SPHOS - A molecule containing ^{1}H, ^{13}C and ^{31}P nuclei

SPHOS (2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl) is a widely used air-stable phosphine ligand employed together with e.g palladium in a range of different catalytic reactions. Figure 1 shows the ^{1}H NMR spectrum of a 800 mM SPHOS sample in $CDCl_3$ measured in a single scan taking 15 seconds to acquire.

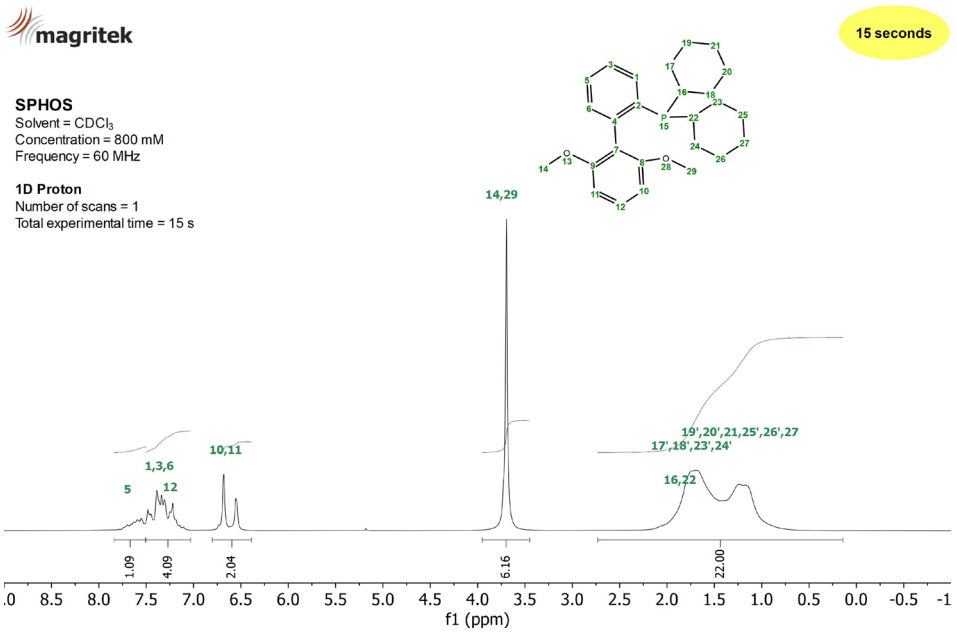

Figure 1: ^{1}H NMR spectrum of a 800 mM SPHOS sample in $CDCl_3$ measured on a Spinsolve 60 MHz system in a single scan.

2D COSY

The 2D COSY experiment allows one to identify coupled ^{1}H nuclei as they generate cross peaks out of the diagonal of the 2D data set. In Figure 2 it can be nicely observed that the aliphatic proton atoms couple to each other (light blue). In the same manner the aromatic protons at position 10, 11 and 12 couple with each other indicated by the respective cross peaks (orange).

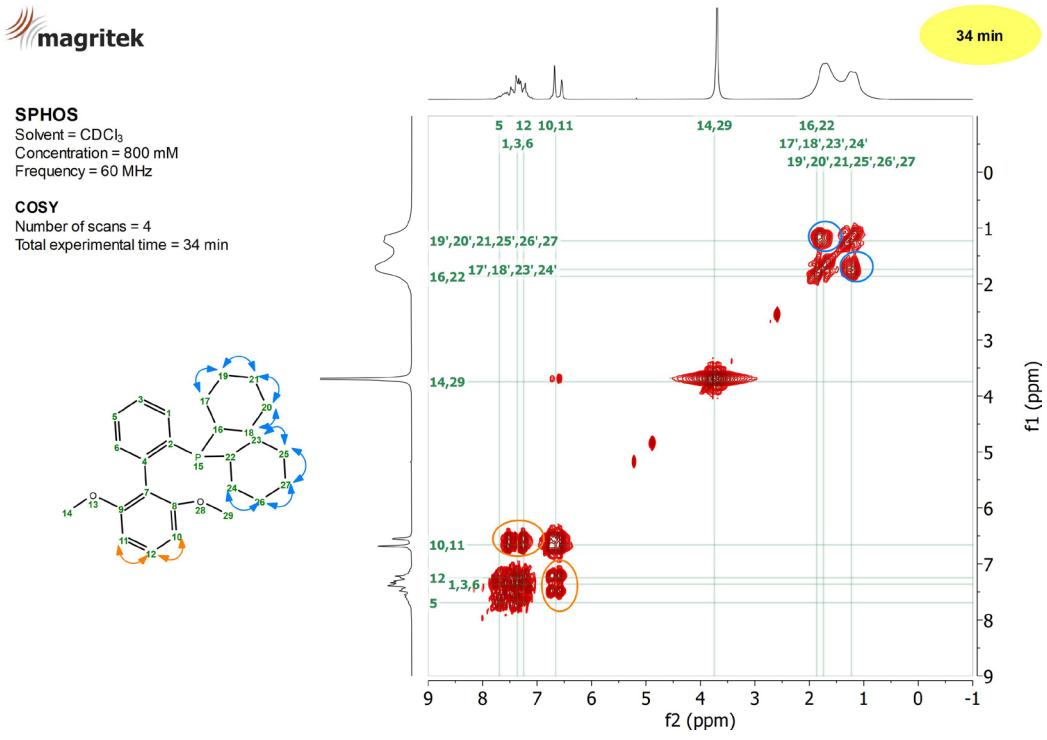

Figure 2: ^{1}H 2D COSY experiment of a 800 mM SPHOS sample in $CDCl_3$ acquired in 34 minutes on a Spinsolve 60 MHz system.

^{13}C Spectra

Figure 3 shows the full ^{13}C NMR spectra of a 800 mM SPHOS sample in $CDCl_3$ acquired using NOE and ^{1}H decoupling (top spectrum). The bottom spectrum shows a zoom of the chemical shift ranges between 110-150 ppm and 20-40 ppm. All expected resonances can be clearly identified even with the multiplicities defined by the different coupling constants between the ^{13}C and the ^{31}P atoms. This underlines the exceptional signal-to-noise ratio and resolution of the Spinsolve spectrometer.

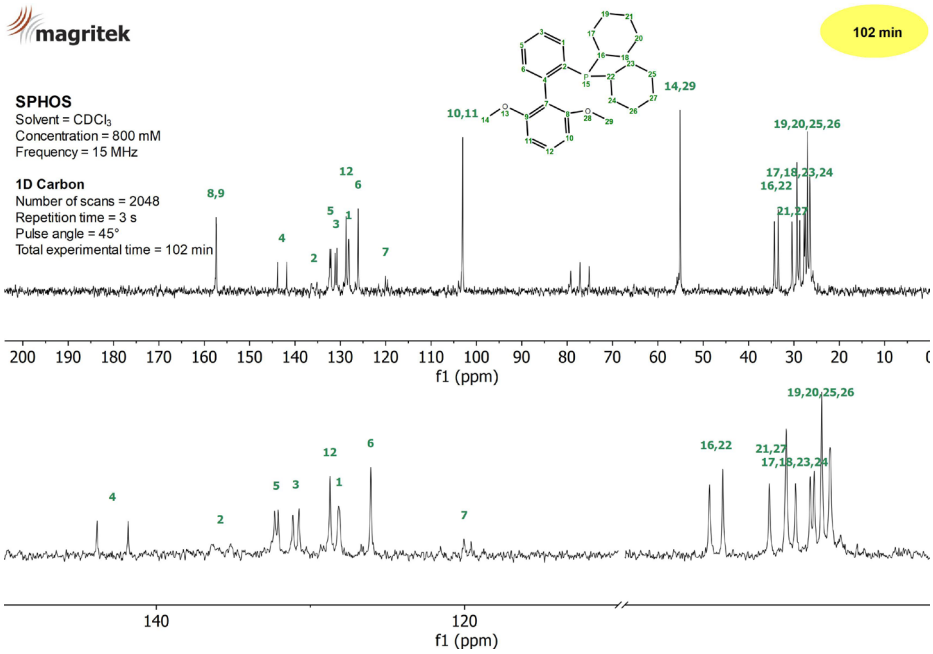

Figure 3: Carbon NMR spectra of a 800 mM SPHOS sample in $CDCl_3$ measured on a Spinsolve 60 MHz system using NOE and ^{1}H decoupling. Full spectrum (top), zoom to 110-150 ppm and 20-40 ppm (bottom).

^{13}C DEPT Spectra

Figure 4 shows the ^{13}C NMR spectra of a 800 mM SPHOS sample in $CDCl_3$ acquired using NOE and DEPT polarization transfer from ^{1}H to ^{13}C and ^{1}H decoupling. While the 1D Carbon experiment using NOE (top spectrum) is sensitive to all ^{13}C nuclei in the sample, the DEPT experiments show only ^{13}C nuclei directly attached to ^{1}H and can be used for spectral editing. Since the peaks for the carbon atoms 2, 4, 7, 8 and 9 do not show in the DEPT spectra they must correspond to the quaternary carbons. The DEPT-90 experiment gives only signal from CH groups, whilst the DEPT-45 and DEPT-135 potentially give signals of CH, CH_2 and CH_3 groups, where the CH_2 groups appear as negative peaks in the DEPT-135.

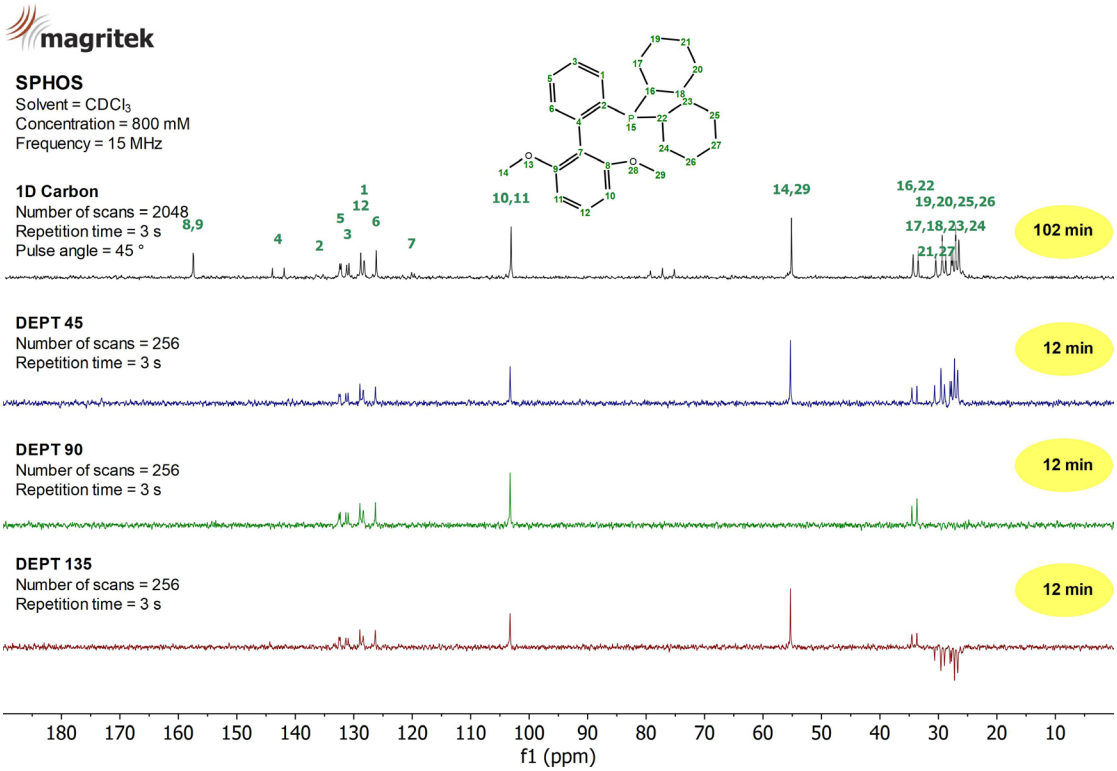

Figure 4: Carbon NMR spectra of a 800 mM SPHOS sample in $CDCl_3$ measured on a Spinsolve 60 MHz using NOE (top) and DEPT-45, -90 and -135 sequences.

2D JRES

The *J*-resolved experiment is useful to identify the chemical groups out of a complex samples mixture with generating a single line for each group by collapsing the *J*-coupling along the direct dimension. The multiplets are generated along the vertical dimension and allow an easier correlation of the signals to the corresponding peaks.

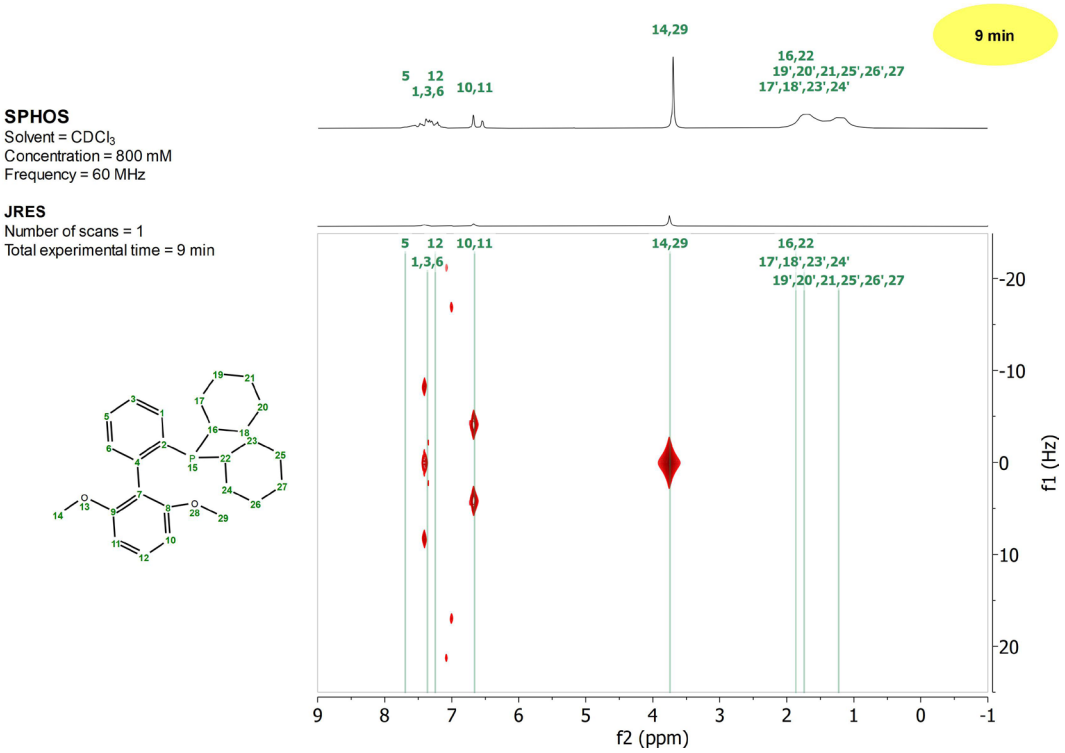

Figure 5: Homonuclear *J*-resolved spectrum of a 800 mM SPHOS sample in $CDCl_3$ measured on a Spinsolve 60 MHz system.

^{31}P spectrum

The ^{31}P spectrum of a 800 mM SPHOS sample in $CDCl_3$ is shown in Figure 6. One can clearly identify the single expected ^{31}P resonance at around -10 ppm for the phosphorus atom at position 15. The spectrum was acquired in 5 minutes with 64 scan cycles. In addition, also an impurity could be observed at around 46 ppm, most likely due to some sample degradation.

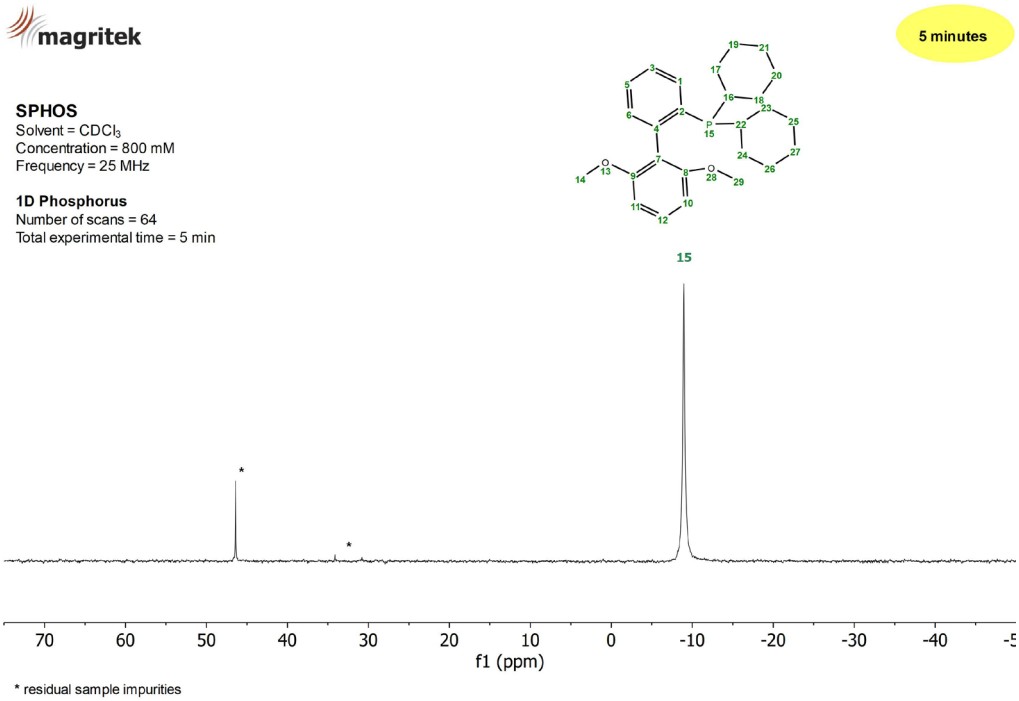

Figure 6: ^{31}P NMR spectrum of a 800 mM SPHOS sample in $CDCl_3$ measured on a Spinsolve 60 MHz system in 64 scans with a total measurement time of 5 minutes.

2D ^{31}P-HMBC

Figure 7 presents the ^{31}P-HMBC (Heteronuclear Multiple Bond Correlation) experiment of a 800 mM SPHOS sample in $CDCl_3$. Here, the long-range ^{1}H-^{31}P correlations can be observed for the phosphorus atom at position 15. It can clearly be seen that both couplings to the aromatic protons 1, 3, 5 and 6 (green) as well as the aliphatic protons (blue) are present.

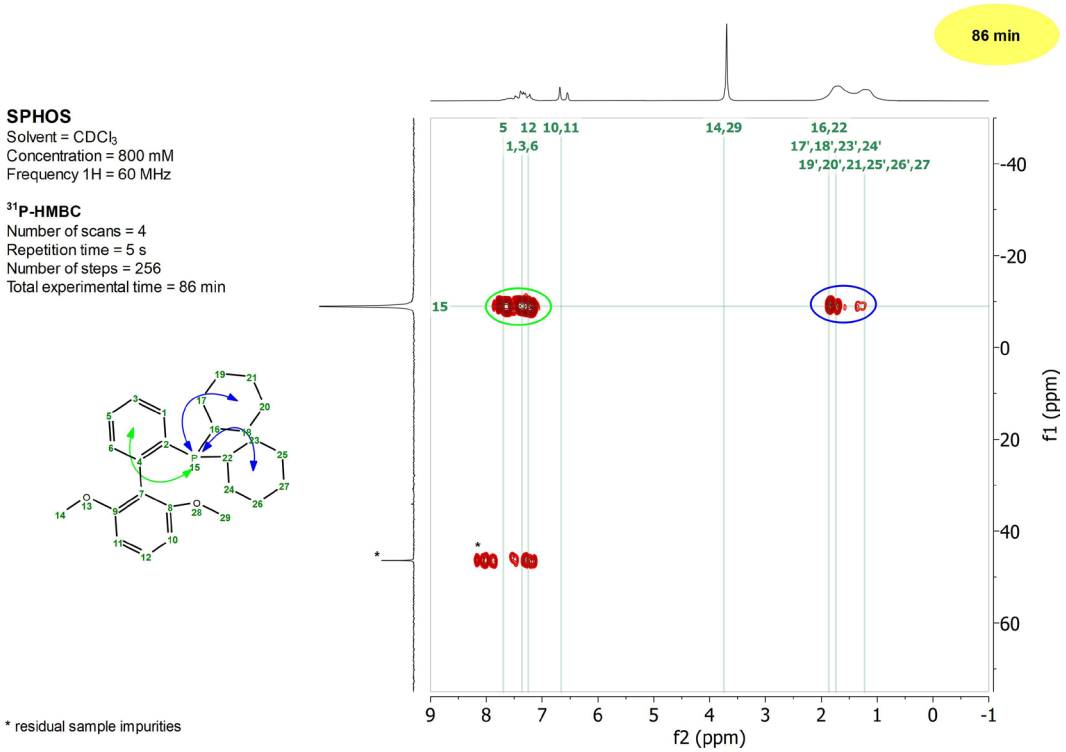

Figure 7: ^{31}P-HMBC NMR spectrum of a 800 mM SPHOS sample in $CDCl_3$ measured on a Spinsolve 60 MHz system showing the long-range couplings between ^{1}H and ^{31}P nuclei.

2D HSQC-ME

The HSQC is a powerful sequence widely used to correlate the ^{1}H with the one-bond coupled ^{13}C nuclei. The Spinsolve is equipped with a multiplicity edited version (HSQC-ME) of this method. It provides the editing power of the DEPT-135 sequence, which is useful to identify the signal of the CH_2 groups (blue) from the CH and CH_3 (red). Figure 8 shows the HSQC-ME spectrum of a 800 mM SPHOS sample in $CDCl_3$ acquired in 34 minutes.

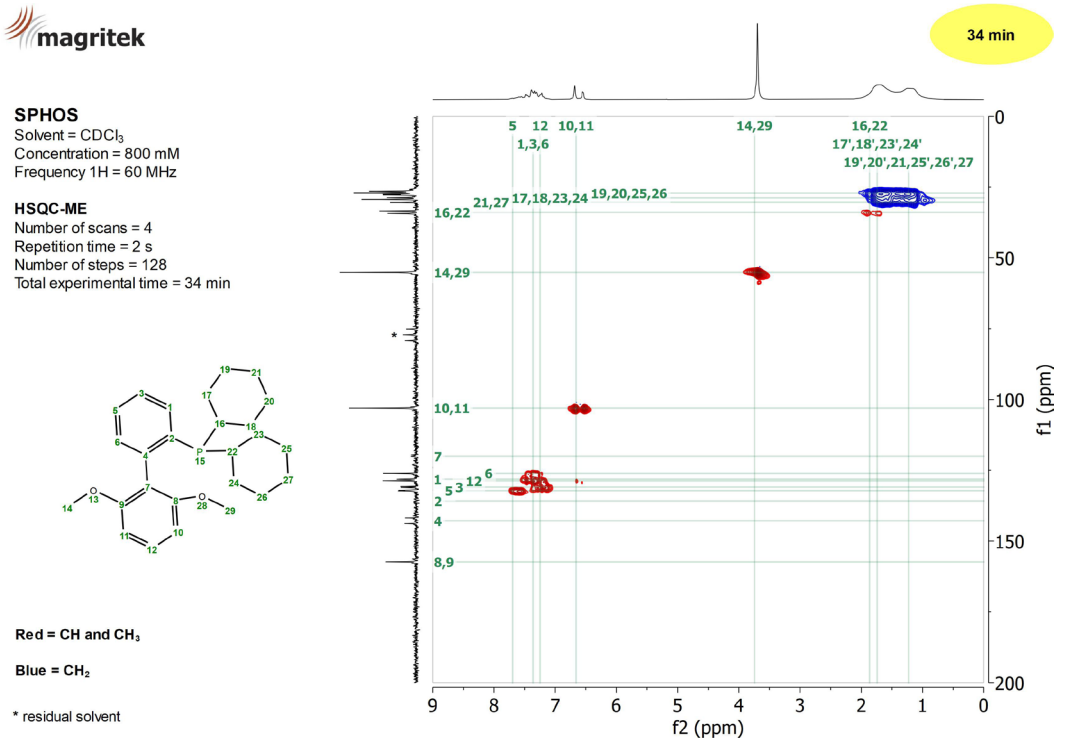

Figure 8: HSQC-ME spectrum of a 800 mM SPHOS sample in $CDCl_3$ showing the correlation between the ^{1}H (horizontal) and ^{13}C (vertical) signals.

2D HMBC

To obtain long-range ^{1}H-^{13}C correlations through two or three bond couplings, the Heteronuclear Multiple Bond Correlation (HMBC) experiment can be used. Figure 9 shows the long-range correlation of protons 10 and 11 with carbons 4, 7, 8, 9 and 12 (the sequence shows the correlation with quaternary carbons, too).

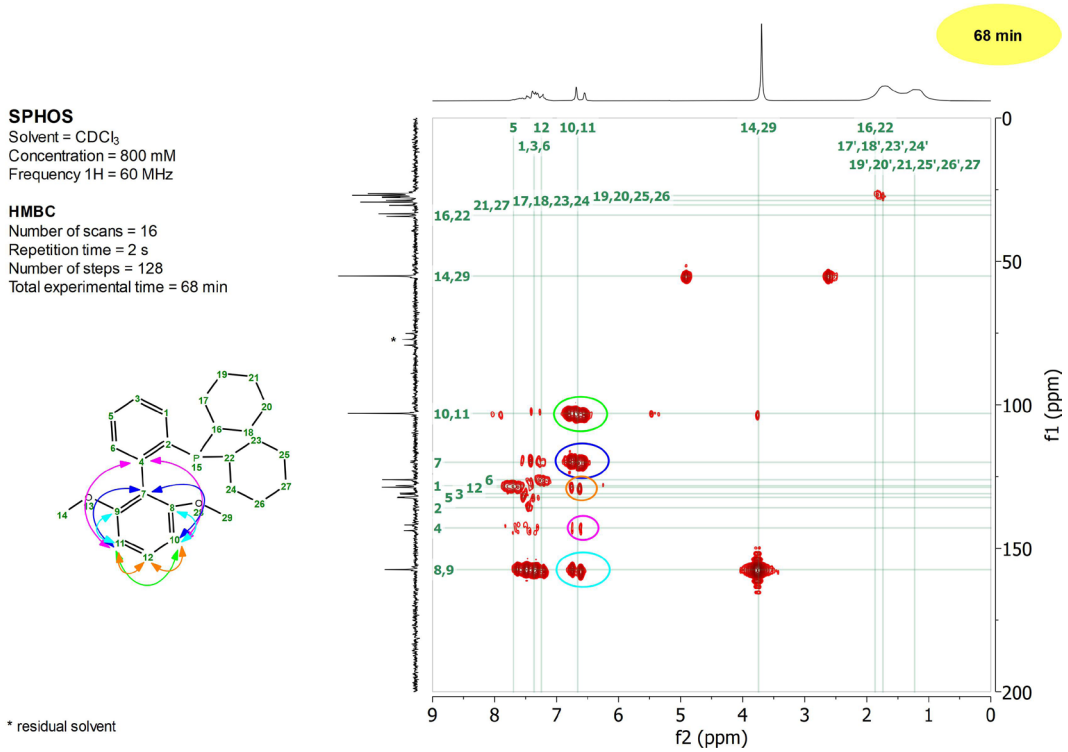

Figure 9: HMBC spectrum of a 800 mM SPHOS sample in $CDCl_3$ showing the long-range couplings between ^{1}H and ^{13}C nuclei.

T_1 proton relaxation

This experiment is used to measure the T_1 relaxation time of each chemical group. Figure 10 shows the T_1 build up curves for all different protons in a 800 mM SPHOS sample in $CDCl_3$. The T_1 value obtained by fitting the build up curve with a single exponential function is shown next to the build up curve. The remarkable quality of the fits demonstrate the high signal-to-noise ratio and reproducibility of the Spinsolve spectrometer.

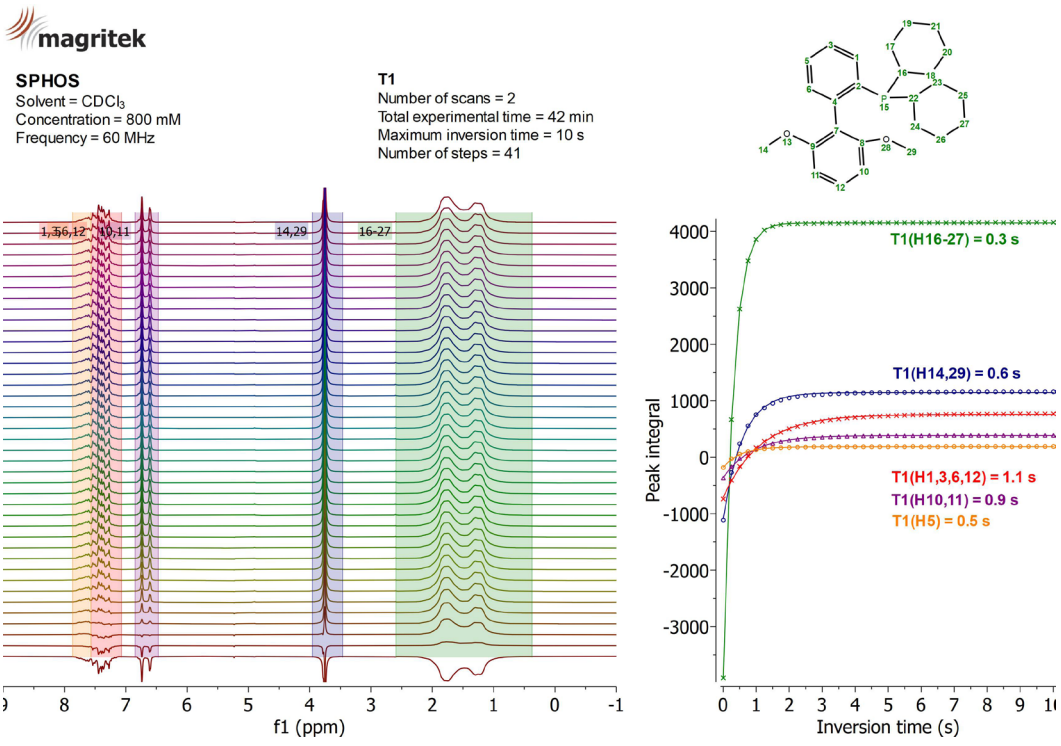

Figure 10: Proton T_1 relaxation measurement done employing a 800 mM SPHOS sample in $CDCl_3$ on a Spinsolve 60 MHz system.

T_2 proton relaxation

This experiment uses a CPMG sequence to allow the protons to relax with the transverse relaxation time T_2 and acquires only the signals during the last echo. To acquire the full data set, it is necessary to repeat the experiment incrementing the duration of the CPMG module by increasing the number of echoes generated during this period. The T_2 values are obtained by fitting the peak integrals of each group as a function of the CPMG evolution time. Figure 11 shows the T2 decay curve for all different protons in a 800 mM SPHOS sample in CDCl3.

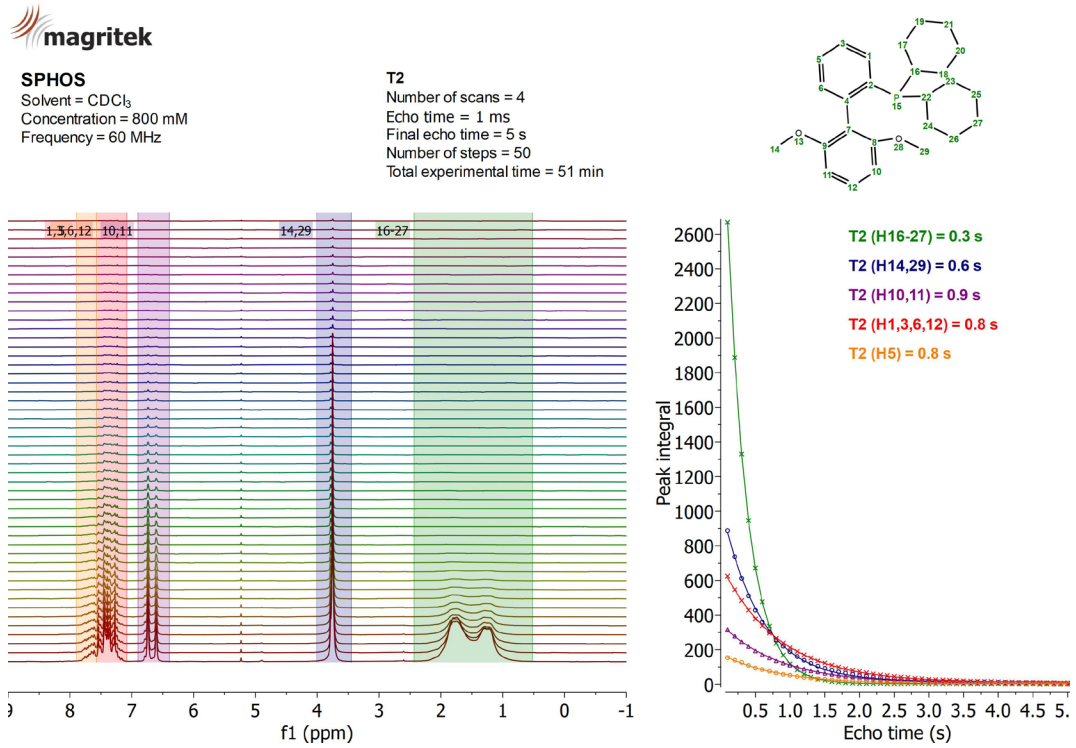

Figure 11: Proton T_2 relaxation curves measured for a 800 mM SPHOS sample in $CDCl_3$ on a Spinsolve 60 MHz system.