- Supporting Information -

Impact of minor amounts of hydroperoxides on rhodium-catalyzed hydroformylation of long-chain olefins

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Materials and general considerations

Chemicals All chemicals were used as delivered without further purification unless otherwise noted. *N,N*-dimethylformamide (DMF, VWR, 99.98 %) and decane (TCI, 99.5 %) were used as solvents and 1-dodecene was used as substrate to constitute the thermomorphic solvent system (TMS) (x_{DMF} : x_{decane} : $x_{1\text{-dodecene}}$ = 49.0/37.7/13.3 mol-%). 1-Dodecene was purchased from different suppliers (abcr, 97.1 %; Acros, 96.9 %; Merck, 94.7 %; TCI, 95.8 %; alphabetical order, no correlation to the article) to investigate the concentration of hydroperoxides and the influence of the same on hydroformylation kinetics. Synthesis gas was used as substrate in a mixture ($CO:H_2$ = 1/1, Linde, CO = (50.0 ± 1) %)). Precatalyst $Rh(acac)(CO)_2$ (Umicore, 38.5…40.0 % in Rh) and ligand (BiPhePhos, Molisa, > 99%) were used to generate the catalyst. 1-Dodecene (Fluka, 97.1 %), tridecanal (Sigma, 99.6 %), dodecane (Sigma, 99.1 %), decane (TCI, 99.5 %), and DMF (VWR, 99.99 %) were used as calibration standards for the gas-chromatographic analysis. All Chemicals for the determination of organic peroxide were commercially available as *PeroxiDetect™ Kit* (Sigma-Aldrich) containing an organic peroxide color reagent (480 µmol butylated hydroxytoluene, 15 µmol xylene orange (XO)), ferrous ammonium sulfate reagent (25 mM $(NH_4)_2Fe(SO_4)_2$ in 2.5 M H_2SO_4) and *tert*-butyl hydroperoxide (TBHP, 70%, aqueous solution). Additionally, methanol (MeOH, Sigma-Aldrich, 99.9 %) was used as a solvent.

Gas chromatography Samples of the reaction mixtures (0.5 mL) were diluted with 2-propanol (1.5 mL) and analyzed using a gas chromatograph (GC, 6890 Series, Agilent) equipped with a flame ionization detector, a polar polyethylene glycol stationary phase (HP-INNOWax, 2x 60 m, d = 250 µm, film = 0.5 µm, Agilent) and helium (Linde, 99.999 %) as a carrier gas. The Inlet temperature was 250 °C and the split ratio was set to 100 : 1. The average carrier gas velocity was set to 15 cm s^{-1} in ramp flow mode. When the sample was injected, the oven was kept isothermal at 130 °C for 30 min, afterwards heated at 35 K min^{-1} to 200 °C for 30 min and finally heated at 35 K min^{-1} to 250 °C for 12 min. The samples were analyzed for the concentrations of 1-dodecene, dodecene isomers, tridecanal, aldehyde isomers and dodecane as well as for the solvents decane and DMF. Decane was used as an internal standard. Due to the lack of commercially available calibration standards, response factors of 1-dodecene and tridecanal were also used for dodecene isomers and aldehyde isomers, respectively. Reference standards with a defined composition of DMF, decane, 1-dodecene and tridecanal were analyzed before and after a measurement series to validate the analytical method. The relative standard deviation in the concentration of all analytes was found to be < 3 %.

NMR spectroscopy NMR spectra were recorded on a Bruker DPX 400 spectrometer. ^1H NMR spectra were referenced to residual protiated solvent signals.^{13}C NMR spectra were referenced to solvent signals and ^{31}P NMR spectra to external 85 % H_3PO_4. NMR spectra are reported as follows: chemical shift (δ / ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are given as follows (or combinations thereof): s: singlet, d: doublet, t: triplet. In addition to 1D NMR experiments the identity of hydroperoxide and branched olefin species were established by 2D NMR experiments (^1H,^1H-COSY, ^1H,^{13}C-HSQC, ^1H,^{13}C-HMBC). Acquired data was processed and analyzed using *Bruker TopSpin* software.

UV/VIS spectroscopy Absorption spectra were recorded on a Macherey-Nagel *NANOCOLOR UV/VIS II* spectral photometer. Characteristic absorption of hydroperoxide indicator was analyzed at 560 and 590 nm for quantification.

Hydroformylation procedure

Hydroformylation experiments were conducted in a 1.8 L stainless steel double-jacketed vessel equipped with a gassing stirrer, PTFE-coated gas cylinder, flexible gas dosing, locking and evacuation system, temperature and pressure controllers. The catalyst solution was prepared by dissolving $Rh(acac)(CO)_2$ and BiPhePhos in solvent DMF. The reactor was filled with the catalyst solution ($Rh(acac)(CO)_2$, BiPhePhos, DMF) and solvent decane. Decane and DMF were used as solvents to constitute a thermomorphic solvents system (TMS). Afterwards the reaction mixture was thoroughly purged and evacuated three times with CO/H2 (1:1) and 50 mbar, respectively. The pretreatment of the catalyst was performed at 105 °C and 20 bar CO/H_2 (1:1) for 30 min. Meanwhile, 1-dodecene was filled into the PTFE-coated gas cylinder and was thoroughly purged and evacuated with CO/H_2 (1:1) and 10 mbar, respectively. The gas cylinder was pressurized with 30 bar CO/H_2 (1:1) and the kinetic experiment was started with the controlled injection of 1-dodecene into the reactor by opening the valve between reactor and gas cylinder. Temperature and pressure were kept constant for the duration of the experiment. Samples were taken in discrete time increments and were analyzed using standard gas chromatography.

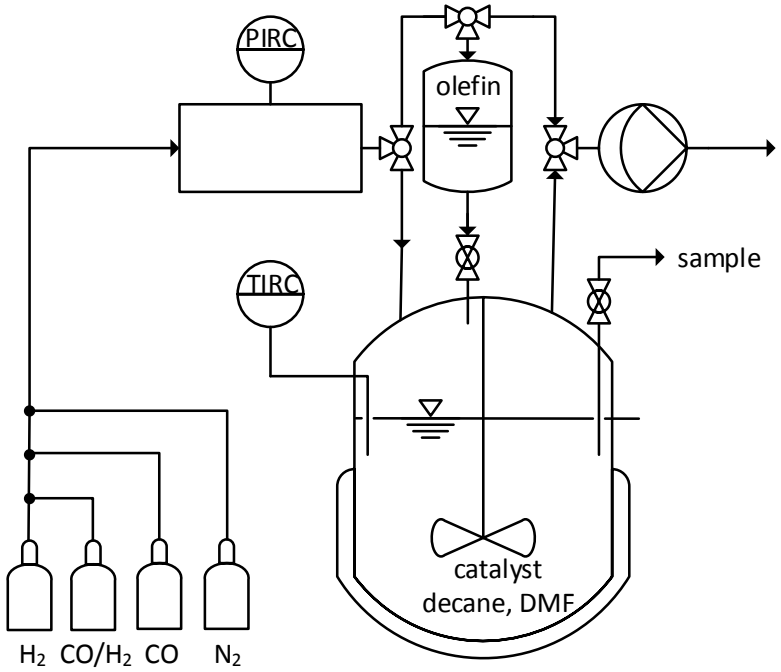


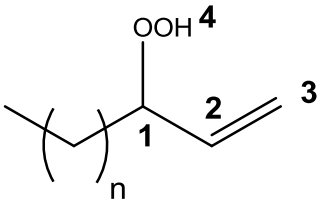
Fig. S1: Experimental setup for hydroformylation reactions.

NMR identification of impurities in olefin feeds

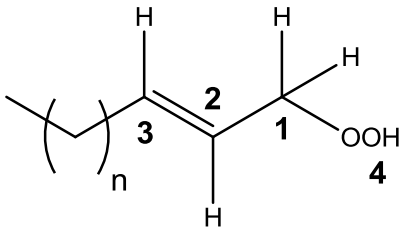
Prior to NMR analysis, impurities in 1-dodecene feeds were purified by vacuum distillation (p = 5 mbar, T = 80 °C). The bottom, containing major amounts of 1-dodecene and significant amounts of impurities, i.e. three hydroperoxide species and two branched olefin species, was analyzed as a mixture. Due to the structural similarity (alkyl chain) of the impurities to 1-dodecene only structural significant and distinct assignable nucleus were assigned in the following. The proton chemical shifts of the hydroperoxide group (ROOH) are in good agreement to reported results of various organic hydroperoxides.[1]

a) Summary of structural analysis

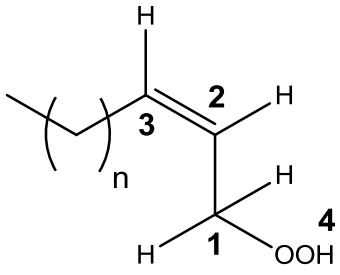
Hydroperoxides



^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.27 (dt, $^{3}J_{HH}$ = 7, $^{3}J_{HH}$ = 7, 1H, H-1), 5.27 (dd, $^{3}J_{HH}$ = 10, $^{2}J_{HH}$ = 1 1H, H-3 *cis*), 5.30 (overlayed w. CD_2Cl_2, 1H, H-3), 5.75 (overlayed w. 1-dodecene, 1H, H-2), 7.82 (s, 1H, H-4). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2)**:** δ 87.5 (s, C-1), 118.9 (s, C-3), 137.9 (s, C-2).

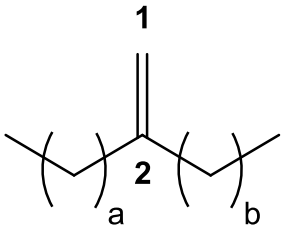


^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.39 (d, $^{3}J_{HH}$ = 7, 2H, H-1), 5.56 (dtt, $^{3}J_{HH}$ = 15, $^{3}J_{HH}$ = 7, $^{4}J_{HH}$ = 1, 1H, H-2), 7.96 (s, 1H, H-4). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2)**:** δ 78.1 (s, C-1), 124.0 (s, C-2), 138.9 (s, C-3).

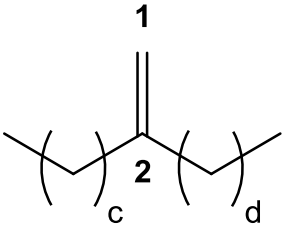


^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.53 (d, $^3J_{HH}$ = 7, 2H, H-1), 5.53 (overlayed w. δ 5.56 (dtt), 1H, H-2), 8.02 (s, 1H, H-4). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2)**:** δ 72.8 (s, C-1), 123.2 (s, C-2), 137.4 (s, C-3).

Branched olefins



^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.67 (s, 2H, H-1). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2)**:** δ 107.4 (s, C-1), 151.7 (s, C-2).



^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.67 (s, 2H, H-1). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2)**:** δ 108.5 (s, C-1), 150.2 (s, C-2).

b) Detailed structural analysis

^{1}H

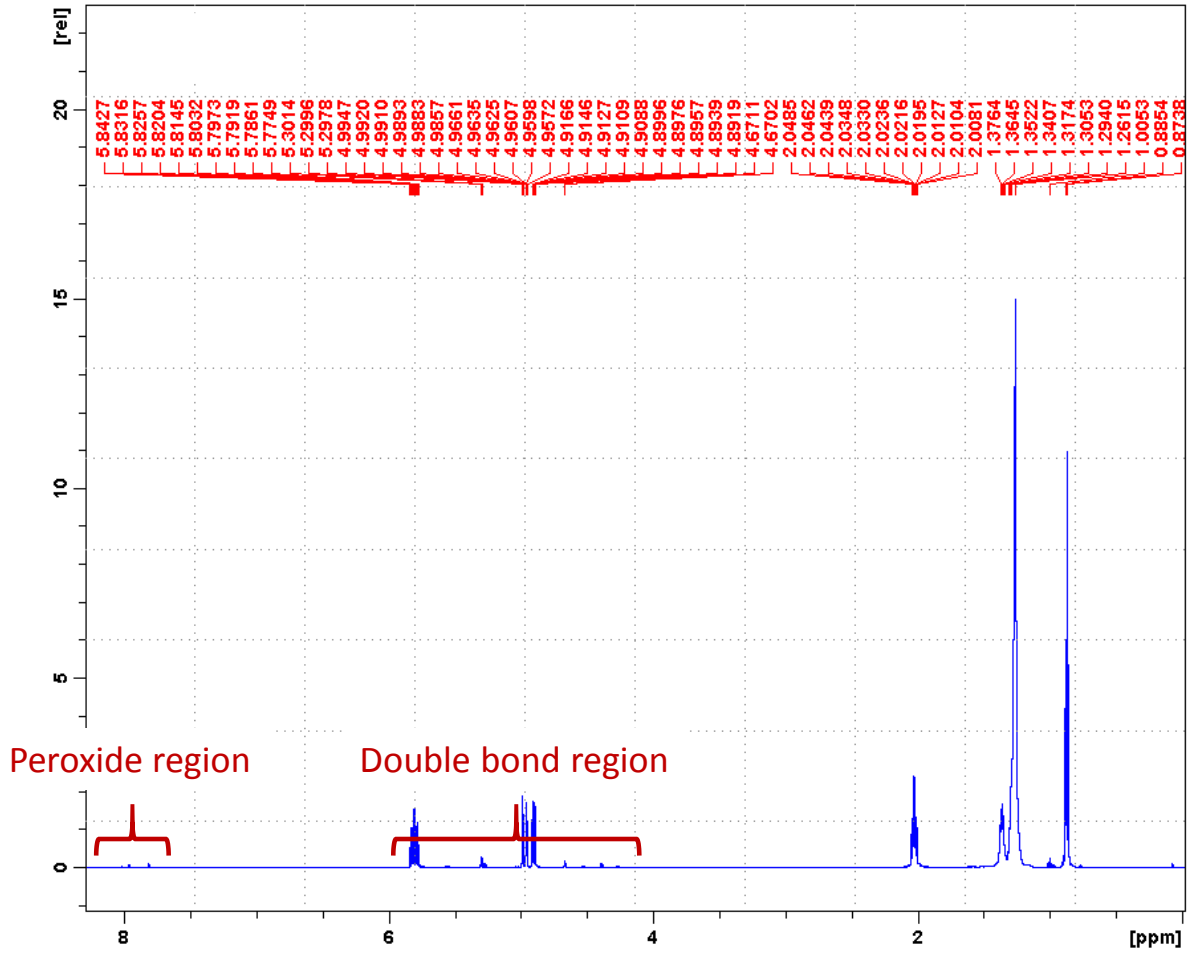


Fig. S2: ^{1}H NMR spectrum of 1-dodecene distillation bottom.

^{1}H

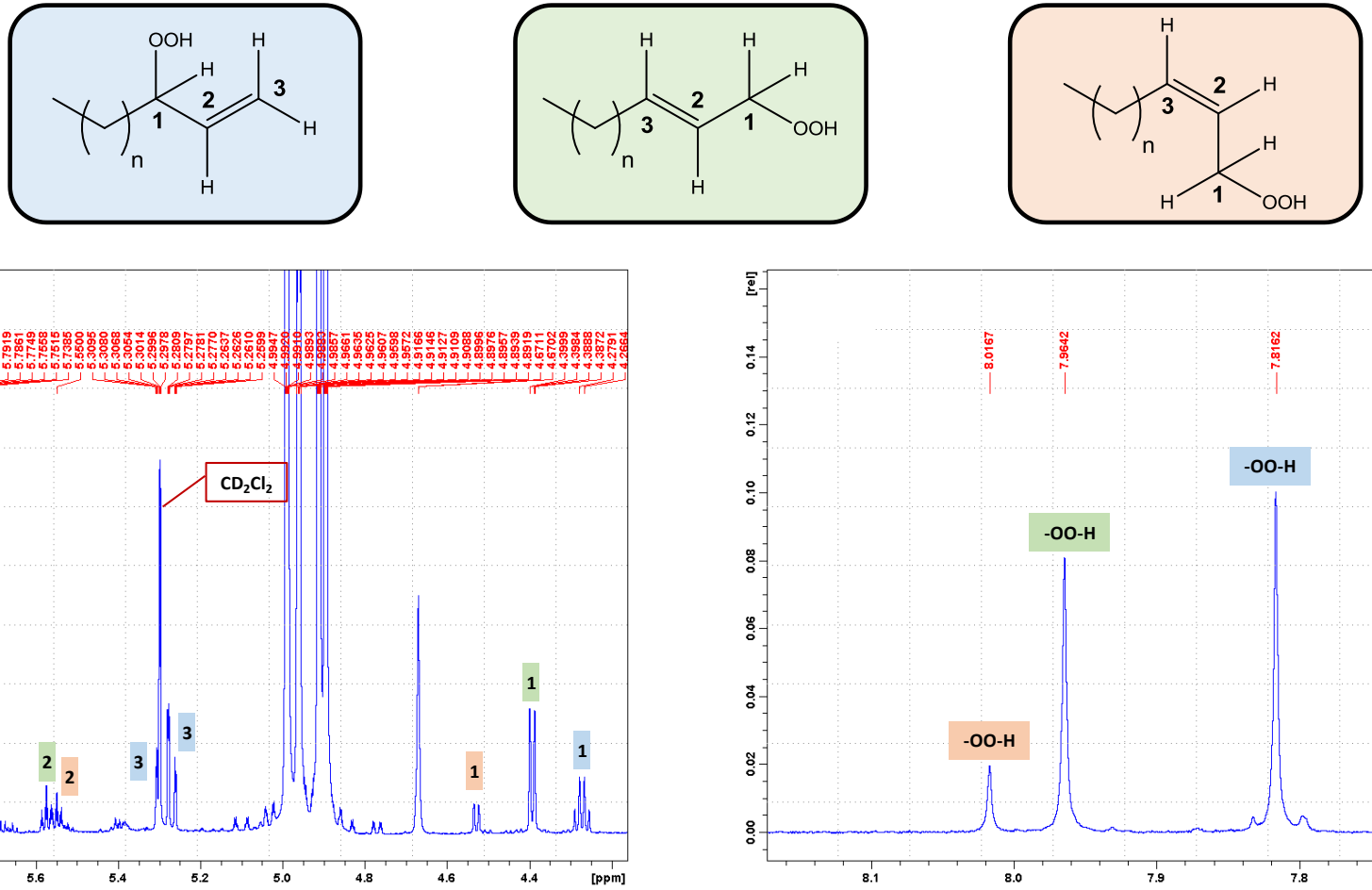


Fig. S3: ^{1}H NMR spectra of 1-dodecene distillation bottom.

^{13}C, DEPT

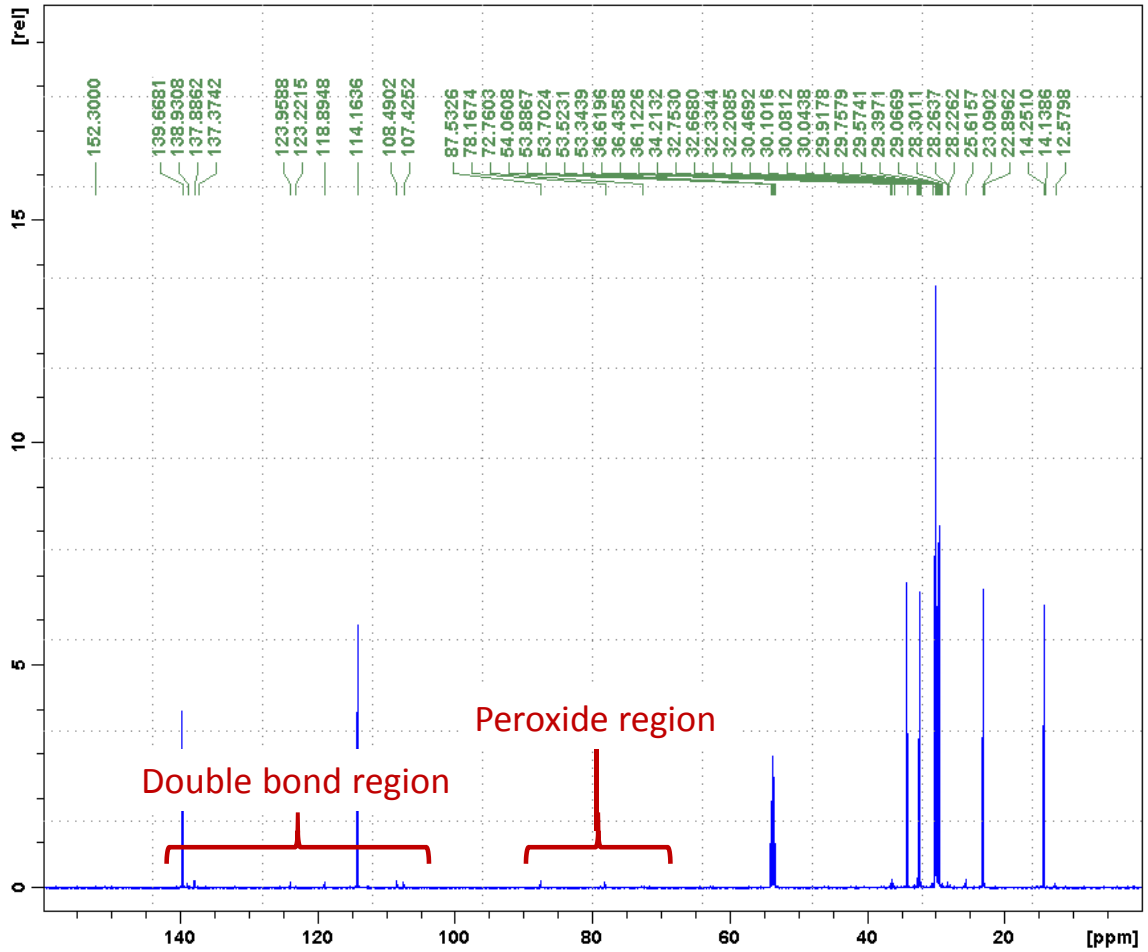


Fig. S4: $^{13}C\{^{1}H\}$ NMR spectrum of 1-dodecene distillation bottom.

^{13}C, DEPT

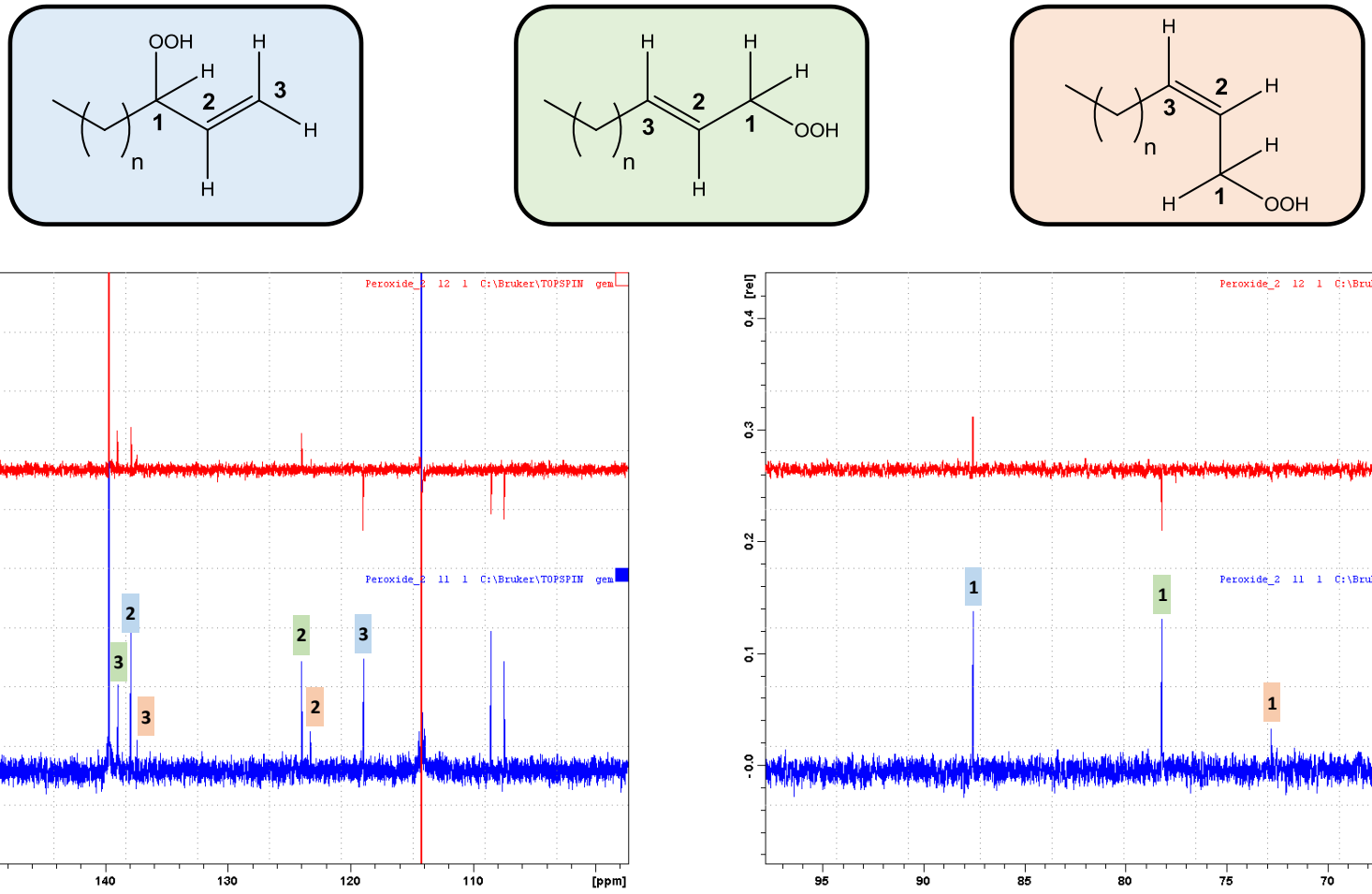


Fig. S5: ^{13}C{^{1}H} NMR (blue) and DEPT-135 (red) spectra of 1-dodecene distillation bottom.

HSQC: F1 – ^{13}C, F2 – ^{1}H

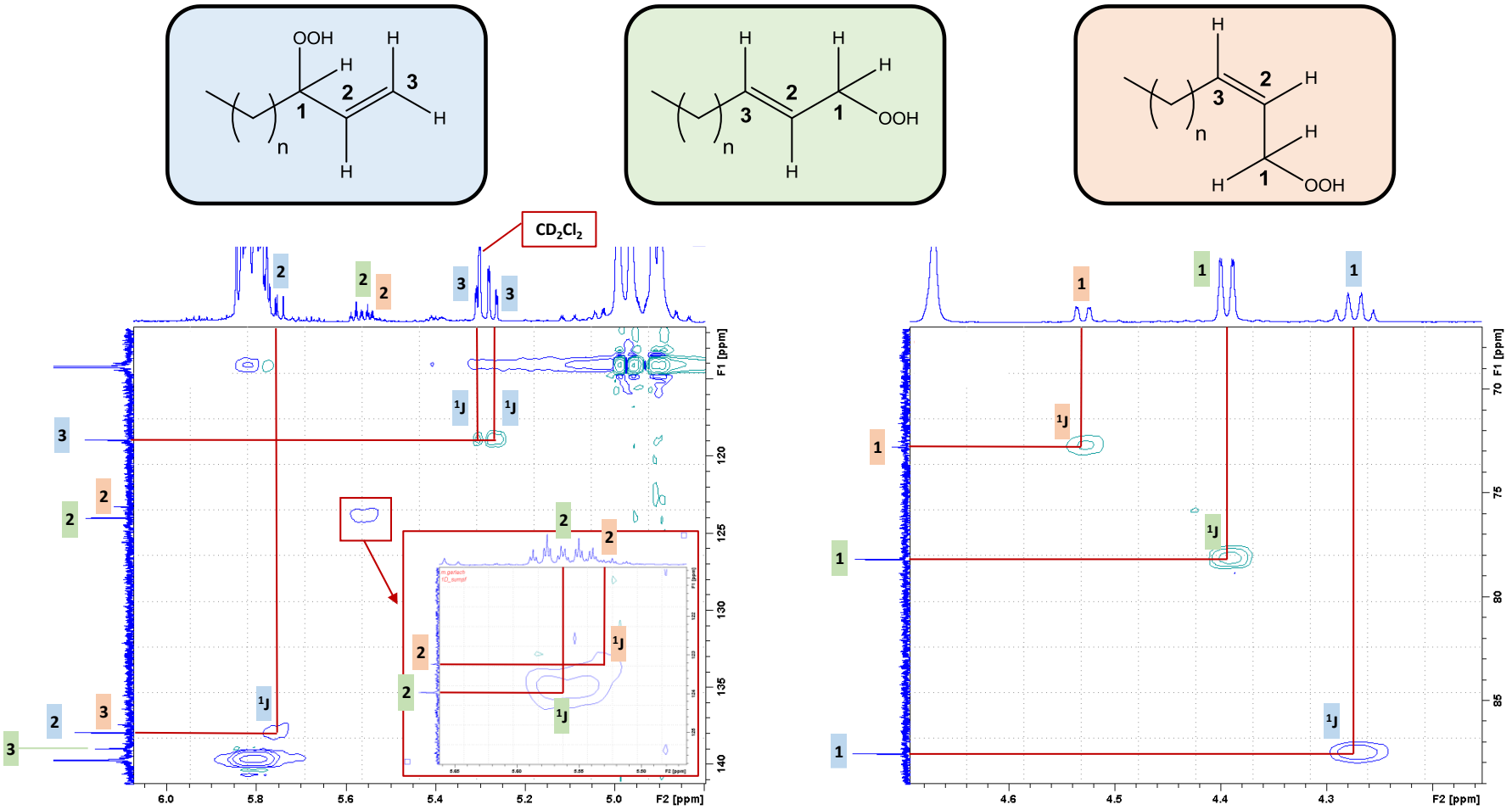


Fig. S6: HSQC spectrum (F1 – ^{13}C, F2 – ^{1}H) of 1-dodecene distillation bottom.

HMBC: F1 – ^{13}C, F2 – ^{1}H

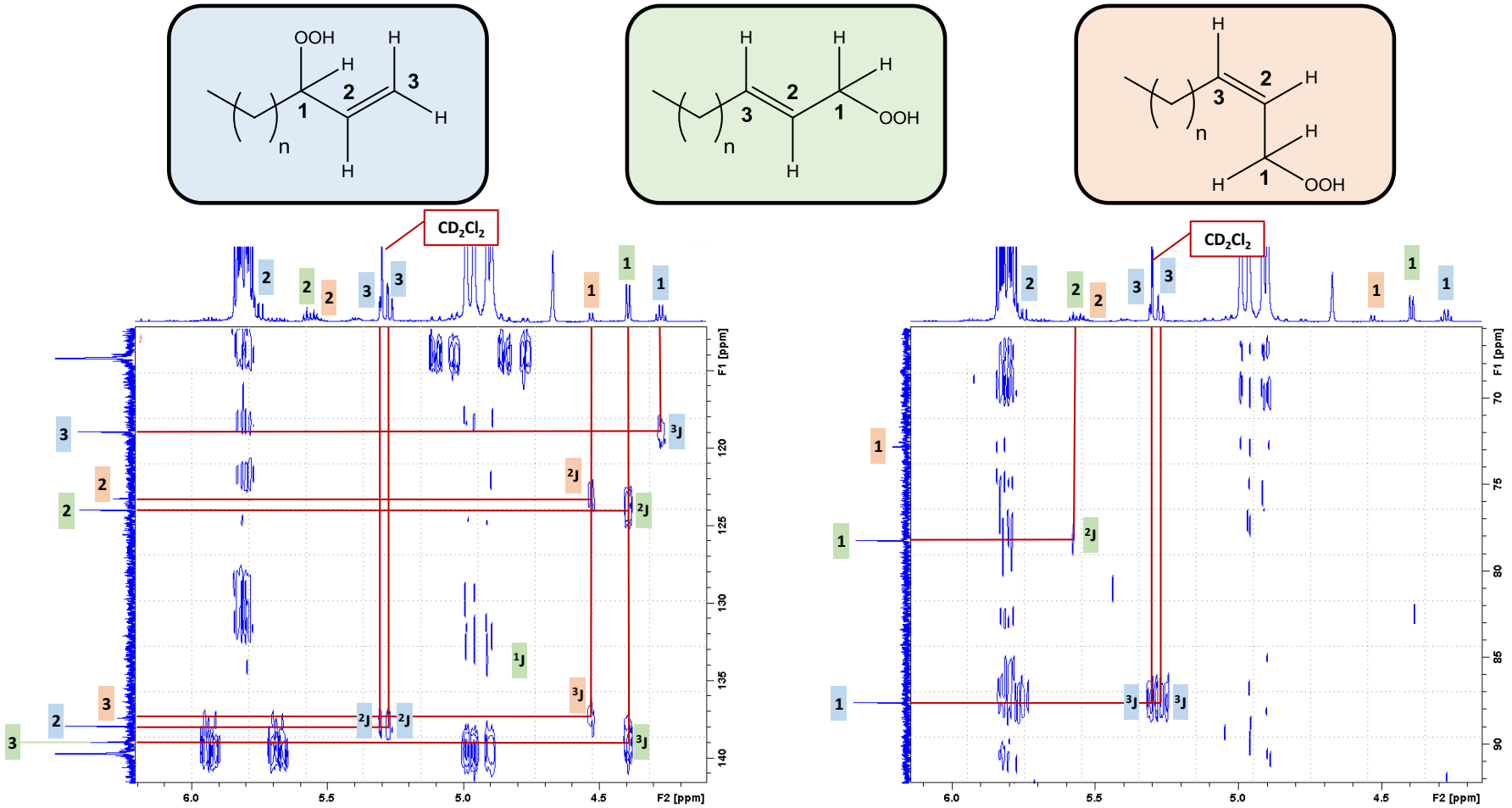


Fig. S7: HMBC spectrum (F1 – ^{13}C, F2 – ^{1}H) of 1-dodecene distillation bottom.

H,H-COSY

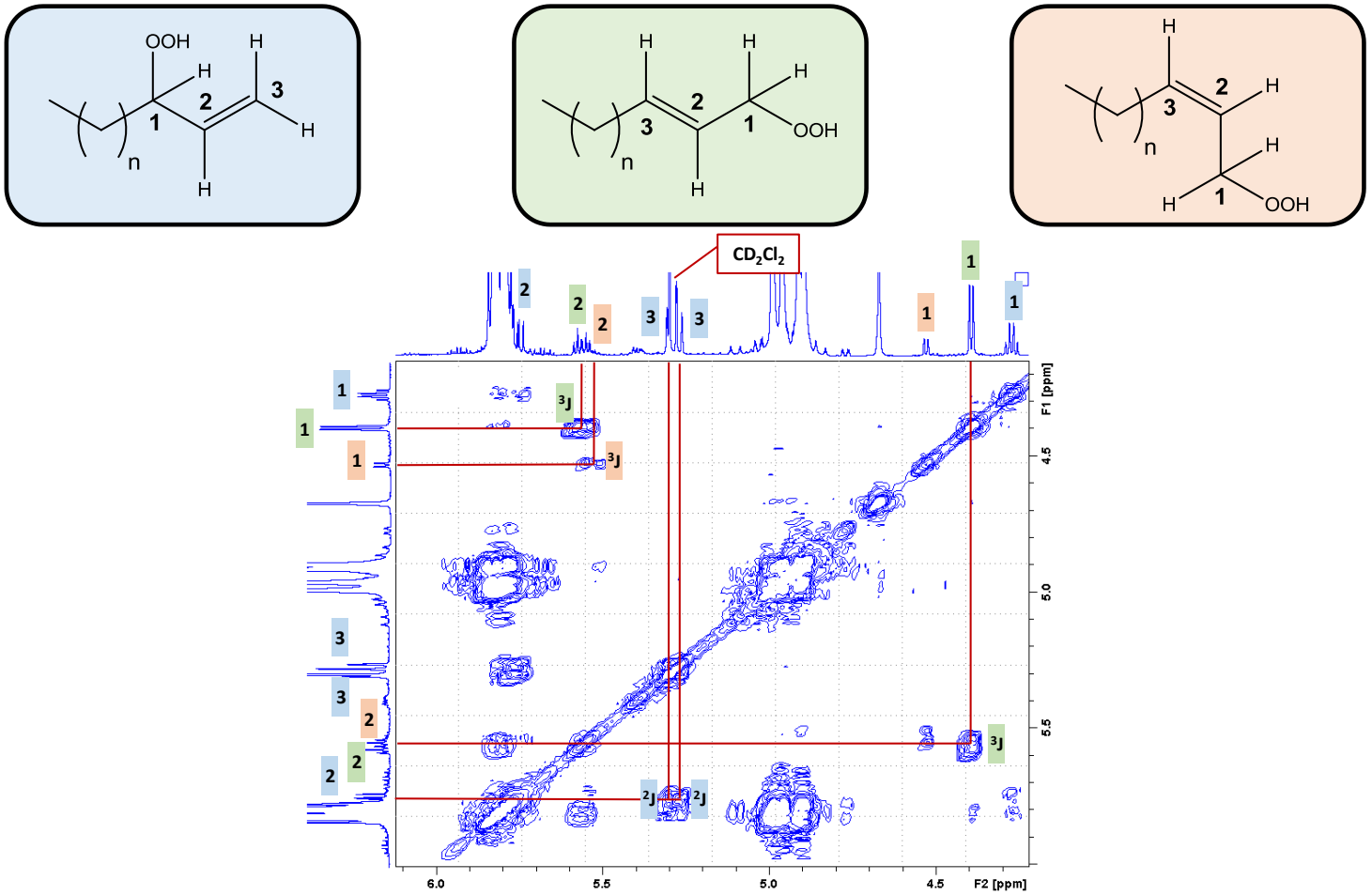


Fig. S8: ^{1}H,^{1}H-COSY spectrum of 1-dodecene distillation bottom.

HSQC: F1 – ^{13}C, F2 – ^{1}H & ^{13}C, DEPT

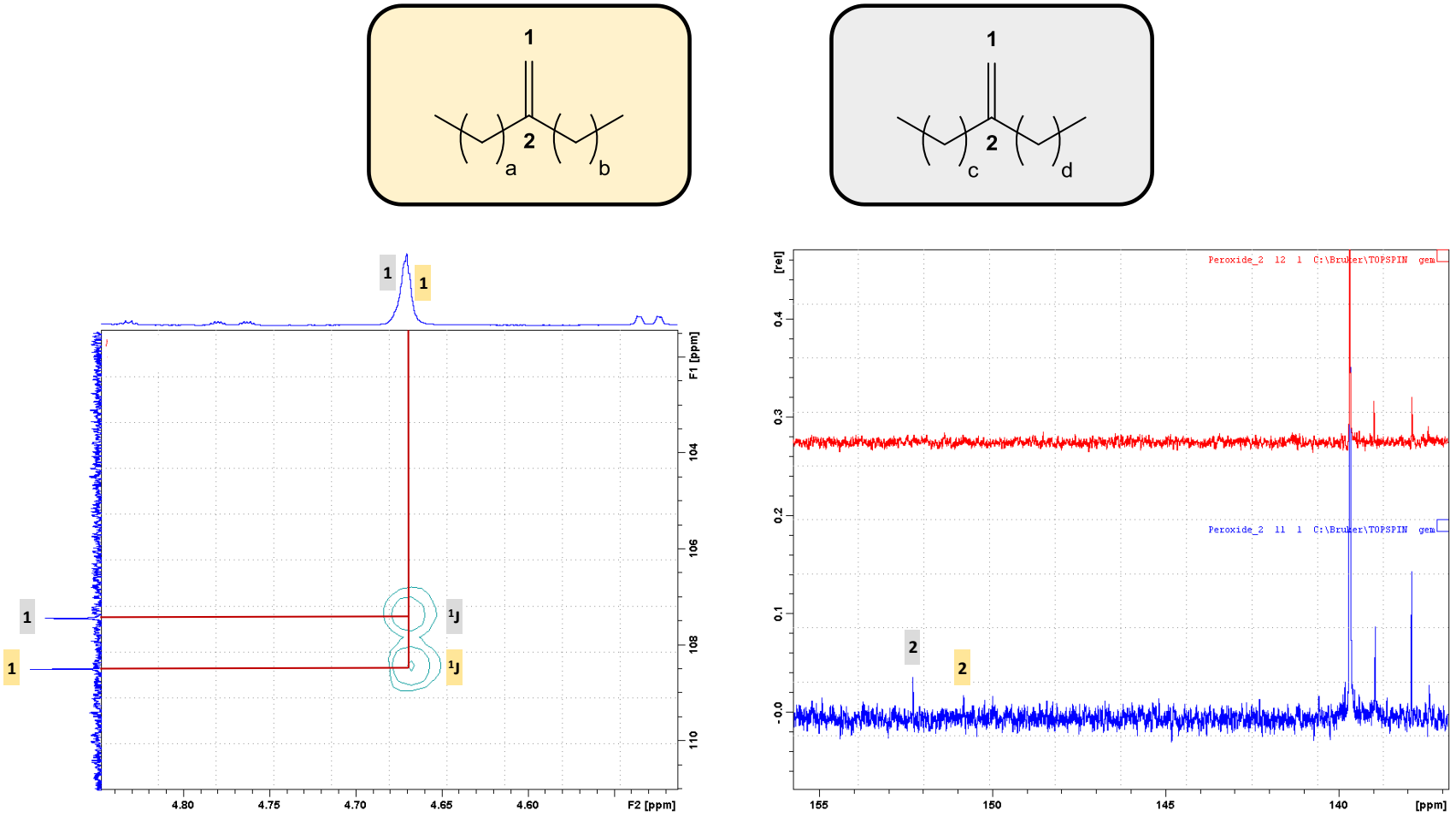


Fig. S9: Left: HSQC spectrum (F1 – ^{13}C, F2 – ^{1}H), right: ^{13}C{^{1}H} NMR (blue) and DEPT-135 (red) spectra of 1-dodecene distillation bottom.

UV/VIS quantification of hydroperoxides

Calibration Following the procedure "Determination of organic or lipid hydroperoxide solutions" (*PeroxiDetect™ Kit*, Sigma-Aldrich, technical bulletin, date: 31.01.2017) a working color reagent and a 200 µM TBHP standard solution were prepared. Calibration solutions were prepared by placing defined volumes of 200 µM TBHP standard solution in a tube and filling the final volume to 200 µL using 90 % MeOH. Afterwards, 200 µL of calibration solution were placed in a cuvette with a magnetic stirrer, mixed with 2 mL working color reagent and stirred for 35 min in a dark room. Finally, the cuvette was placed in the UV/VIS spectrometer. 90 % MeOH was used as reference. Mean values of absorbances at 560 and 590 nm (A_{560nm}, A_{590nm}) from five different measurements with a variation coefficient < 0.1% are given in Tab. 1 for different TBHP concentrations. The graphical representation of linear regressions for 560 and 590 nm are given in Fig. 1.

Quantitative analysis Depending on the concentration of hydroperoxides in the different olefin feeds, 1 – 20 µL of olefin sample were transferred to a cuvette with a magnetic stirrer and filled to a final volume of 200 µL using 90 % MeOH. Afterwards, 2 mL of working color reagent were added and the solution was stirred for 35 min in a dark room. Finally, the cuvette was placed in the UV/VIS spectrometer. 90 % MeOH was used as a reference. Mean values of A_{560nm} and A_{590nm} from five measurements and linear regression parameters (Fig. 1) were used to determine the concentration of peroxides c_{HP} in different olefin feeds (Eq. 1).

$$c_{HP} = \frac{(185.87 \cdot \bar{A}_{560nm} - 100.18) + (180.38 \cdot \bar{A}_{590nm} - 63.68)}{2} \cdot \frac{\left(V_{90\%\,MeOH} + V_{olefin}\right)}{V_{olefin}} \qquad (1)$$

Tab. 1: Calibration of hydroperoxides for UV/VIS quantification.

Calibration level	200 µM TBHP	90 % MeOH	Working color reagent	TBHP	$A_{560\ nm}$	A_{590nm}
-	µL	µL	mL	µmol L^{-1}	-	-
1	0	200	2	0.0	0.521	0.338
2	5	195	2	0.5	0.560	0.376
3	10	190	2	10.0	0.596	0.410
4	20	180	2	20.0	0.643	0.457
5	40	160	2	40.0	0.776	0.597
6	80	120	2	80.0	0.982	0.808
7	120	80	2	120.0	1.197	1.039
8	160	40	2	160.0	1.377	1.212

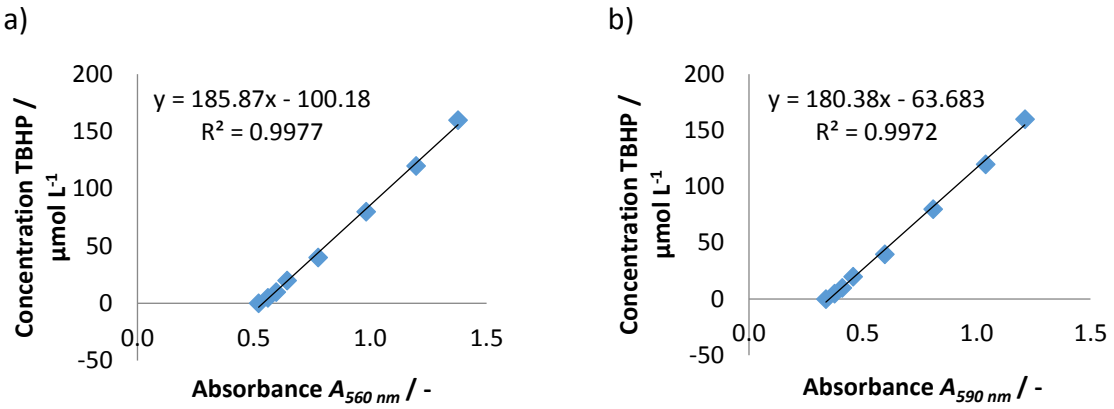


Fig. S10: TBHP calibration curves, linear regression parameters and residuals for different UV/VIS absorbances: a) 560 nm, b) 590 nm.

^{31}P NMR analysis of catalyst solutions

The catalyst solution was prepared according to "Hydroformylation procedure" (p. S3). For ^{31}P NMR analysis, a sample of the catalyst solution was analyzed before it was transferred to the reactor. Another sample of the catalyst solution was analyzed after the hydroformylation reaction. Therefore, the reaction solution was cooled down to room temperature to initiate the phase separation of the TMS. Afterwards the reactor was depressurized and a sample of the catalyst solution was taken. The comparison of spectra indicated a complete decomposition of BiPhePhos (δ = 145.0 ppm) to unknown phosphorous species (δ_1 = -3.8 ppm, δ_2 = -8.8 ppm). According to general ^{31}P NMR spectroscopy literature these chemical shifts can be correlated with phosphate species.[2]

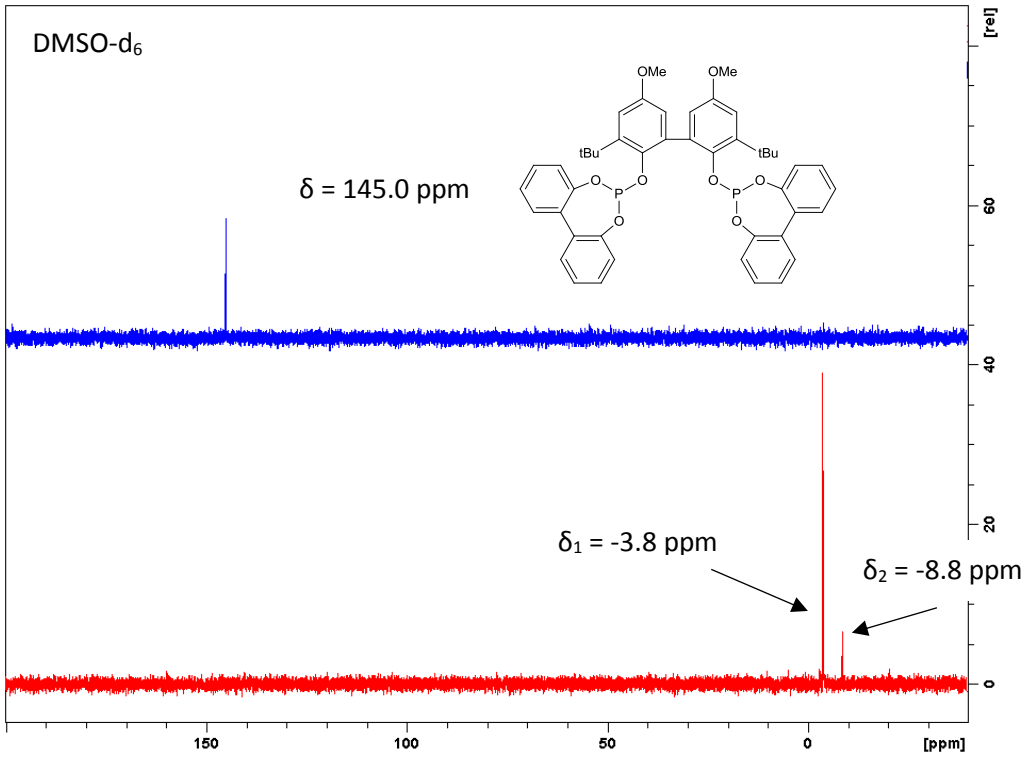


Fig. S11: ^{31}P{^{1}H} NMR spectra of the catalyst solution before (blue) and after the reaction (red).

References

1 D. Swern, A. H. Clements and T. M. Luong, *Anal. Chem.*, 1969, **41**(3), 412.

2 O. Kühl, *Phosphorus-31 NMR Spectroscopy: A Concise Introduction for the Synthetic Organic and Organometallic Chemist*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009, p 32.