Electronic Supplementary Material (ESI) for Dalton Transactions.

New approach for the synthesis of water soluble of *fac*-$\{M^{I}(CO)_3\}^+$ bis(diarylphosphino)alkylamine complexes (M=^{99}Tc, Re)

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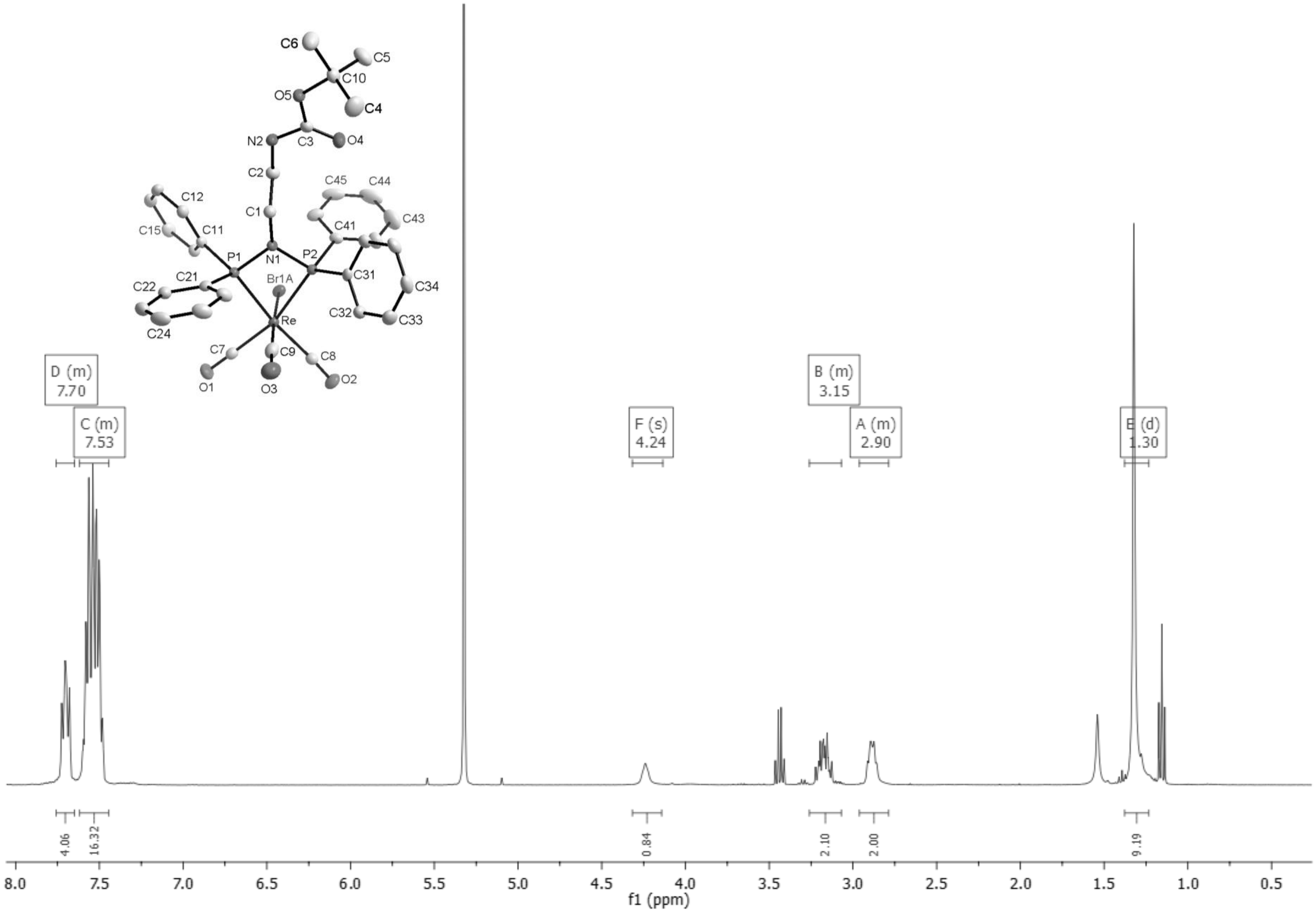
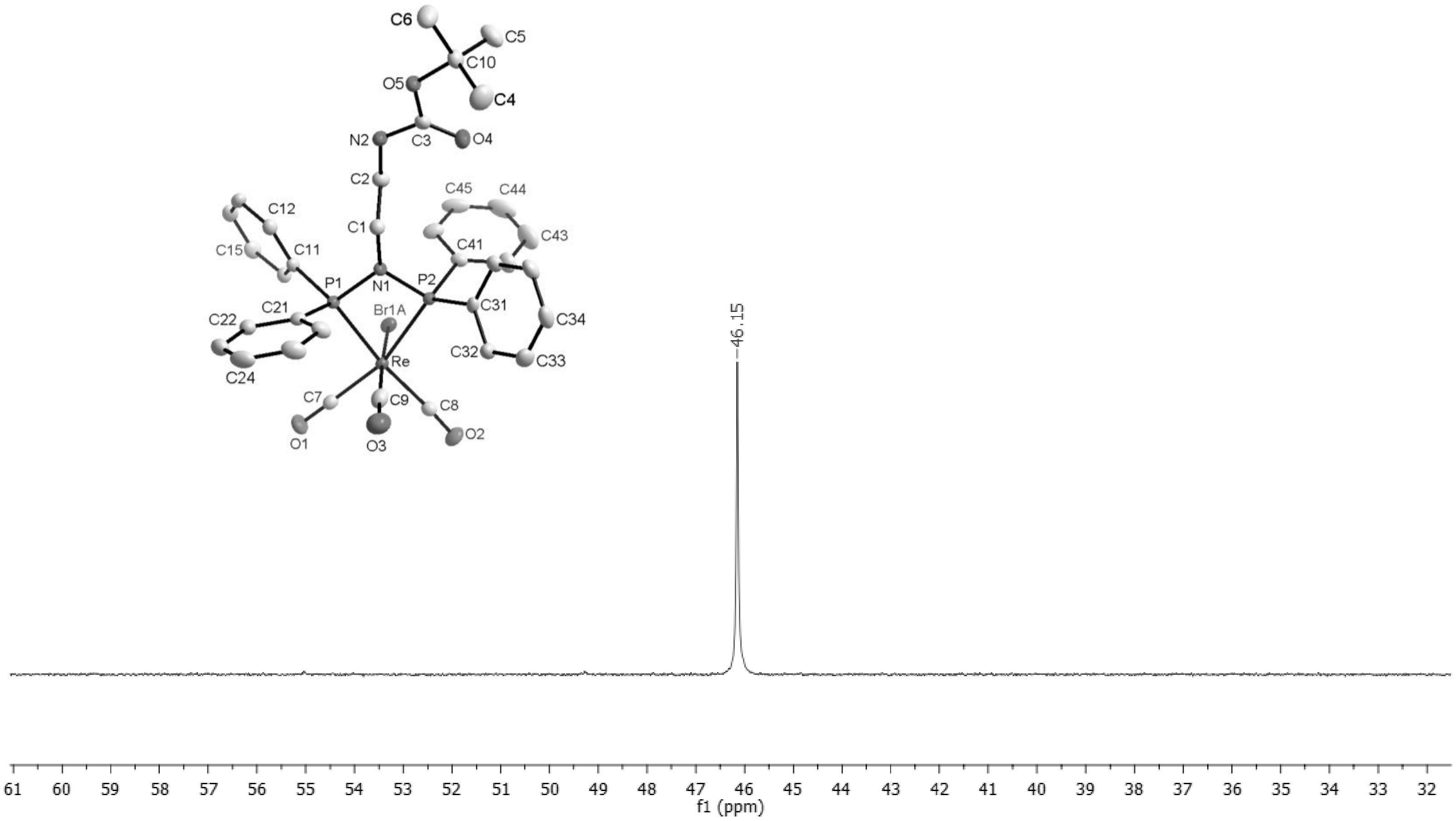
Table of Contents

1. NMR/IR Data for 1A

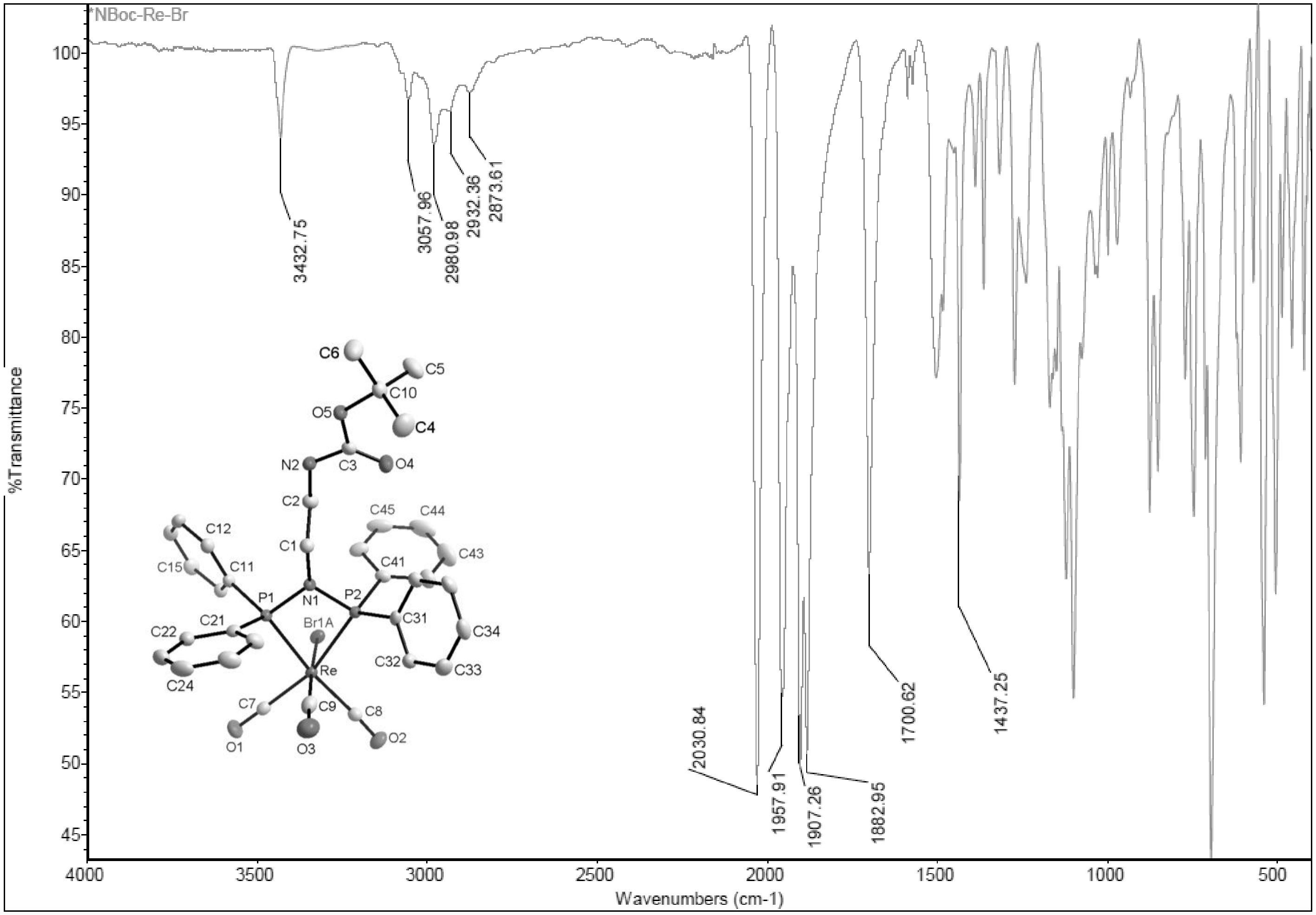
1.1. ^{1}H NMR spectrum for *fac*-[Re(NBoc-PNP)(CO)$_3$Br] (1A)



1.2. ^{31}P NMR spectrum for *fac*-[Re(NBoc-PNP)(CO)$_3$Br] (1A)

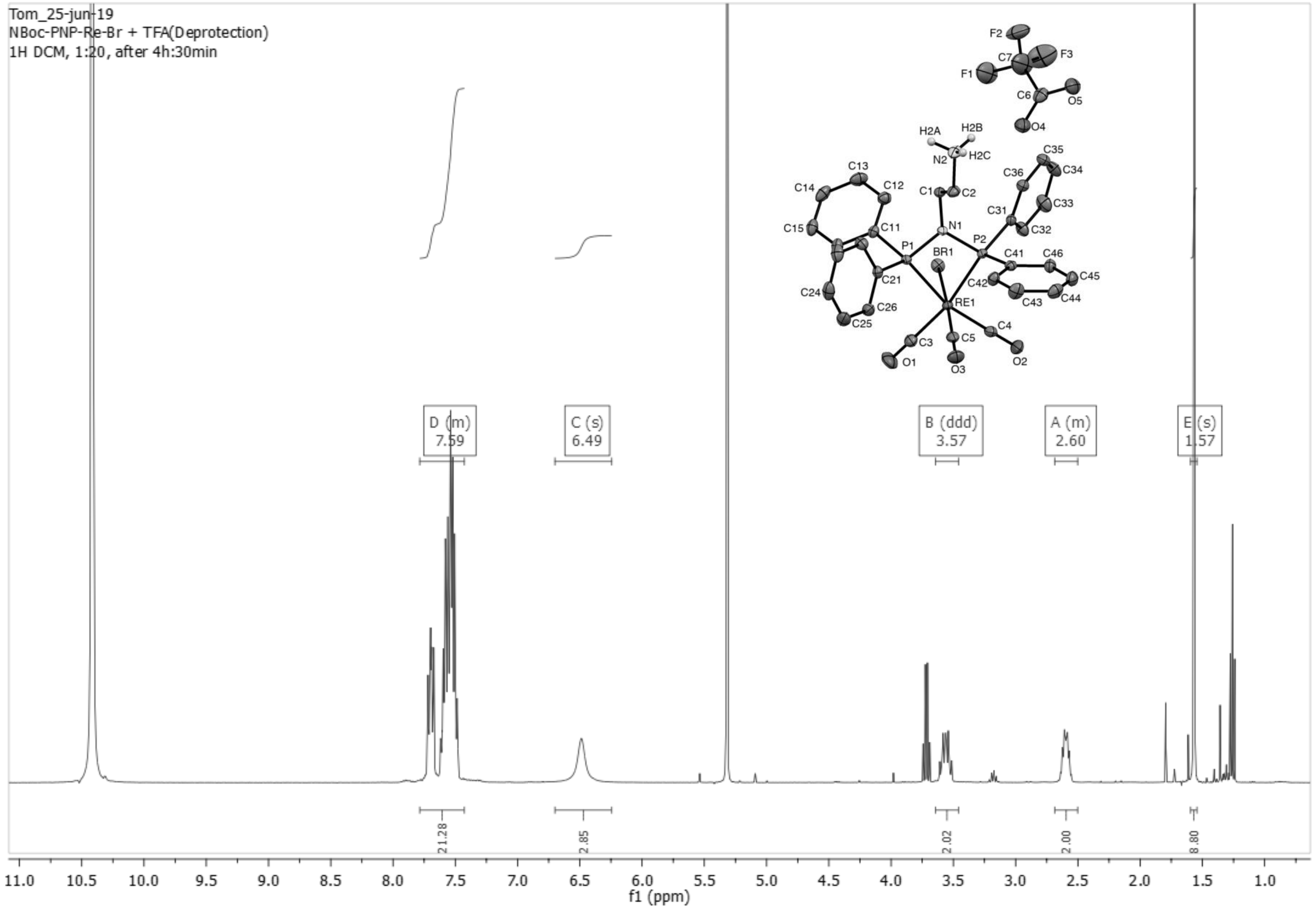


1.3. IR spectrum for *fac*-[Re(NBoc-PNP)(CO)$_3$Br] (1A)

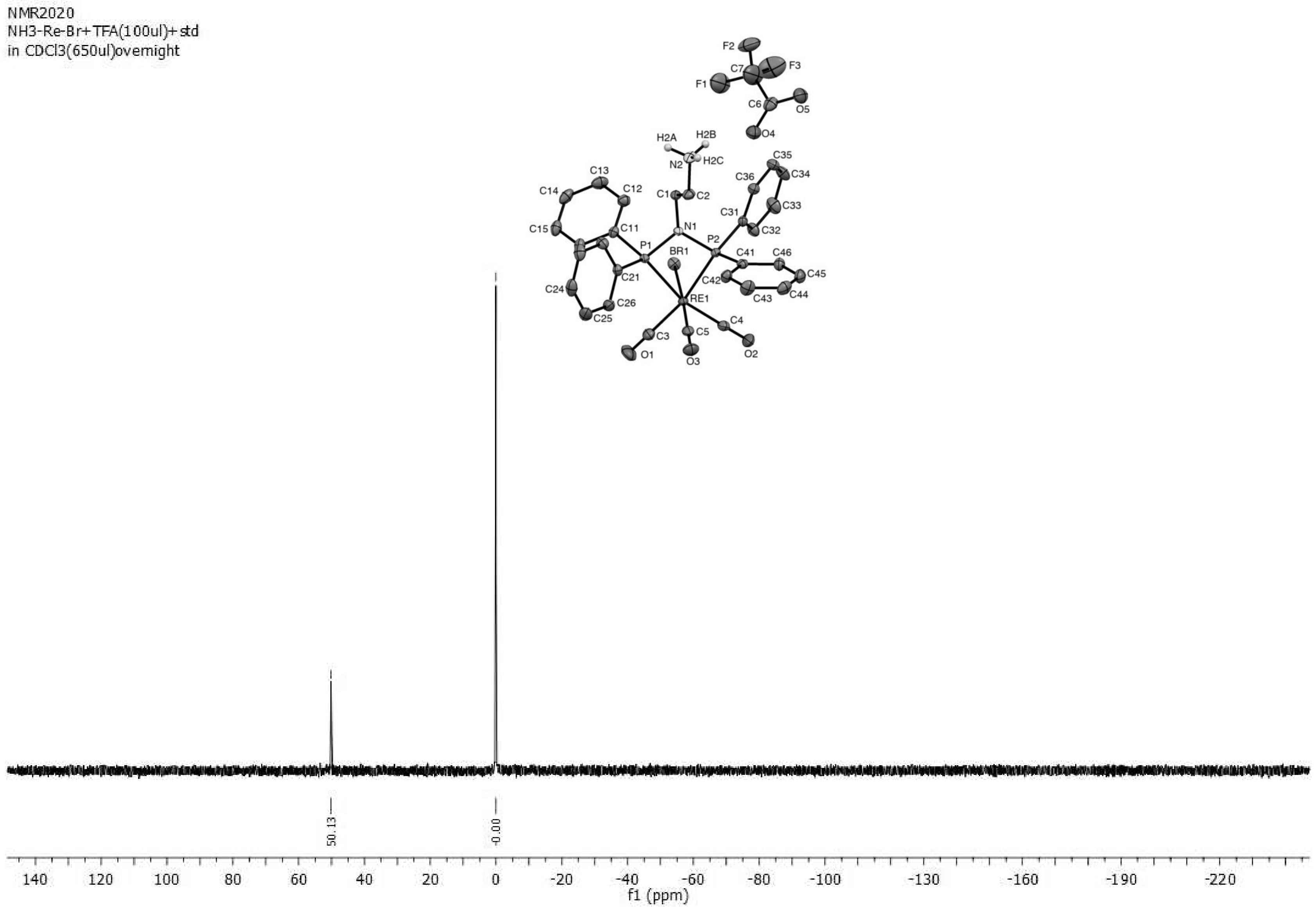


2. NMR/IR Data for 1B

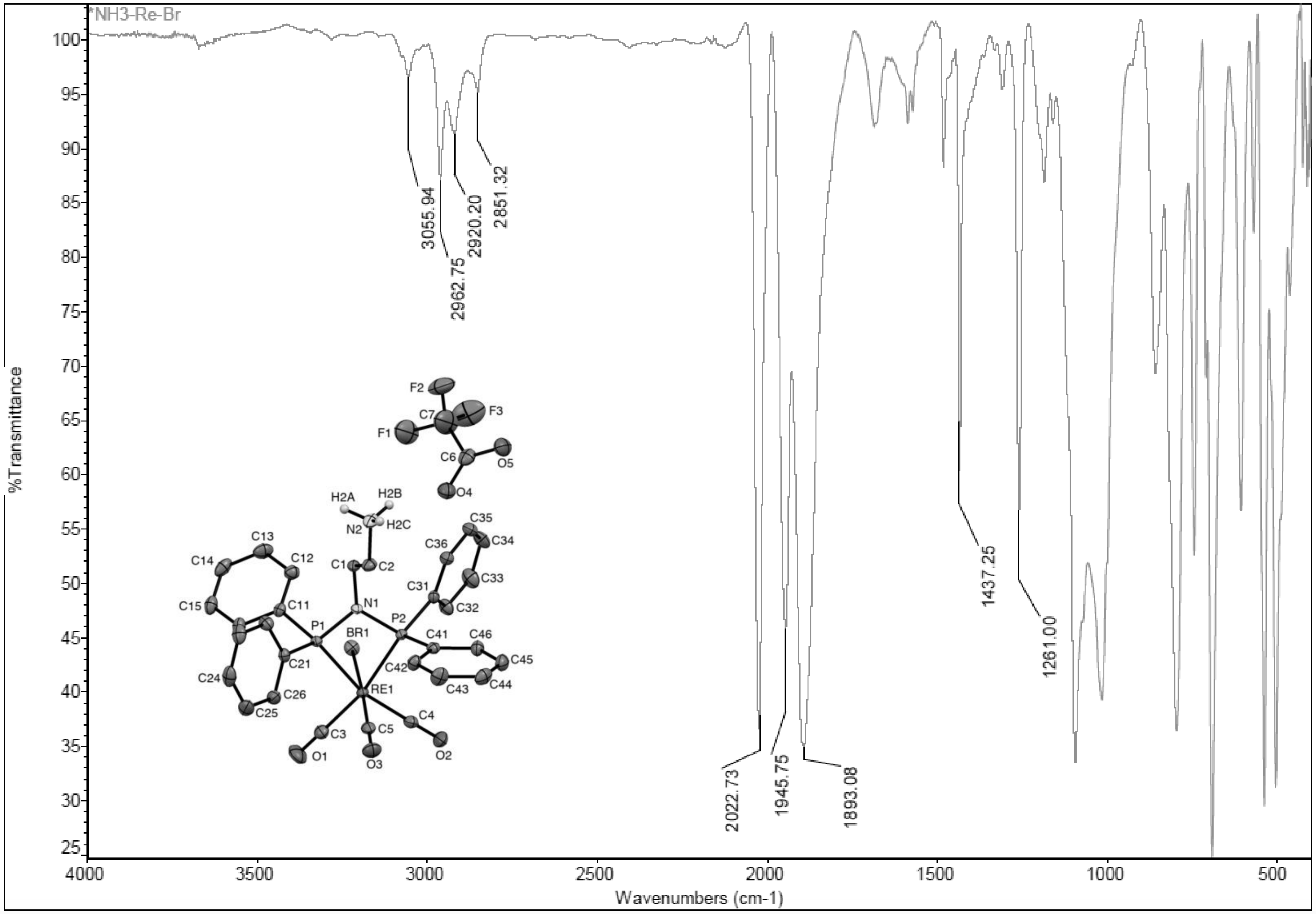
2.1. ^{1}H NMR spectrum of *fac*-[Re(NH$_3$-PNP)(CO)$_3$Br] (1B)



2.2. ^{31}P NMR spectrum of *fac*-[Re(NH$_3$-PNP)(CO)$_3$Br] (1B)

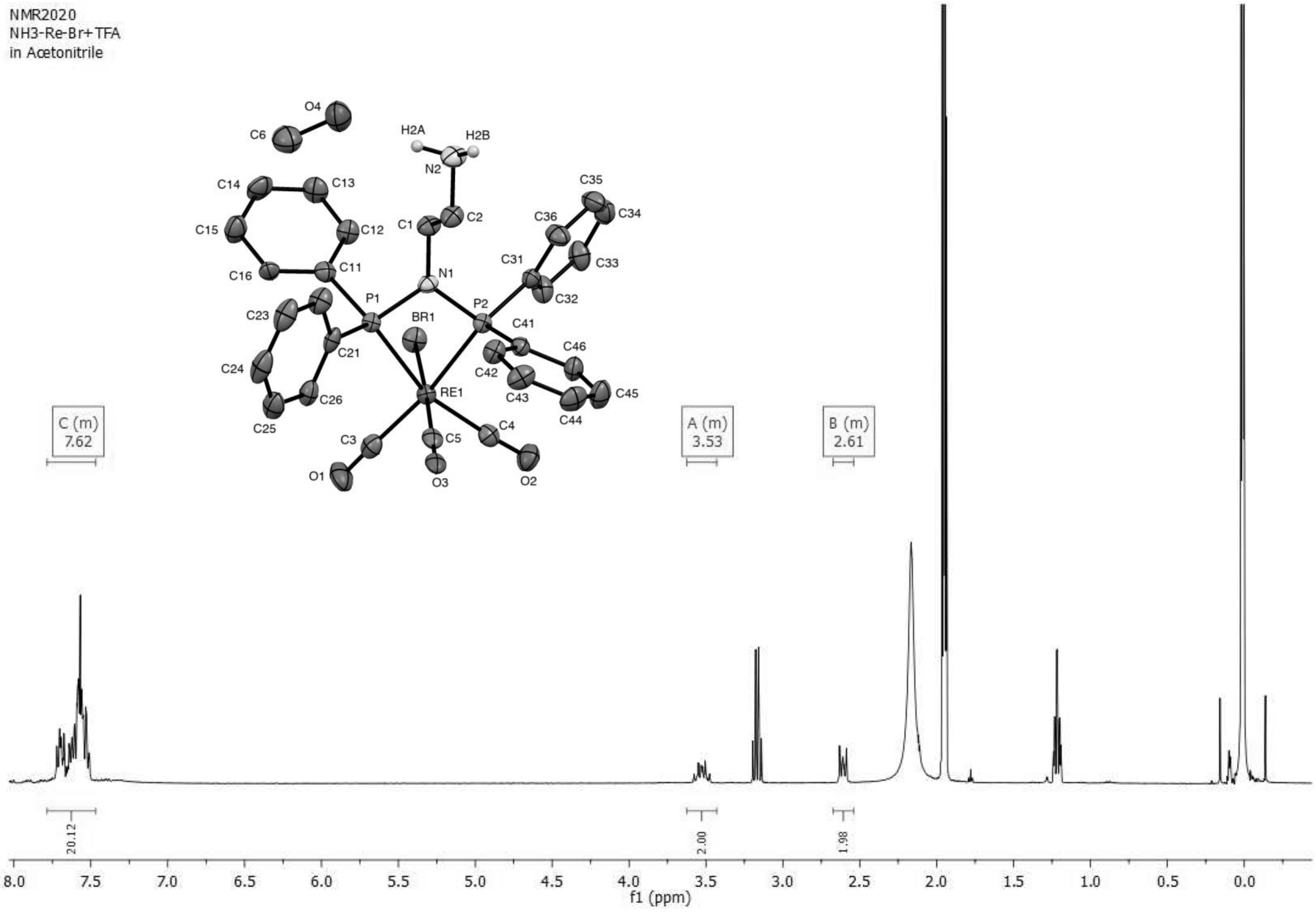


2.3. IR spectrum for *fac*-[Re(NH$_3$-PNP)(CO)$_3$Br] (1B)

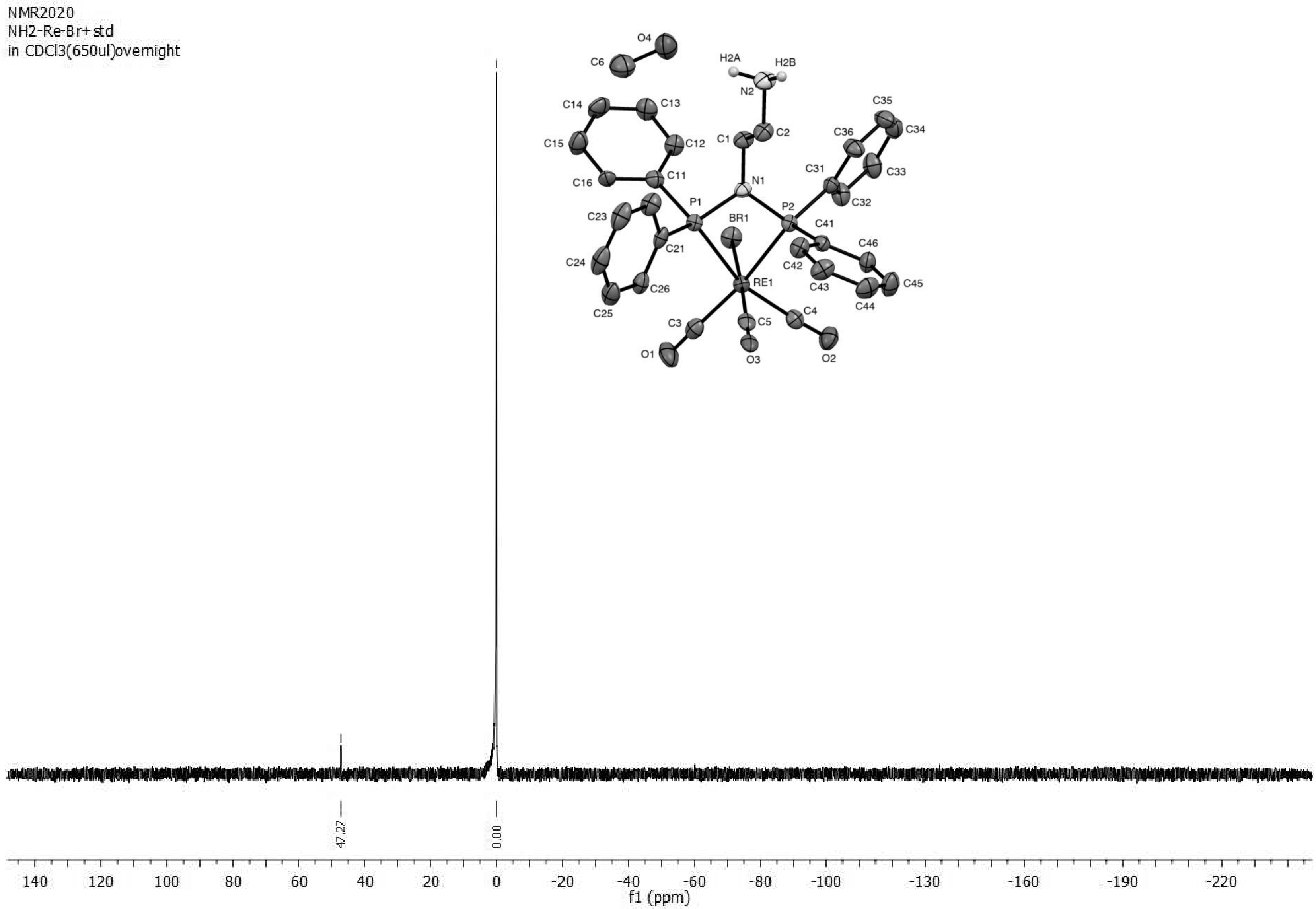


3. NMR/IR data for 1C

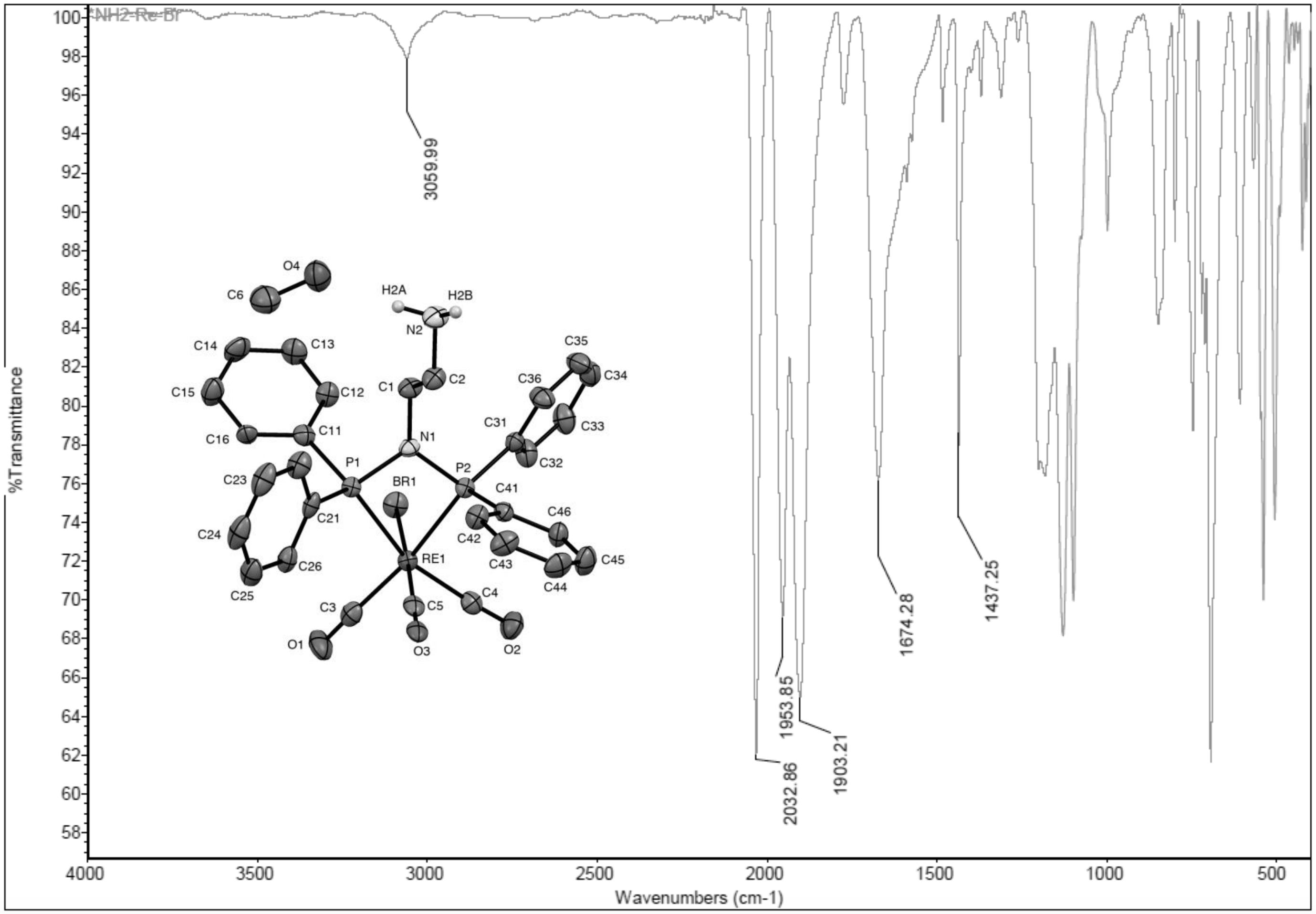
3.1 ^{1}H NMR spectrum for *fac*-[Re(NH$_2$-PNP)(CO)$_3$Br] (1C)



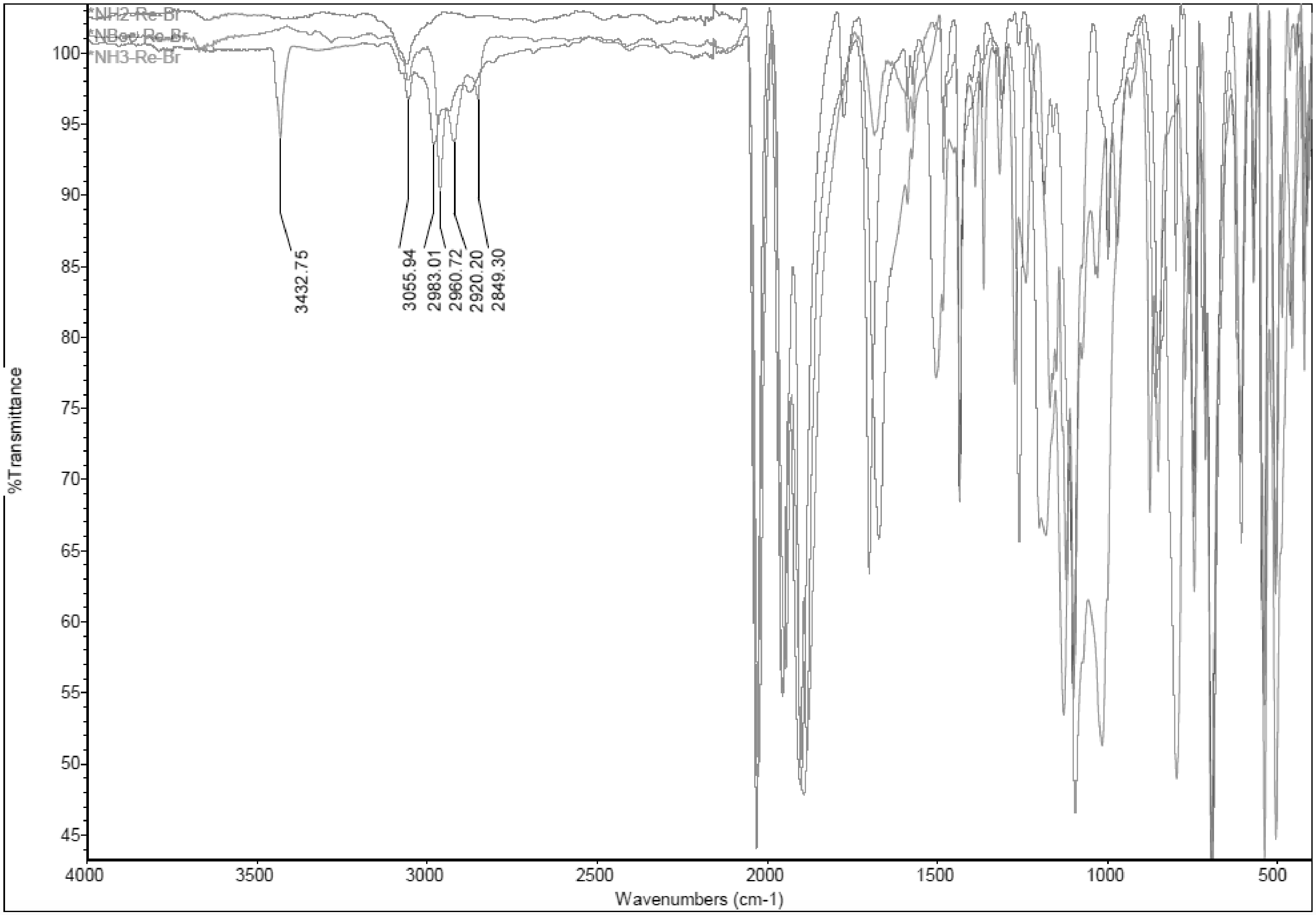
3.2 ^{31}P NMR spectrum for *fac*-[Re(NH$_2$-PNP)(CO)$_3$Br] (1C)



3.3 IR spectrum for *fac*-[Re(NH_2-PNP)$(CO)_3$Br] (1C)

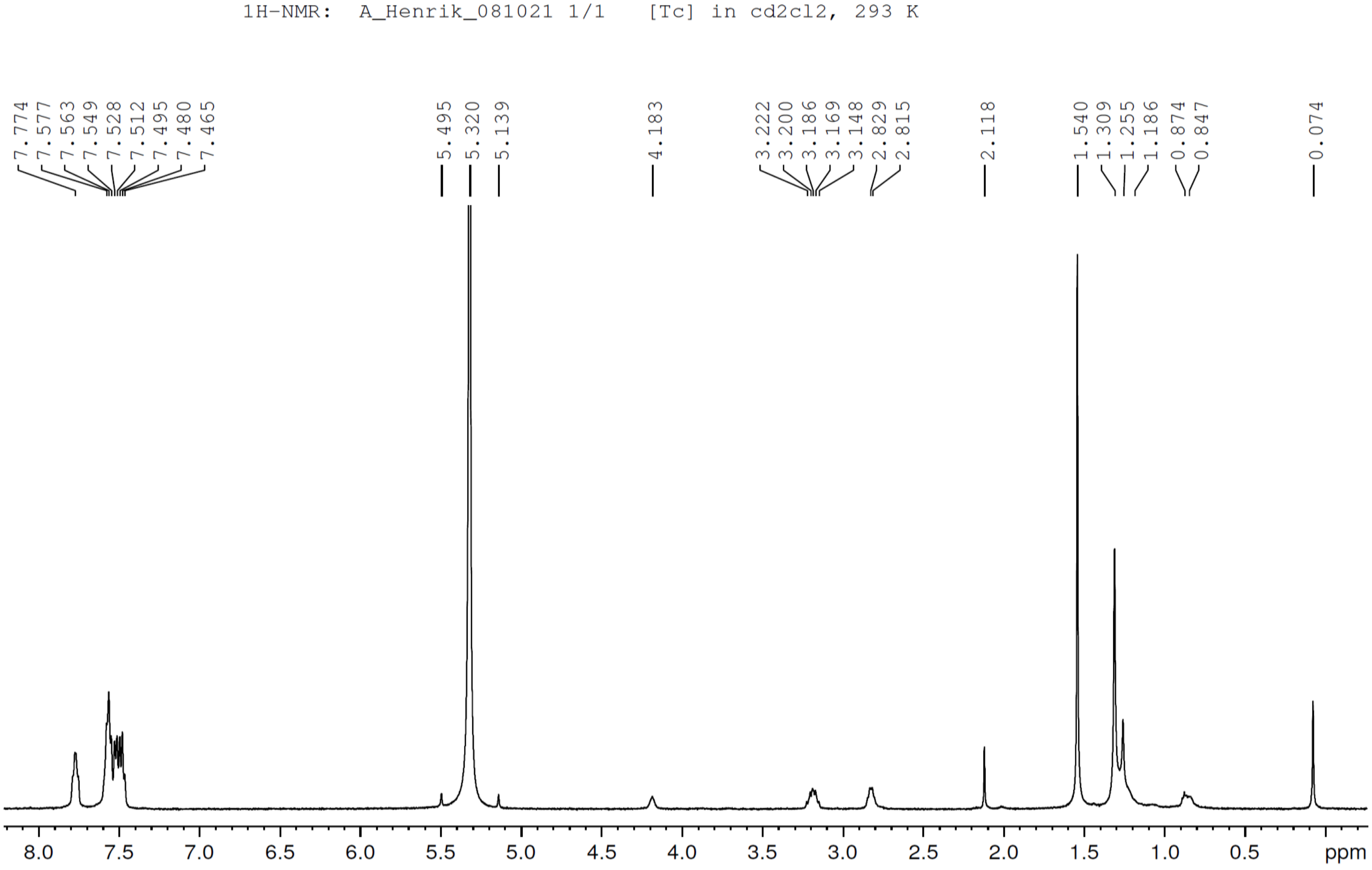


IR overlay of 1A (Red), 1B (Green) and 1C (Blue)



4. NMR/IR data for 1C

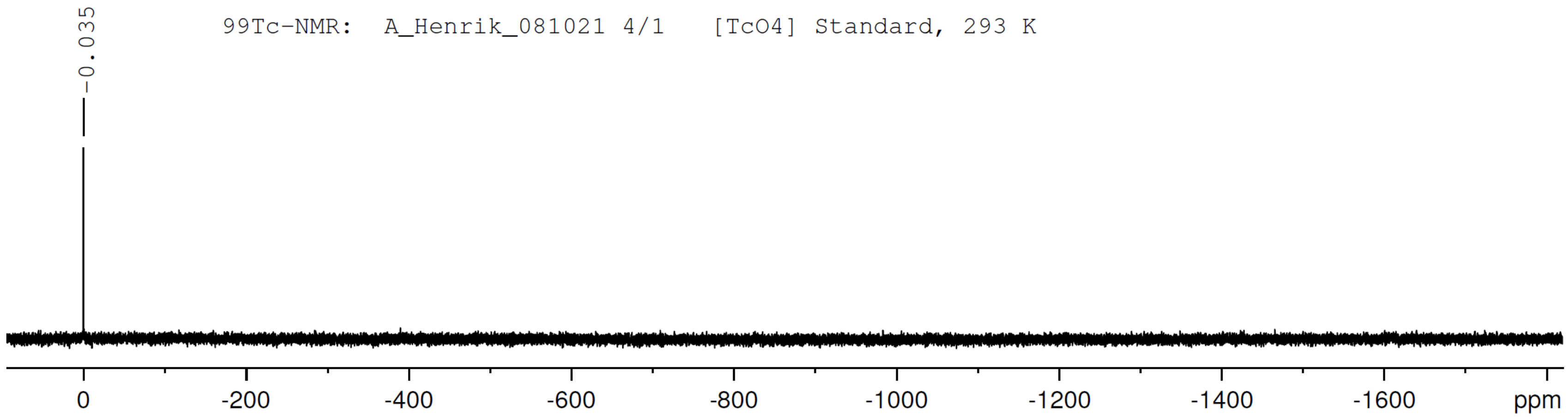
4.1 H-1 NMR *fac*-[^{99}Tc(NBoc-PNP)(CO)$_3$Cl] (1D)

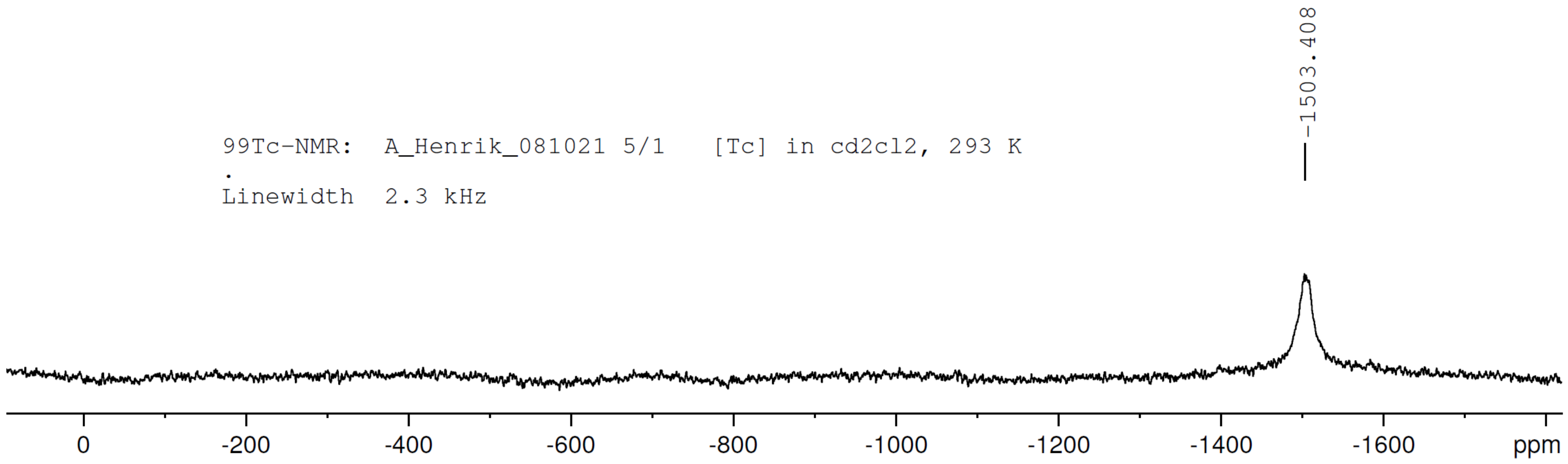


4.2 P-31 NMR *fac*-[^{99}Tc(NBoc-PNP)(CO)$_3$Cl] (1D)

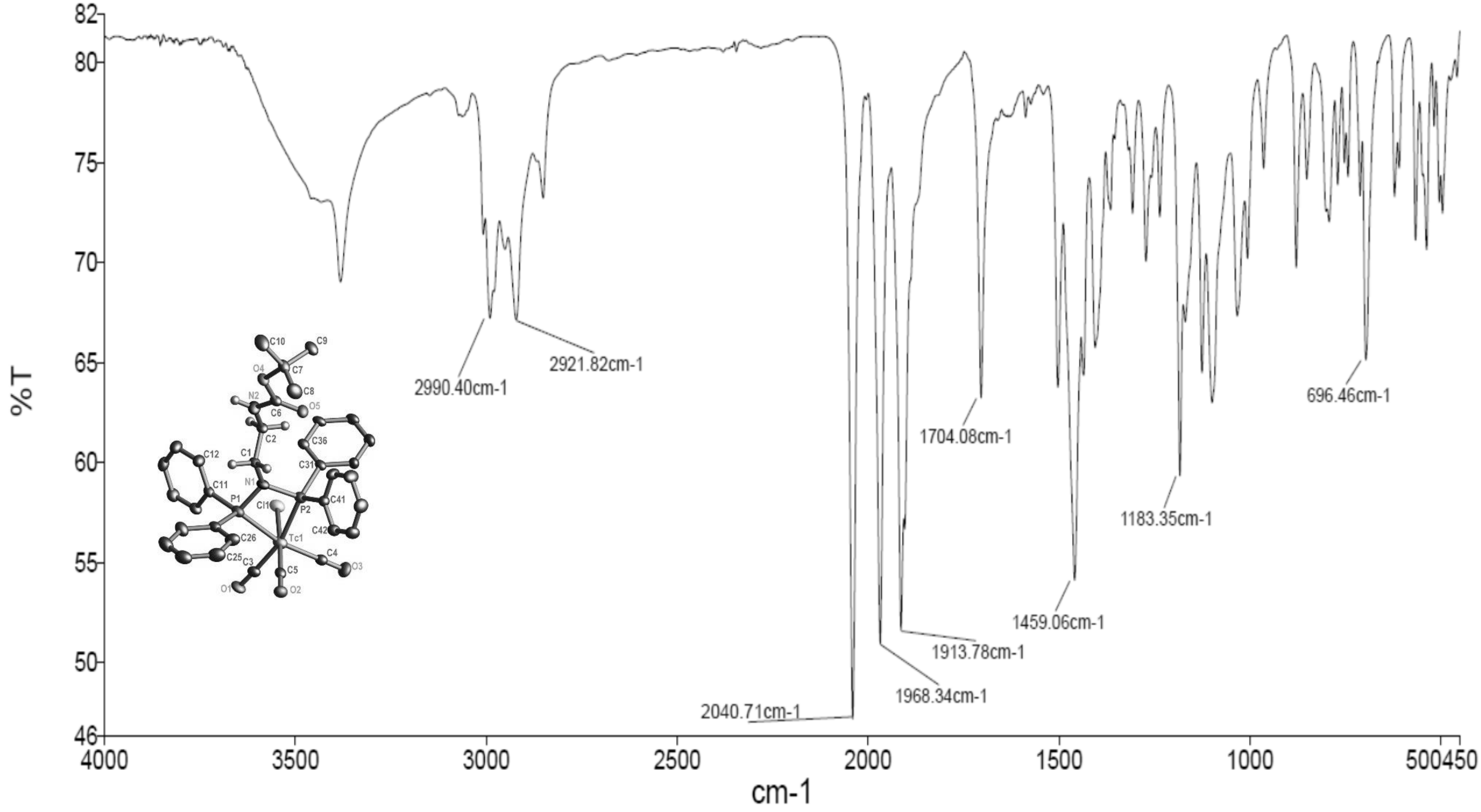
No signal was observed due to the non-symmetry within the complex and the significant quadropolar moment of the Tc-99 nucleus.

4.3 Tc-99 NMR *fac*-[^{99}Tc(NBoc-PNP)(CO)$_3$Cl] (1D)





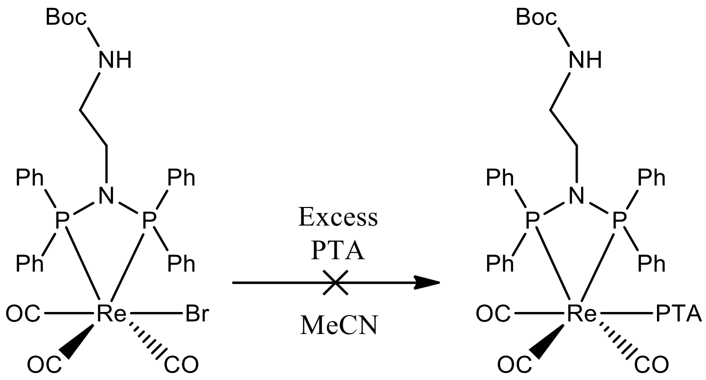
4.4 IR spectrum for *fac*-[^{99}Tc(NBoc-PNP)(CO)$_3$Cl] (1D)



5. Preliminary substitution kinetic evaluation

All ^{31}P NMR spectra were analyzed on 400 MHz AVANCE III nuclear magnetic resonance spectrometer operation at a temperature of 25 C using deuterated acetonitrile as a solvent. Chemical shifts are reported in parts per million (ppm) while the MestReNova (V 6.02-5475) program was used for graphical illustrations.

5.1. 1,3,5-triaza-7-phosphaadamantane (PTA) as the entering ligand



4c

Figure S 1 Reaction scheme of attempted Bromido substitution on 1A with PTA.

The potential substitution of the bromido ligand from **1A** (7.5 x 10^{-3} M) with PTA (0.075 M) was investigated in deuterated MeCN for 4 hours at 25 °C using ^{31}P NMR on a 400 MHz AVANCE III NMR spectrometer under *pseudo* first-order conditions. From the ^{31}P NMR results illustrated **Fig. S2**, two distinct single peaks were observed. However, these peaks correspond only to **1A** (46.15 ppm) and the entering ligand **PTA** (-102.10 ppm).

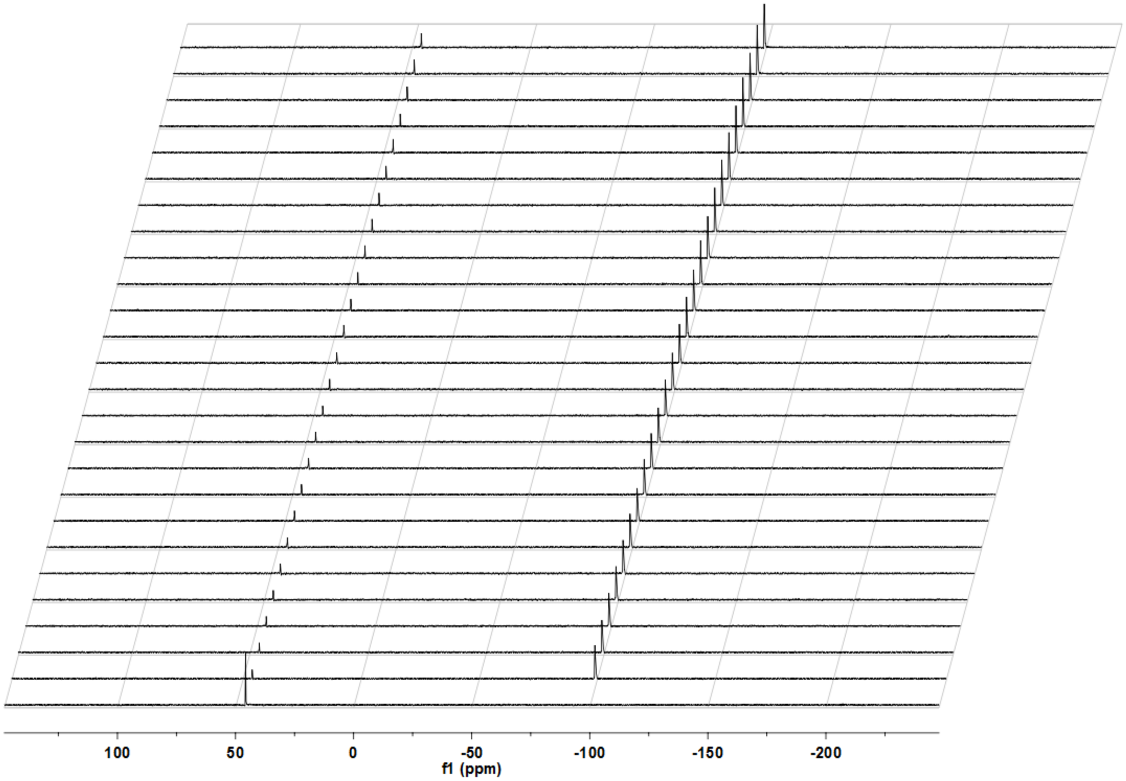


Figure S 2 Stacked plot of ^{31}P NMR spectra as a function of time (Δt= 140 s) for the reaction between 1A and PTA. The first spectrum denotes the undiluted starting concentration of 1A while the remaining spectra illustrates only the last hour of the 4 hour reaction.

The same substitution reaction was performed at various concentrations on a Varian 50 Conc UV/Vis spectrophotometer. As anticipated, no absorbance change was observed. Both the UV/Vis and the ^{31}P NMR studies were performed in triplicate for reproducibility purposes

5.2. Pyridine as the entering ligand

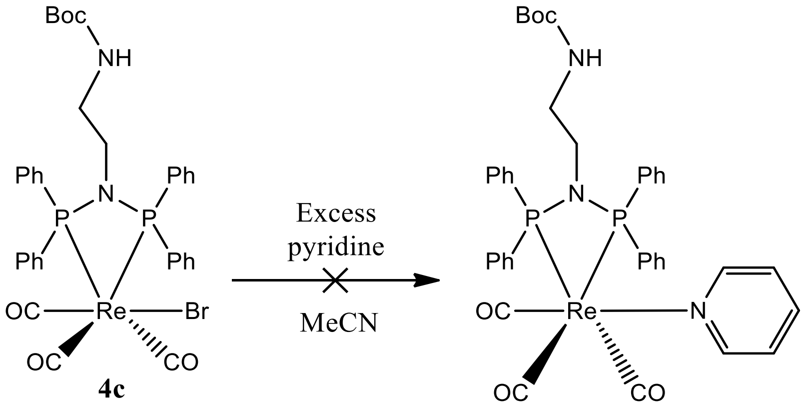


Figure S 3 Reaction scheme of attempted Bromido substitution on 1A with Pyridine**.**

Similar to the PTA substitution reaction, the substitution reaction of the bromide moiety in **1A** (0.015 M) by pyridine (0.045 M) in deuterated MeCN was investigated for 4 hours at 25 °C using ^{31}P NMR technique on a 400 MHz AVANCE III NMR spectrometer under *pseudo* first-order conditions. Similar to the PTA substitution reaction, again a distinct single peak at 46.15 ppm corresponding to only **1A** indicating that no substitution of the Br$^-$ ligand took place (**Fig. S4**). The same substitution reaction was performed at various concentrations on a Varian 50 Conc UV/Vis spectrophotometer. As anticipated, no absorbance change was observed. Both the UV/Vis and the ^{31}P NMR studies were performed in triplicate for reproducibility purposes.

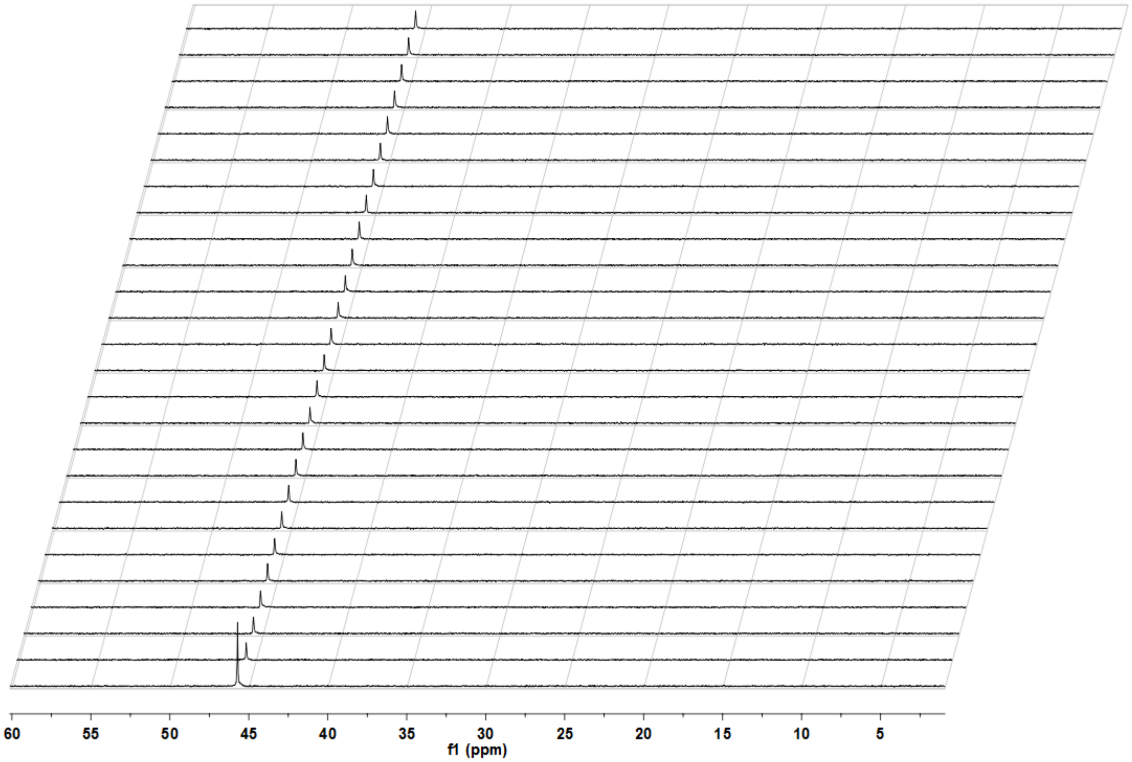
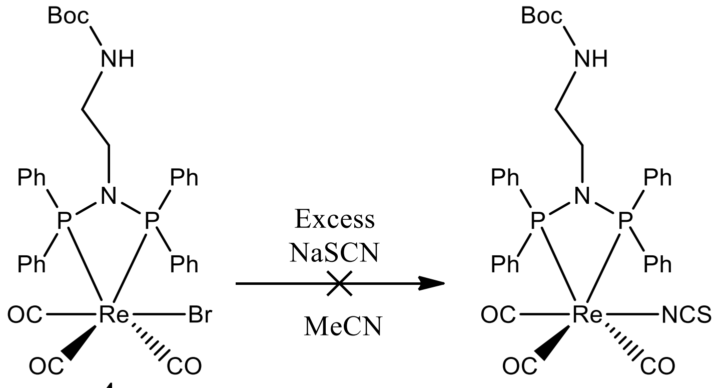


Figure S 4 Stacked plot of ^{31}P NMR spectra as a function of time (Δt= 140 s) for monitoring the kinetics for the reaction between 1A and pyridine. The first spectrum denotes the undiluted starting concentration of 1A while the remaining spectra illustrates only the last hour of the 4 hour reaction.

5.3. Thiocyanate anion (using NaSCN) as the entering ligand



4c

Figure S 5 Reaction scheme of attempted Bromido substitution on 1A with NaSCN.

Similar to the PTA substitution reaction, the substitution reaction of the bromide moiety in **1A** (5x10^{-3} M) with sodium NaSCN (0.075 M) in deuterated MeCN was investigated for 4 hours at 25 °C using ^{31}P NMR on a 400 MHz AVANCE III NMR spectrometer under *pseudo* first-order conditions**.** Again, only a distinct single peak at 45.69 ppm corresponding to **1A** was observed as illustrated below indicating that no substitution reaction took place (**Fig. S6**).

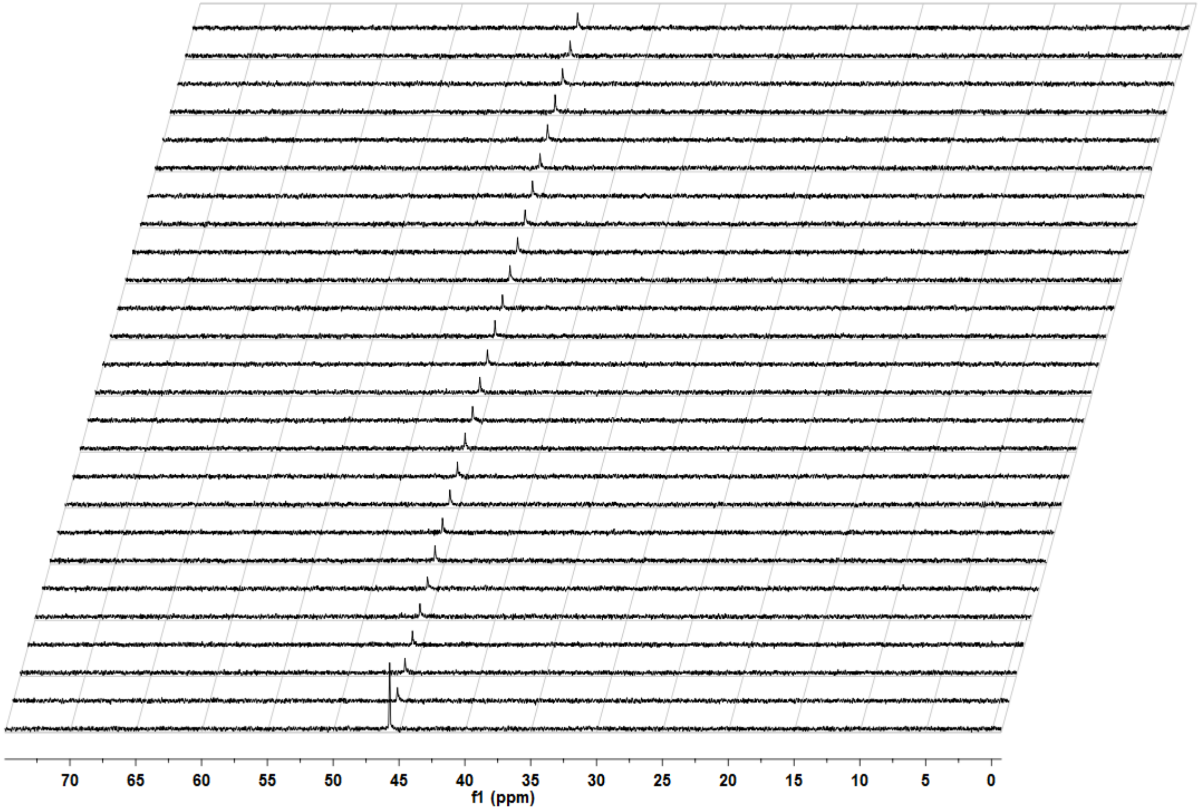


Figure S 6 Stacked plot of ^{31}P NMR spectra as a function of time ($\Delta t = 140$ s) for monitoring the kinetics for the reaction between 1A and NaSCN. The first spectrum denotes the undiluted starting concentration of 1A while the remaining spectra illustrates only the last hour of the 4 hour reaction.

The same substitution reaction was performed at various concentrations on a Varian 50 Conc UV/Vis spectrophotometer. As anticipated, no absorbance change was observed. Both the UV/Vis and the ^{31}P NMR studies were performed in triplicate for reproducibility purposes