	82	0.18
32	3.02	60	1.84	83	0.38
37	0.39	61	0.11	84	2.57
38	1.32	62	0.30	85	20.61
39	35.78	63	0.16	86	15.97
40	16.99	64	0.14	87	18.53
41	71.11	65	0.58	88	2.42
42	47.72	66	0.34	89	0.19
43	100.00	67	0.55	100	0.13
44	56.00	68	1.09	114	0.18
45	23.96	69	1.93	115	4.02
46	2.01	70	9.53	116	5.80
50	0.81	71	17.66	117	1.28
51	2.86	72	14.56		
52	2.02	73	12.48		
53	2.61	74	2.11		
54	3.36	75	0.26		
55	15.23	77	0.76		
56	23.01	78	0.26		

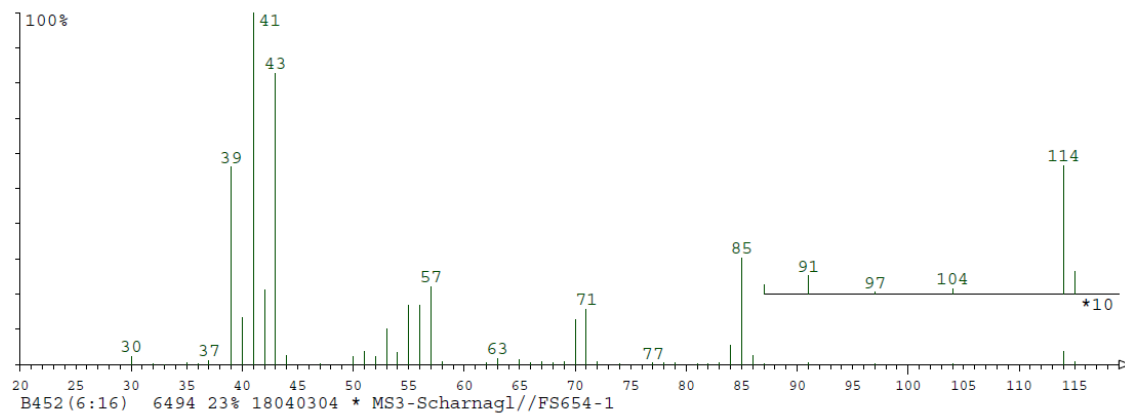
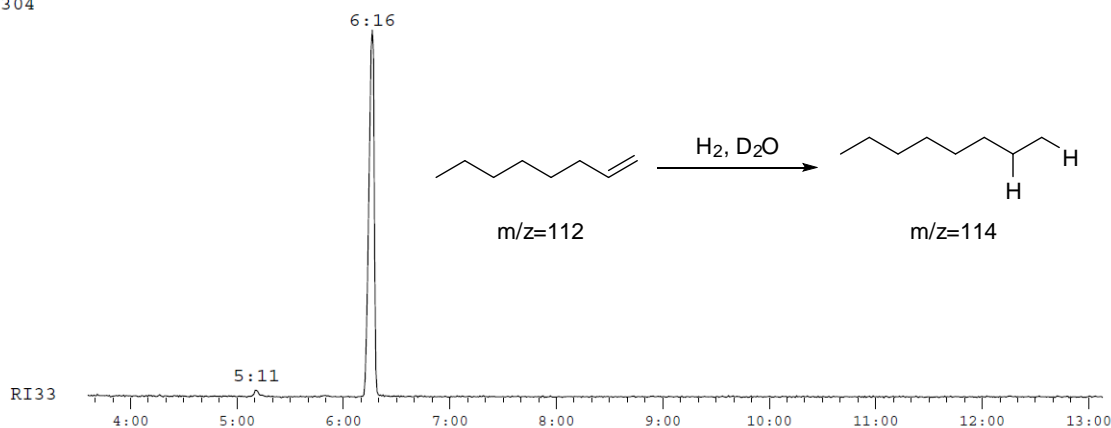
B125 (5:42) 1936 14% 18012314 * MS6-Scharnagl FS 563

GCMS-spectrum for the hydrogenation of 1-octene with D₂ in H₂O.



*1

18040304 * MS3-Schornagl//FS654-1
18040304



B452 (6:16) 6494 23% 18040304 * MS3-Schornagl//FS654-1

30	2.33	58	0.66	87	0.25
32	0.12	62	0.45	91	0.52
33	0.04	63	1.65	97	0.05
35	0.36	65	1.32	104	0.15
36	0.18	66	0.38	114	3.66
37	1.18	67	0.76	115	0.63
39	56.09	68	0.37		
40	13.32	69	0.90		
41	100.00	70	12.66		
42	21.09	71	15.64		
43	82.75	72	0.69		
44	2.58	74	0.23		
47	0.08	77	0.44		
50	2.09	78	0.34		
51	3.77	79	0.42		
52	2.14	81	0.20		
53	10.09	82	0.15		
54	3.32	83	0.35		
55	16.81	84	5.45		
56	16.83	85	30.32		
57	22.18	86	2.45		

B452 (6:16) 6494 23% 18040304 * MS3-Schornagl//FS654-1

GCMS-spectrum for the hydrogenation of 1-octene with H₂ in D₂O.

Leaching analysis

After the reaction in water, the organic fraction was separated. The aqueous one was washed with hexane (2-3 mL) three times. The aqueous phase was diluted with H₂O to 10 mL total volume and submitted to AAS. From the organic fraction the volatiles were removed in vacuum in a high pressure tube. 4 mL aqua regia was added and the tube was heated to 140 °C for 4 h. After cooling to room temperature, the acidic mixture was diluted to 25 mL total volume with H₂O and submitted to AAS.

For the other solvents and neat conditions, the same method was applied, without the separating step at the beginning.

Table S4. Leached metal content in different reaction media detected by AAS.

Solvent	used m (catalyst) [mg]	detected c (cobalt) [mg/L]
H ₂ O (aqueous fraction)	8.86 mg	0.1367
H ₂ O (organic fraction)	8.86 mg	0.0045
MeOH	8.86 mg	0.3050
Neat (1-octene)	55.36 mg	0.0060
Heptane	8.85 mg	0.0024