Biomass Oxidation to Formic Acid in Aqueous Media Using Polyoxometalate Catalysts – Boosting FA Selectivity by In-situ Extraction

Supplementary Information

Determination of distribution coefficients

A model reaction solution containing 0.91 g of the HPA-5 catalyst, 10.18 g FA and 50.0 g water was prepared. This solution was stirred with 50.91 g of the extracting solvent at 363 K for one hour and then transferred into a separation funnel. After phase separation, a sample of each phase was taken and analysed by means of ^{1}H-NMR to determine the formic acid concentration.

Extraction Solvent Screening

Table S1: Solvent screening to identify a suitable extraction solvent - extraction of a simulated product solution.

Extracting agent	Distribution coefficient K $c_{FA,org.}/c_{FA,aqu}$ [a]	Selectivity K_{FA}/K_{water} [b]
1-Hexanol	0.94	8.6
1-Heptanol	0.67	4.4
Butylethylether	0.49	2.7
Benzyl formate	0.46	2.6
Heptyl formate	0.42	2.2
Di-isopropylether	0.40	2.5
Di-n-butylether	0.22	1.2

Conditions: 10.18 g formic acid, 0.91 g (0.5 mmol) HPA-5 catalyst dissolved in 50.0 mL H_2O, together with 50.91 g of the extracting solvent; stirred at 363 K; 1 h. [a)] as determined by ^{1}H-NMR using benzene as external standard; [b)] ratio of the distribution coefficients of formic acid and water.

Table S2: Esterification activity of formic acid with 1-hexanol and 1-heptanol, respectively.

Time [h]	Content FA [a)] [wt%]	Phase	Esterification 1-hexanol [%]	Esterification 1-heptanol [%]
0.08	5	Aqueous	0	0
		Organic	0	0
	15	Aqueous	0	0
		Organic	4	3
12	5	Aqueous	0	0
		Organic	12	11
	15	Aqueous	0	0
		Organic	14	14

Procedure: Preparation of 1 g aqueous formic acid (5 or 15 wt% FA) and 1 g 1-hexanol/1-heptanol; measuring degree of esterification in both phases directly or after 12 h respectively by ^{13}C-NMR.

NMR spectra of the esterification tests

All ^{13}C-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectra show the ^{13}C-NMR of esterification experiments of aqueous formic acid with 1-hexanol and 1-heptanol, respectively. Both phases were analysed using 1000 scans and a frequency of 100.61 MHz.

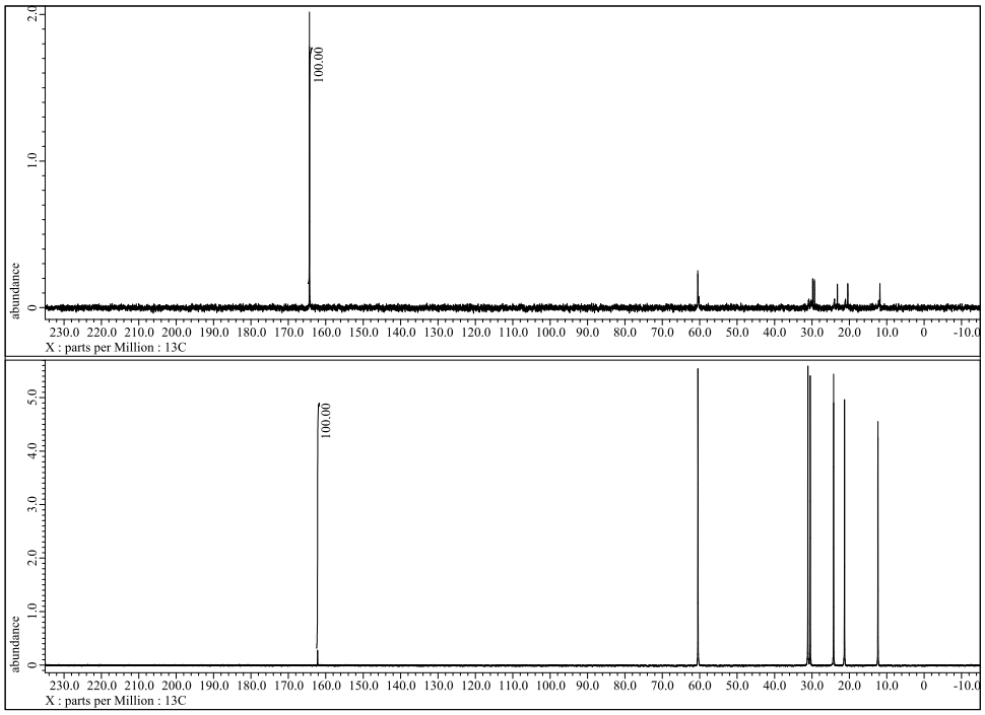


Figure S1: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (5 wt% FA) contacted with 1 g 1-hexanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) directly after sample preparation.

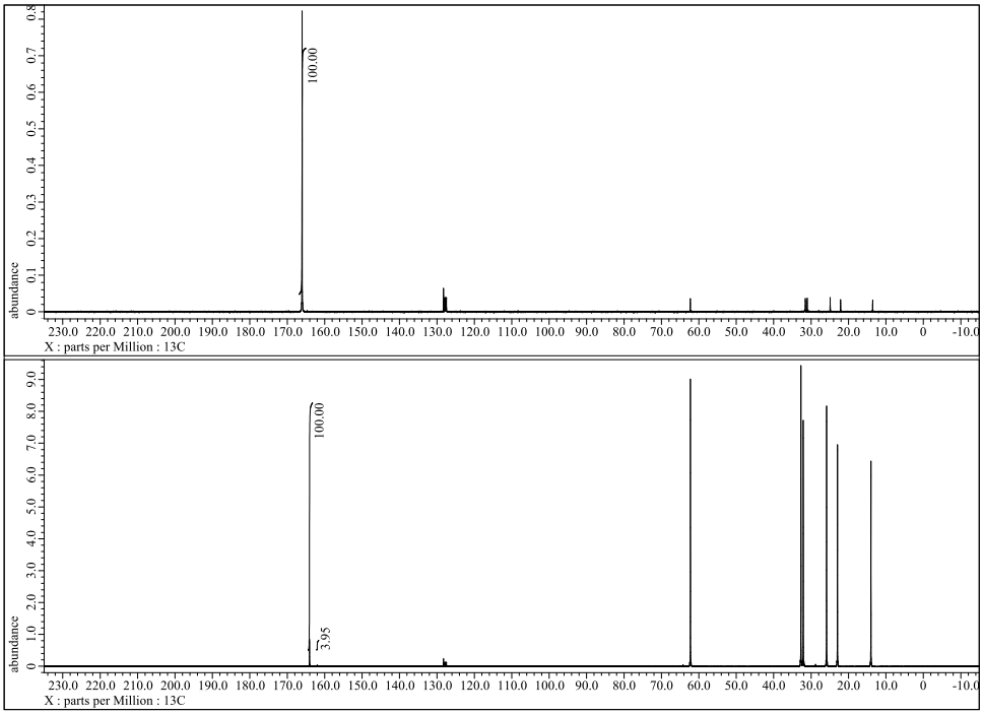


Figure S2: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (15 wt% FA) contacted with 1 g 1-hexanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) directly after sample preparation (peak at 128.5 ppm: external standard benzene).

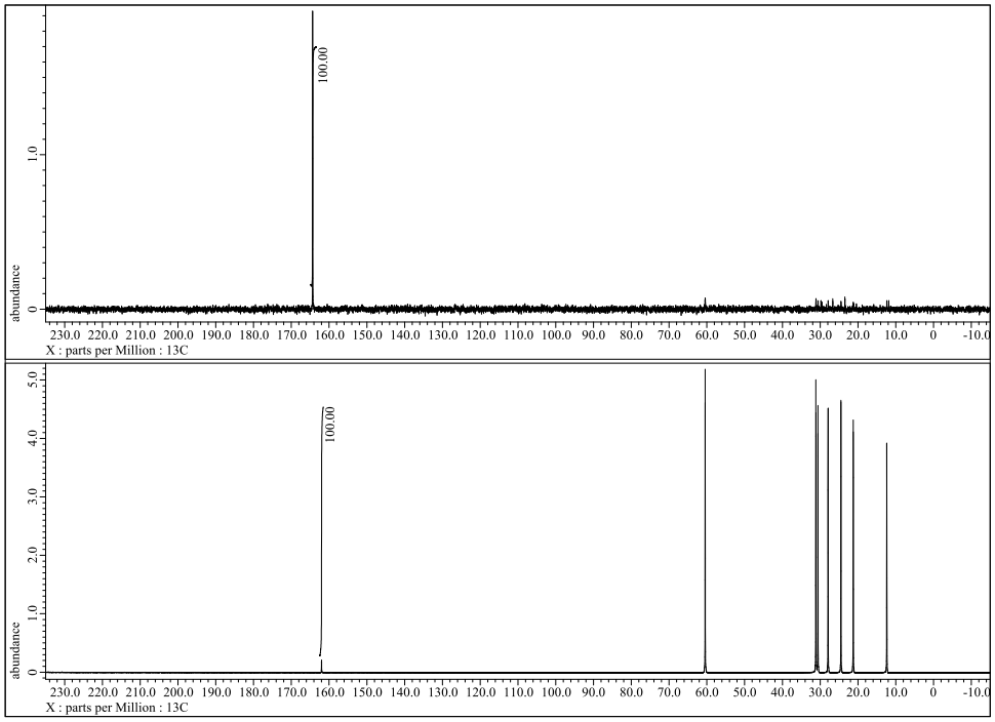


Figure S3: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (5 wt% FA) contacted with 1 g 1-heptanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) directly after sample preparation.

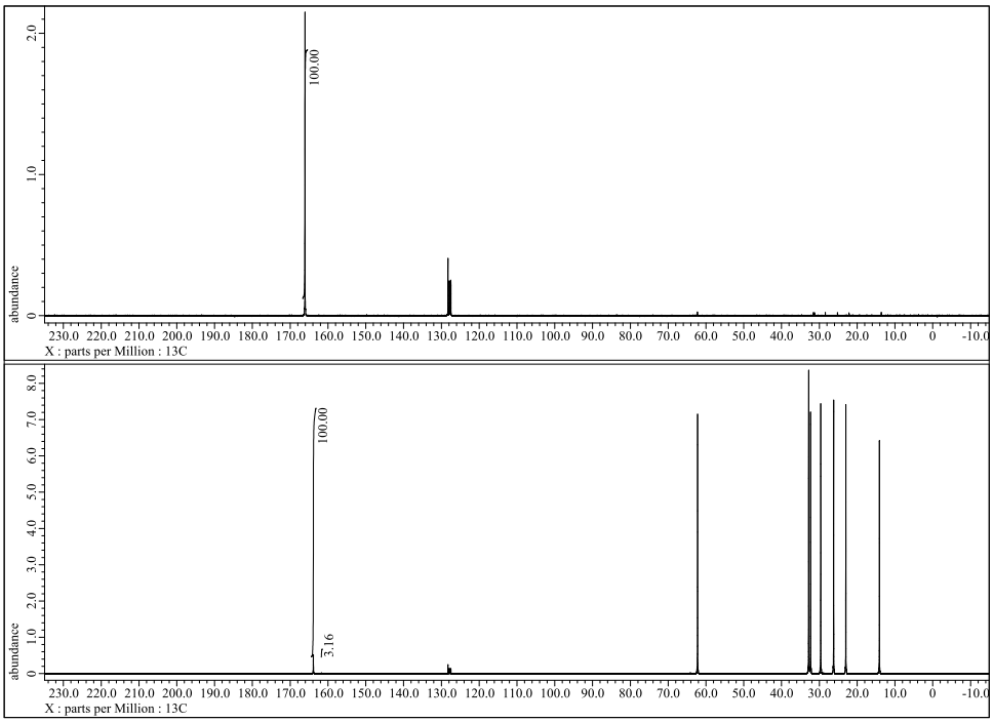


Figure S4: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (15 wt% FA) contacted with 1 g 1-heptanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) directly after sample preparation (peak at 128.5 ppm: external standard benzene).

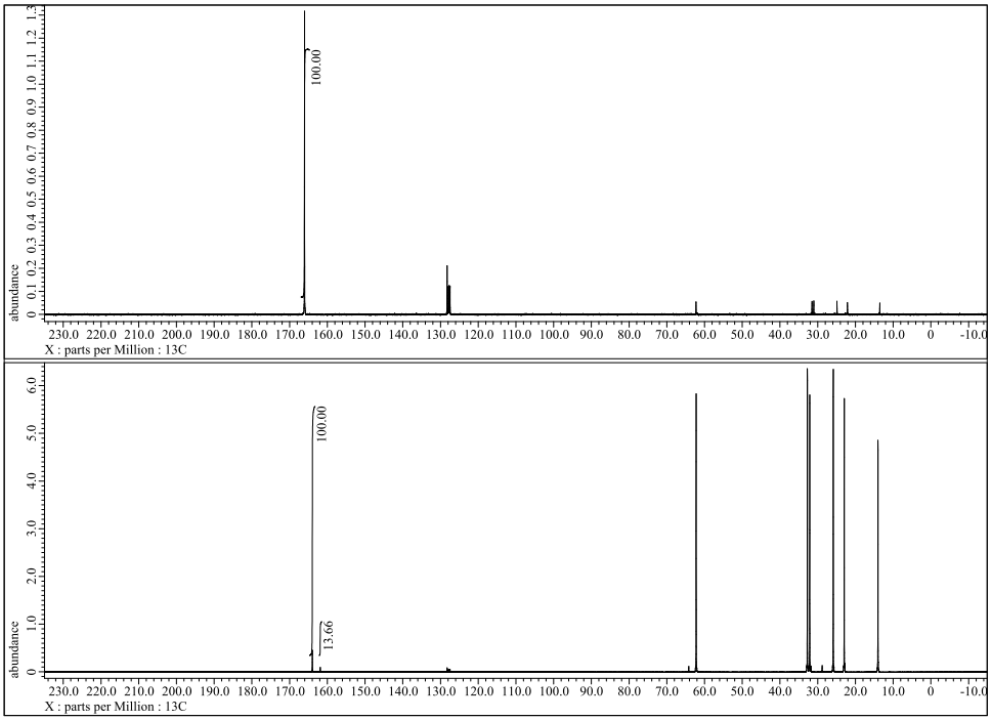


Figure S5: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (5 wt% FA) contacted with 1 g 1-hexanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) 12 hours after sample preparation (peak at 128.5 ppm: external standard benzene).

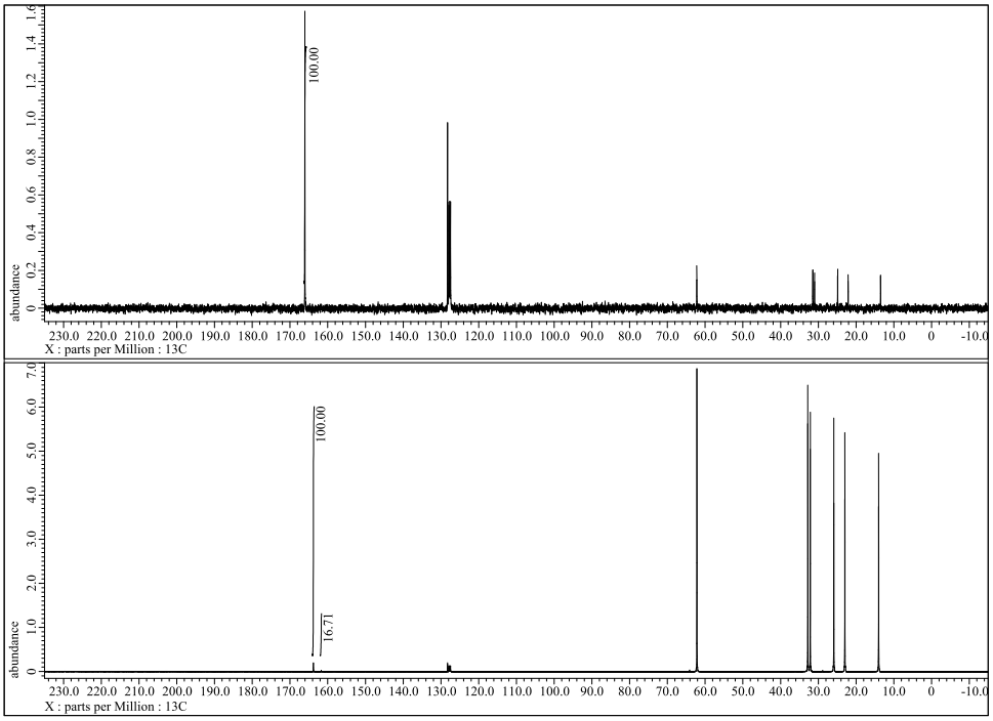


Figure S6: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (15 wt% FA) contacted with 1 g 1-hexanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) 12 hours after sample preparation (peak at 128.5 ppm: external standard benzene).

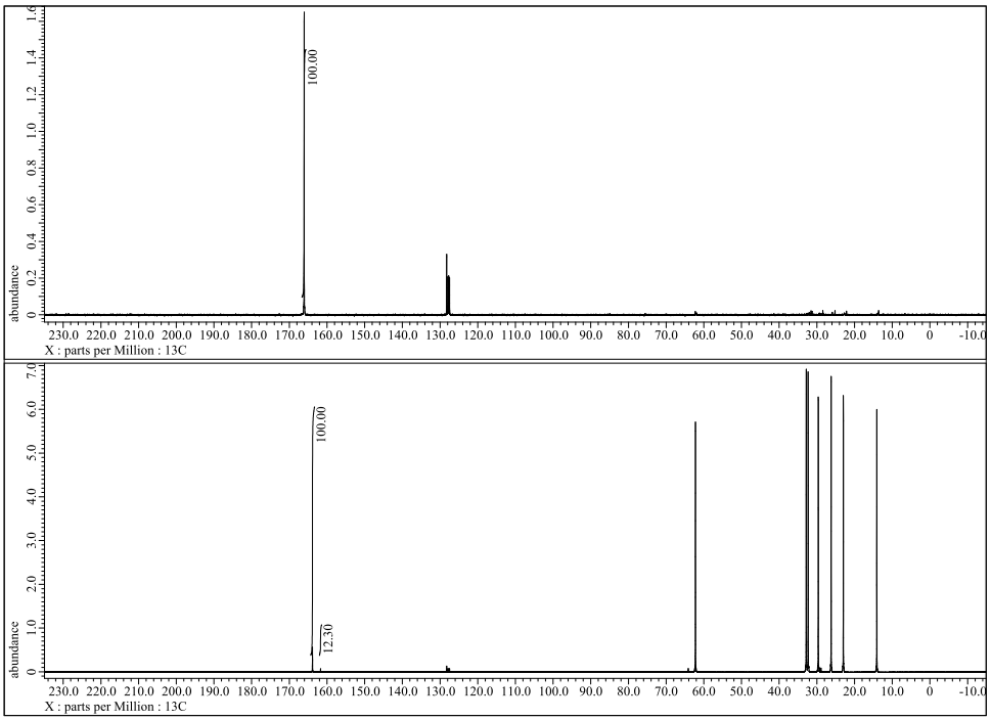


Figure S7: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (5 wt% FA) contacted with 1 g 1-heptanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) 12 hours after sample preparation (peak at 128.5 ppm: external standard benzene).

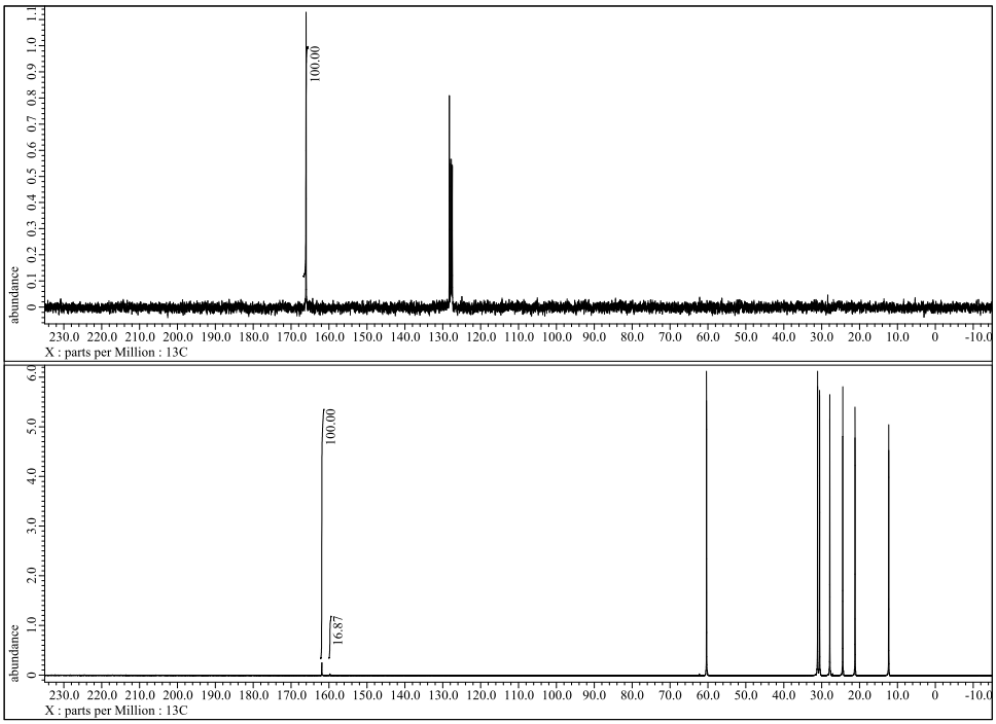


Figure S8: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous formic acid (15 wt% FA) contacted with 1 g 1-heptanol; measuring degree of esterification in both phases (aqueous: top, organic: bottom) 12 hours after sample preparation (peak at 128.5 ppm: external standard benzene).

NMR spectra of 1-hexanol, 1-heptanol stability tests

The ^{13}C-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectra show the ^{13}C-NMR of 1-hexanol and 1-heptanol before and after the stability test using 1000 scans and a frequency of 100.61 MHz.

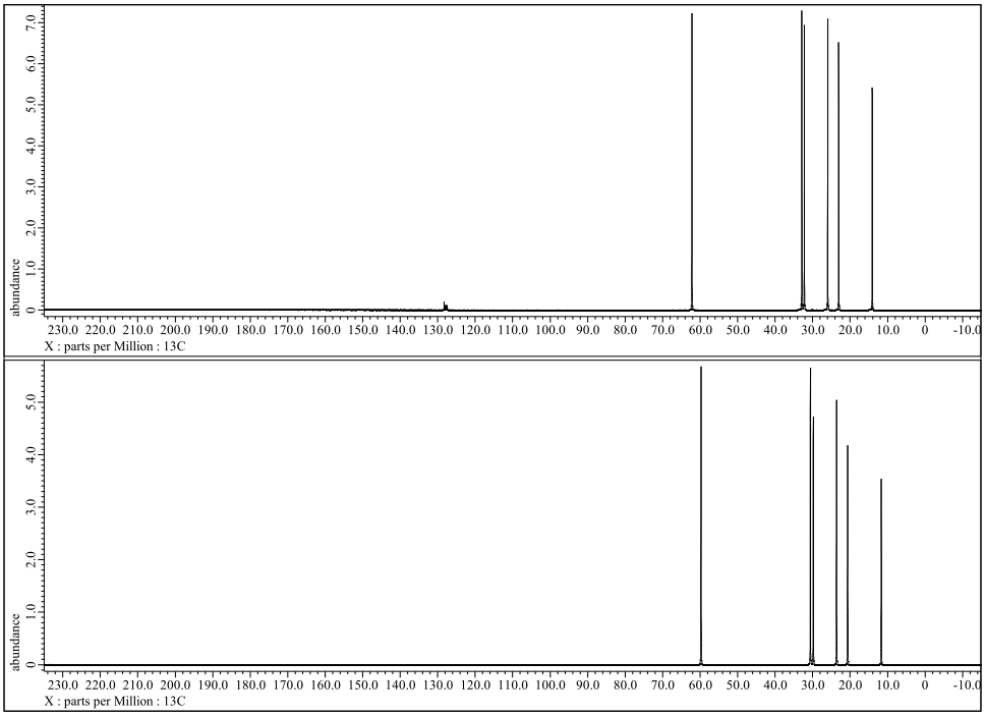


Figure S9: ^{13}C NMR spectra of 1-hexanol before (top) and after the stability test at 363 K, 20 bar O_2, 1000 rpm for 72 h reaction time (bottom); peak at 128.5 ppm: external standard benzene.

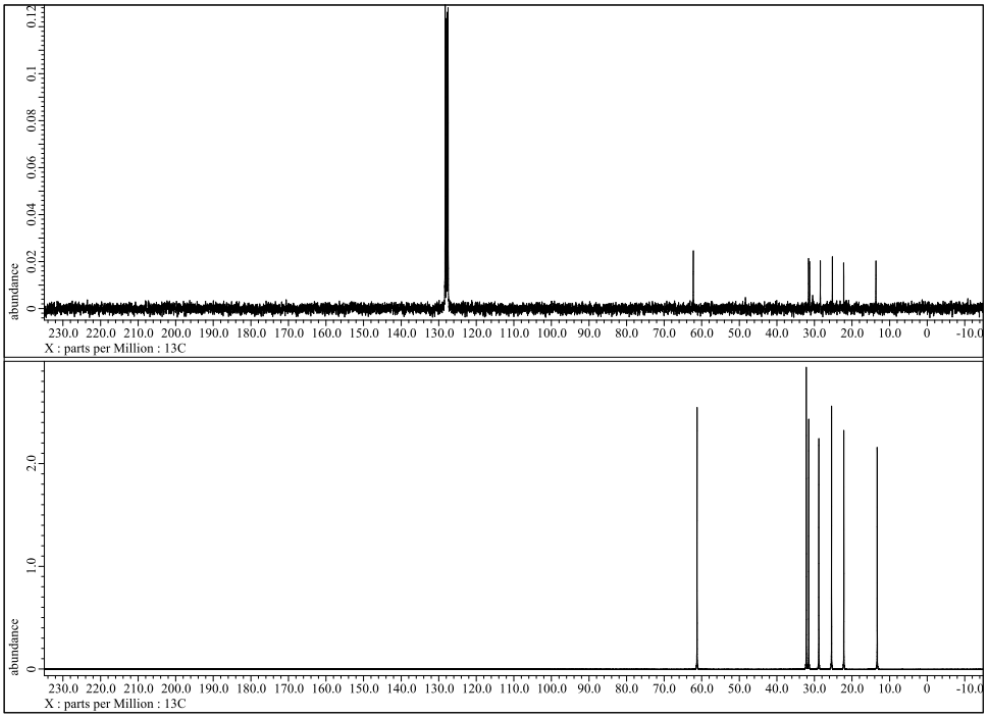


Figure S10: ^{13}C NMR spectra of 1-heptanol before (top) and after the stability test at 363 K, 20 bar O_2, 1000 rpm for 72 h reaction time (bottom); peak at 128.5 ppm: external standard benzene.

The following spectra show the ^{13}C-NMR after the stability test (aqueous and organic phase) of 1-heptanol in the presence of the catalyst HPA-5 and formic acid using 1000 scans and a frequency of 100.61 MHz.

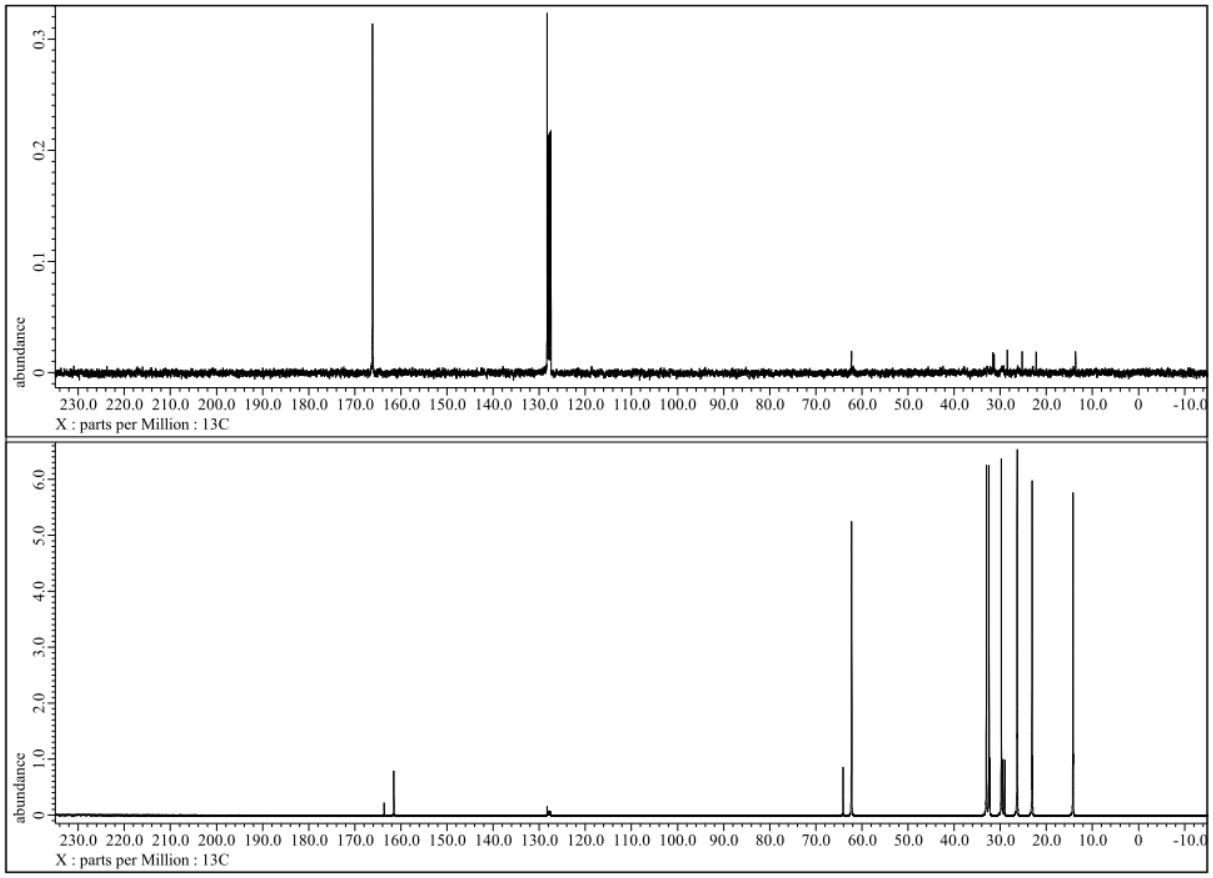


Figure S11: ^{13}C NMR spectra of the stability tests in the presence of HPA-5 and formic acid; 100 g 1-heptanol were processed in 100 g aqueous formic acid (10 wt% FA) at 363 K and 20 bar oxygen pressure for 72 h; measuring whether 1-heptanol is converted in both phases (aqueous: top, organic: bottom); peak at 128.5 ppm: external standard benzene.

GC-MS analysis of products from ^{13}C glucose oxidation

The following spectra show the results of the experiment using ^{13}C glucose as substrate and HPA-5 as catalyst applying the in-situ extraction method. The gaseous sample was investigated in a Agilent 7890B GC/ 5977A MSD-system using a 30 m x 0.25 mm x 0.25 µm column and a single quadrupole MS. For the liquid samples a Varian CP-800 GC, Saturn 2200 MS CP-SIL 8CB equipped with a 30 m x 0.25 mm x 0.25 µm column and ion trap was used.

Figure S12: GC-MS spectra of a pure $^{12}CO_2$ gas sample (top) and the gas phase after the experiment (bottom) containing a large amount of $^{13}CO_2$ (amounts of $^{12}CO_2$ found in the sample origin from manual sampling with some remaining air volume in the probe volume). For this experiment, 2.0 g ^{13}C glucose as substrate were processed in 100 g water and 100 g 1-hexanol at 363 K and 20 bar oxygen pressure for 24 h using 0.5 mmol HPA-5 as catalyst to examine whether only $^{13}CO_2$ (and ^{13}CO) is present in the gas phase.

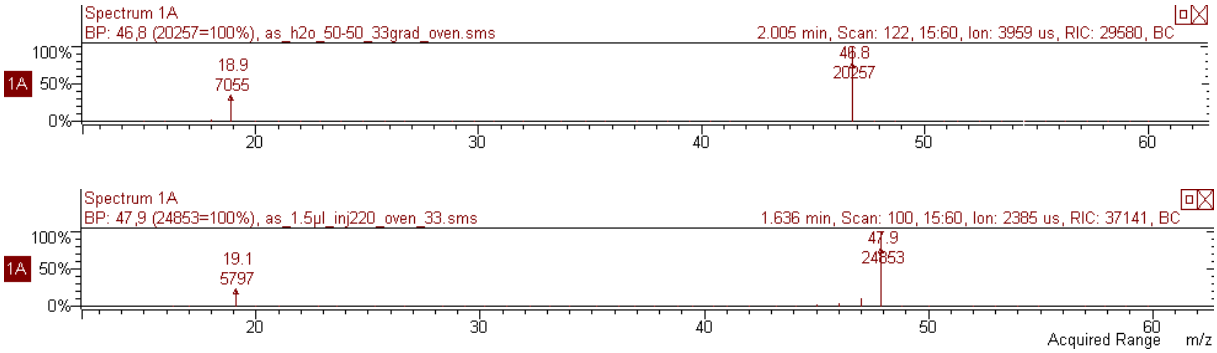
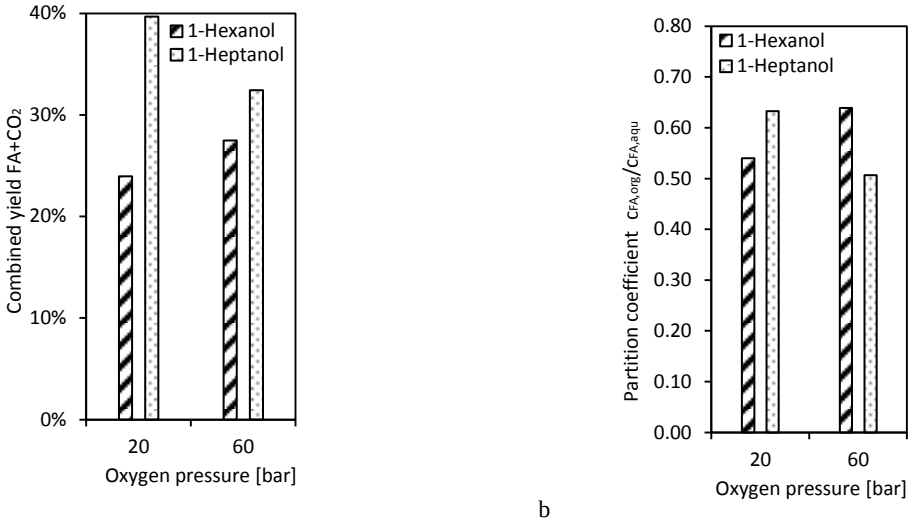


Figure S13: GC-MS spectra of aqueous ^{12}C FA (top) and a liquid sample from the oxidation experiment with ^{13}C glucose (bottom) containing only ^{13}C FA. ^{13}C glucose was processed in 100 g water and 100 g 1-hexanol at 363 K and 20 bar oxygen pressure for 24 h using 0.5 mmol HPA-5 as catalyst; water served as reference component having a m/z ratio of 19 in this GC-MS, FA found after the oxidative conversion was only ^{13}C FA .



a b

Figure S14: Oxidative conversion of glucose to formic acid in the presence of alcohols as in-situ extracting agent - comparison of combined yields and partition coefficients at 20 and 60 bar O_2 pressure (1.8 g glucose and 0.91 g (0.5 mmol) HPA-5 catalyst dissolved in 100.0 mL H_2O, 100 g extracting agent, 363 K, 1000 rpm, 6 h); a: combined yield FA + CO_2 applying different oxygen partial pressures; b: partition coefficient $c_{FA,aqu}/c_{FA,org}$ applying different oxygen partial pressures.

FA product stability in the reaction phase

The ^{13}C-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectrum shows the ^{13}C-NMR after the stability test (10 wt% formic acid in aqueous HPA-5 solution) at 20 bar CO_2 pressure using 1000 scans and a frequency of 100.61 MHz.

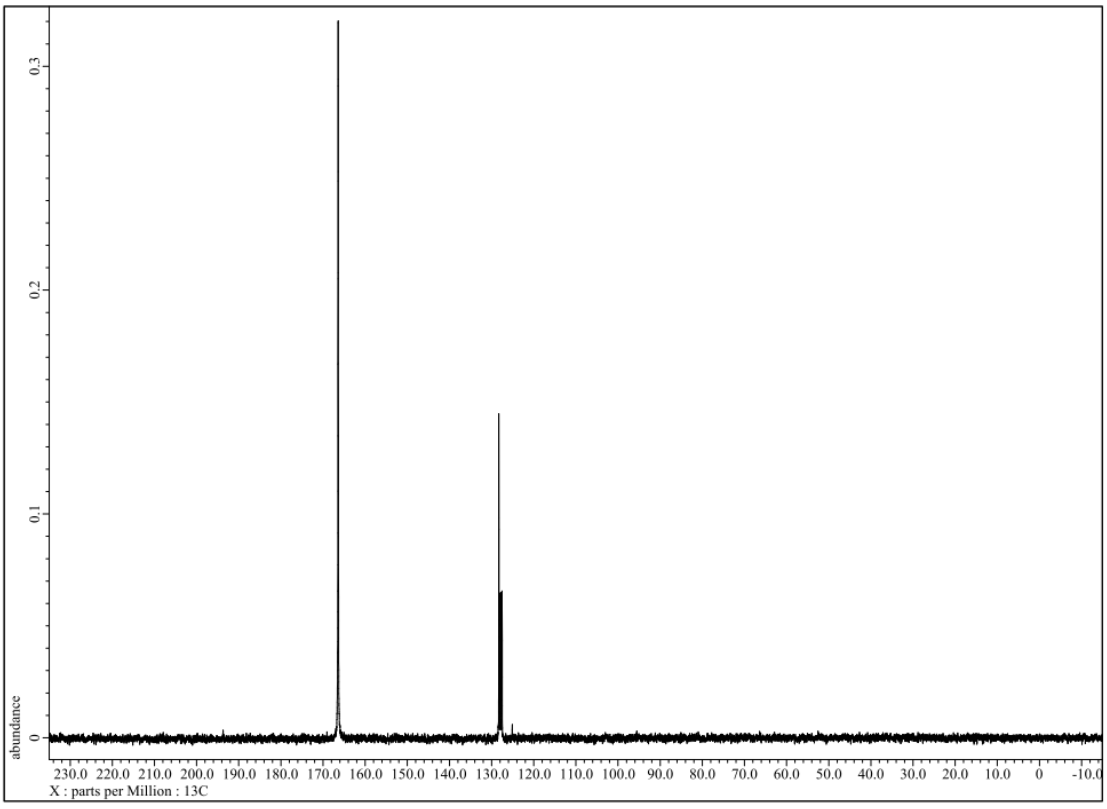


Figure S15: ^{13}C NMR spectrum of the stability test of 10 wt% FA in the presence of HPA-5 in 100 g aqueous solution at 363 K and 20 bar CO_2 pressure for 48 h; measuring whether FA is stable under CO_2 pressure at reaction conditions; peak at 128.5 ppm: external standard benzene.

Ester formation between toluenesulfonic acid and the alcoholic extraction solvent

The ^{13}C-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectra show the ^{13}C-NMR of esterification experiments of aqueous *p*-toluenesulfonic acid solution with 1-hexanol and 1-heptanol, respectively. Both phases were analysed using 1000 scans and a frequency of 100.61 MHz.

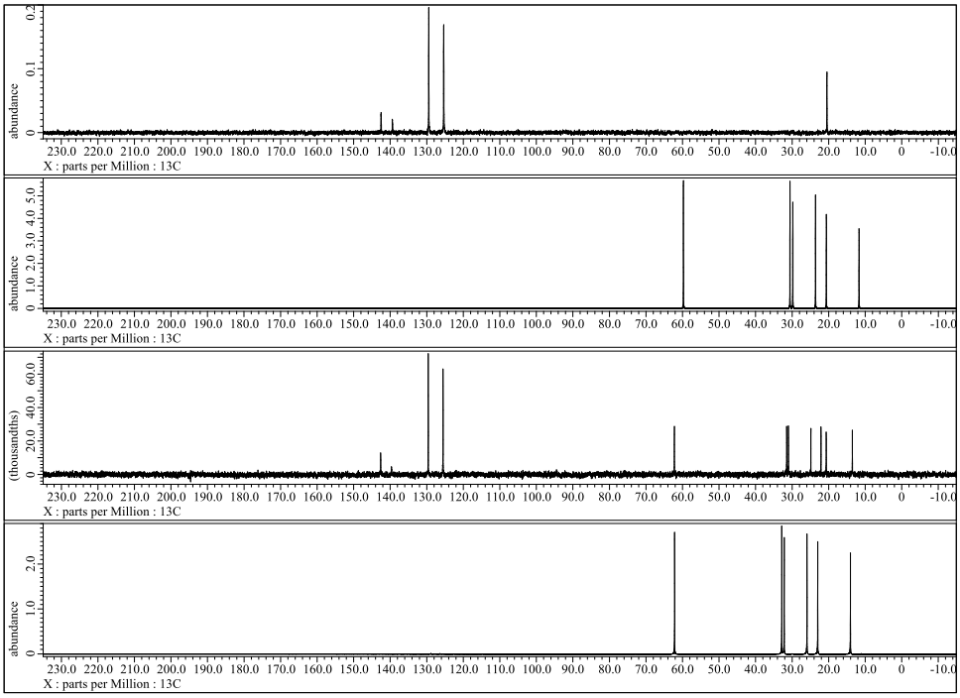


Figure S16: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous *p*-toluenesulfonic acid (0.17 wt% TSS) contacted with 1 g 1-hexanol; measuring degree of esterification in both phases (from top to bottom: pure TSS, pure 1-hexanol, aqueous phase, organic phase) 12 hours after sample preparation.

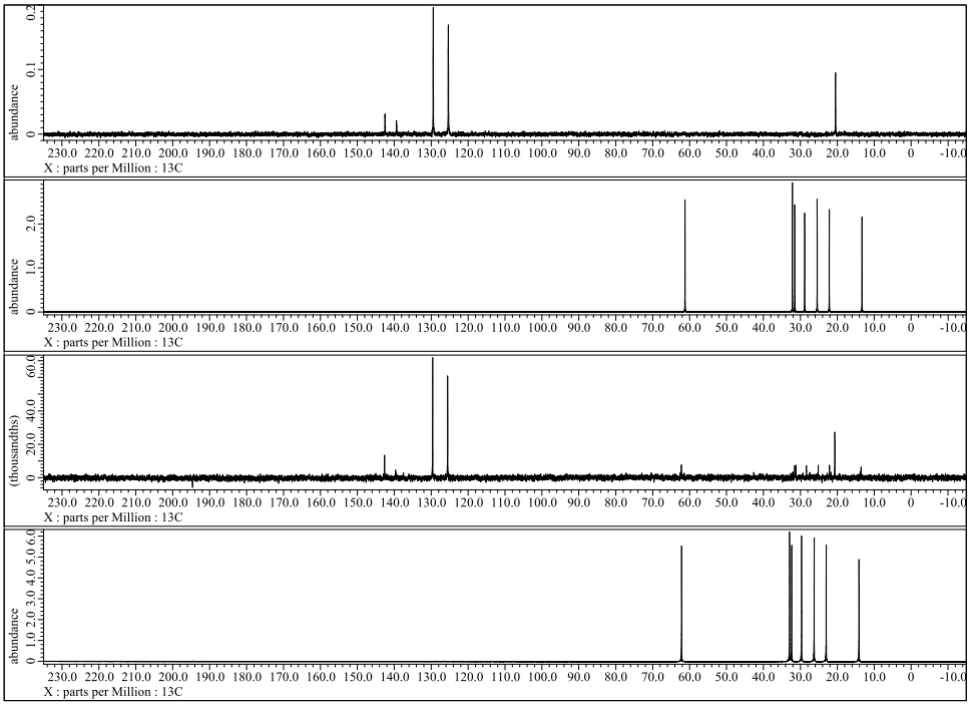


Figure S17: ^{13}C NMR spectra of the esterification experiments; 1 g aqueous *p*-toluenesulfonic acid (0.17 wt% TSS) contacted with 1 g 1-heptanol; measuring degree of esterification in both phases (from top to bottom: pure TSS, pure 1-heptanol, aqueous phase, organic phase) 12 hours after sample preparation.

Solubility of the polyoxometalate catalyst in the organic extraction phase during and after the biphasic oxidation reaction

The ^{31}P-and ^{51}V-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectra show the ^{51}V-NMR (top) and ^{31}P-NMR spectra (bottom) of the aqueous catalyst phase and the organic extraction phase during the glucose oxidation reaction (see Table 1).

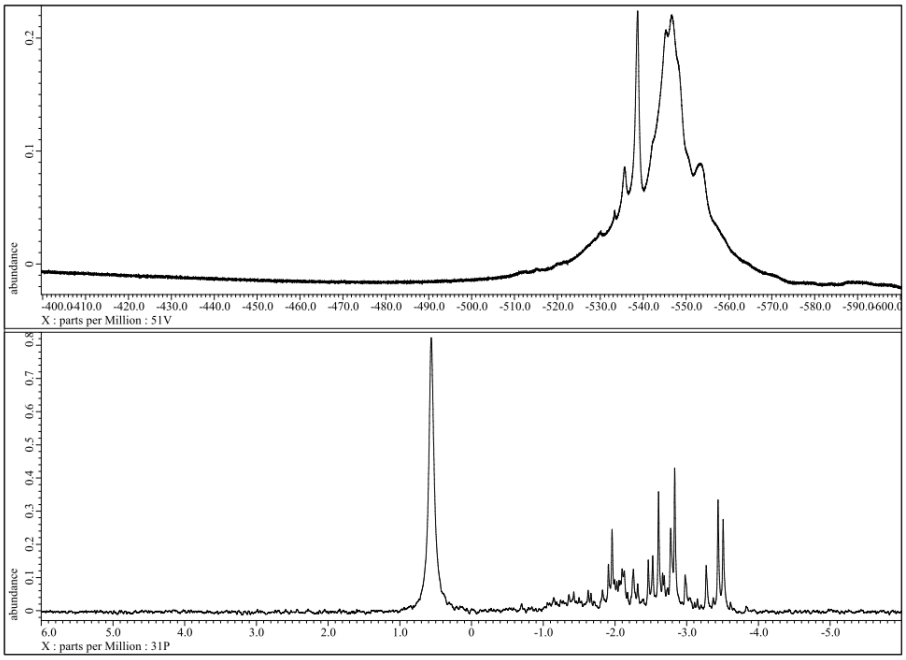


Figure S18: ^{51}V-NMR (top) and ^{31}P-NMR (bottom) spectra of the aqueous catalyst phase from an experiment with 1.80 g glucose and 0.91 g (0.5 mmol) HPA-5 dissolved in 100.0 mL H_2O, 100 g 1-hexanol as primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm during the oxidation reaction.

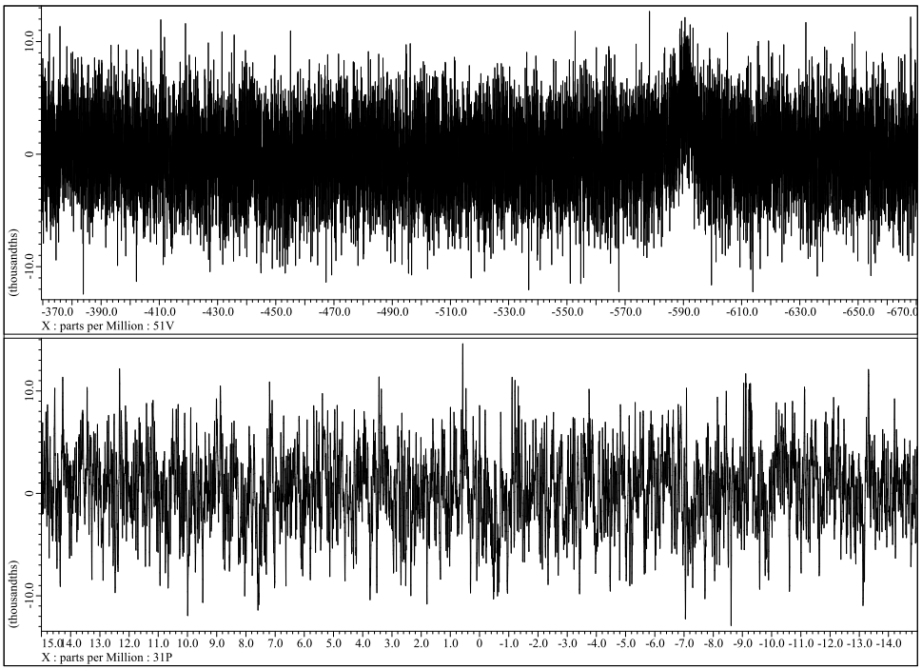


Figure S19: ^{51}V-NMR (top) and ^{31}P-NMR (bottom) spectra of the organic extraction phase from an experiment with 1.80 g glucose and 0.91 g (0.5 mmol) HPA-5 dissolved in 100.0 mL H_2O, 100 g 1-hexanol as primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm during the oxidation reaction.