

# Synthesis of nixantphos core-functionalized amphiphilic nanoreactors and application to rhodium-catalyzed aqueous biphasic 1-octene hydroformylation

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SUPPORTING INFORMATION

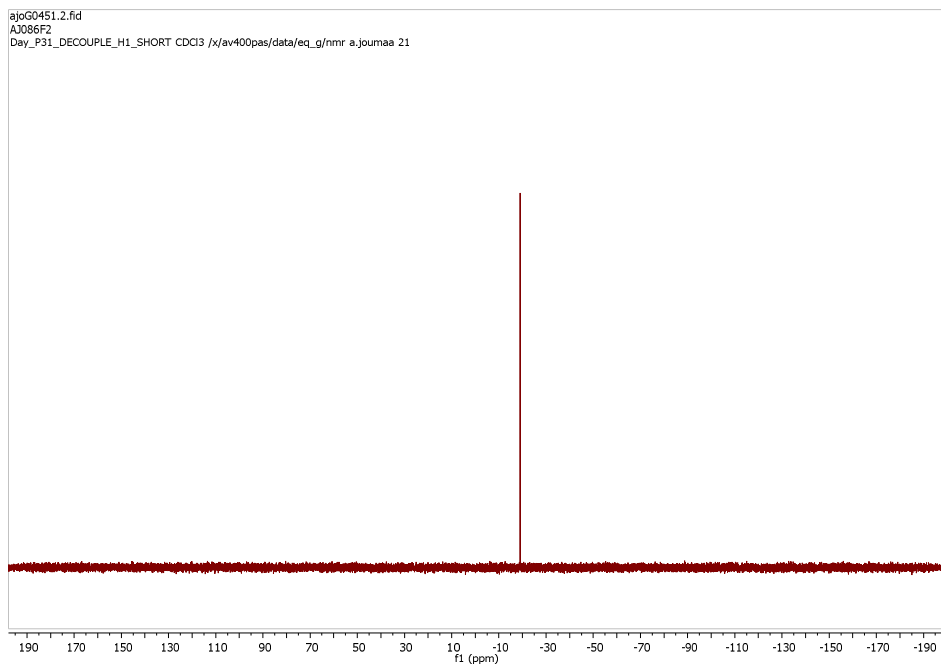


Figure S1.  $^{31}\text{P}\{^1\text{H}\}$  NMR of compound **1** in  $\text{CDCl}_3$ .

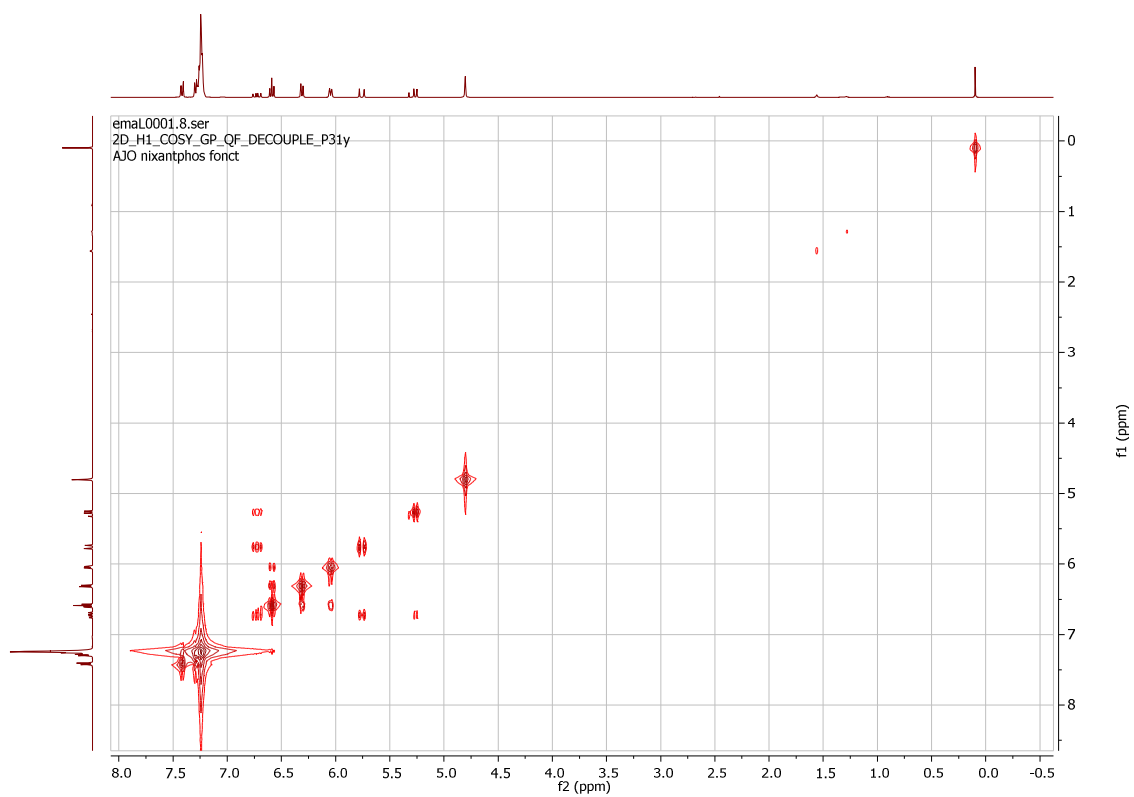


Figure S2.  $^1\text{H}\{^{31}\text{P}\}$  COSY NMR of compound **1** in  $\text{CDCl}_3$ .

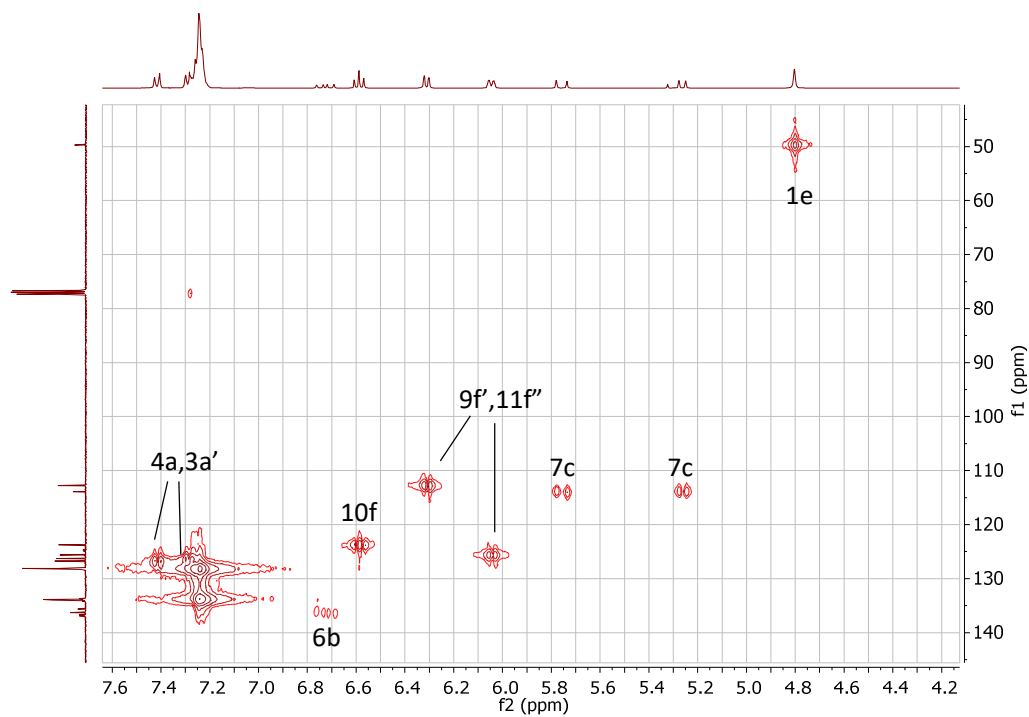


Figure S3.  $^1\text{H}$ - $^{13}\text{C}\{^{31}\text{P}\}$  HMQC of compound **1** in  $\text{CDCl}_3$ .

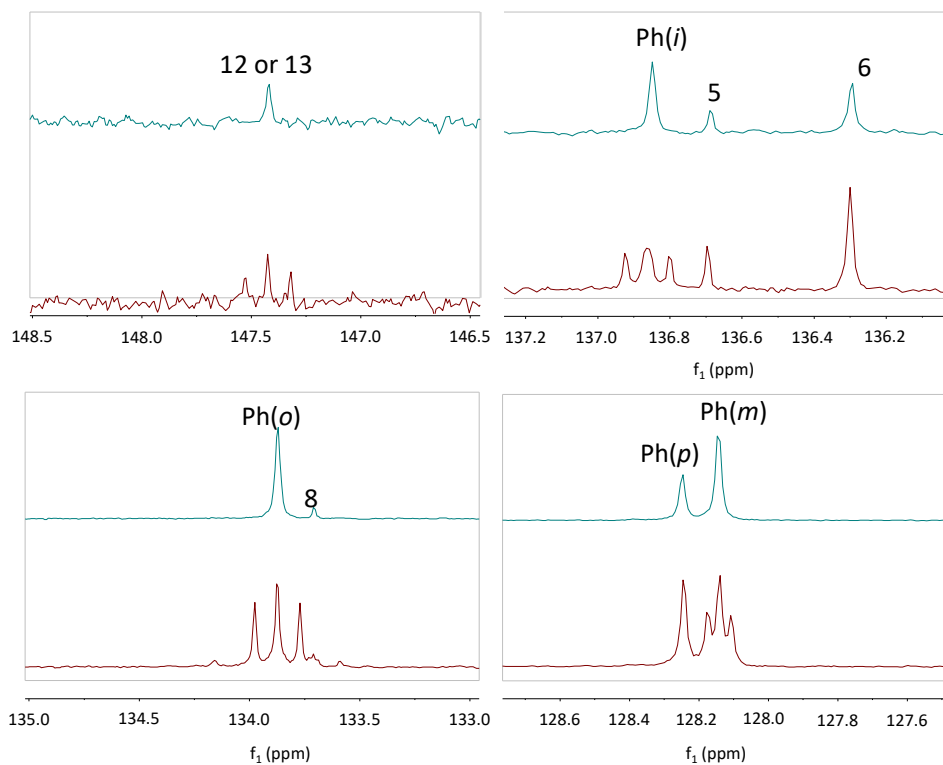


Figure S4. Comparison of  $^{13}\text{C}\{^1\text{H}\}$  (below) and  $^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$  (above) NMR spectra of **1** in  $\text{CDCl}_3$  for selected expanded regions of the spectrum.

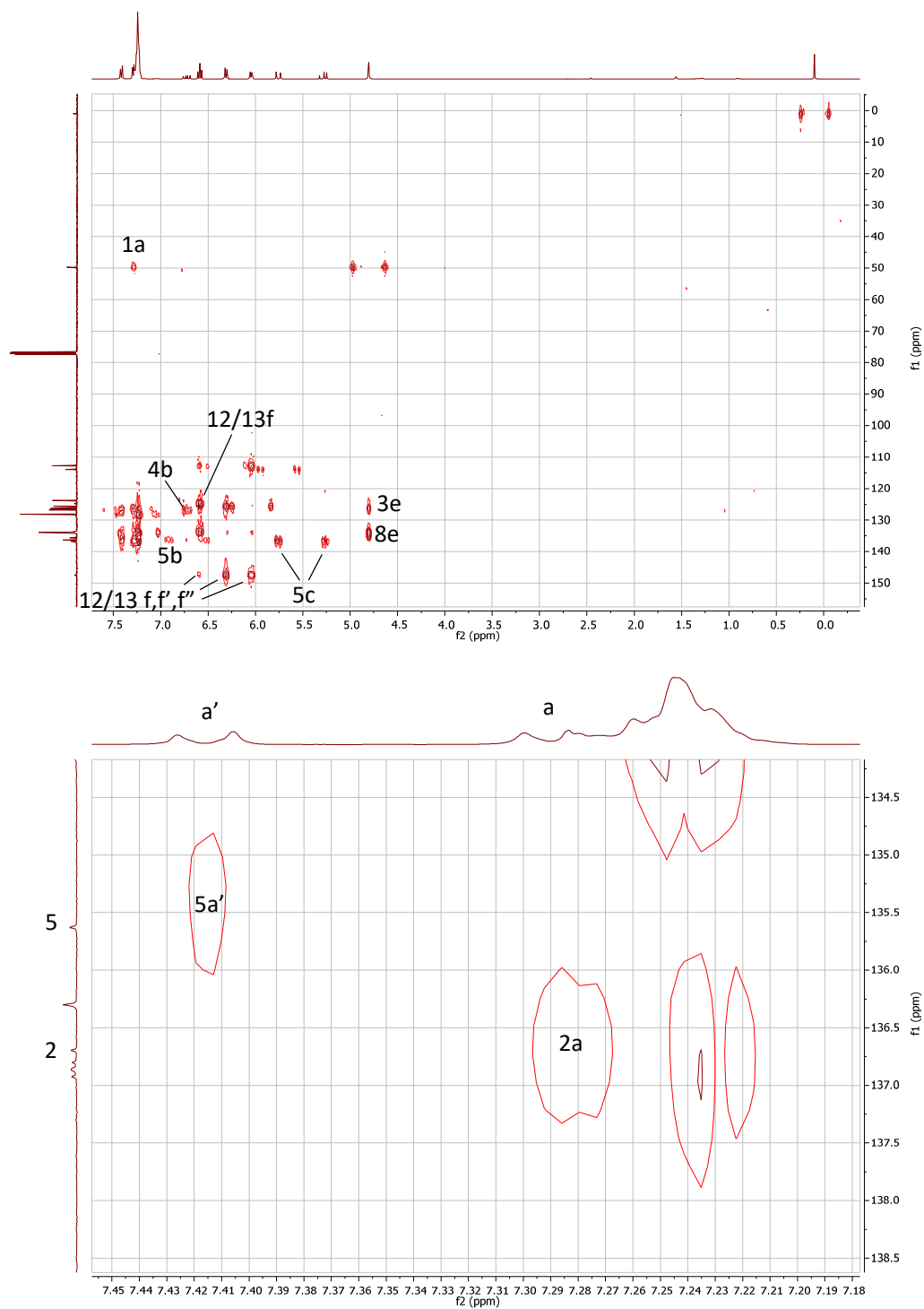


Figure S5.  $^1\text{H}$ - $^{13}\text{C}$  HMBC of compound **1** in  $\text{CDCl}_3$ .

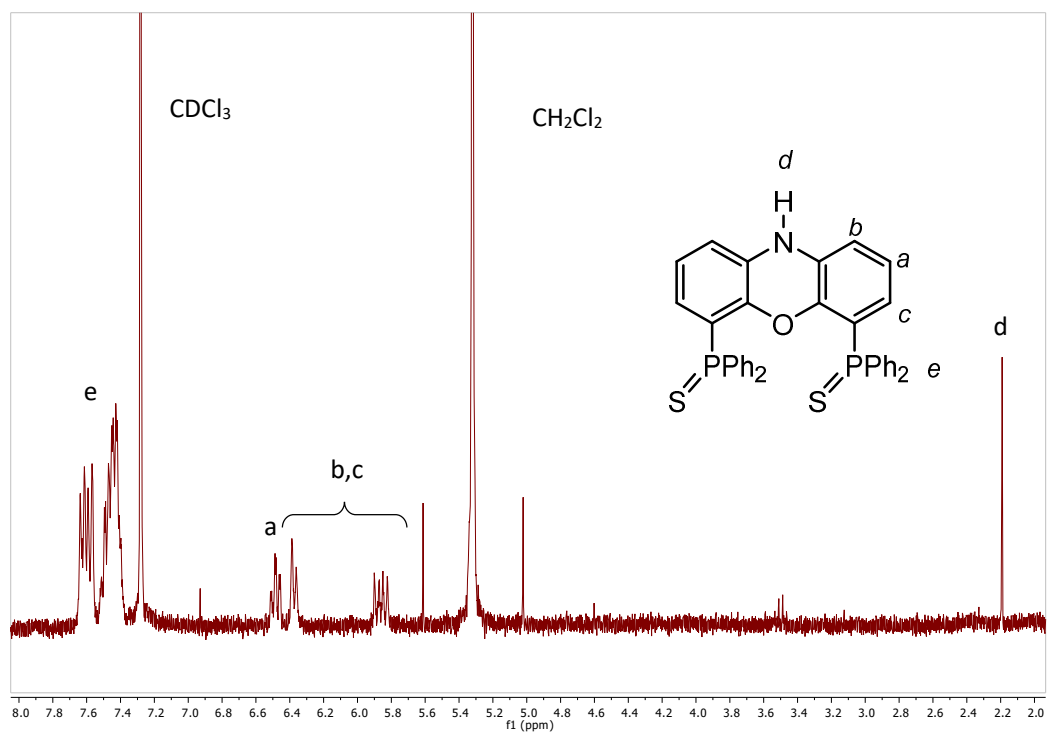


Figure S6.  $^1\text{H}$  NMR of compound **2** in  $\text{CDCl}_3$ .

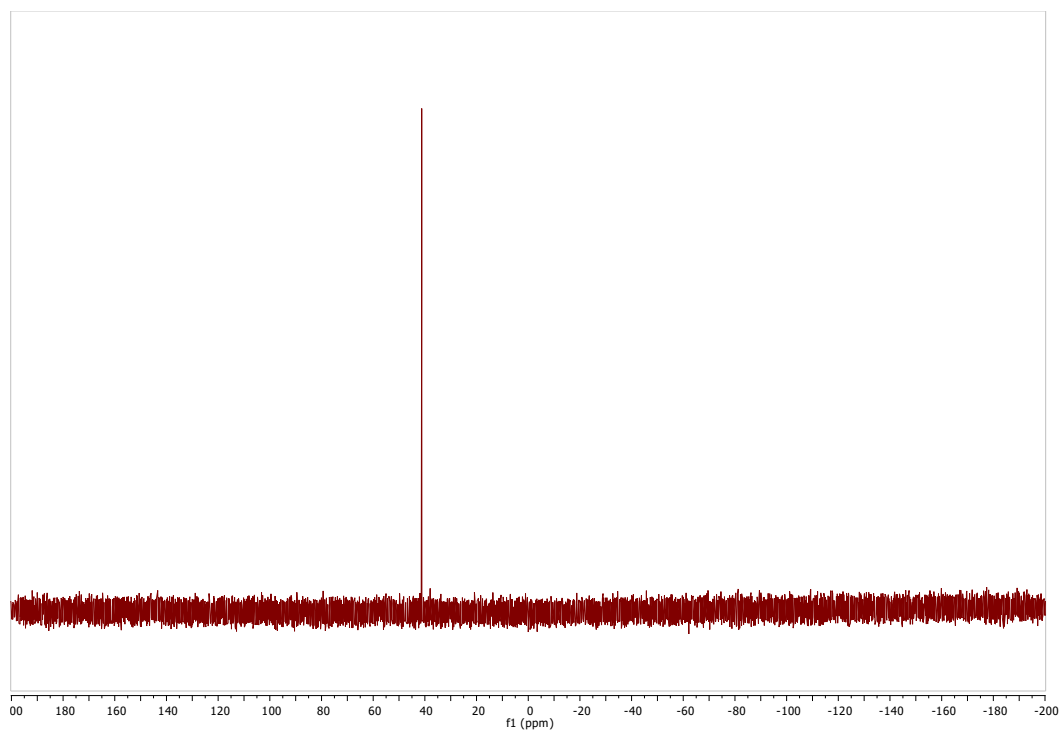


Figure S7.  $^{31}\text{P}\{^1\text{H}\}$  NMR of compound **2** in  $\text{CDCl}_3$ .

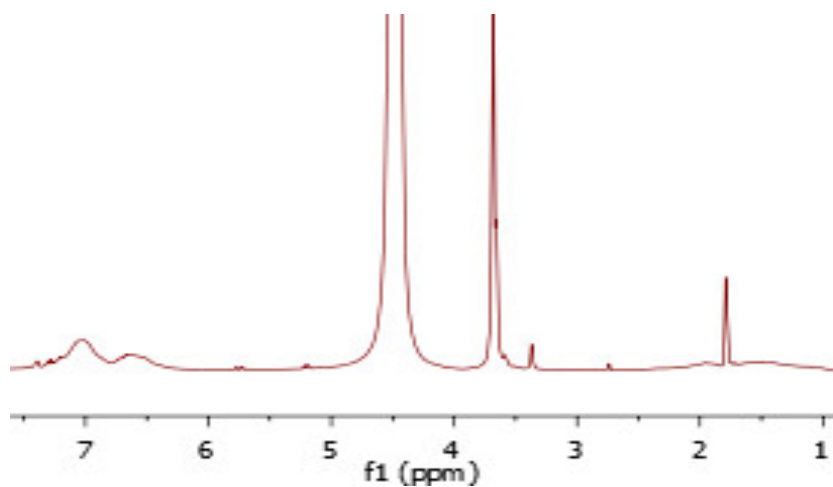


Figure S8.  $^1\text{H}$  NMR spectrum of Nixantphos@CCM in  $\text{THF-}d_8$ .

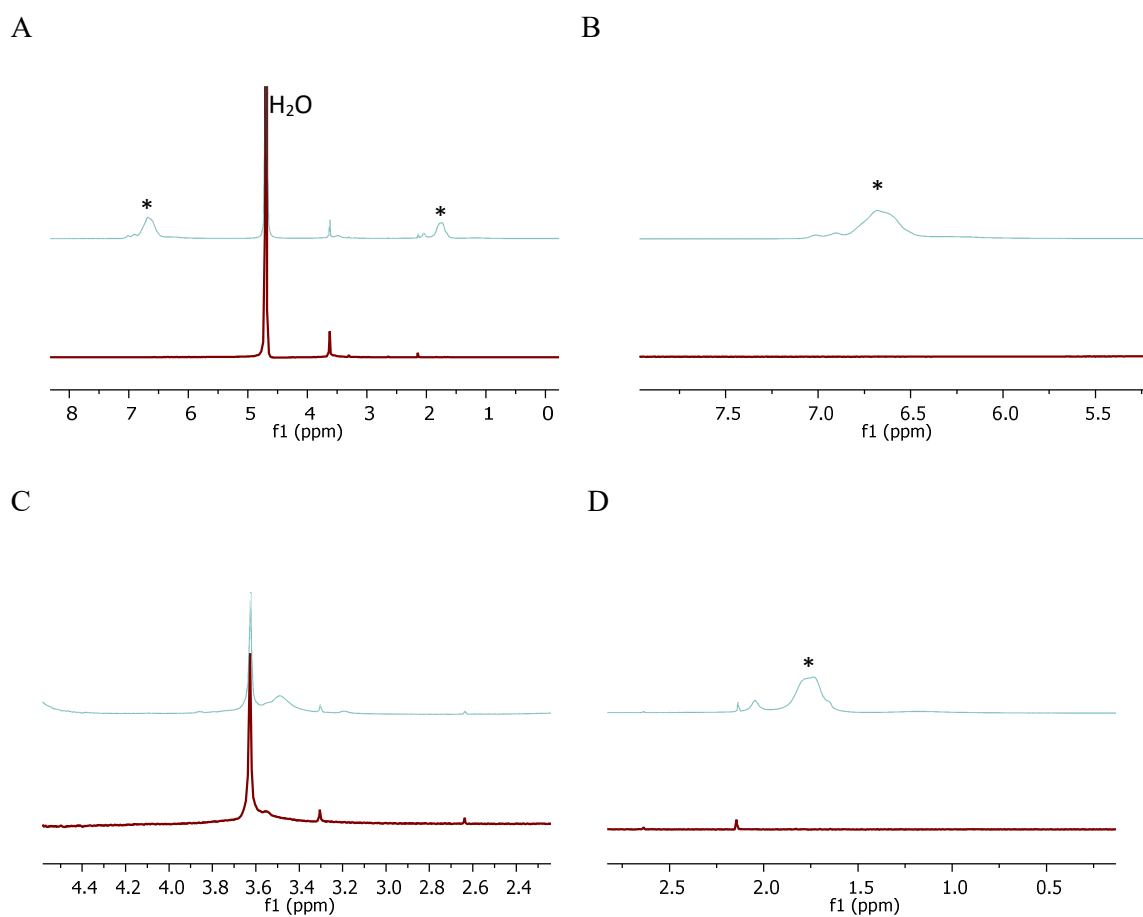


Figure S9. A:  $^1\text{H}$  NMR spectrum of Nixantphos@CCM in  $\text{D}_2\text{O}$  before (red) and after (light blue) toluene swelling. B-D: Expansions of selected regions. The resonances marked by an asterisk belong to the swelling toluene molecules.

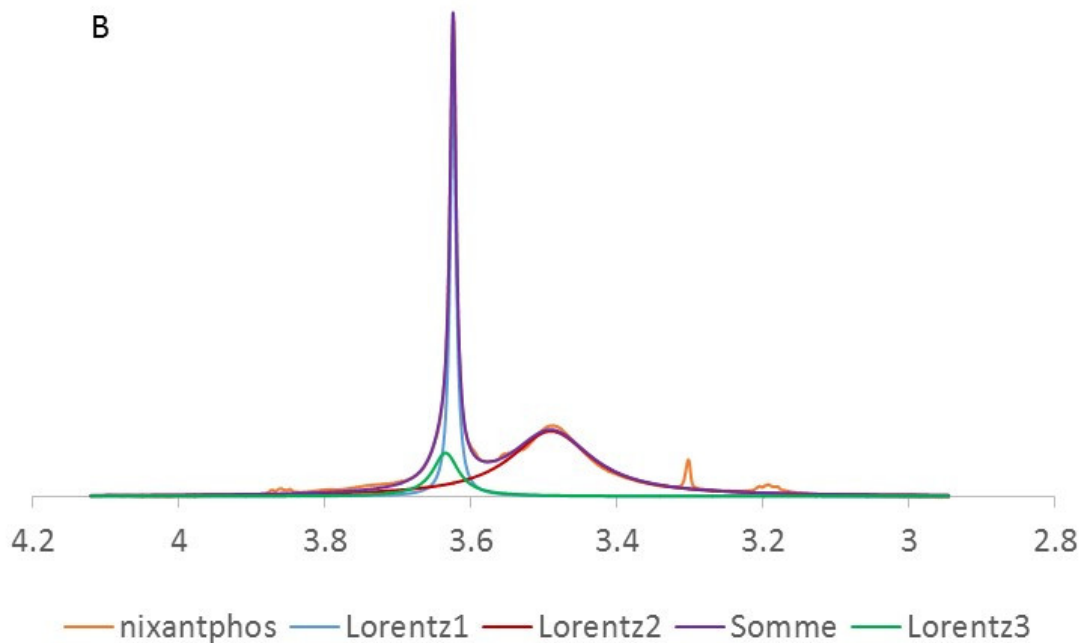
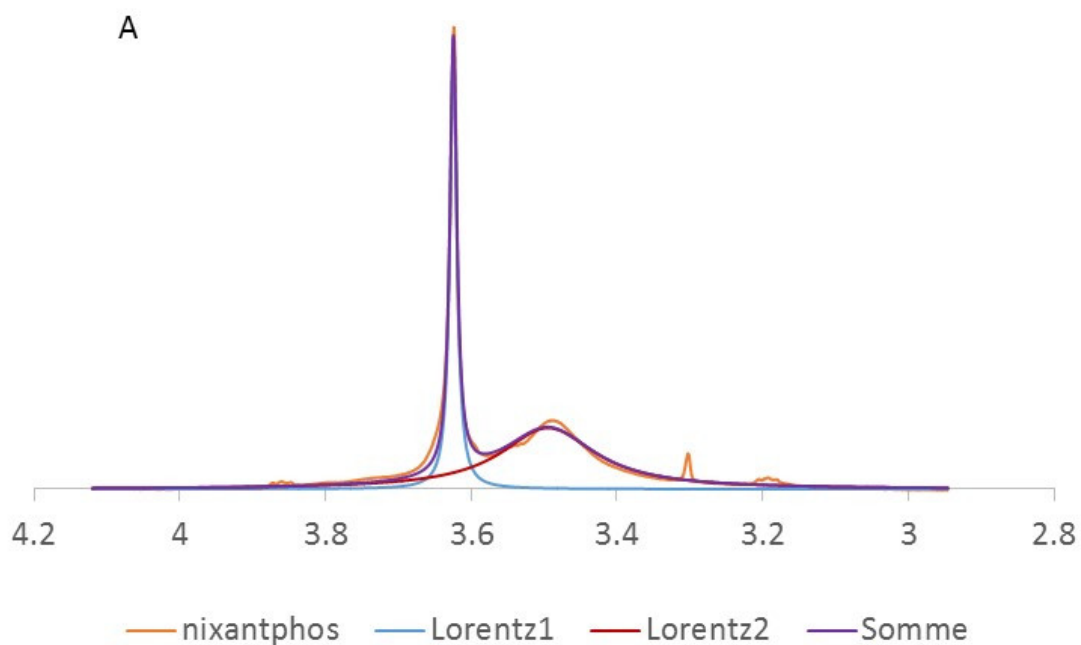


Figure S10. Expansion of the  $^1\text{H}$  NMR spectrum of toluene-swollen Nixantphos@CCM in  $\text{D}_2\text{O}$  in the PEO resonance region and deconvolution of the  $\text{CH}_2$  proton resonance as sum of two (A) or three (B) Lorentzian functions.

### Interpretation of the PEO resonance region (following ref. [1])

The proton resonances of the PEO chains (CH<sub>2</sub> and CH<sub>3</sub>) are split into two signals, one broader and one sharper, because of a core-shell interface structuring, placing a fraction of the chains inside the core while the others are solvated in the aqueous phase. The sharper resonances at  $\delta$  3.62 (for the CH<sub>2</sub> protons) and 3.30 (for the CH<sub>3</sub> protons at the chain end) are assigned to the more mobile chains in the water phase and the broader ones at  $\delta$  3.49 (for the CH<sub>2</sub> protons) and 3.19 (for the CH<sub>3</sub> protons) belong to the chains solvated by toluene within the core. The deconvolution of the larger CH<sub>2</sub> resonance as sums of Lorentzian functions provides the fraction of the chains in each phase. While the use of two Lorentzian functions was found to provide an excellent fit for the <sup>1</sup>H NMR spectrum of the previously reported TPP@CCM,<sup>[1]</sup> in the present case the agreement between experimental and simulated spectrum is of lower quality, see Figure S7A. A better fit can be obtained using the sum of three Lorentzian functions, as shown in Figure S7B. The optimized fractions are of 29.7 % for the sharp peak of the water-solvated protons (Lorentz 1 at  $\delta$  3.62), 57.5 % for the broader peak of the toluene-solvated protons in the core (Lorentz 2 at  $\delta$  3.49) and 12.8 % for the third population (Lorentz 3 at  $\delta$  3.64). This latter population is probably caused by a few CH<sub>2</sub> functions that are located near the water-toluene interphase.

[1] S. Chen, F. Gayet, E. Manoury, A. Joumaa, M. Lansalot, F. D'Agosto and R. Poli, *Chem. Eur. J.* **2016**, *22*, 6302 – 6313.