SPHOS - A molecule containing $^1\text{H}$, $^{13}\text{C}$ and $^{31}\text{P}$ 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 $^1\text{H}$ NMR spectrum of a 800 mM SPHOS sample in CDCl$_3$ measured in a single scan taking 15 seconds to acquire.

**2D COSY**

The 2D COSY experiment allows one to identify coupled $^1\text{H}$ 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 1: $^1\text{H}$ NMR spectrum of a 800 mM SPHOS sample in CDCl$_3$ measured on a Spinsolve 60 MHz system in a single scan.

Figure 2: $^1\text{H}$ 2D COSY experiment of a 800 mM SPHOS sample in CDCl$_3$ acquired in 34 minutes on a Spinsolve 60 MHz system.
**13C Spectra**

Figure 3 shows the full 13C NMR spectra of a 800 mM SPHOS sample in CDCl3 acquired using NOE and 1H 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 13C and the 31P 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 CDCl3 measured on a Spinsolve 60 MHz system using NOE and 1H decoupling. Full spectrum (top), zoom to 110-150 ppm and 20-40 ppm (bottom).](image)

**13C DEPT Spectra**

Figure 4 shows the 13C NMR spectra of a 800 mM SPHOS sample in CDCl3 acquired using NOE and DEPT polarization transfer from 1H to 13C and 1H decoupling. While the 1D Carbon experiment using NOE (top spectrum) is sensitive to all 13C nuclei in the sample, the DEPT experiments show only 13C nuclei directly attached to 1H 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, CH2, and CH3 groups, where the CH3 groups appear as negative peaks in the DEPT-135.

![Figure 4: Carbon NMR spectra of a 800 mM SPHOS sample in CDCl3 measured on a Spinsolve 60 MHz using NOE (top) and DEPT-45, -90 and -135 sequences.](image)
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.

**2D JRES**

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**31P 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 5: Homonuclear J-resolved spectrum of a 800 mM SPHOS sample in CDCl$_3$ measured on a Spinsolve 60 MHz system.

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.

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.
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).

**2D HMBC**

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 9: HMBC spectrum of a 800 mM SPHOS sample in CDCl$_3$ showing the long-range couplings between $^1$H and $^{13}$C nuclei.

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 $T_2$ decay curve for all different protons in a 800 mM SPHOS sample in CDCl$_3$.

Figure 11: Proton $T_2$ relaxation curves measured for a 800 mM SPHOS sample in CDCl$_3$ on a Spinsolve 60 MHz system.