Supporting Information

Introducing SulfoShvo: Synthesis and Catalytic Testing of the First Sulfonated Derivative of Shvo's Catalyst

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General Information

Unless noted otherwise, all reactions were carried out under inert conditions. Solvents and all other reagents were purchased from Sigma Aldrich, Acros, TCI, and abcr and used as received without any additional purification. The microwave-assisted reations were carried out in a CEM Discover 2.0 microwave synthesizer. The reactions with H_2 as the hydrogen source were carried out in a parallel autoclave system from Parr.

NMR Spectroscopy (NMR): ^{1}H and ^{13}C NMR spectra were recorded in DMSO-*d6* using Bruker 400 and 600 MHz spectrometers. All chemical shifts are quoted in parts per million referenced to the DMSO solvent residue (δH = 2.50 ppm, δC = ppm). ^{1}H NMR splitting patterns are abbreviated as follows: broad signal (br), singlet (s), doublet (d), triplet (t), doublet of doublets (dd), doublet of triplets (dt), triplet of triplets (tt), quartet (q), quintet (quint), heptet (hept), multiplet (m).

Hight Resolution Mass Spectrometry (HR-MS): Samples for HRMS were dissolved in methanol (100 $\mu g \cdot mL^{-1}$) and measured with an LTQ-Orbitrap (Thermo Scientific).

X-ray crystallography: X-ray crystallographic data collections for the compound 7 were conducted on a Bruker D8 Venture four-circle diffractometer by Bruker AXS GmbH using a PHOTON II CPAD detector by Bruker AXS GmbH. X-ray radiation was generated by a microfocus source IμS Mo by Incoatec GmbH with HELIOS mirror optics and a single-hole collimator by Bruker AXS GmbH. MicroGrippers from MiTeGen were used for mounting. For the data collection, the programs APEX 4 Suite with the integrated programs SAINT (integration) and SADABS (absorption correction) by Bruker AXS GmbH were used. Using Olex2.1,[1] the structures were solved with the ShelXT 2 structure solution program by Intrinsic Phasing and refined with the XL 3 refinement package using Least Squares minimization.[2]

Gas Chromatography (GC): Conversion and yield of levulinic acid to GVL were determined *via* GC on an Agilent Technologies INC. chromatograph of the type 7890B with a thermal conductivity detector (TCD). A HP-INNOWAX column was used (30 m long, 0.25 mm diameter, 0.25 μm thickness of the layer).

Table 1: Heating profile for the GC-TCD analysis of the conversion of levulinic acid to GVL.

	Rate [°C/min]	Value [°C]	Hold Time [min]
Initial		50	2
Ramp 1	7	110	0
Ramp 2	60	250	5

The split was set to 15:1. *Tert*-amylalcohol was chosen as internal standard and response factors of the substrates and products were obtained experimentally by analyzing known quantities of the substances (calibration).

Table 2: Calibration curve for the GC of levulinic acid.

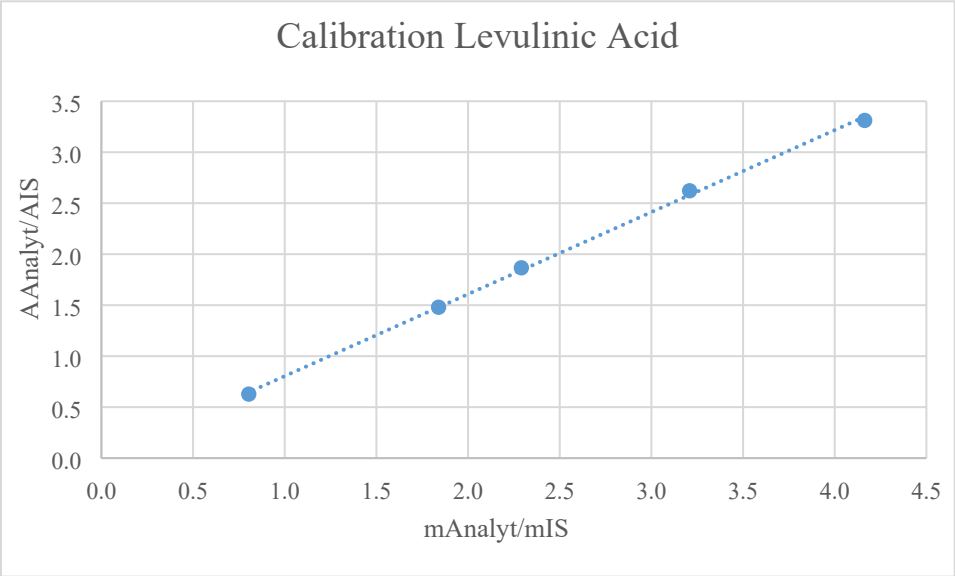
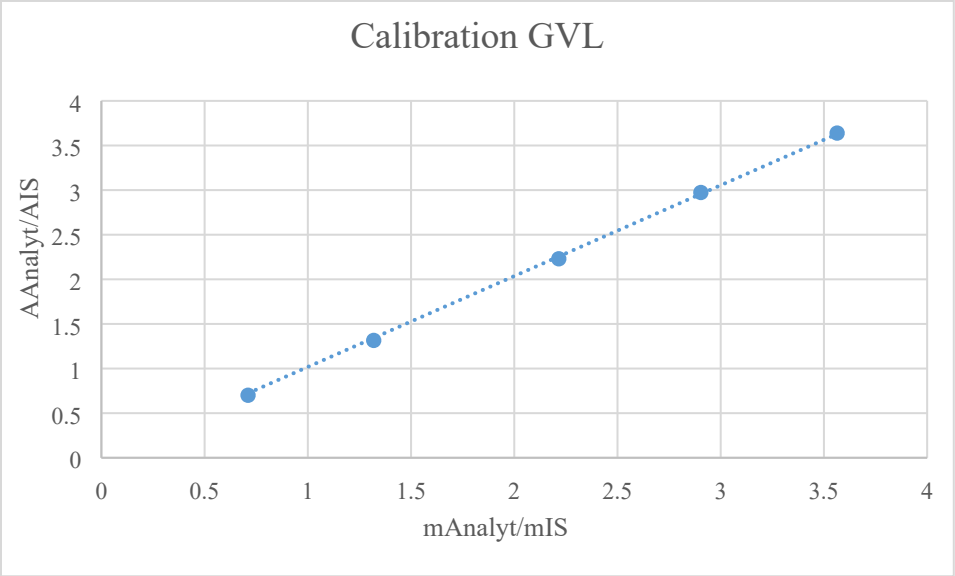


Table 3: Calibration curve for the GC of levulinic acid.



Conversion and yield of undecanal to undecanol were determined *via* GC on an Agilent Technologies INC. chromatograph of the type 7890A with a flame ionization detector (FID). A HP-5 column was used (30 m long, 0.25 mm diameter, 0.25 µm thickness of the layer).

Table 4: Heating Profile for the GC-FID analysis of the conversion of undecanal to undecanol.

	Rate [°C/min]	**Value [°C]**	**Hold Time [min]**
Initial		40	3
Ramp 1	7.5	150	0
Ramp 2	40	320	8

The split was set to 50:1. *n*-Decane was chosen as internal standard and response factors of the substrates and products were obtained experimentally by analyzing known quantities of the substances (calibration).

Table 5: Calibration curve for the GC of undecanal.

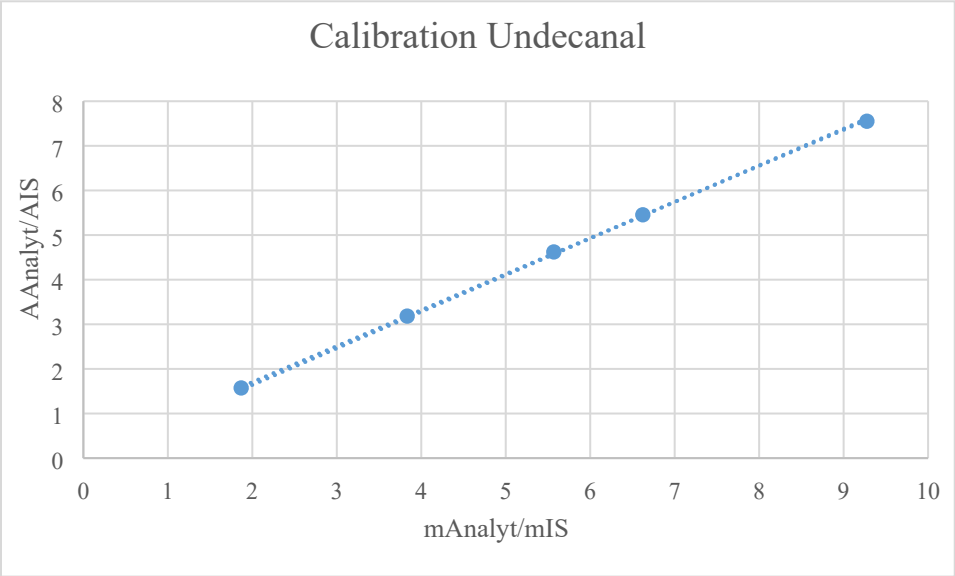
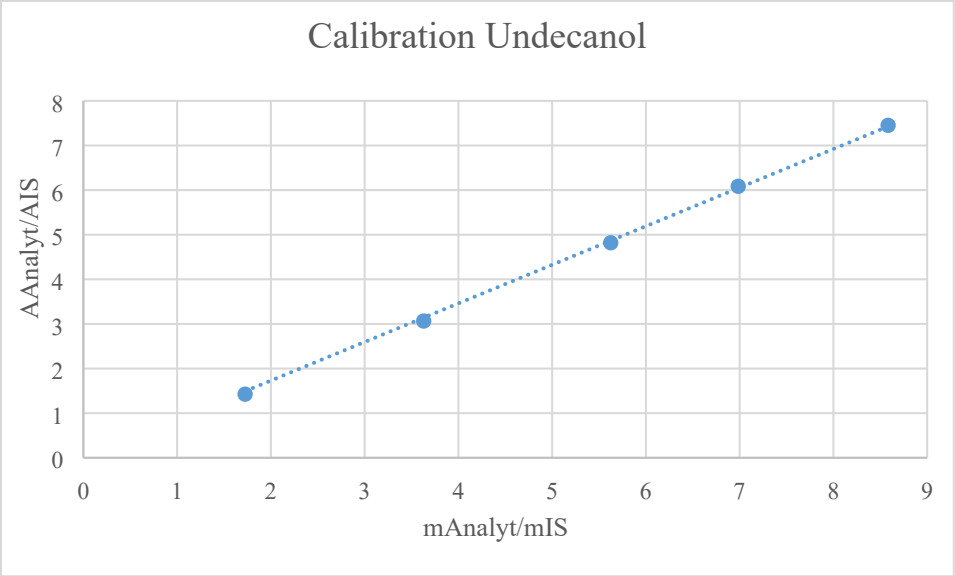


Table 6: Calibration curva for the GC of undecanal.



The conversion of (*R*)-1-phenylethanol to acetophenone was determined *via* GC on an Agilent Technologies INC. chromatograph of the type 7890B with a flame ionization detector (FID). A HP-INNOWAX column was used (30 m long, 0.25 mm diameter, 0.25 µm thickness of the layer).

Table 7: Heating Profile for the GC-FID analysis of the conversion of undecanal to undecanol.

	Rate [°C/min]	Value [°C]	Hold Time [min]
Initial		50	2
Ramp 1	25	120	0
Ramp 2	40	250	1

The split was set to 73:1.

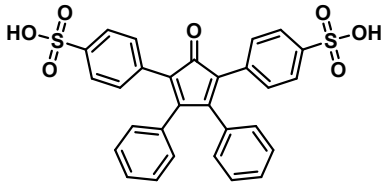
High Pressure Liquid Chromatography (HPLC): The *ee* of the racemisation reaction were determined *via* HPLC on a Shimadzu liquid chromatograph of the type NexeraXR LC-20AD XR with a UV-Vis detector. A Lux 5µ Cellulose-1 column was used.

Since the response factors of both enantiomers is the same, the areas were directly compared without a calibration.

Infrared Spectroscopy (IR): IR-ATR measurements (diamond) were performed in reflection mode on a Bruker Alpha II inside a glovebox, wavenumbers are given in cm^{-1}.

Ligand and Complex Synthesis

4,4'-(2-oxo-4,5-diphenylcyclopenta-3,5-diene-1,3-diyl)dibenzenesulfonic acid (4)



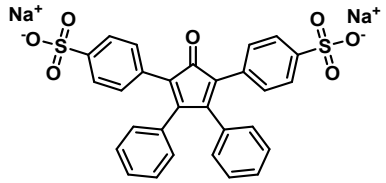
The disulfonic acid **4** was synthesised accordingly to the procedure reported by Skalski et al.[3] Our workup deviated from their procedure. After the quenching, the solution was concentrated and stored at 6 °C. The product crystallized, was filtered off and washed with cold heptane. The resulting dark violet solid (Y = 81 %), was dried in a vacuum oven at 100 °C. NMR studies revealed residues of solvent, which were not removed since the following neutralisation yielded a pure product without purification of the disulfonic acid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.76 (br, 2H), 7.47 (d, *J* = 7.8 Hz, 4H), 7.25 (tt, *J* = 8.8, 4.8 Hz, 6H), 7.12 (d, *J* = 7.9 Hz, 4H), 6.97 (d, *J* = 6.7 Hz, 4H) ppm.

^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6) δ = 199.5, 155.0, 147.1, 132.6, 130.7, 129.2, 128.9, 128.7, 128.1, 125.2, 124.6, 39.5 ppm.

HR-MS (ESI): calcd. $[M-2H]^{2-}$ = 271.0252, found $[M-2H]^{2-}$ = 271.0244.

Disodium 4,4'-(2-oxo-4,5-diphenylcyclopenta-3,5-diene-1,3-diyl)dibenzenesulfonate (5)



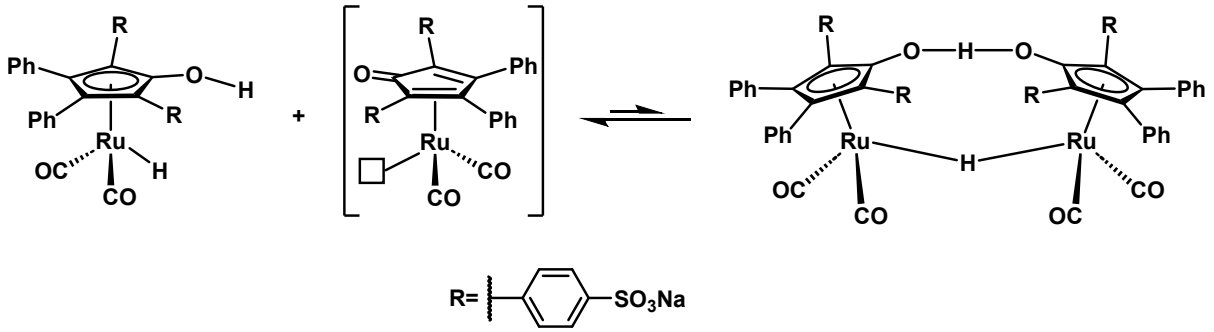
2 g of the disulfonic acid **4** (5.2 mmol, 1 eq.) were dissolved 50 mL EtOH. 520 mg of NaOH (13 mmol, 2.5 eq.) were dissolved in 100 mL EtOH. The NaOH solution was added to the solution of **4** under constant stirring. The product precipitated instantly. The solid was filtered off, washed with EtOH, and dried in a vacuum oven at 110 °C yielding a grey-violet powder (Y = 90 %).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.48 (d, *J* = 8.4 Hz, 4H), 7.32 – 7.20 (m, 7H), 7.12 (d, *J* = 8.4 Hz, 4H), 6.97 (dd, *J* = 8.0, 1.6 Hz, 4H) ppm.

^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ = 199.5, 155.0, 147.1, 132.6, 130.6, 129.2, 128.9, 128.7, 128.1, 125.2, 124.6 ppm.

HR-MS (ESI): calcd. $[M-2Na]^{2-}$ = 271.0252, found $[M-2Na]^{2-}$ = 271.0249.

Synthesis of the Complex



A 500 mL Schlenk flask was charged with a stirring bar, 589 mg of the disulfonated ligand **5** (1 mmol, 3 eq.), and 213 mg of $Ru_3(CO)_{12}$ (0.33 mmol, 1 eq.). 250 mL of dry methanol were added and the resulting mixture was refluxed for 40 h. Afterwards, the solvent was removed *in vacuo* yielding an orange solid which was washed with diethyl ether and dryed under high vacuum.

Suitable crystals for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution of the solid in MeOH. For further details see the crystallography appendix.

The structure of the isolated solid is not consistent with the results of the NMR measurements and the HR-MS spectrum due to the formation of the monomeric hydride complex, which was observed *via* NMR. Therefore all NMR and HR-MS measurements refer to that structure found in solution (Figure 1). For the NMR spectrum, the measurement after 20.5 h in solution (DMSO-d6) was analysed. The undefined solid will be referred to as compound **8.**

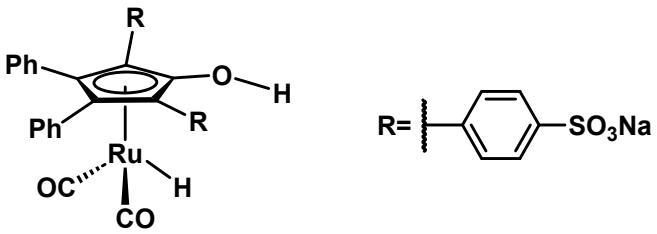


Figure 1: Structure of the monomeric hydride complex, which forms in solution *via* dehydrogenation of MeOH.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.10 (s, 2H, formaldehyde), 7.50 – 7.01 (m, 18H, CH_{aryl}), 3.33 (s, 1H, OH), 3.17 (d, J = 5.1 Hz, 3H, CH_3),-9.83 (s,1H, RuH) ppm.

^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6): δ = 202.1, 194.7, 173.5, 147.1, 146.8, 136.8, 132.6, 132.3, 131.9, 131.4, 131.1, 130.9, 129.7, 129.7, 128.5, 128.0, 127.6, 127.4, 125.0, 125.0, 124.2, 107.8, 104.0, 91.0, 80.2, 64.9, 48.6, 40.1, 39.9, 39.8, 39.7, 39.5, 39.4, 39.2, 39.1, 15.2 ppm.

HR-MS (ESI): calcd. $[M-2Na]^{2-}$ = 350.9805, found $[M-2Na]^{2-}$ = 350.9782.

FTIR: v = 2088, 2020, 1631 cm^{-1}.

Catalytic Reactions

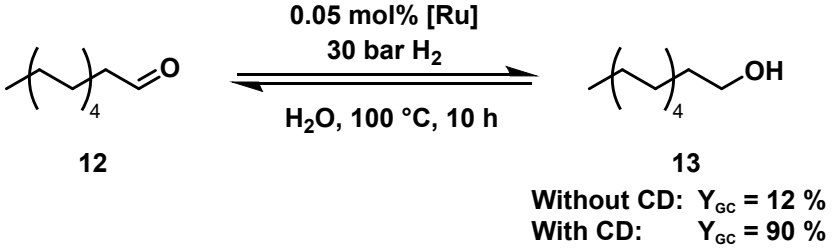
Biphasic Hydrogenation of Undecanal

A 75 mL hastelloy C pressure autoclave was equipped with a glas inlet and flushed with argon three times and put under vacuum afterwards. A 50 mL roundbottom schlenk flask was charged with 37.3 mg (0.0005 eq. Ru/Substrate) of orange compound **8**. The solid was dissolved in 10 mL degassed water. The solution was sucked into the autoclave *via* cannula. The autoclave´s dropping funnel was charged with 17.029 g of undecanal (**12**) (100 mmol, 1 eq.). The stirrer was set to 1000 rpm. Then the autoclave was pressurised with 20 bar of

hydrogen and heated up to 100 °C for 30 min. Afterwards the pressure was increased to 30 bar and the reaction was started by the addition of the substrate. The hydrogen consumption was tracked with a mass flow controller. After 19 h, a GC sample was taken and the consumption curve was normalised to the GC result.

Biphasic, Cyclodextrin-mediated Hydrogenation of Undecanal

A 75 mL hastelloy C pressure autoclave was equipped with a glas inlet and flushed with argon three times and put under vacuum afterwards. A 100 mL roundbottom schlenk flask was charged with 35.8 mg (0.0005 eq. Ru/Substrate) of orange compound **8** and 6.5 g (100 eq./Ru) of RAME-β-cyclodextrine. The solids were dissolved in 10 mL degassed water. The solution was sucked into the autoclave *via* cannula. The autoclave´s dropping funnel was charged with 17.029 g of undecanal (**12**) (100 mmol, 1 eq.). The stirrer was set to 1000 rpm. Then the autoclave was pressurised with 20 bar of hydrogen and heated up to 100 °C for 30 min. Afterwards the pressure was increased to 30 bar and the reaction was started by the addition of the substrate. The hydrogen consumption was tracked with a mass flow controller. After 10 h a GC sample was taken and the consumption curve was normalised to the GC result.



Scheme 1. Additional experiment to determine the effect of RAME-β-cyclodextrine on the biphasic hydrogenation of undecanal with the SulfoShvo catalyst in an aqueous phase

Biphasic, Cyclodextrin-mediated Hydrogenation of Undecanal and Recycling of the Catalyst Phase

A 75 mL hastelloy C pressure autoclave was equipped with a glas inlet and flushed with argon three times and put under vacuum afterwards. A 100 mL roundbottom schlenk flask was charged with 71.6 mg (0.0005 eq. Ru/Substrate) of orange compound **8** and 6.5 g (100 eq./Ru) of RAME-β-cyclodextrine. The solids were dissolved in 10 mL degassed water. The solution was sucked into the autoclave *via* cannula. The autoclave´s dropping funnel was charged with 17.029 g of undecanal (**12**) (100 mmol, 1 eq.). The stirrer was set to 1000 rpm. Then the autoclave was pressurised with 20 bar of hydrogen and heated up to 100 °C for 30 min. Afterwards the pressure was increased to 30 bar and the reaction was started by the addition of the substrate. After 4 h the reaction was stopped by cooling down to 20 °C. The autoclave was depressurised and the reaction mixture was transferred to a separating funnel. The catalyst Phase was separated and reused for the next run as described above. The product phase was analysed *via* GC.

Hydrogenation of Levulinic Acid

A 75 mL hastelloy C pressure autoclave was equipped with a glas inlet and flushed with argon three times and put under vacuum afterwards. A 100 mL roundbottom schlenk flask was charged with 71.8 mg (0.001 eq. Ru/Substrate) of compound **8**. The solid was dissolved in 20 mL of degassed water. 11.611 g (100 mmol, 1 eq.) of levulinic acid (**9**) were dissolved in 20 mL of water and degassed. The catalyst solution was sucked into the autoclave *via* cannula. The autoclave´s dropping funnel was charged with the solution of levulinic acid (**9**). The stirrer was set to 1000 rpm. Then the autoclave was pressurised with 20 bar of hydrogen and heated up to 100 °C for 30 min. Afterwards the pressure was increased to 30 bar and the reaction was

started by the addition of the substrate. The hydrogen consumption was tracked with a mass flow controller. After 43 h a GC sample was taken and the consumption curve was normalised to the GC result.

Transfer Hydrogenation of Levulinic Acid

A 100 mL three-neck round bottom flask was equipped with a stopcock and a magnetic stirring bar. Afterwards, it was charged with 71.8 mg (0.001 eq. Ru/Substrate) of compound **8**. The complex was dissolved in a degassed mixture of 20 mL water and 9.206 g (200 mmol, 2 eq.) of formic acid. 11.611 g (100 mmol, 1 eq.) of levulinic acid (**9**) were dissolved in 20 mL of water and degassed. The catalyst solution was refluxed for 10 min. Then, the substrate solution was added *via* syringe through a rubber septum. Samples were taken *via* syringe, filled in a pre-cooled GC vial, frozen and stored at -20 °C to avoid further reactions. For analysis, the samples were melted, prepared for GC and measured one by one to keep the potential reaction time to a minimum.

Transfer Hydrogenation of Levulinic Acid in a Microwave Synthesiser (Comparison Shvo vs. SulfoShvo)

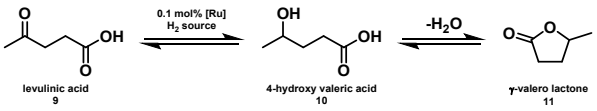
A 35 mL microwave reaction vessel was equipped with a magnetic stirring bar. Afterwards, it was charged with 2.2 mg (4.2×10^{-3} mmol, 0.0333 mol%) of $Ru_3(CO)_{12}$ and 0.1 mol% ligand (**1** or **5**). The vessel was flushed with argon and the solids were suspended in 1.5 mL of the preferred solvent (water for **5** and toluene for **1**) and 4.5 mL *i*PrOH. The septum cap was placed on the vessel and the mixture was heated to 110 °C for 30 min. Afterwards the vessel was cooled down to 40 °C and a degassed mixture of 1.185 g (10 mmol) of levulinic acid (**9**), 1 mL of the preferred solvent and 3 mL of *i*PrOH were added *via* syringe through the septum cap. The reaction mixture was heated to 110 °C for 2 h. Samples were taken *via* syringe, filled in a pre-cooled GC vial, frozen and stored at -20 °C to avoid further reactions. For analysis, the samples were warmed up to room temperature, prepared for GC and measured one by one to keep the potential reaction time to a minimum.

Transfer Hydrogenation of Levulinic Acid in a Microwave Synthesiser with Different Solvent Mixtures

A 35 mL microwave reaction vessel was equipped with a magnetic stirring bar. Afterwards, it was charged with 2.7 mg (4.2×10^{-3} mmol, 0.0167 mol%) of $Ru_3(CO)_{12}$ and 7.4 mg of ligand **5** (12.5×10^{-3} mmol, 0.05 mol%). The vessel was flushed with argon and the solids were suspended in 8 mL of degassed solvent 1. The septum cap was placed on the vessel and the mixture was heated to 110 °C for 30 min. Afterwards the vessel was cooled down to 40 °C and a degassed mixture of 2.962 g (25 mmol) of levulinic acid (**9**) and 6 mL of solvent 2 were added *via* syringe through the septum cap. The reaction mixture was heated to 110 °C for 24 h. Samples were taken *via* syringe, filled in a pre-cooled GC vial, frozen and stored at -20 °C to avoid further reactions. For analysis, the samples were melted, prepared for GC and measured one by one to keep the potential reaction time to a minimum.

Entry	Solvent 1	Solvent 2
1	MeOH	MeOH
2	MeOH	IPA
3	IPA/H_2O (4:1)	IPA/H_2O (4:1)

Results of the (Transfer) Hydrogenation of Levulinic Acid



Entry	H_2-source	Cat.	Solvent	Reaction Set-up	t [h]	T [°C]	Y_{GVL}[a] [%]
1	H_2 (30 bar)	SulfoShvo	H_2O	pressure autoclave	37	100	98
2	H_2 (30 bar)	Shvo	toluene	pressure autoclave	4	100	97
3	FA	SulfoShvo	H_2O	reflux	43	100	90
4	iPrOH[c]	SulfoShvo	H_2O	MW[b]	2	40	0
5	iPrOH[c]	SulfoShvo	H_2O	MW[b]	2	70	2
6	iPrOH[c]	SulfoShvo	H_2O	MW[b]	2	80	5
7	iPrOH[c]	SulfoShvo	H_2O	MW[b]	2	90	7
8	iPrOH[c]	SulfoShvo	H_2O	MW[b]	2	100	10
9	iPrOH[c]	SulfoShvo	H_2O	MW[b]	2	110	21
10	iPrOH[c]	Shvo	toluene	MW[b]	2	40	<1
11	iPrOH[c]	Shvo	toluene	MW[b]	2	70	6
12	iPrOH[c]	Shvo	toluene	MW[b]	2	80	9
13	iPrOH[c]	Shvo	toluene	MW[b]	2	90	15
14	iPrOH[c]	Shvo	toluene	MW[b]	2	100	12[d]
15	iPrOH[c]	Shvo	toluene	MW[b]	2	110	41
16	MeOH/iPrOH	SulfoShvo[e]	MeOH/iPrOH	MW[b]	24	110	24
17	MeOH	SulfoShvo[e]	MeOH	MW[b]	24	110	29
18	iPrOH	SulfoShvo[e]	iPrOH/H_2O	MW[b]	24	110	75

[a] GC yield. [b] *in situ* catalyst formation in microwave (MW) (110 °C, 30 min). [c] 5 mL iPrOH. [d] Not following the trend, possible weighing error due to the small amounts of precursor. [e] 0.05 mol% catalyst.

Racemisation of (*R*)-1-Phenylethanol

A 10-mL Schlenk-tube was equipped with a magnetic stirring bar and charged with 57.4 mg (0.01 eq. Ru/Substrate) of compound **8**. The solid was dissolved in 3 mL of degassed water. 1 g of (*R*)-1-Phenylethanol (**(*R*)-14**) (8.2 mmol) was added and the reaction mixture was refluxed at 100 °C for 48 h. 10 mL of water and 10 mL of ethyl acetate were added to the reaction mixture. The two phases were separated in a separating funnel. The water phase was extracted with 10 mL of ethyl acetate three times. The combined organic fractions were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The remaining product was analysed by GC-FID and chiral HPLC.

Appendix

NMR Spectra

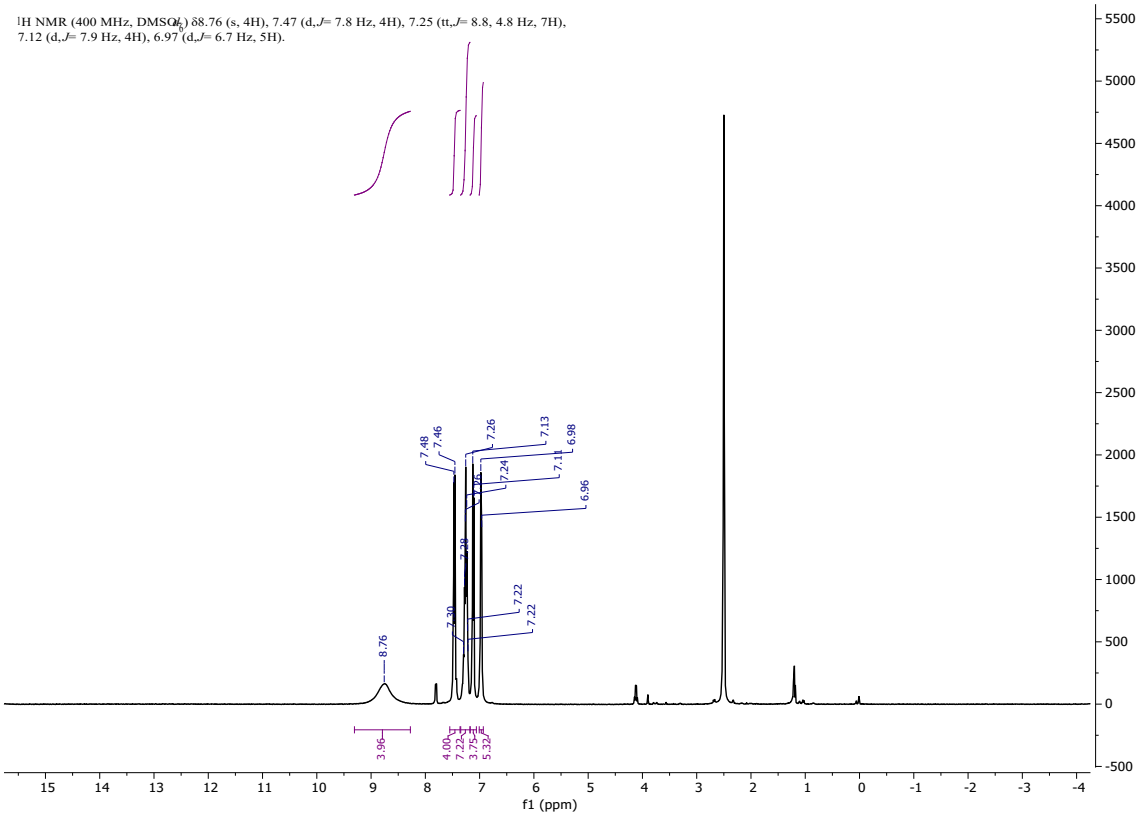


Figure 6: ^{1}H NMR spectrum (400 MHz) of the disulfonic acid **4**.

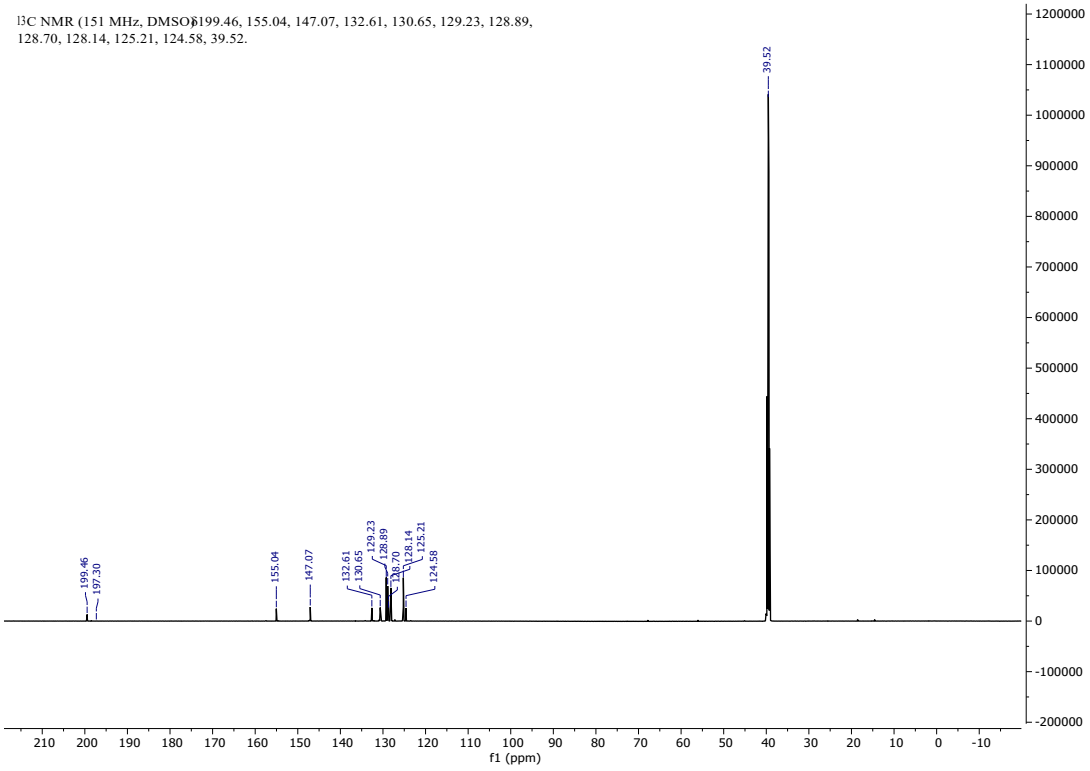


Figure 7: ^{13}C NMR spectrum (151 MHz) of the disulfonic acid **4**.

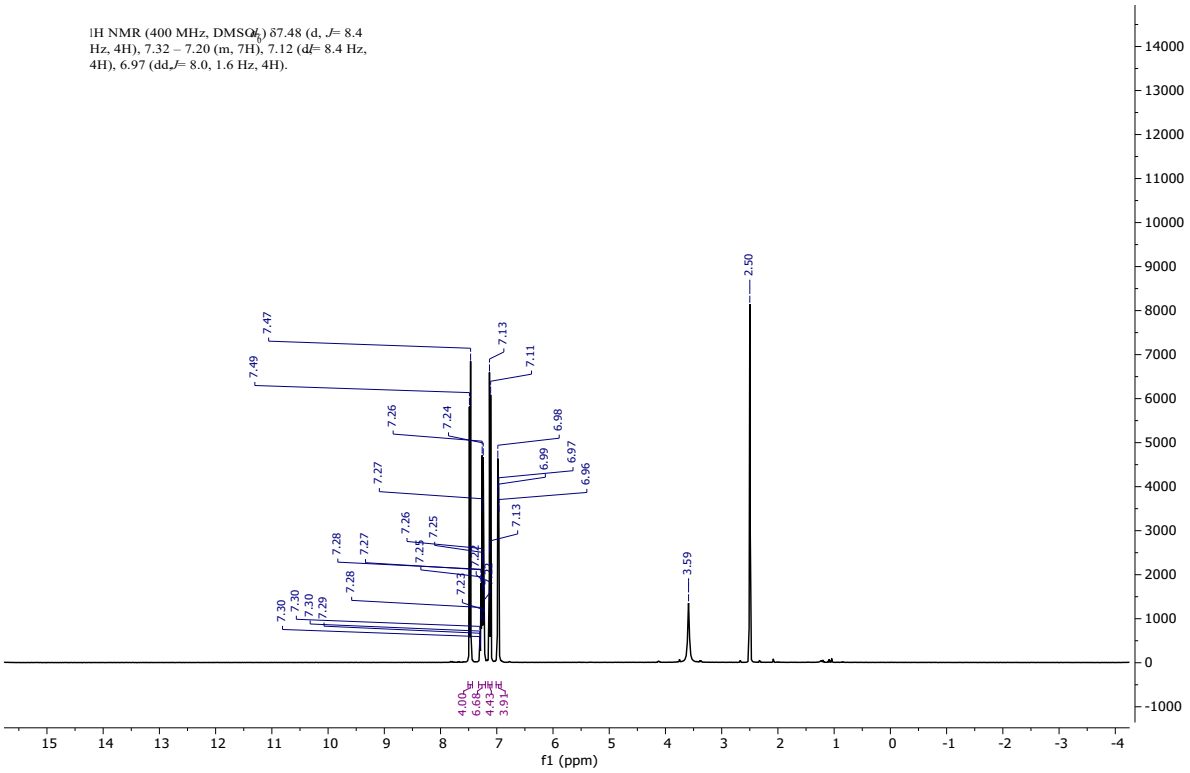


Figure 8: [1]H NMR spectrum (400 MHz) of the disodium sulfonate ligand **5**.

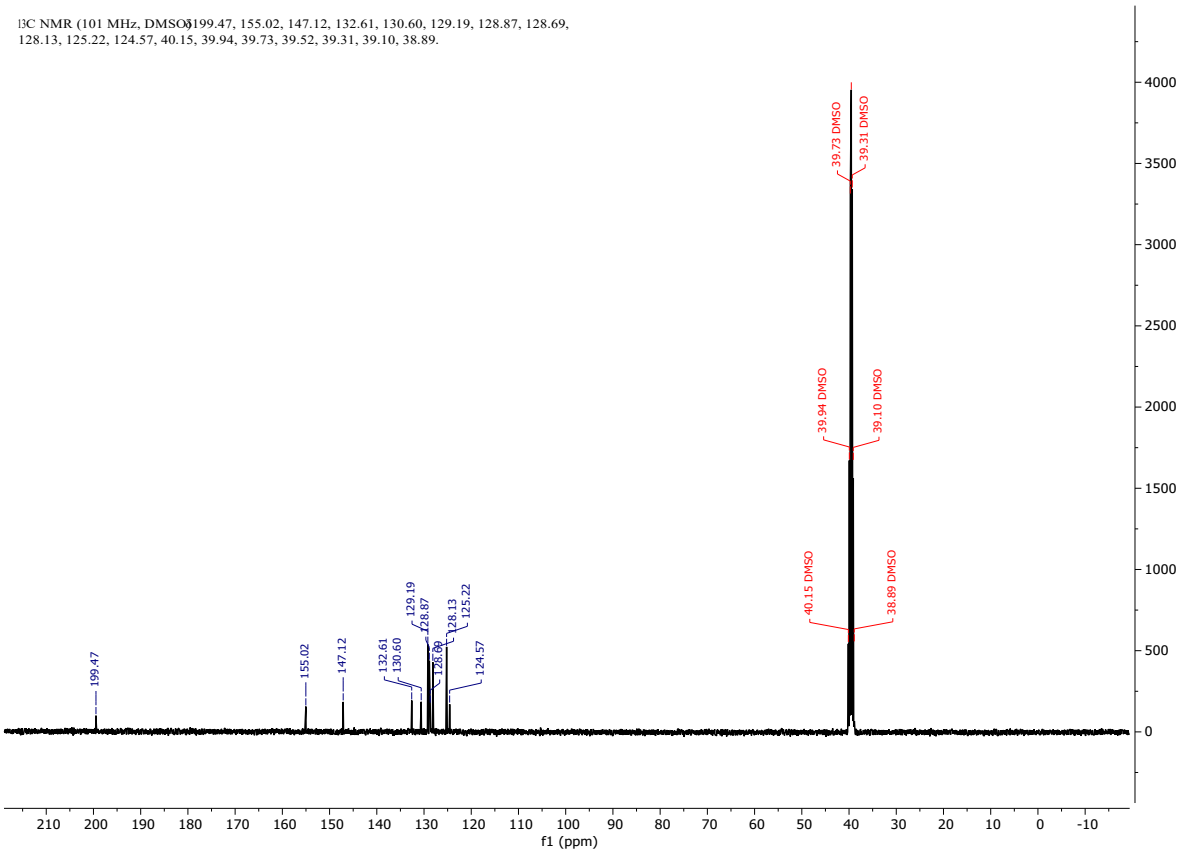


Figure 9: [13]C NMR spectrum (101 MHz) of the disodium sulfonate ligand **5**.

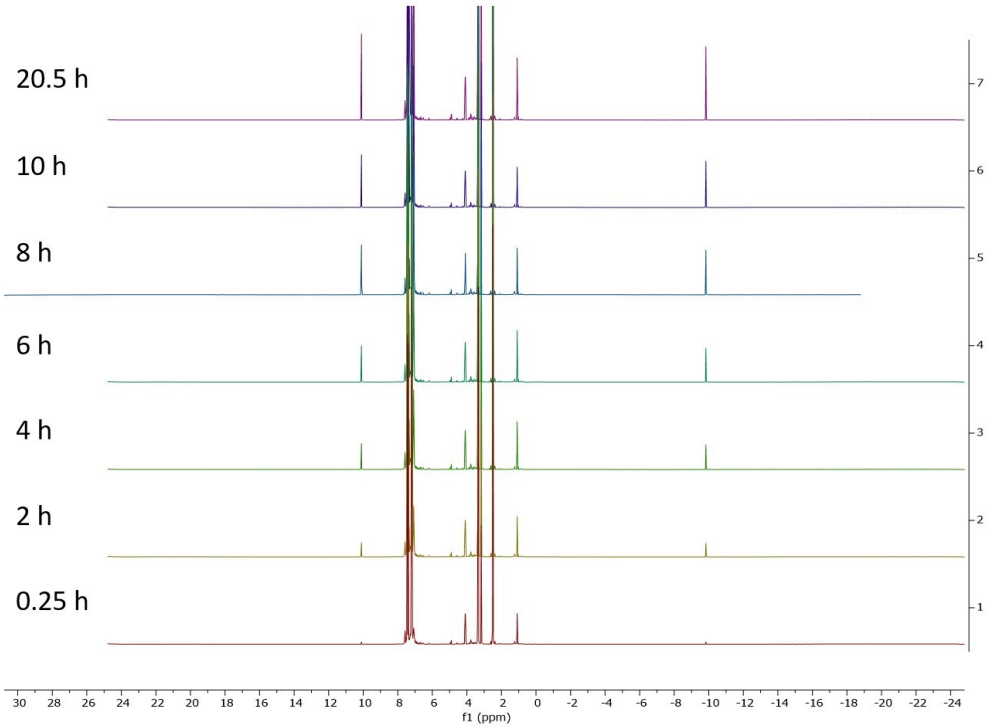


Figure 10: ^{1}H NMR spectra (600 MHz) of the orange compound **8** over 20.5 h (DMSO-d6, 25 °C). The formation of the monomeric hydride species can be seen through the growth of the signal at -9.83 ppm and the simultaneous appearance of the formaldehyde signal at 10.01 ppm.

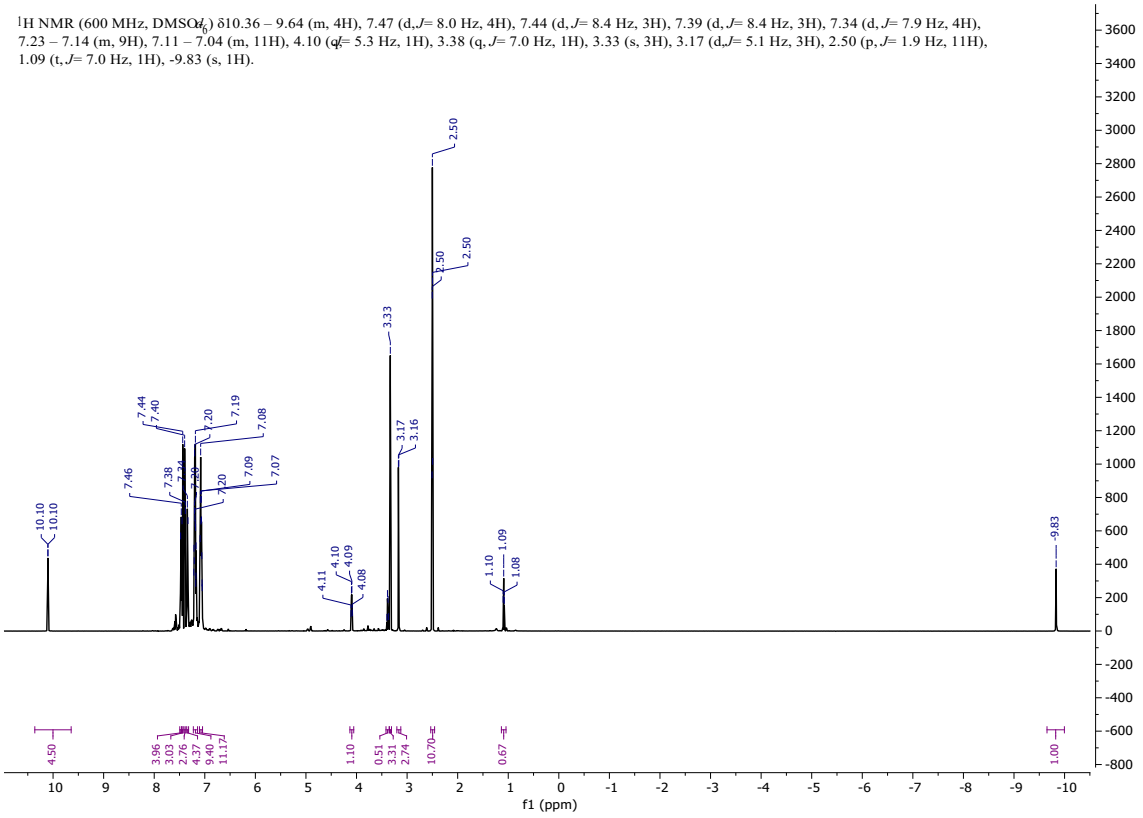


Figure 11: ^{1}H NMR spectrum (600 MHz) of the orange compound **8** after 20.5 h (DMSO-d6, 25 °C).

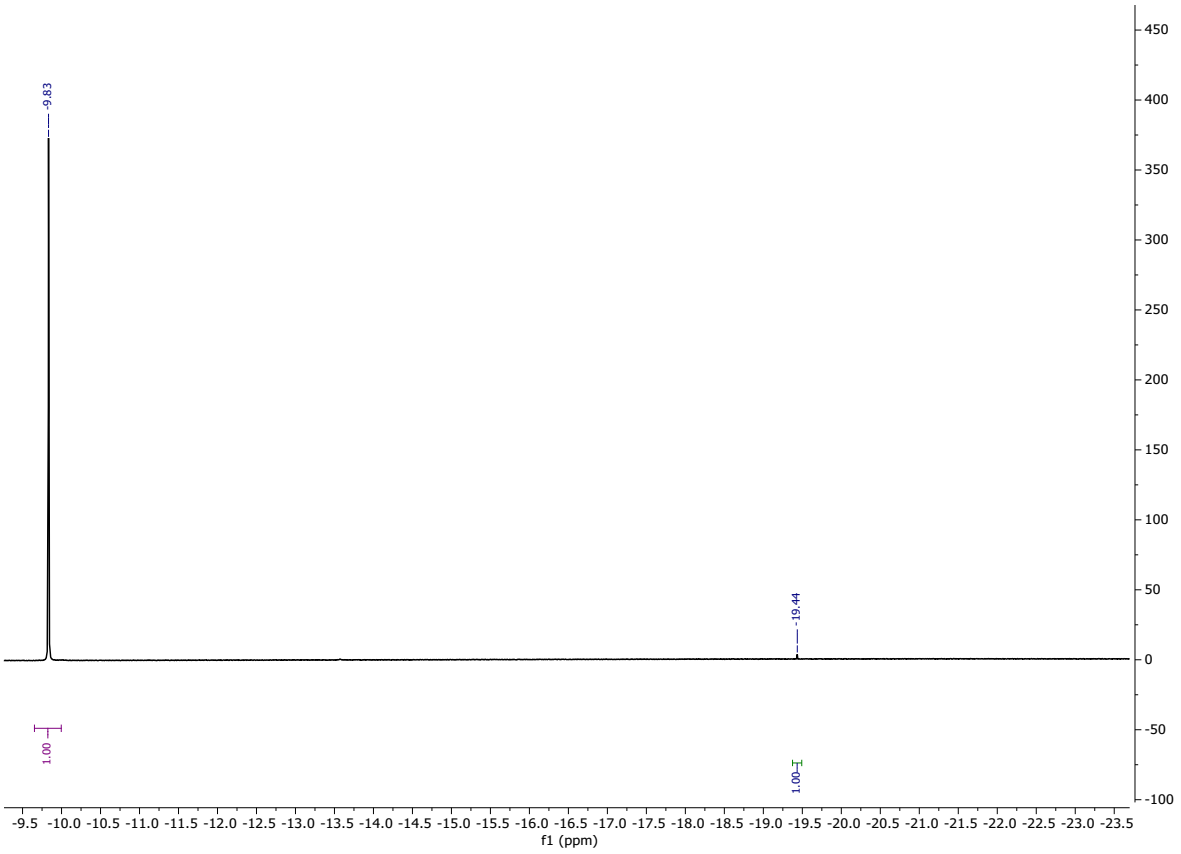


Figure 12: Detail of the metal hydride signals in the ^{1}H NMR spectrum (600 MHz) of the orange compound **8** after 20.5 h (DMSO-d6, 25 °C). The residual signal at -19.44 ppm can be attributed to the dimeric hydride complex **7**, while the larger signal at -9.83 ppm stems from the monomeric hydride species.

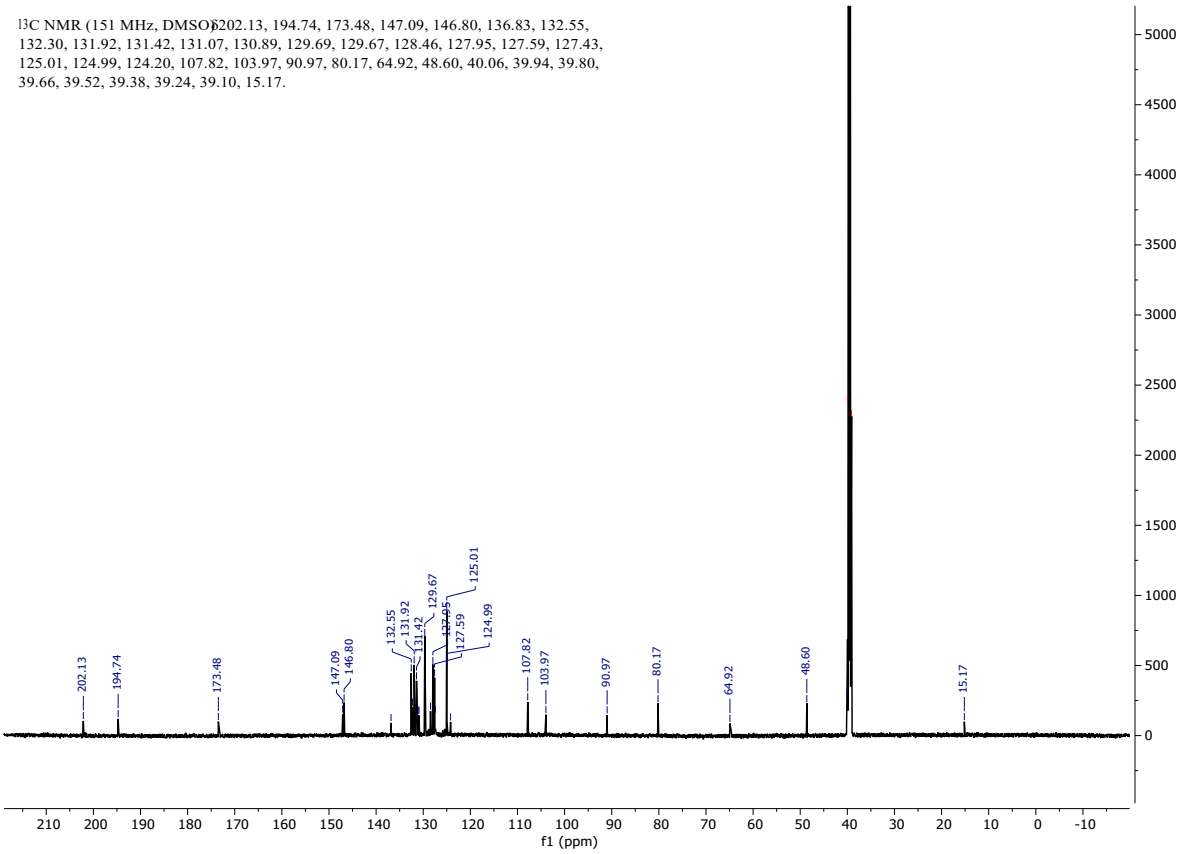


Figure 13: ^{13}C NMR spectum(151 MHz) of the orange compound **8** after 20.5 h (DMSO-d6, 25 °C).

IR Spectra

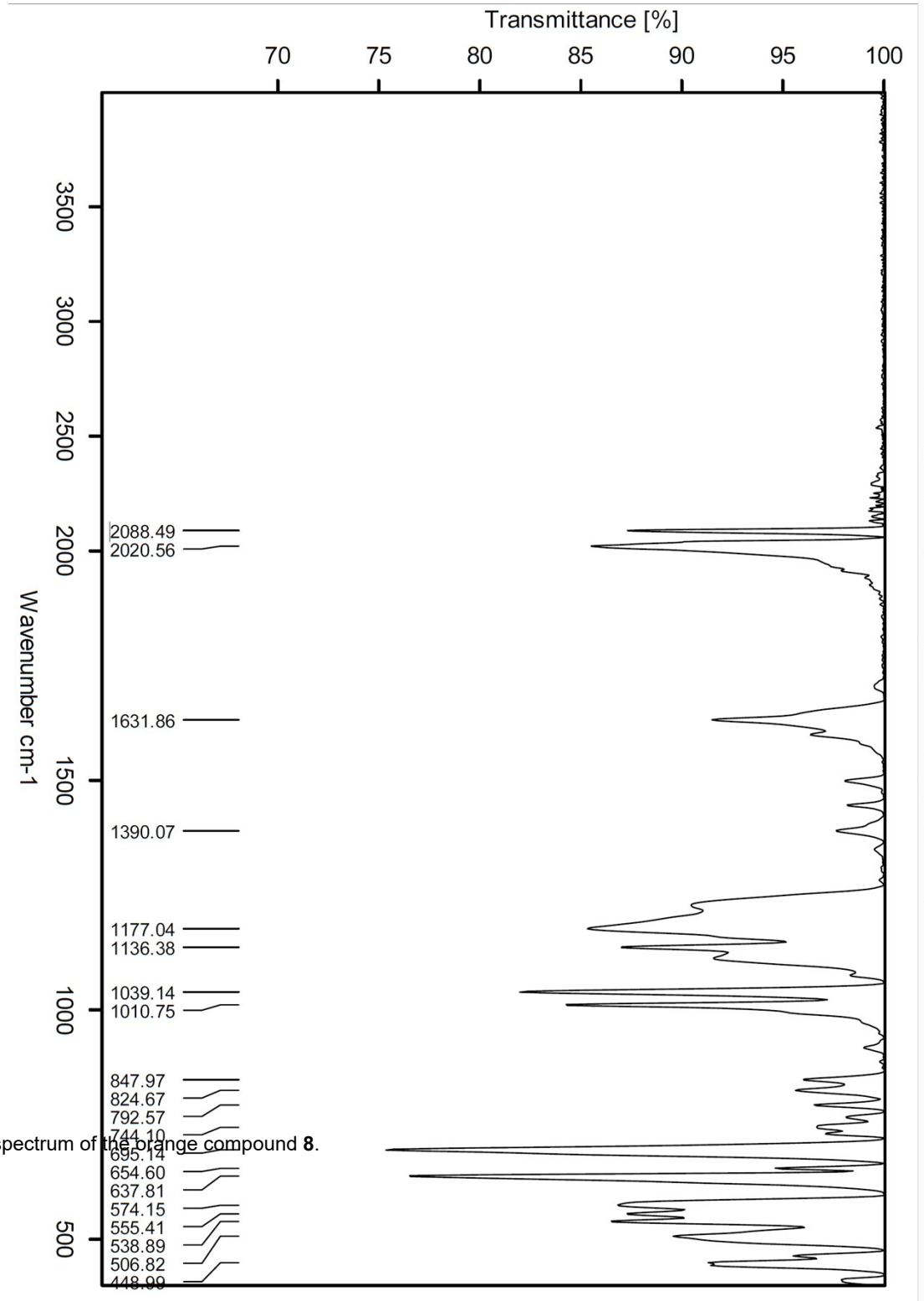


Figure 14: IR-ATR spectrum of the brange compound **8**.

X-ray Crystallographic Analysis

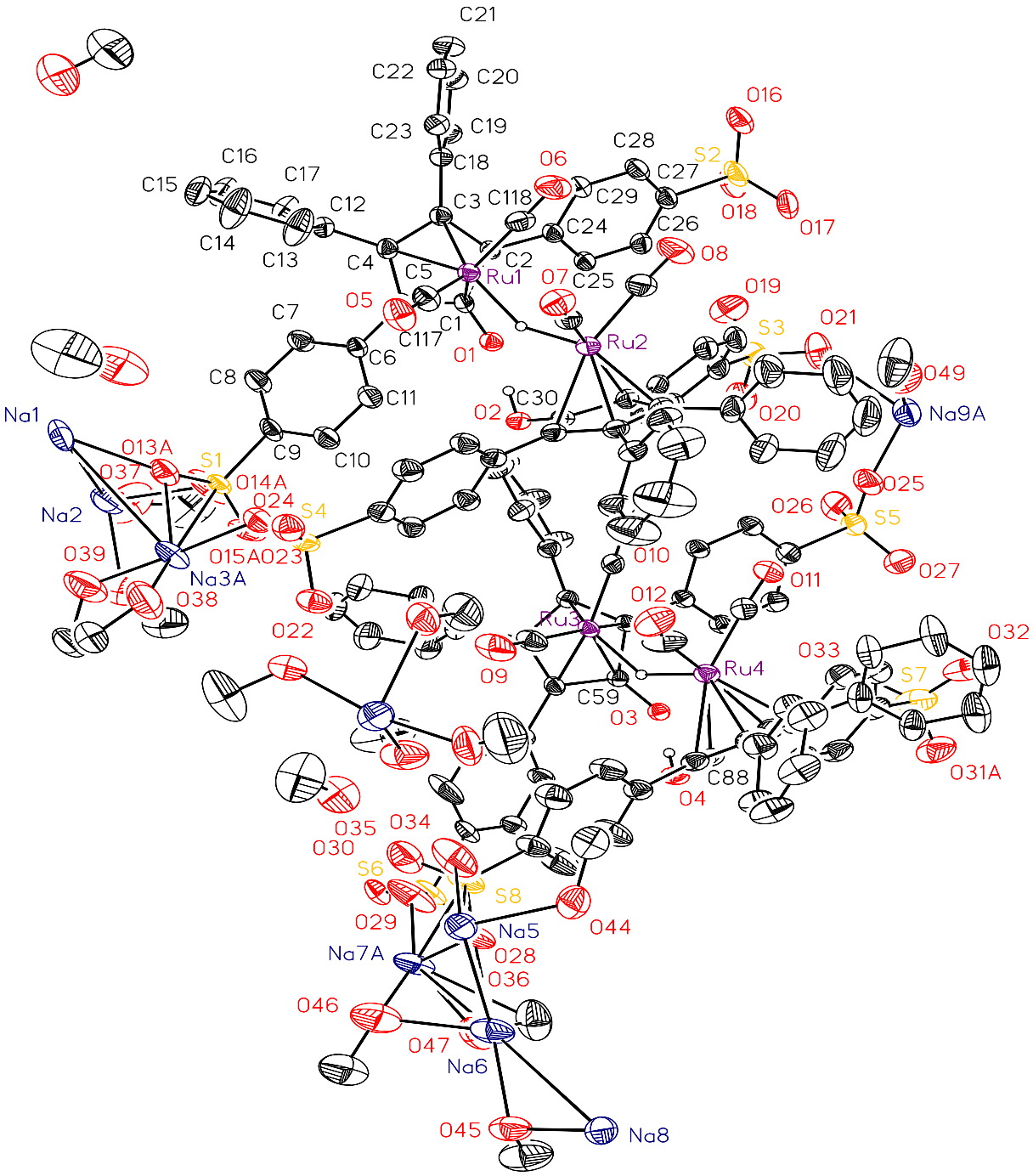


Figure 15. ORTEP generated displacement ellipsoid plot of compound **7** in the crystal with ellipsoids drawn at 50% probability. Only parts with no disorder or main occupancy are shown. Numbering of less relevant parts and less relevant hydrogen atoms were omitted for clarity, but can be obtained from the data deposited at CCDC with deposition number 2336908. Selected distances [Å] and [°]: Ru1–H 1.72(7) Å, Ru3–HA 1.74(5) Å, O1–C1 1.287(4) Å, O2–C30 1.300(4) Å, O3–C59 1.276(4) Å, O4–C88 1.308(5) Å, Ru1–Ru2 3.1758(4) Å, Ru3–Ru4 3.1872(4) Å, Ru1–H–Ru2 140(4)°, Ru3–Ha–Ru4 136(3)°.

The hydride can be refined freely adjacent to Ru1 and Ru3 in the coordination-polymer form of Figure 15. The obtained bond distances correspond to literature known structures.[4] Especially, the $C1_{ring}$–O bond distances show both short distances of 1.276(4) Å and 1.287(4) Å and longer distances of 1.300(4) Å and 1.308(5) Å, equivalent to a dehydrogenated and hydrogenated form respectively.

Structure **7** shows some disorders, that have been modeled with the use of 3 parts and 5 free variables. The phenyl rings of one SulfoShvo ligand are disordered with a ratio 50:50 as refined with constraint free variables 2 and -2. The sulfate groups around sulfur atoms S1, S2, S4, S7 and S8 are disordered and the disorder is described with constraint free variables of either 2 and -2 or 3 and -3. The groups around S1, S2 and S4 are disordered with a ratio of 70:30, while the groups are S7 and S8 are disordered with a ratio of 50:50. The bond lengths around S2 and S7 are further described with a restraint to equalize the bond lengths. Still, O33 adjacent to S7 could not be refined anisotropically. Sodium counterions and solvent methanols are further disordered and are equally described with constraint free variables of ratios 50:50 or 70:30. Methanol O41 is disordered by 3 parts and was described with a restraint to sum the 3 parts to an occupancy of 1 with free variables 4, 5 and 6. Two out three of these methanols are further treated to restraint the U_{ij} of neighboring C and O atoms.

Table S1. Crystallographic data and structural refinements for **7**.

	7
Empirical formula	$C_{139.25}H_{137}Na_8O_{51.25}Ru_4S_8$
Formula weight	3475.16
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	14.6295(5)
b/Å	19.7444(6)
c/Å	26.6859(10)
α/°	80.3110(10)
β/°	84.209(2)
γ/°	87.5740(10)
Volume/Å^3	7557.0(4)
Z	2
ρ_{calc} g/cm^3	1.527
μ/mm^{-1}	0.611
F(000)	3549.0
Crystal size/mm^3	0.293 × 0.228 × 0.154
Radiation	MoK*α* (*λ* = 0.71073)
2Θ range for data collection/°	3.834 to 59.452
Index ranges	-20 ≤ h ≤ 20 -27 ≤ k ≤ 27 -37 ≤ l ≤ 36
Reflections collected	345772
Independent reflections	42728 [R_{int} = 0.0599, R_{sigma} = 0.0376]
Data/restraints/parameters	42728/2415/2405
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2*σ* (I)]	R_1 = 0.0628, wR_2 = 0.1497
Final R indexes [all data]	R_1 = 0.0822, wR_2 = 0.1608
Largest diff. peak/hole / e Å^{-3}	1.68/-0.80

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[4] a) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana, *J. Am. Chem. Soc.* **2001**, *123*, 1090; b) C. Cesari, L. Sambri, S. Zacchini, V. Zanotti, R. Mazzoni, *Organometallics* **2014**, *33*, 2814.