Supplementary Information

Anion templating from a silver(I) dithiophosphate 1D polymer forming discrete cationic and neutral octa- and decanuclear silver(I) clusters

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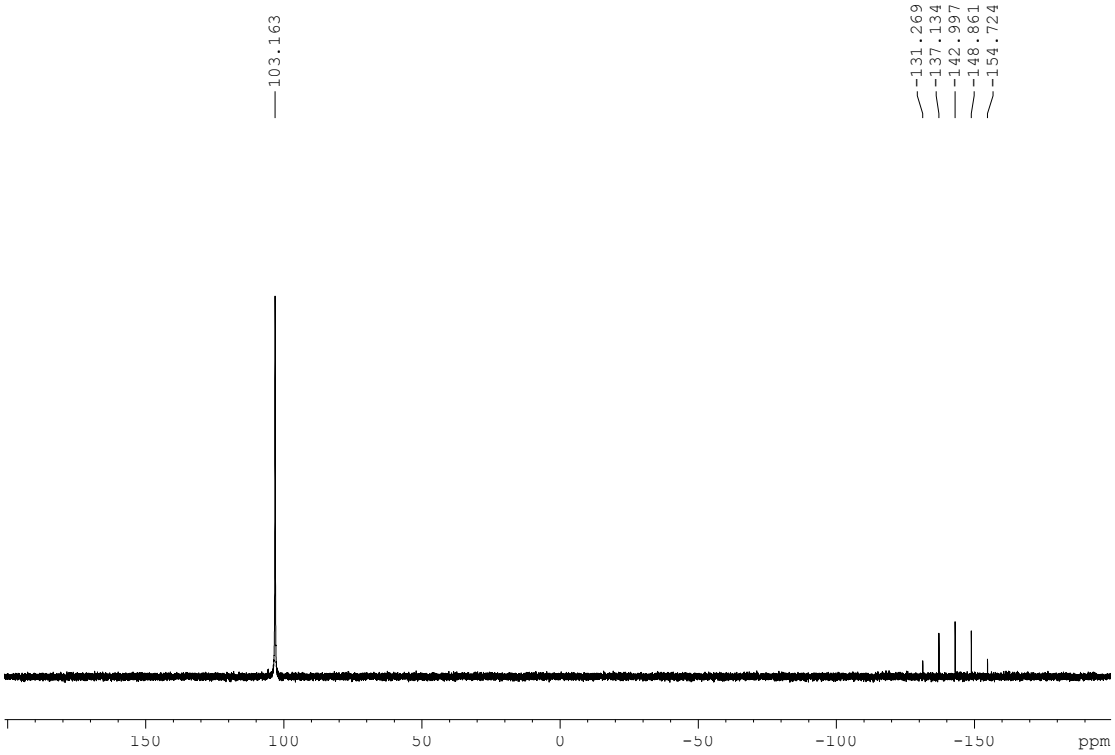

Figure S1 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_5\{S_2P(O^iPr)_2\}_4]_n(PF_6)_n$, **1**.

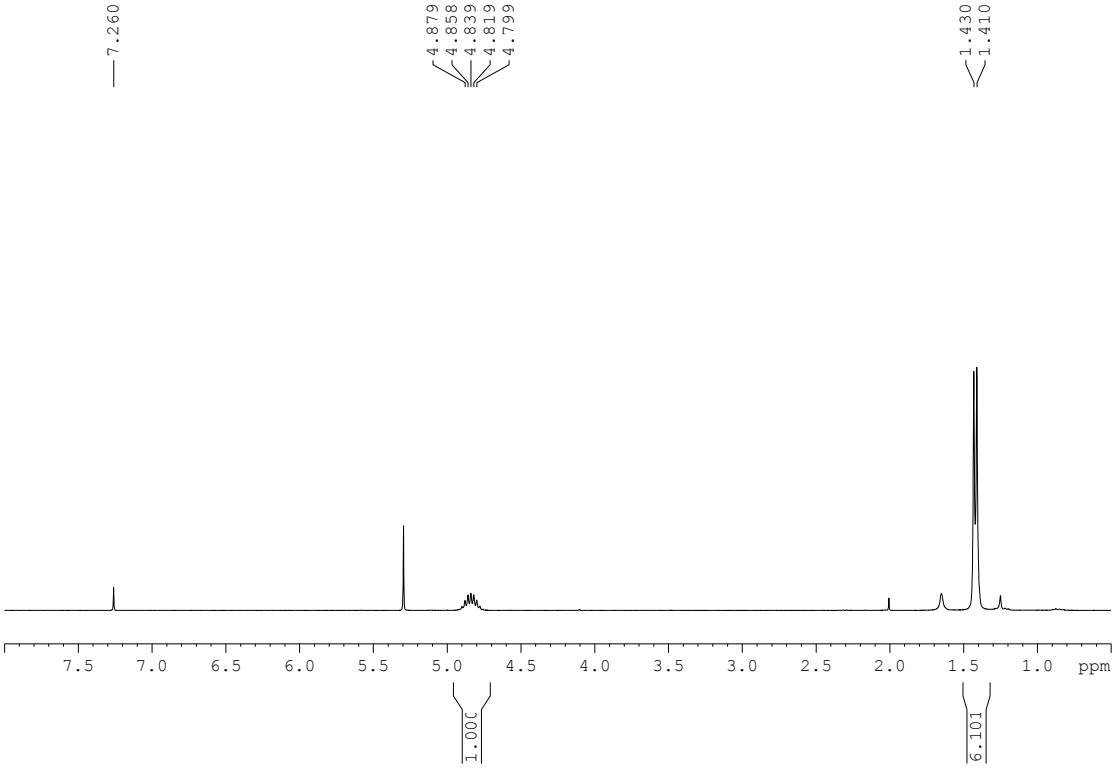

Figure S2 ^{1}H NMR spectrum of $[Ag_5\{S_2P(O^iPr)_2\}_4]_n(PF_6)_n$, **1**.

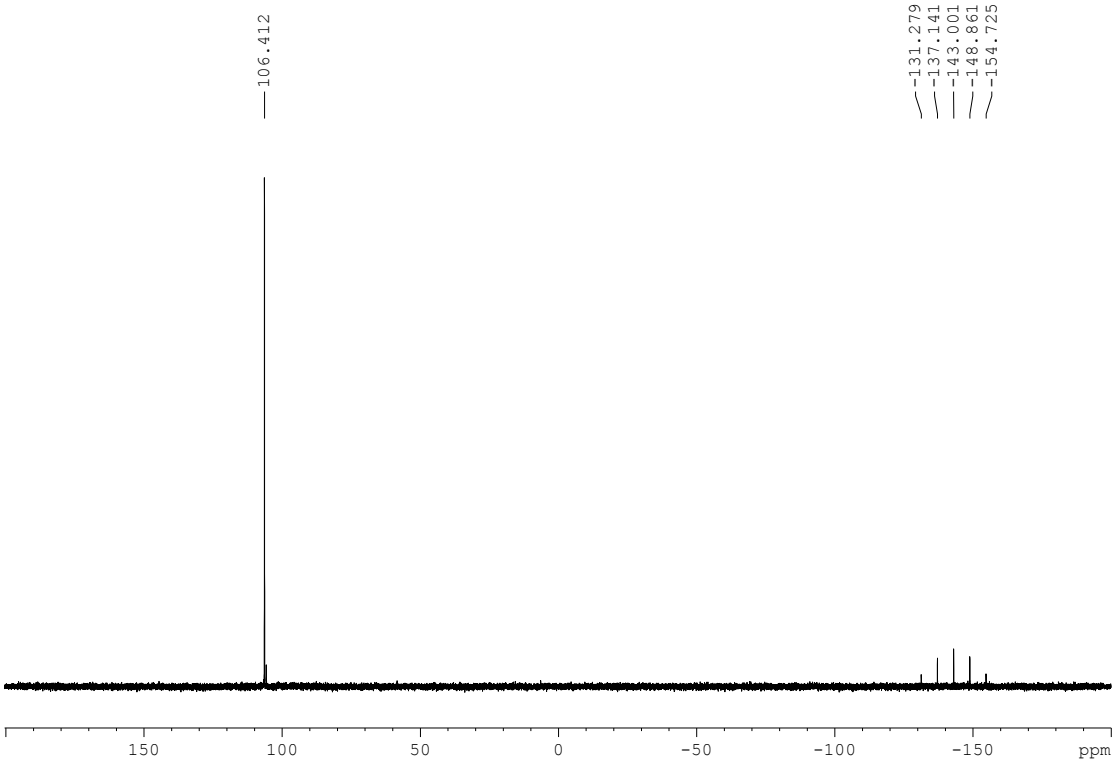

Figure S3 ^{31}P{^{1}H} NMR spectrum of $[Ag_8(\mu_8\text{-}F)\{S_2P(O^iPr)_2\}_6](PF_6)$, **2**.

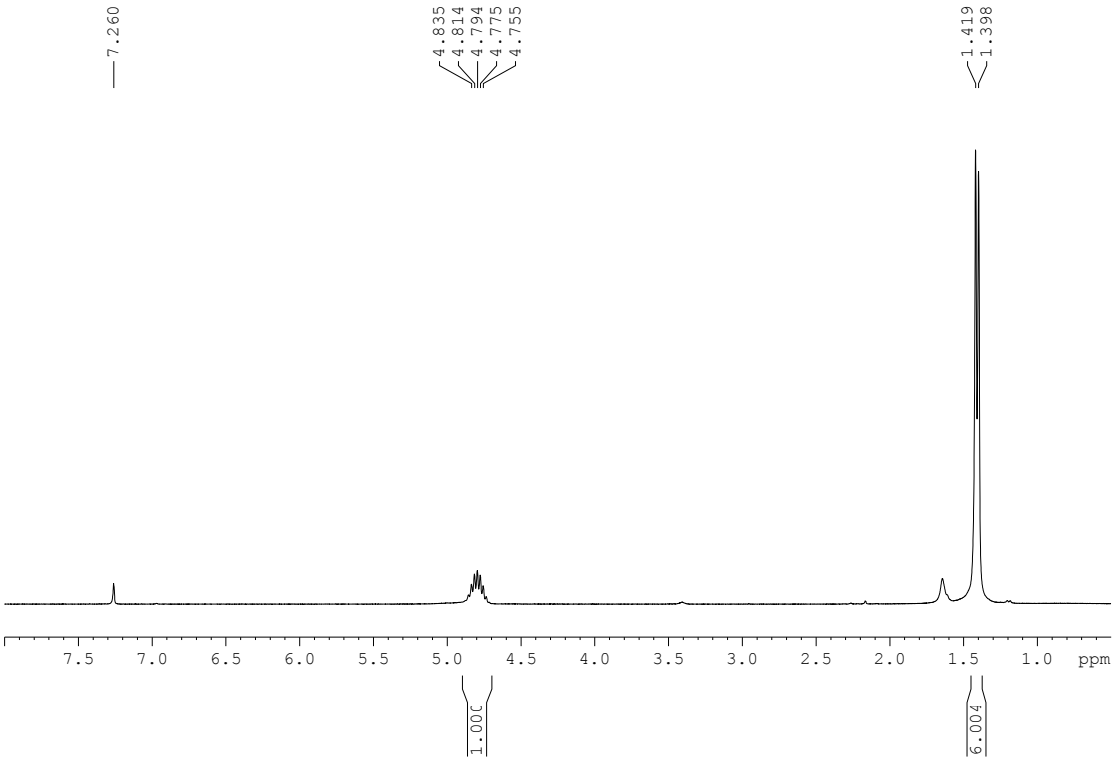

Figure S4 ^{1}H NMR spectrum of $[Ag_8(\mu_8\text{-}F)\{S_2P(O^iPr)_2\}_6](PF_6)$, **2**.

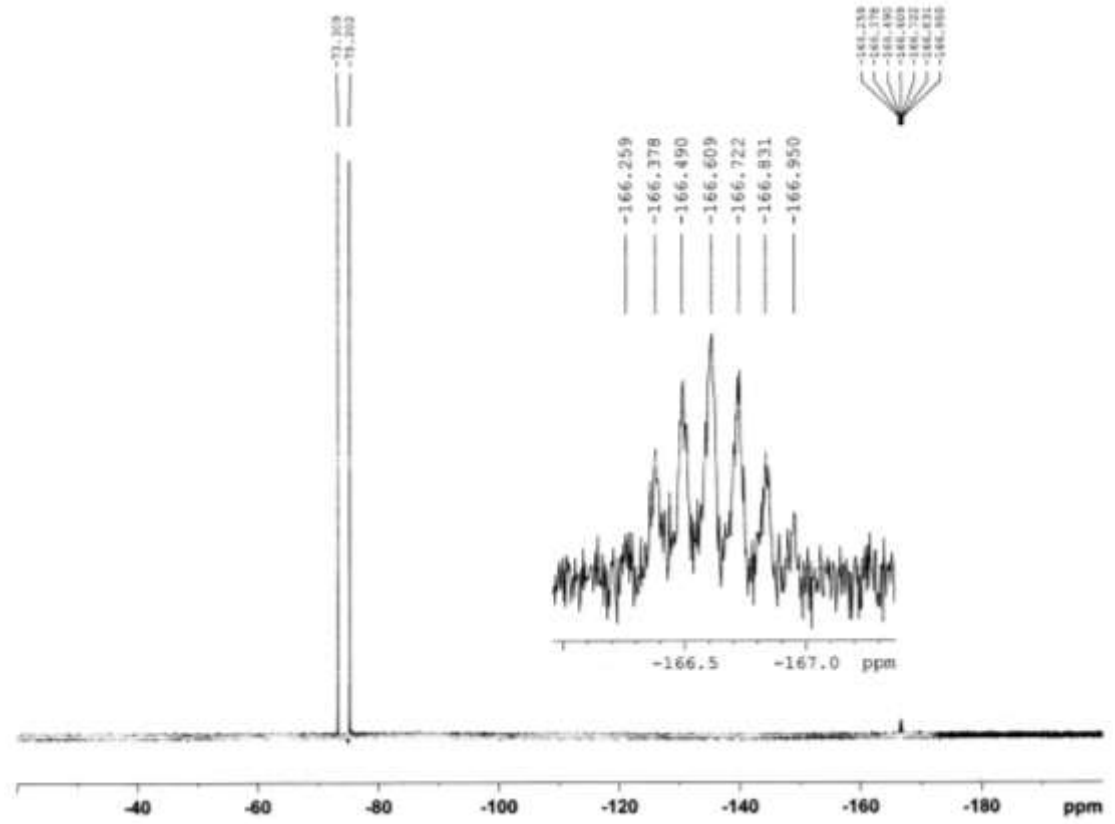

Figure S5 ^{19}F NMR spectrum of $[Ag_8(\mu_8\text{-}F)\{S_2P(O^iPr)_2\}_6](PF_6)$, **2**. Inset is the magnetude around -166 ppm.

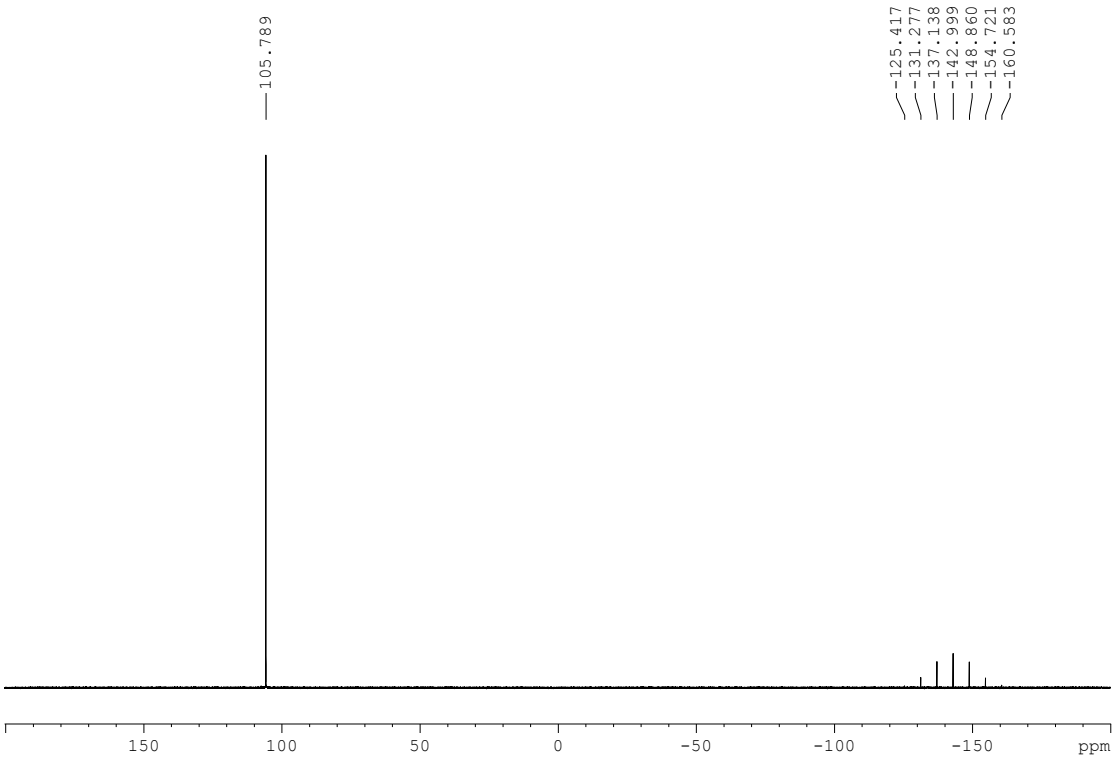

Figure S6 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_8(\mu_8\text{-}Cl)\{S_2P(O^iPr)_2\}_6](PF_6)$, **3**.

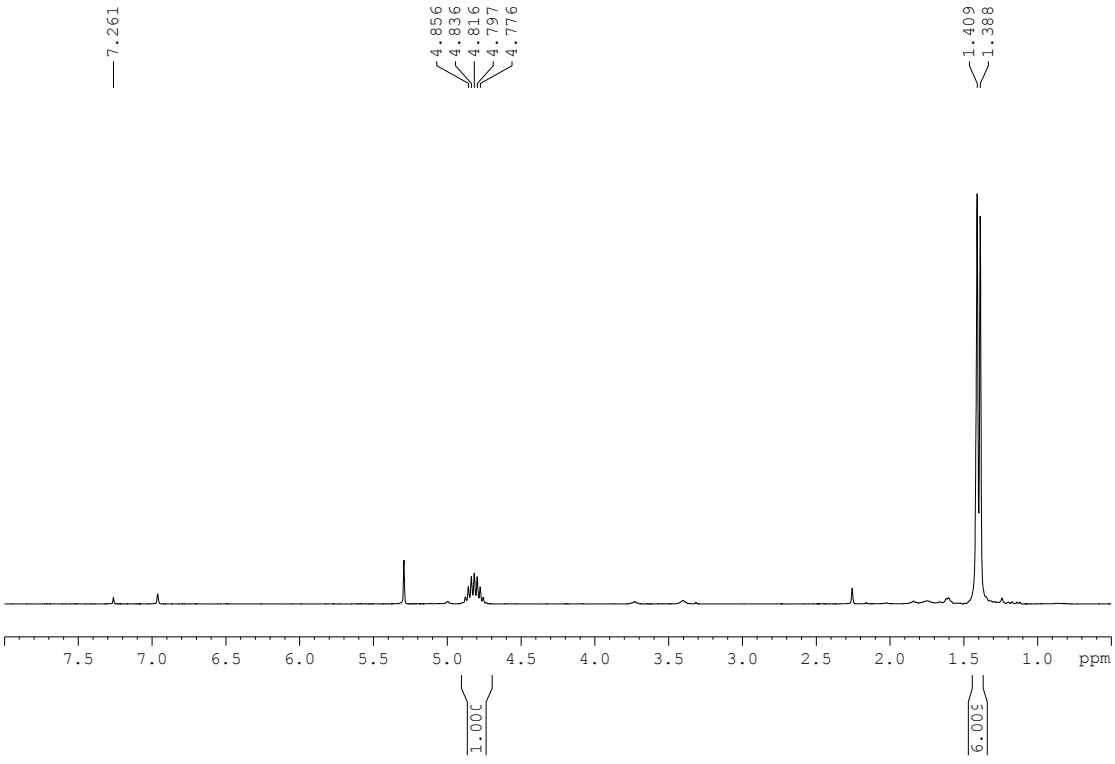

Figure S7 ^{1}H NMR spectrum of $[Ag_8(\mu_8\text{-}Cl)\{S_2P(O^iPr)_2\}_6](PF_6)$, **3**.

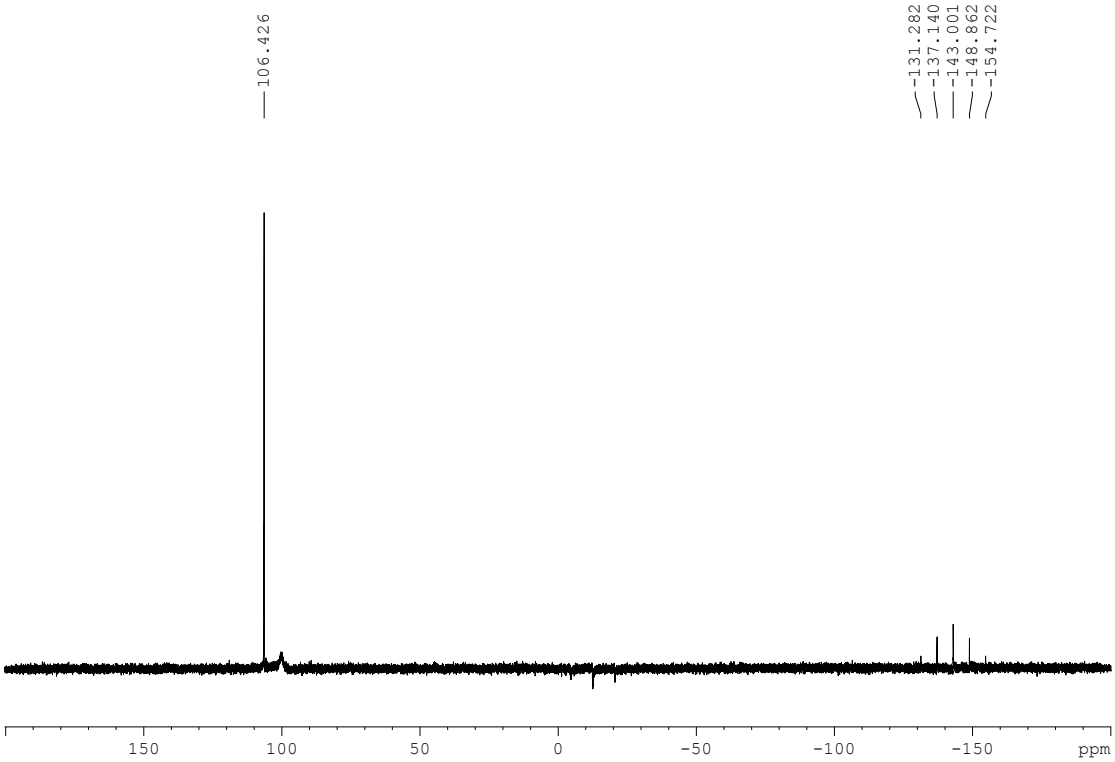

Figure S8 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_8(\mu_8\text{-}Br)\{S_2P(O^iPr)_2\}_6](PF_6)$, **4**.

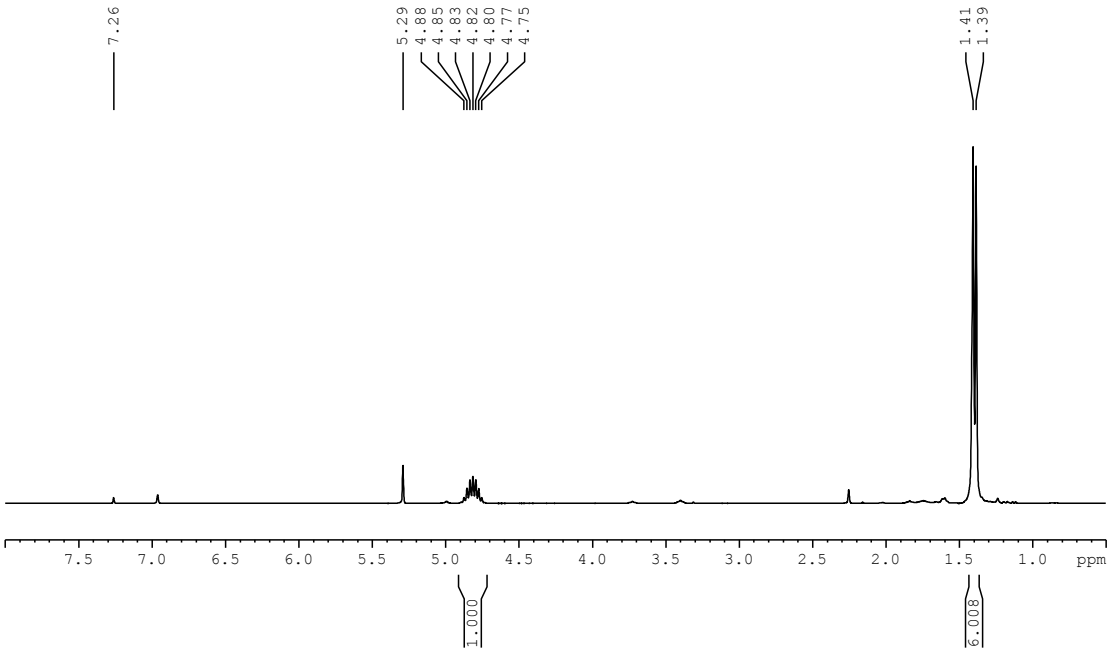

Figure S9 ^{1}H NMR spectrum of $[Ag_8(\mu_8\text{-}Br)\{S_2P(O^iPr)_2\}_6](PF_6)$, **4**.

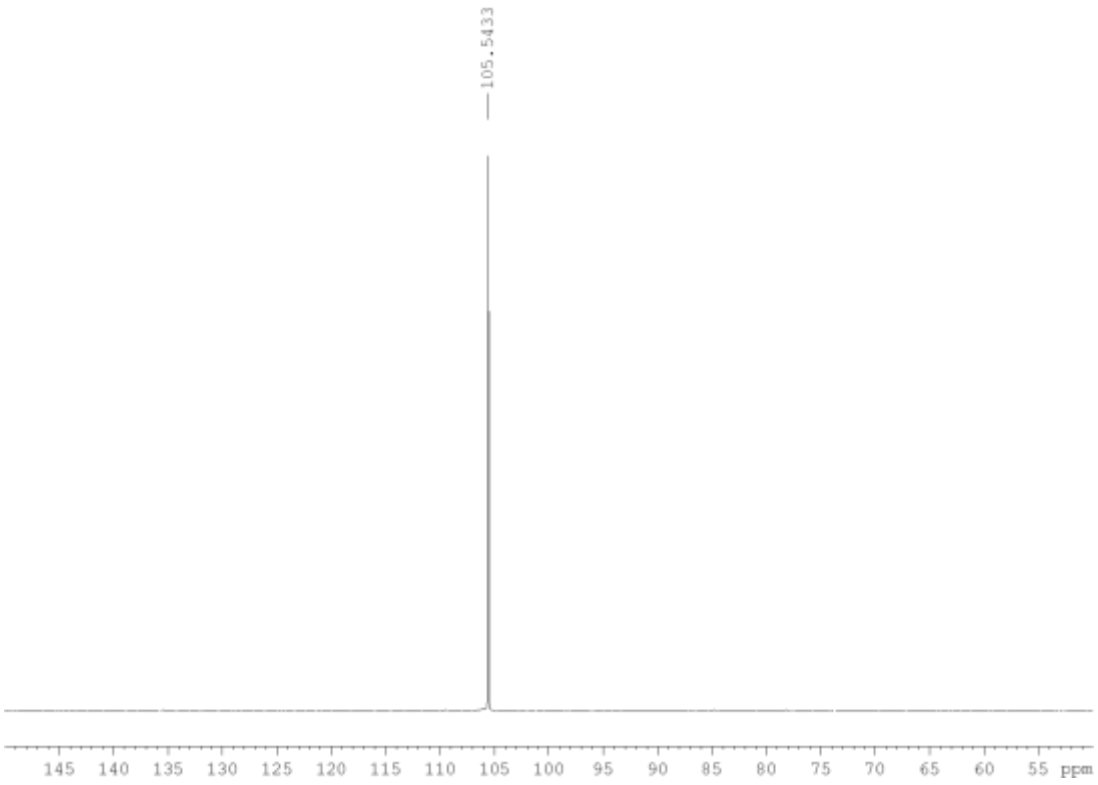

Figure S10 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_8(\mu_4\text{-}H)\{S_2P(O^iPr)_2\}_6](PF_6)$, **5**.

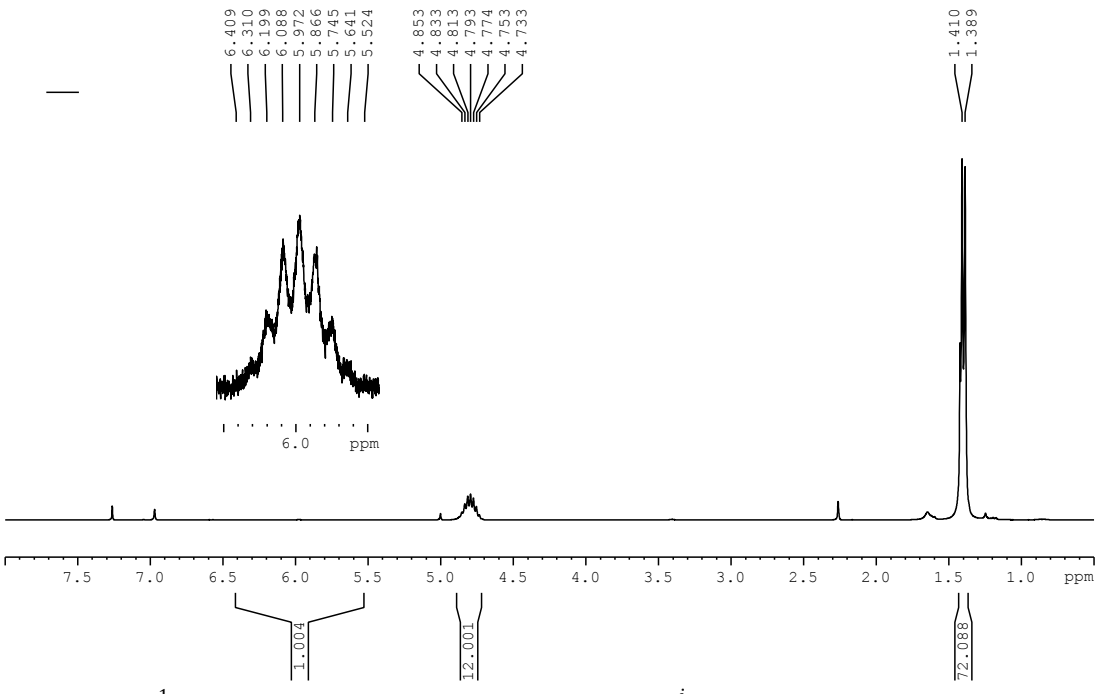

Figure S11 ^{1}H NMR spectrum of $[Ag_8(\mu_4\text{-}H)\{S_2P(O^iPr)_2\}_6](PF_6)$, **5**. Inset is the magnitude around 6.0 ppm.

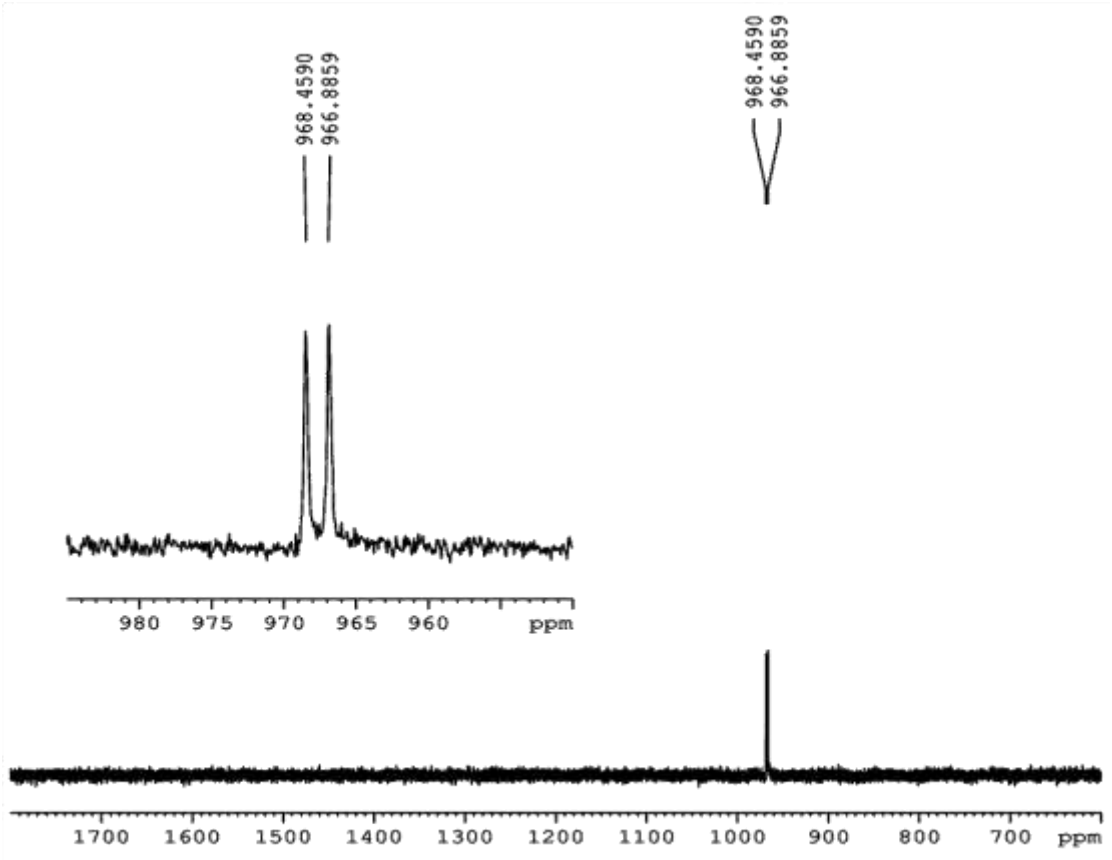

Figure S12 ^{109}Ag{^{1}H} NMR spectrum of $[Ag_8(\mu_4\text{-H})\{S_2P(O^iPr)_2\}_6](PF_6)$, **5**. Inset is the magnitude around 967 ppm.

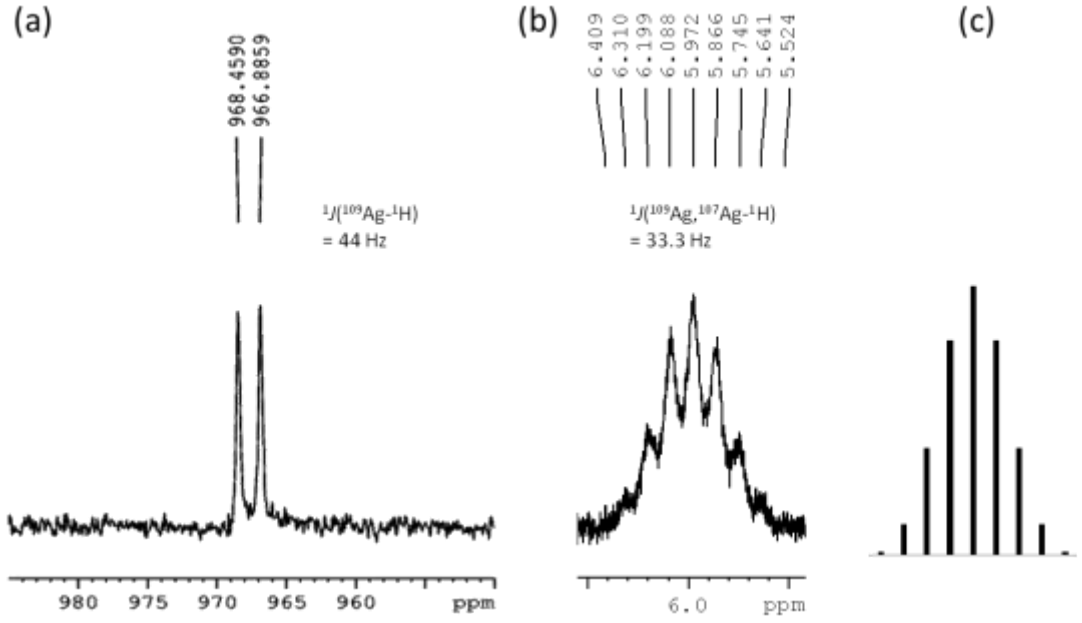

Figure S13 The splitting patterns of compound 5 that consisting one doublet in (a) ^{109}Ag NMR and one nonet in (b) ^{1}H NMR spectra. (c) Simulated Intensity ratio for a nonet resonance.

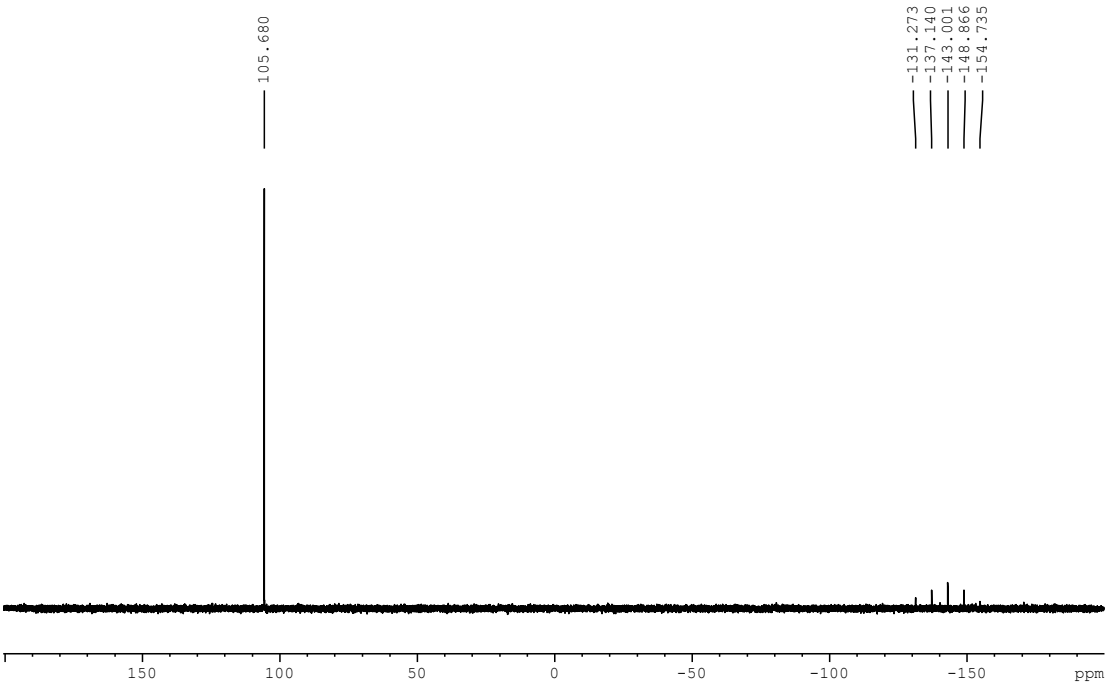

Figure S14 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_8(D)\{S_2P(O^iPr)_2\}_6](PF_6)$, **5'**.

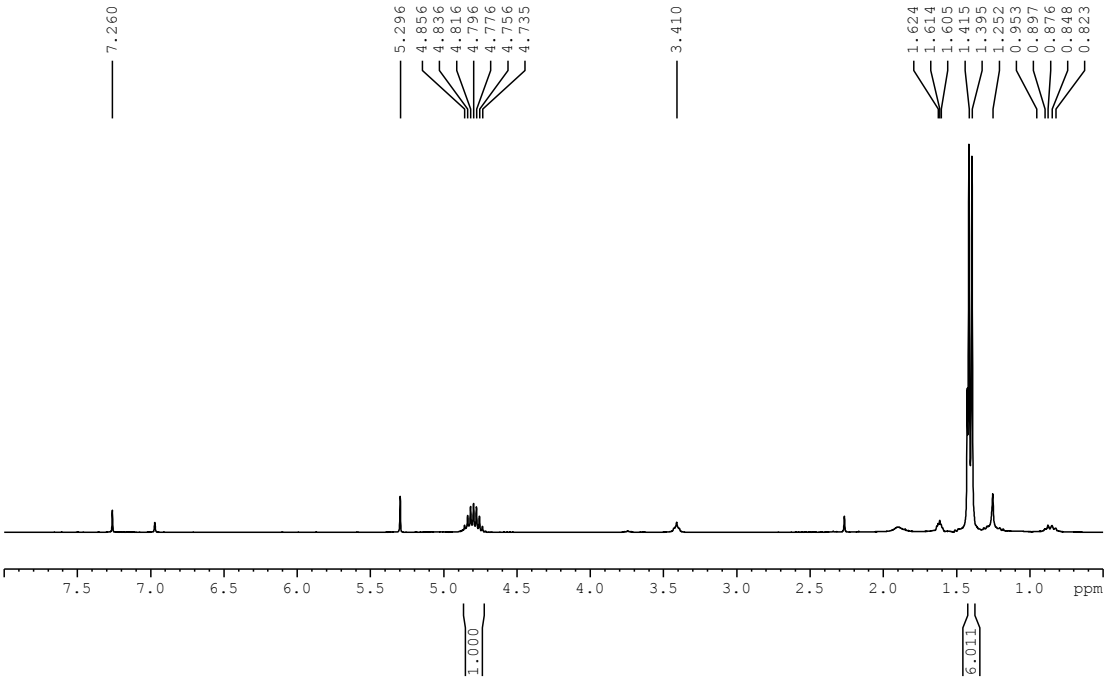

Figure S15 ^{1}H NMR spectrum of $[Ag_8(D)\{S_2P(O^iPr)_2\}_6](PF_6)$, **5'**.

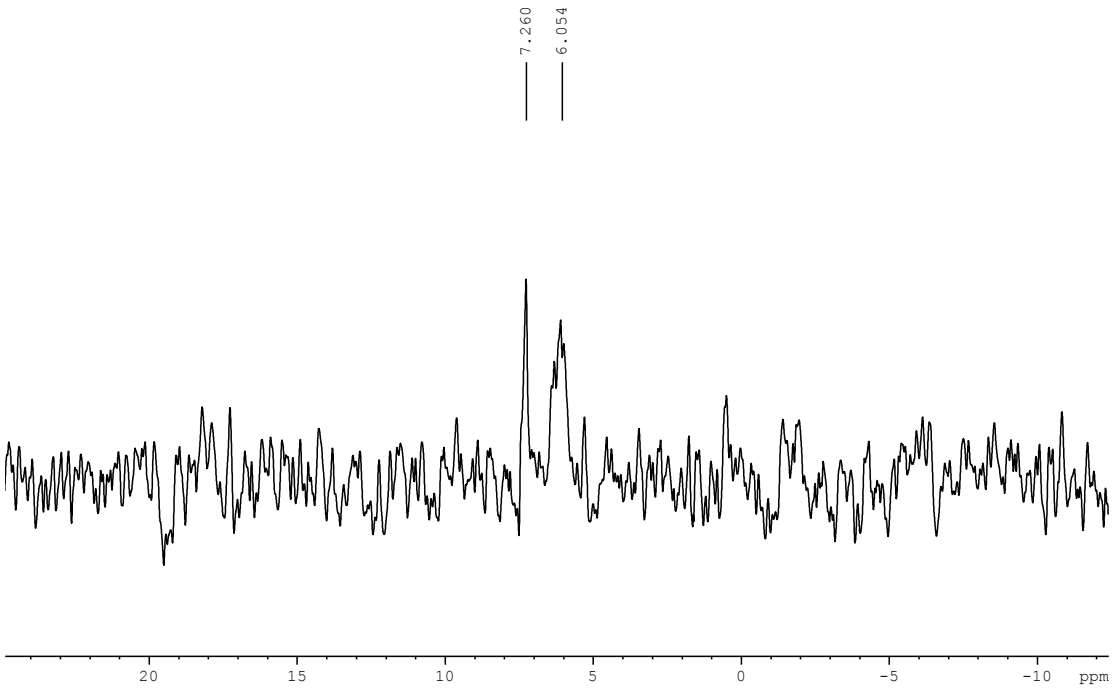

Figure S16 ^{2}H NMR spectrum of $[Ag_8(D)\{S_2P(O^iPr)_2\}_6](PF_6)$, **5'**.

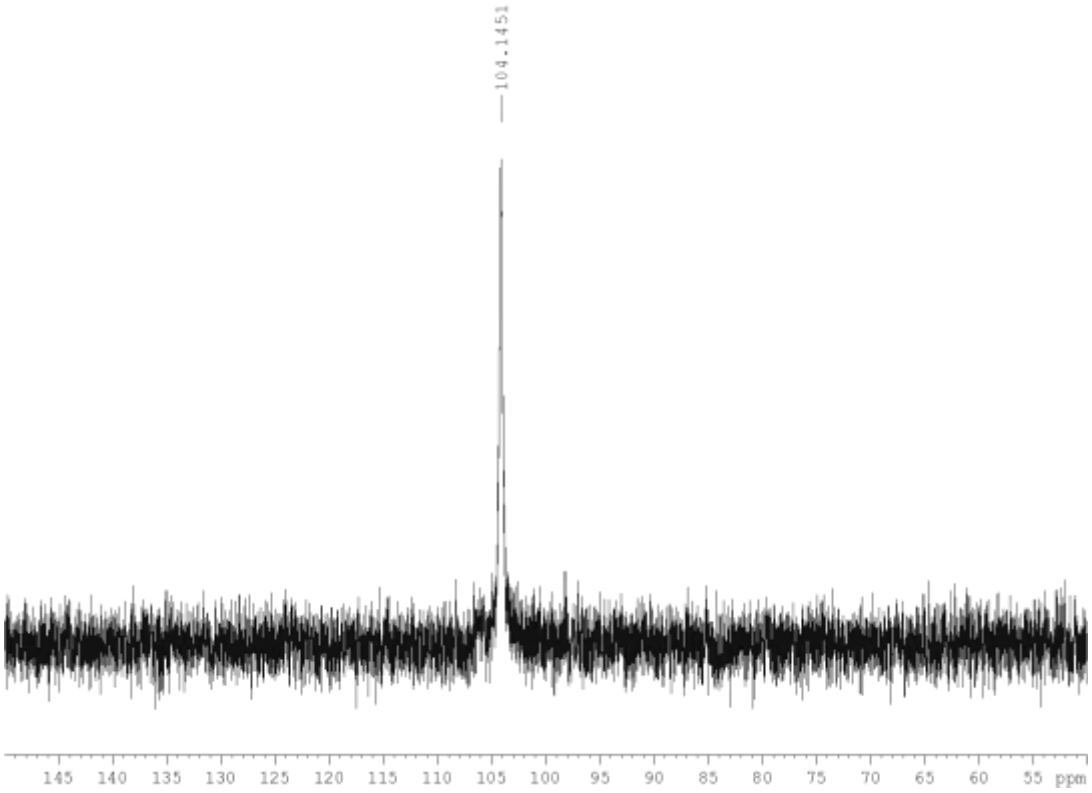

Figure S17 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_8(\mu_8\text{-}S)\{S_2P(O^iPr)_2\}_6]$, **6**.

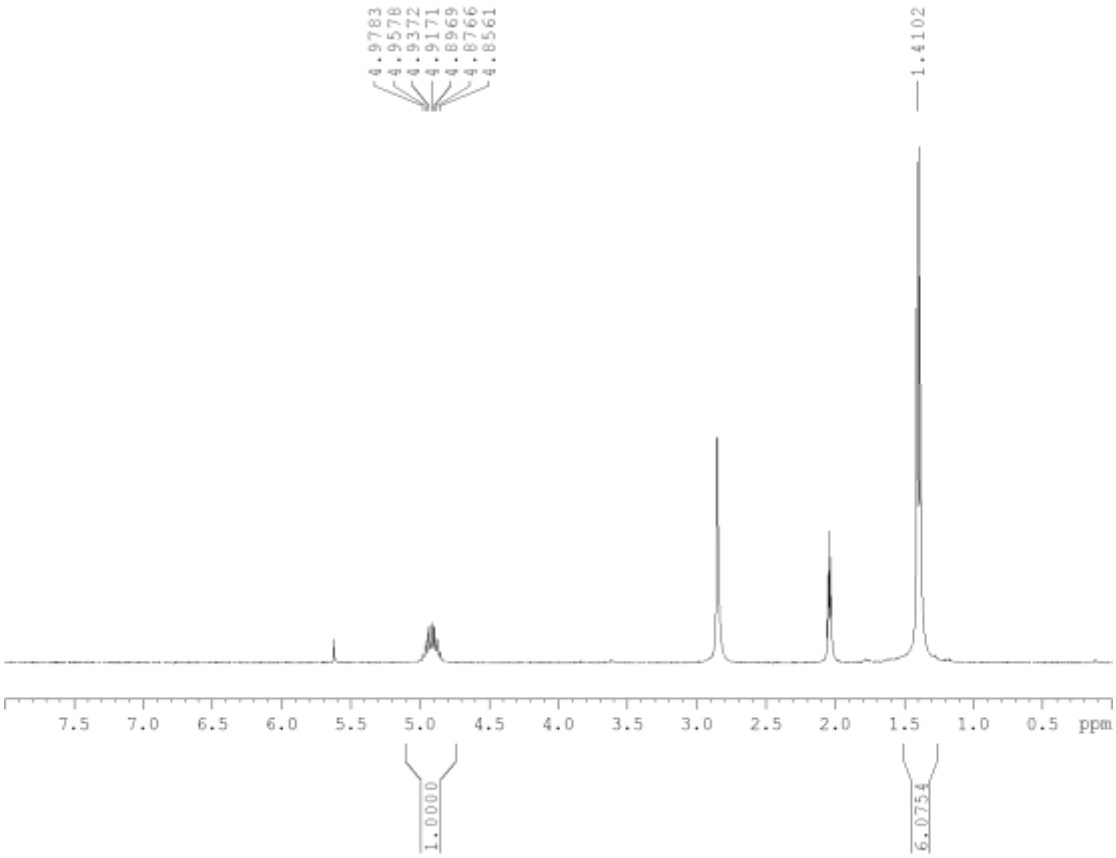

Figure S18 ^{1}H NMR spectrum of $[Ag_8(\mu_8\text{-}S)\{S_2P(O^iPr)_2\}_6]$, **6**.

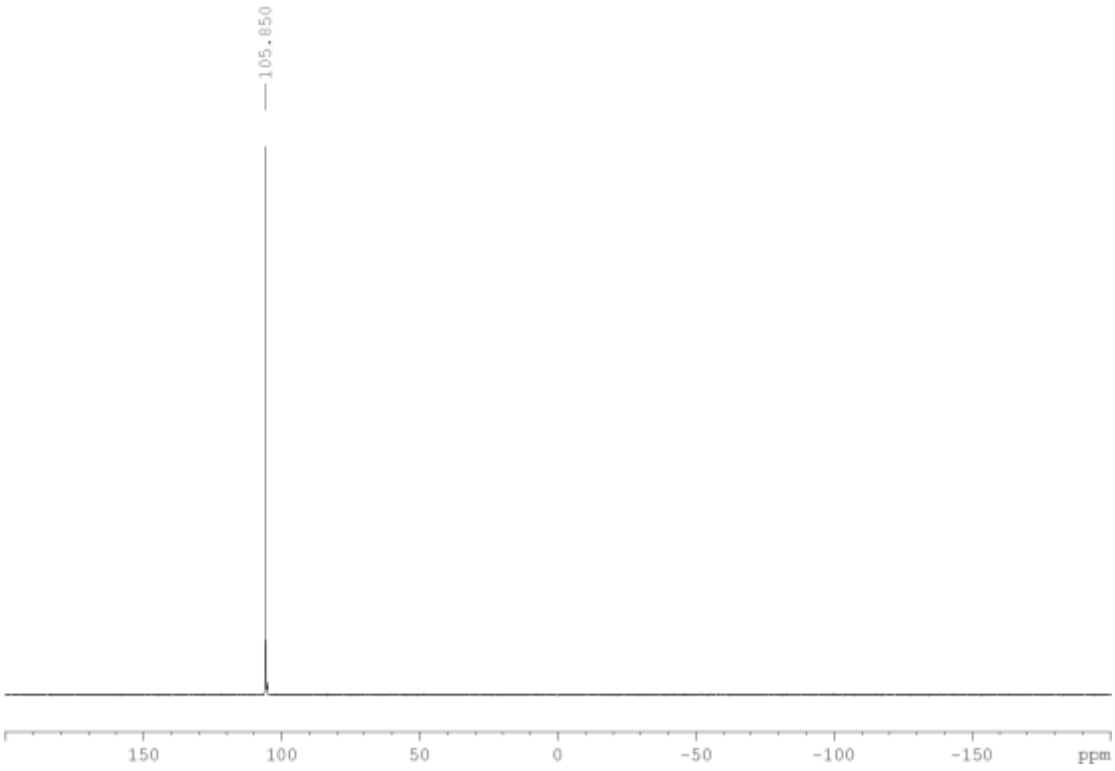

Figure S19 $^{31}P\{^{1}H\}$ NMR spectrum of $[Ag_{10}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]$, **7**.

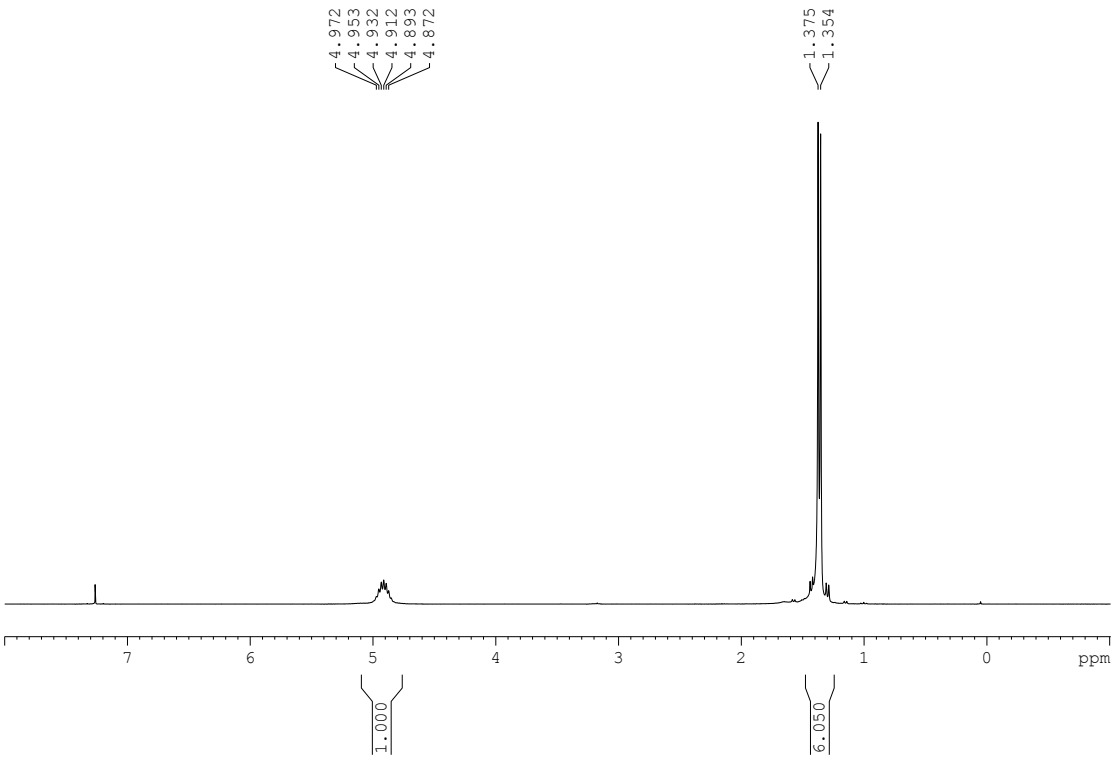

Figure S20 ^{1}H NMR spectrum of $[Ag_{10}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]$, **7**.

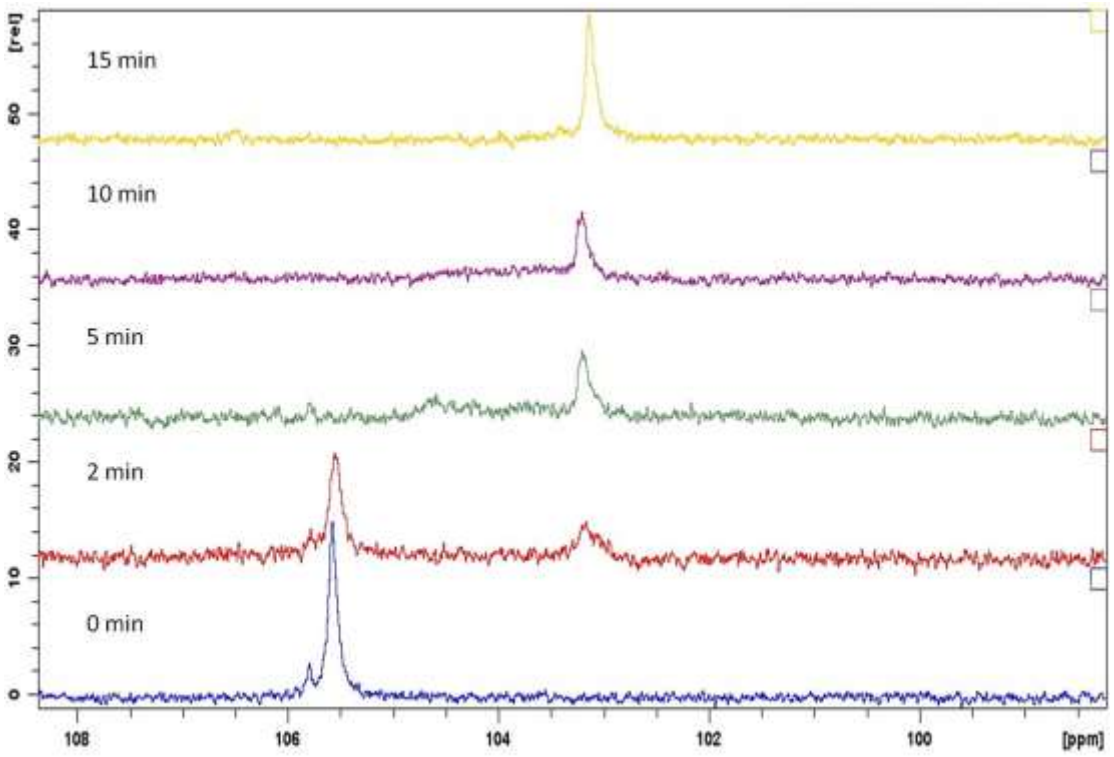

Figure S21 $^{31}P\{^{1}H\}$ NMR spectra of monitoring the conversion within 15 minutes from $[Ag_{10}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]$ to $[Ag_{11}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]PF_6$ by adding one equivalent (relative to $[Ag_{10}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]$) of $[Ag(CH_3CN)_4]PF_6$.