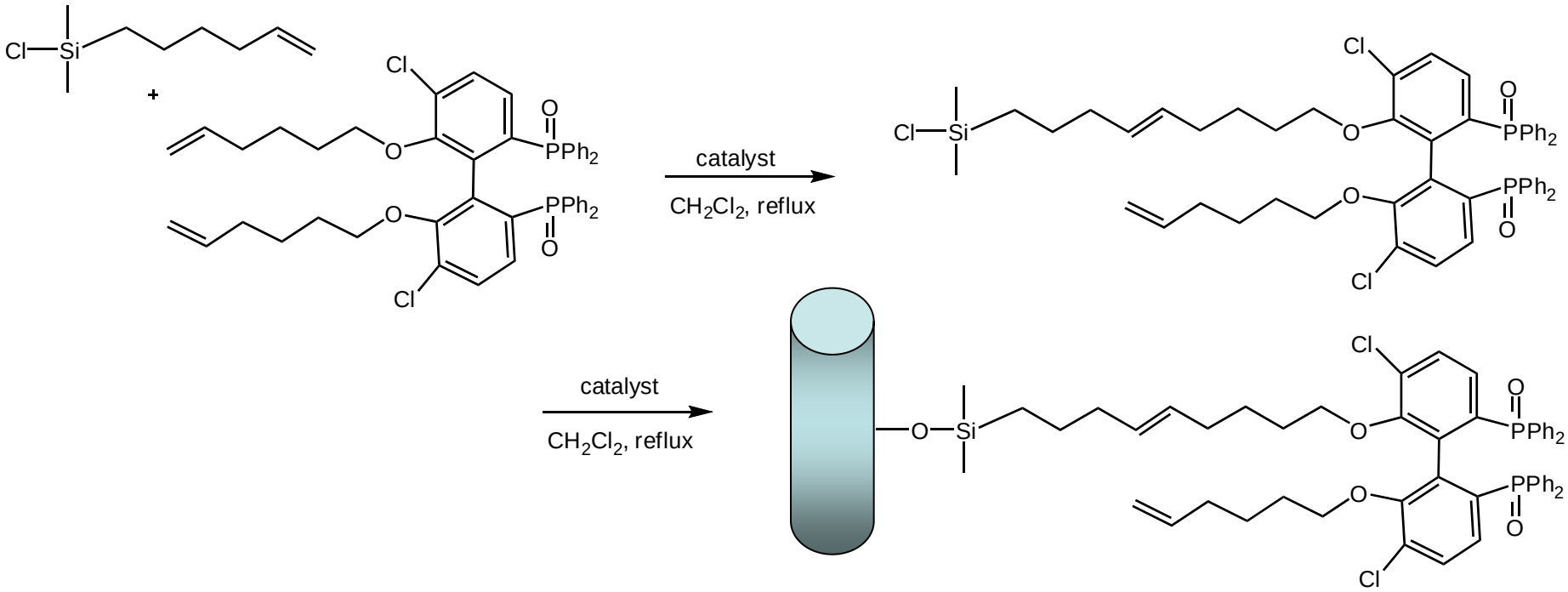
Literature Report 2009-10-13

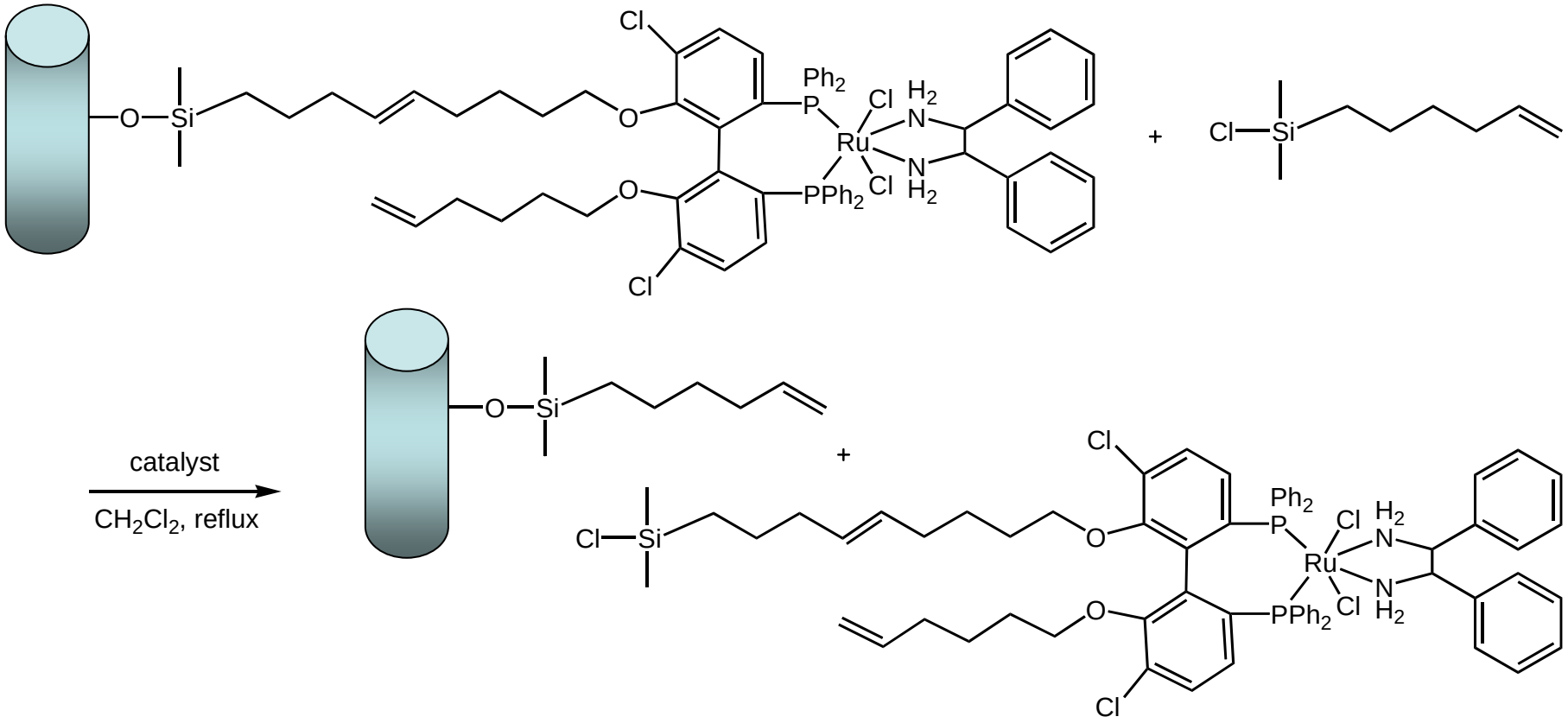
Reversible Immobilization of a Molecular Catalyst and Challenges of Catalyst Characterization

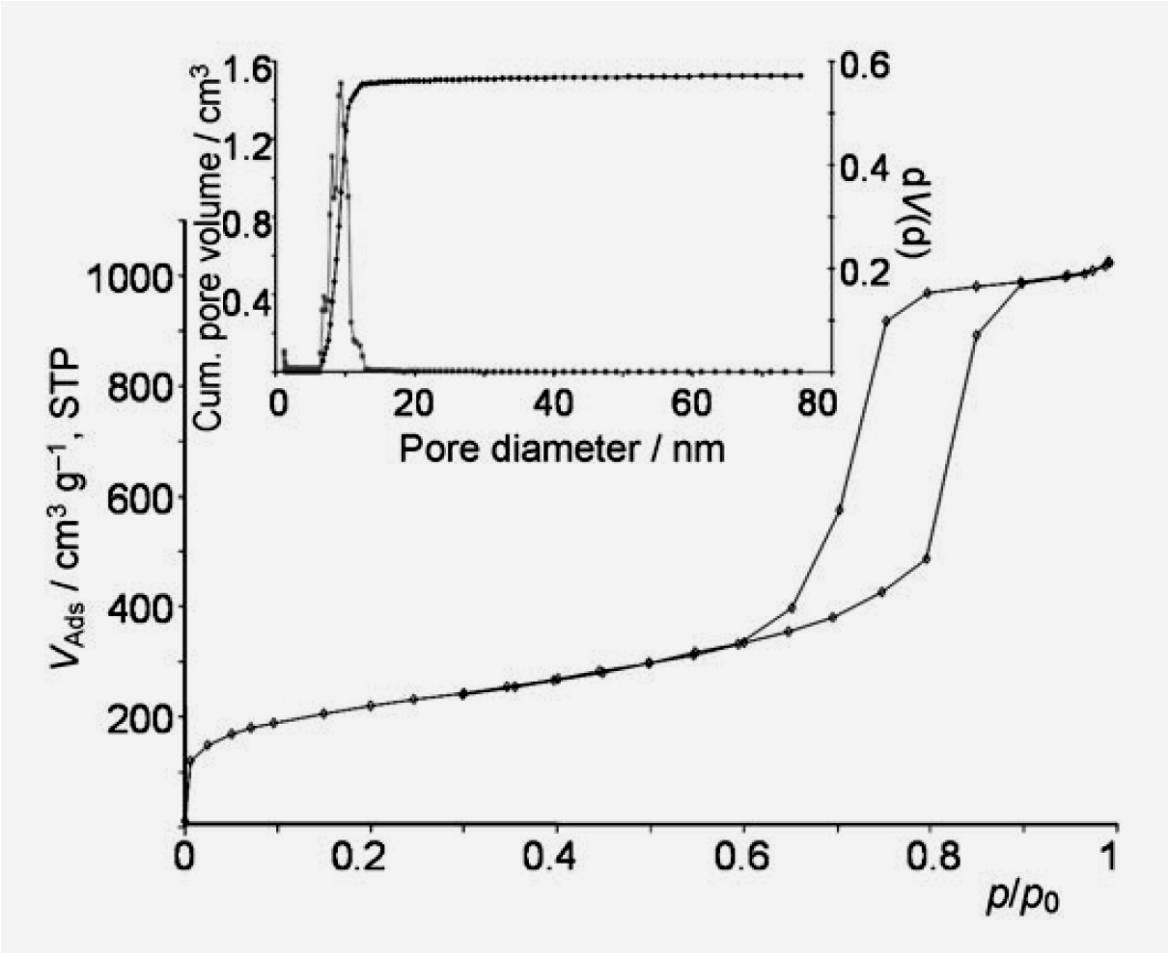
Yang Yan

F. Schüth* *et al*

Chem. Eur. J. **2009**, *15*, 9183-9190


Cl
Si
+
Cl
O
PPh2
O
PPh2
O
Cl
catalyst
CH2Cl2, reflux
Cl
Si
Cl
O
O
PPh2
PPh2
O
Cl
catalyst
CH2Cl2, reflux
O
Si
Cl
O
O
PPh2
PPh2
O
Cl


catalyst
CH2Cl2, reflux



	S_{BET} (m^2g^{-1})	Pore size (nm)	V_t (cm^3g^{-1})
SBA-15	743	9.4	1.5

$Q^1(SiO_{1/2}(OH)_3)$, Q^2 $(SiO(OH)_2)$,
Q^3 $(SiO_{3/2}OH)$ and Q^4 (SiO_2)

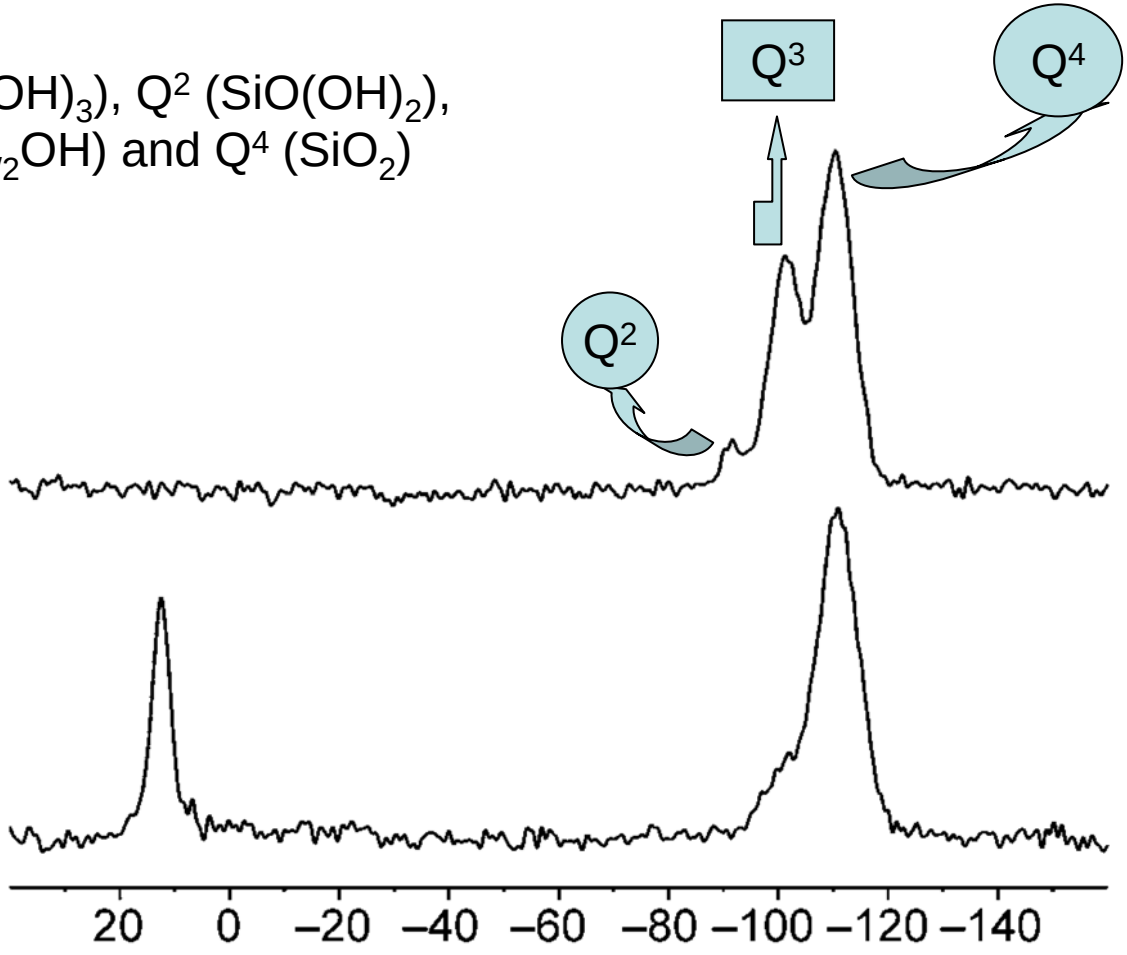


Figure 2. ^{29}Si MAS NMR spectra of blank (top) and trimethylsilylated (bottom) SBA-15 (number of scans: 3200; spinning rate: 12000).

24% of the silicon atoms are present as surface silanol groups

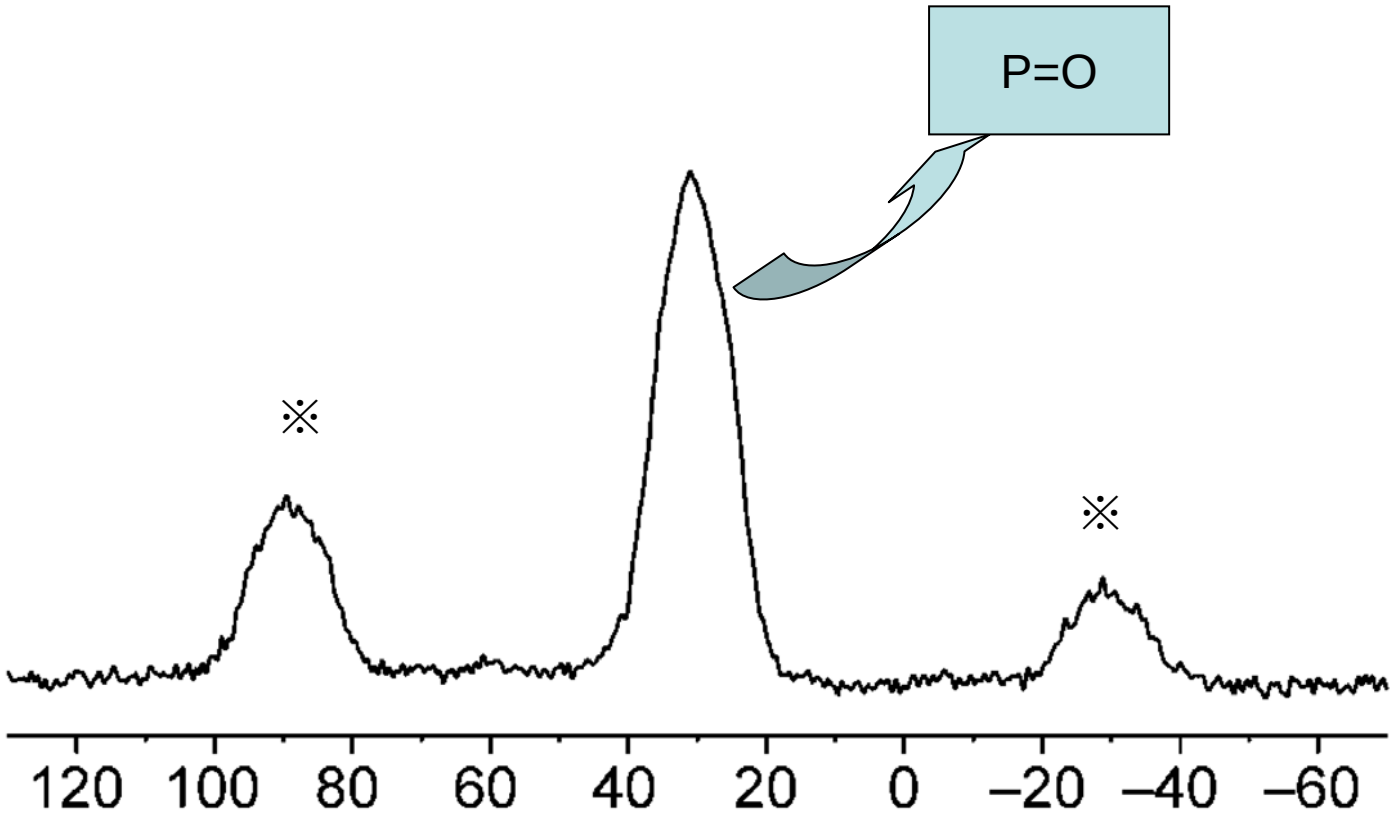


Figure 3. Solid-state ^{31}P MAS NMR spectrum of the phosphine oxide ligand immobilized on SBA-15 (number of scans: 4000, spinning rate 12000).

Spinning side bands at 30 and 90 ppm

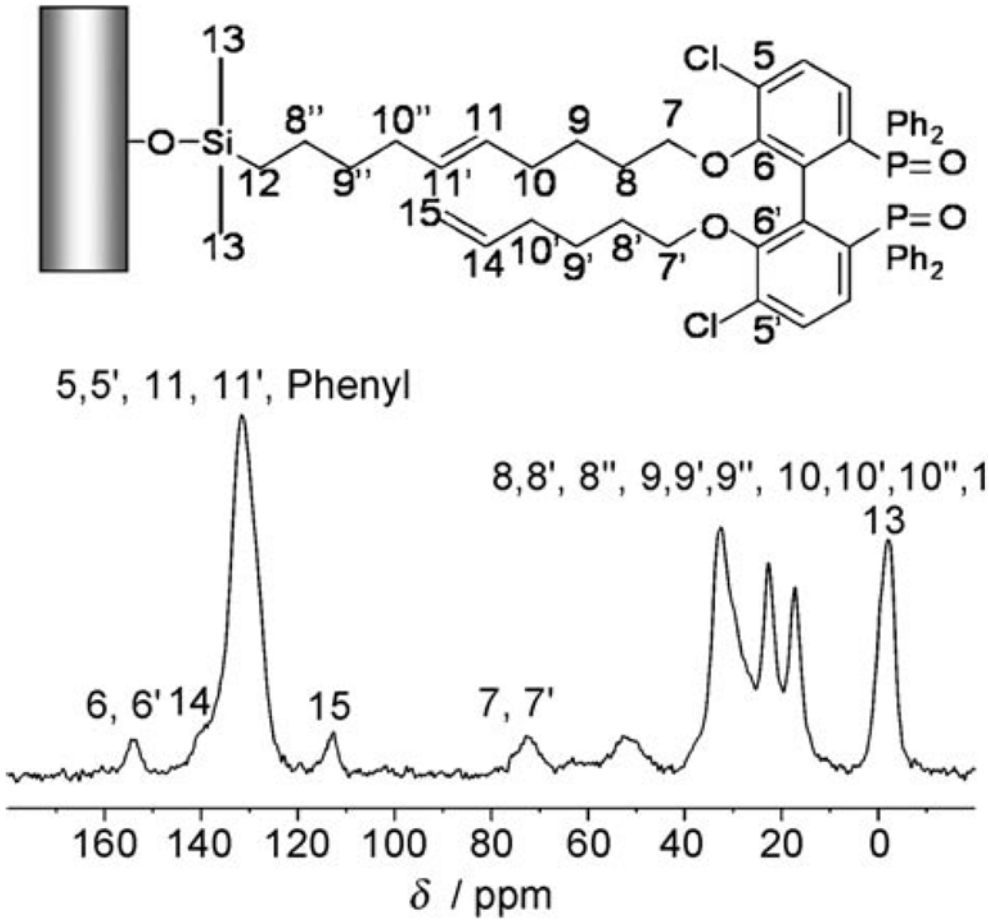


Figure 4. Solid-state ^{13}C CP/MAS NMR spectrum of the phosphine oxide ligand immobilized on SBA-15 with assignment of the resonances to the corresponding carbon atoms (number of scans: 36000, spinning rate:10000).

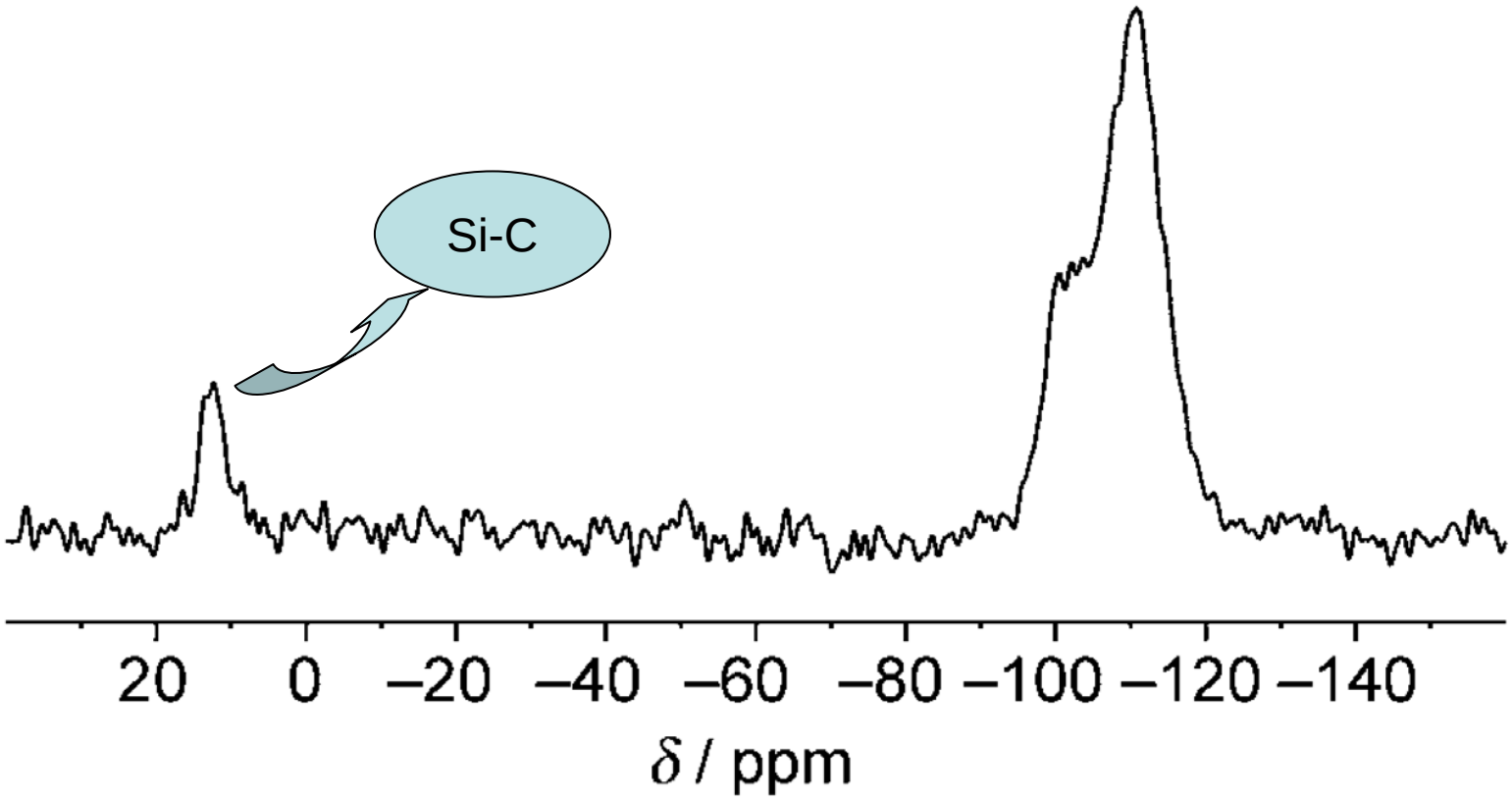


Figure 5. Solid-state ^{29}Si MAS NMR spectrum of the phosphine oxide ligand immobilized on SBA-15 (number of scans: 2400, spinning rate: 10000).

Confirms the successful covalent immobilization of the ligand

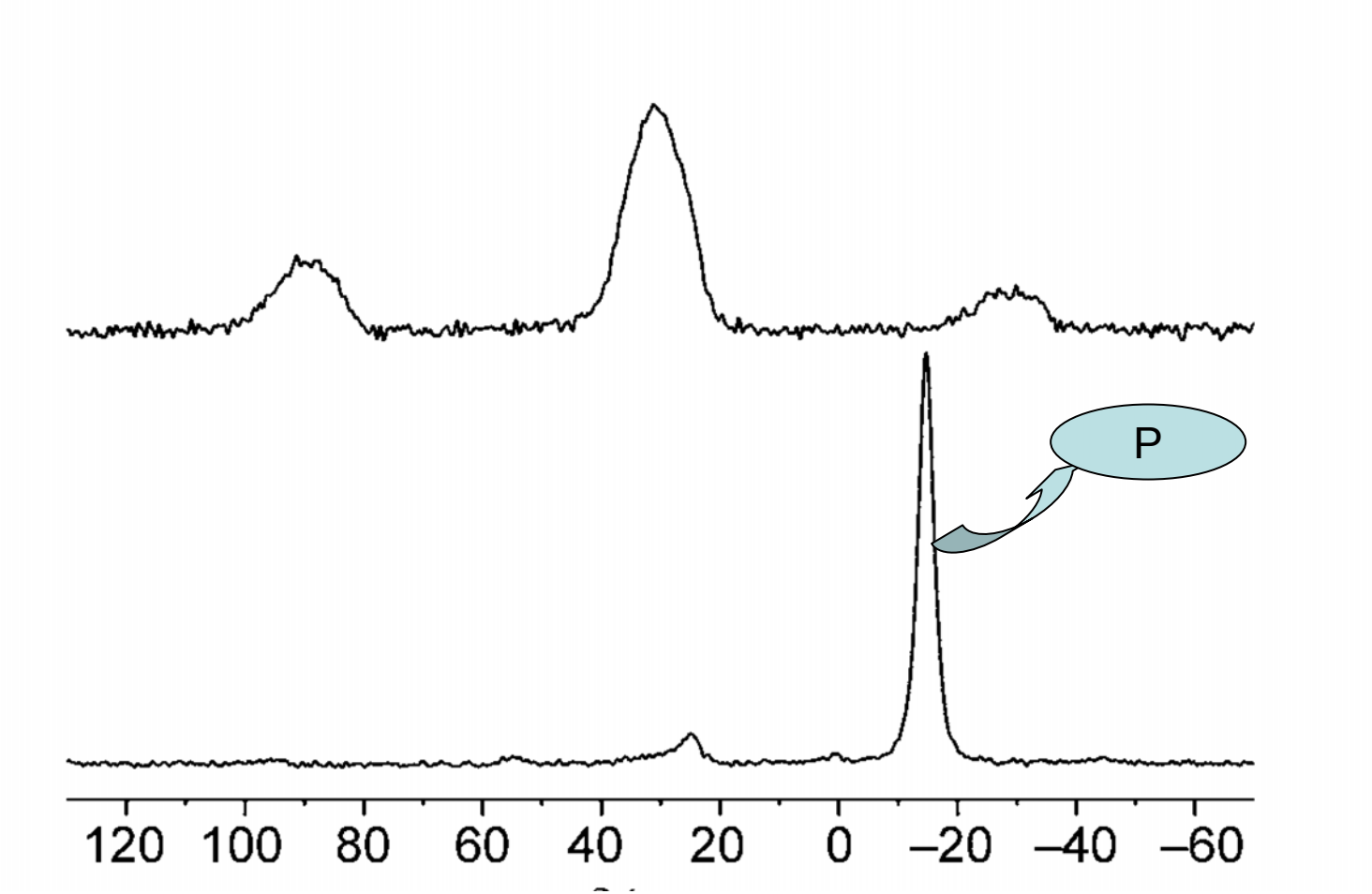


Figure 6. Solid-state ^{31}P MAS NMR spectra of the immobilized phosphine ligands before (top) and after (bottom) the reduction (number of scans: 4000, spinning rate: 12000).

More than 95% of the phosphorus atoms were reduced

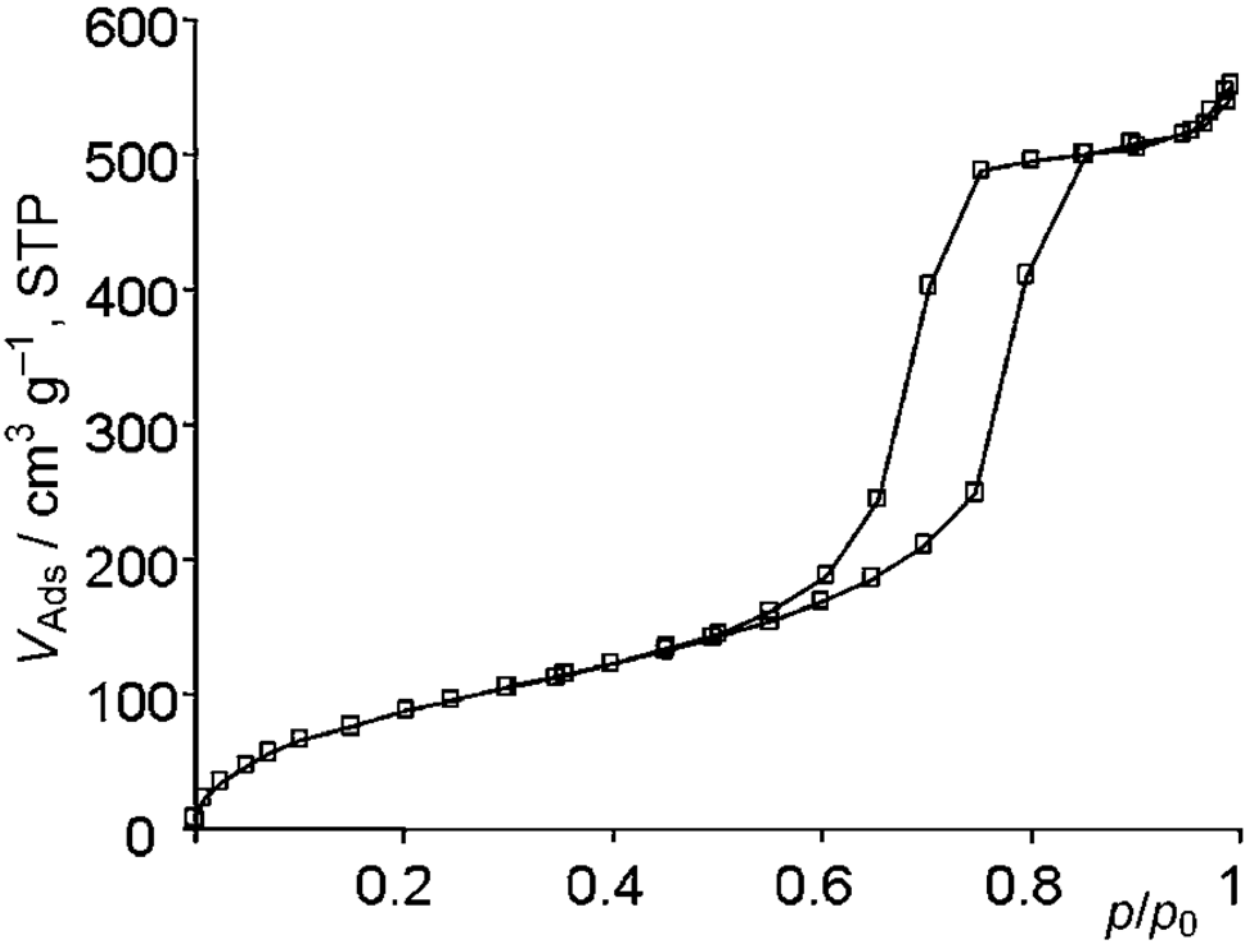


Figure 7. Nitrogen sorption isotherm of the SBA-15 after immobilization and reduction of the phosphine ligand.

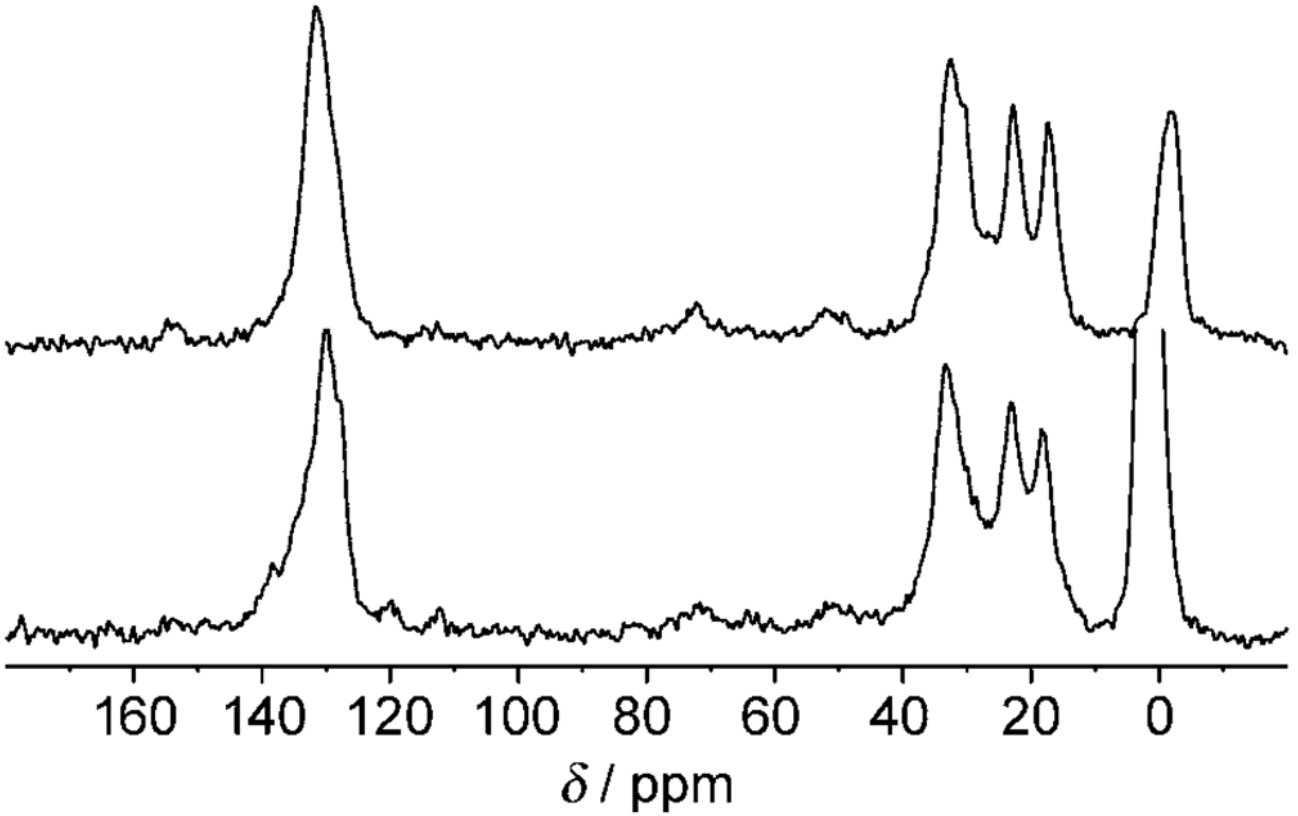


Figure 8. ^{13}C CP/MAS NMR spectra of the immobilized ligand before (top) and after (bottom) the reduction procedure (number of scans: 36000, spinning rate: 10000).

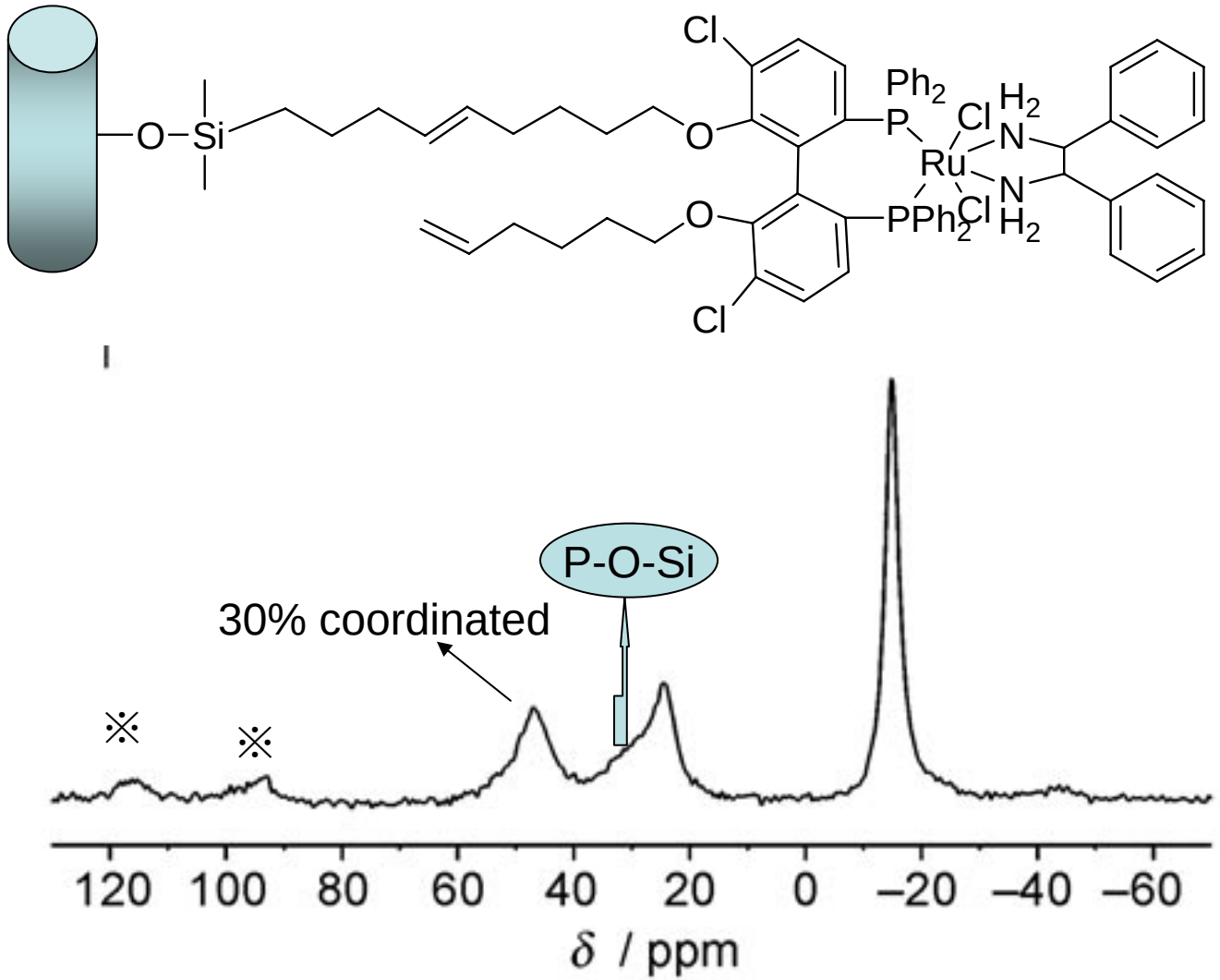


Figure 9. Solid-state ^{31}P MAS NMR spectrum of the immobilized catalyst after reaction with the ruthenium precursor and Dpen (number of scans: 4000, spinning rate 14000).

Catalytic activity of homogeneous and immobilized molecular catalysts with different ligands in the hydrogenation of acetophenone to phenylethanol.

Entry	Ligand	TON	TOF[h^{-1}]	Ee [%]
1	tol-Binap	8200	342	61
2	hexO-biphep	10000	417	62
3	SBA15-(hexO -biphep)	3000	125	75

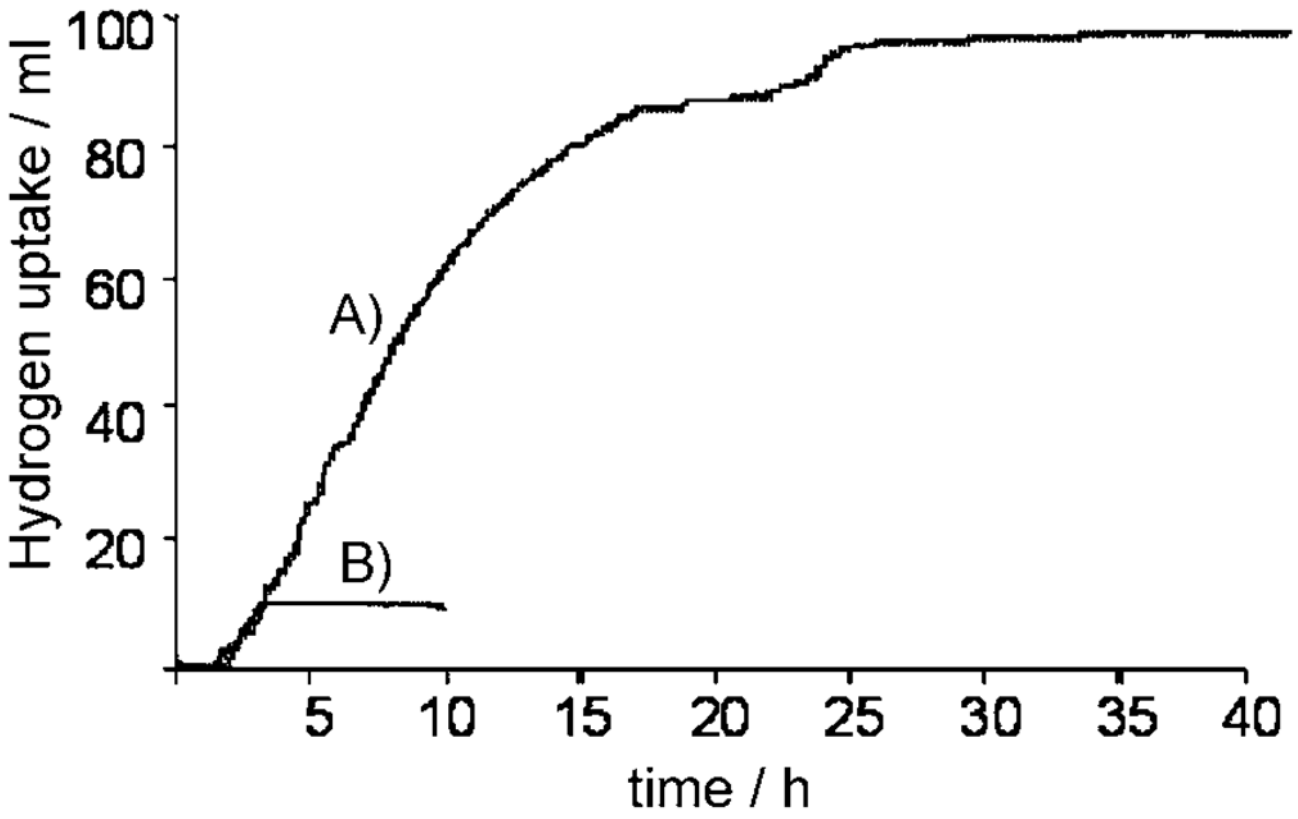


Figure 10. Hydrogen uptake with reaction time for the hydrogenation of acetophenone applying the immobilized molecular catalyst (A) and hydrogen uptake of the liquid phase after filtration (after 3 h) (B).

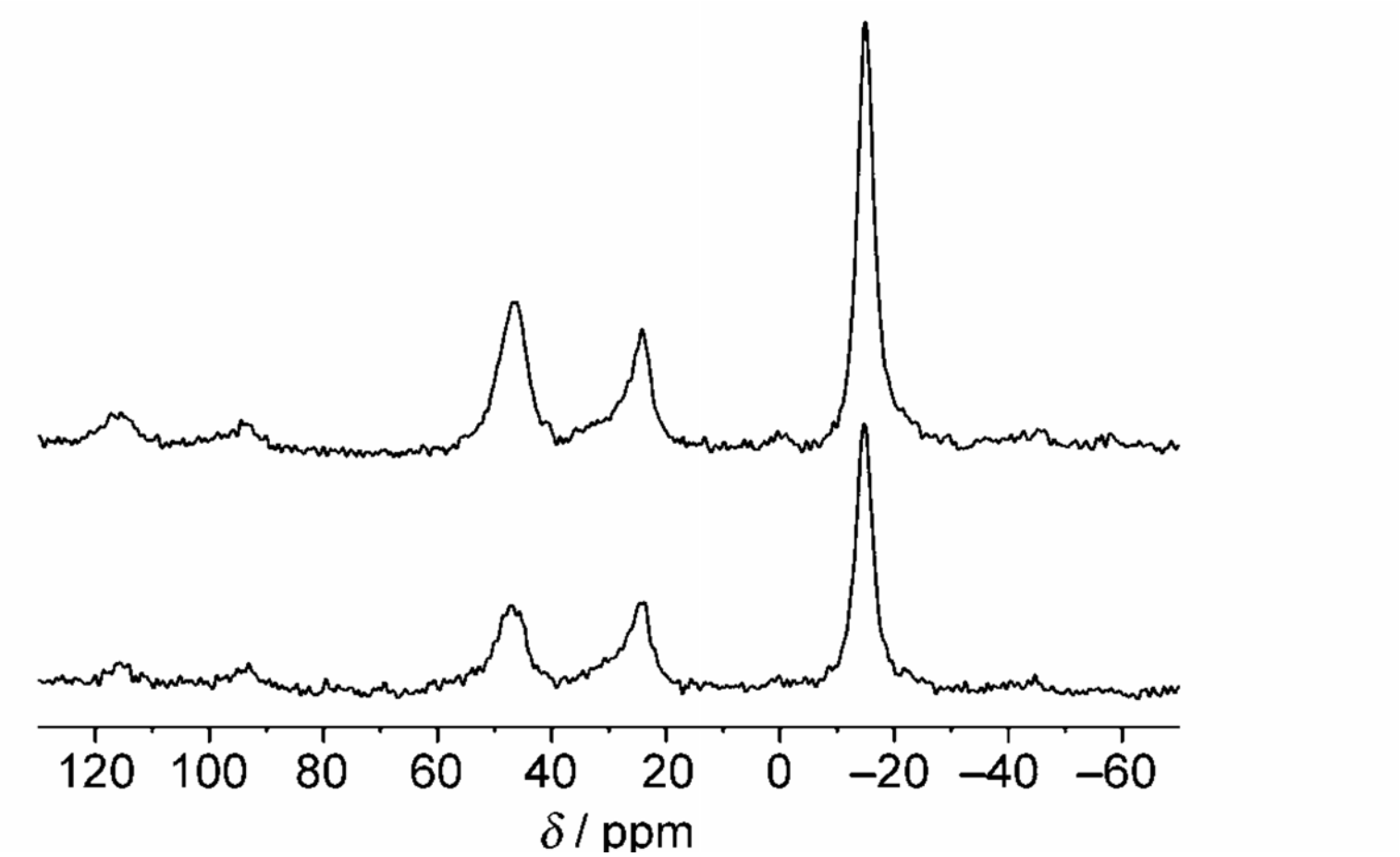


Figure 11. Solid-state ^{31}P MAS NMR spectra were measured before (top) and after (bottom) the back-metathesis reaction (number of scans: 4000, spinning rate: 14000).

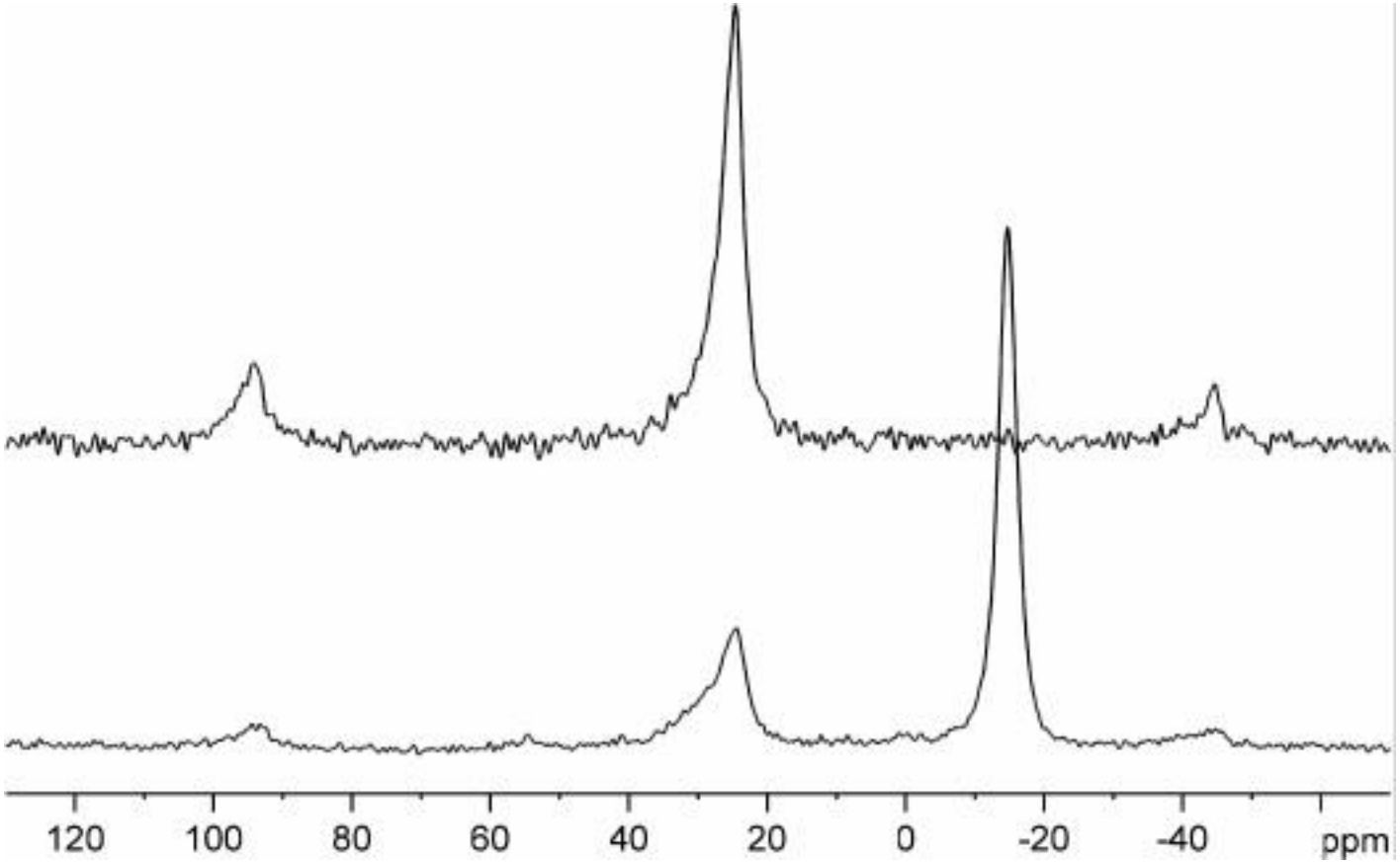


Figure S3. Solid-state ^{31}P MAS NMR spectrum of the molecular catalyst re-immobilized onto fresh support material before (top) and after reduction (bottom), (number of scans: 4000, spinning rate 14000).

We therefore studied a concept to covalently immobilize molecular catalysts through a reversible anchoring reaction. If successful, the molecular catalysts could be removed from the support after use, re-purified and subsequently be re-immobilized. In this approach, we investigated the cross-metathesis reaction between alkene-chlorosilanes and molecular catalysts bearing a terminal olefin group as a tool with which to reversibly immobilize molecular catalysts. In this reaction, an alkene-modified ligand and an alkenyl-chlorosilane are reacted through a cross metathesis reaction and the reaction product is immobilized on a silica support. Since cross-metathesis reactions are reversible, a back-metathesis reaction becomes possible to cut-off the molecular catalyst from the support after use. Accordingly, the molecular catalyst could be recycled and immobilized on fresh support material. The only prerequisite for this approach is the presence of olefin groups. Hence, it can widely be used to reversibly immobilize various. types of ligand molecules or complexes.

Cross-metathesis reactions could be applied for a reversible, but covalent immobilization of molecular catalysts. Hexenoxy functionalized biphepO type ligands and hexenyldimethylchlorosilane were reacted in a cross-metathesis reaction and the reaction product was subsequently anchored on a silica support material. The immobilized phosphine oxide ligands could be reduced and the desired ruthenium-based hydrogenation catalysts could be formed. The immobilized molecular catalyst was tested in the hydrogenation of acetophenone to phenylethanol. The immobilized molecular catalyst showed slightly reduced activity compared to the homogeneous system, the enantiomeric excess, however, was improved. Additionally, the envisaged back metathesis to allow cleavage of the complex from the support followed by re-immobilization on a fresh support material could be achieved. Although further optimizations of the single reaction steps are necessary, we believe that the method is widely applicable and offers an interesting approach to covalently, but reversibly, immobilize various. molecular catalysts.