

# Electronic supplementary data to accompany

## Self-Assembly of heteroleptic dinuclear silver(I) complexes bridged by bis(diphenylphosphino)-acetylene

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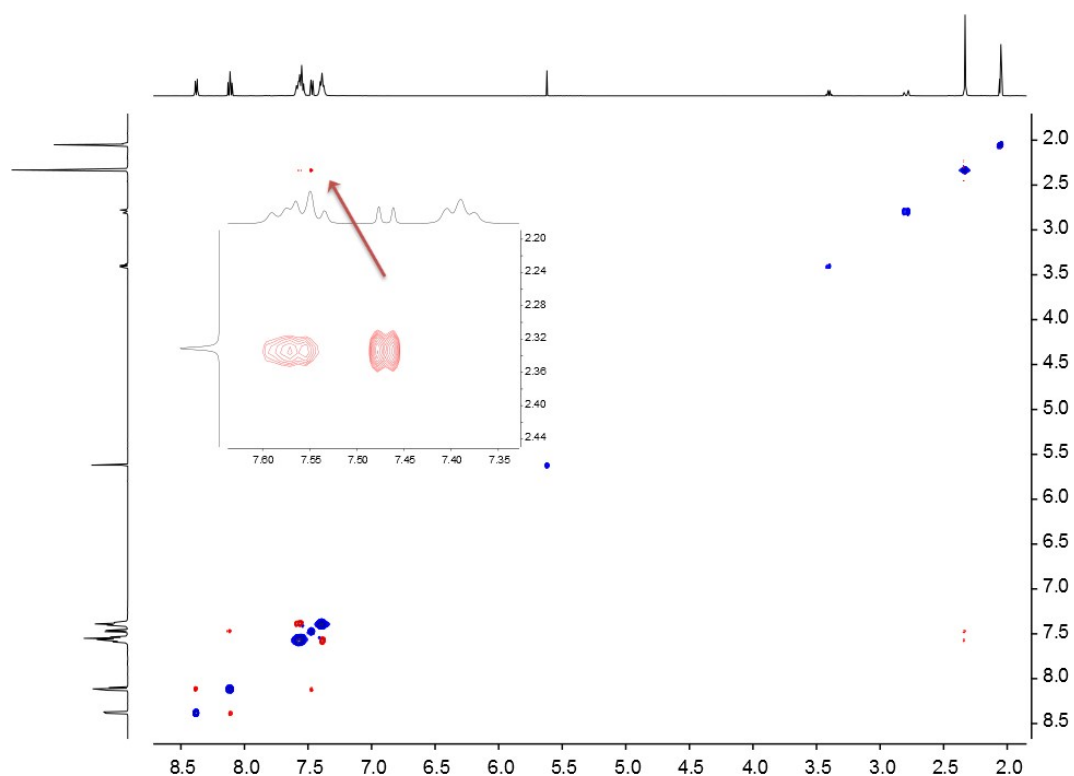


Fig. S1: NOESY spectrum of  $[\text{Ag}_2(\text{dppa})_2(6,6'\text{-Me}_2\text{bpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz. The NOESY cross peaks between the Me signal at  $\delta$  2.33 ppm and the  $\text{H}^{\text{C}2+\text{C}4}$  signal at  $\delta$  7.57 ppm are clearly visible.

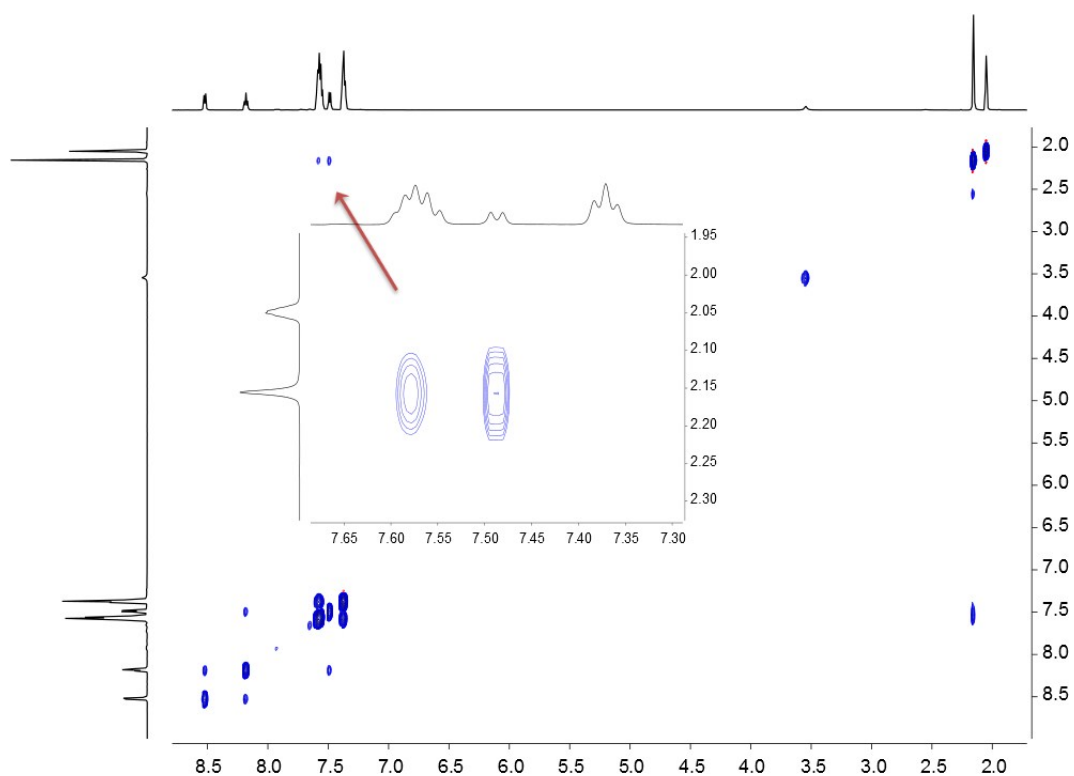


Fig. S2: NOESY spectrum of  $[\text{Ag}_2(\text{dppa})_2(6,6'\text{-Me}_2\text{bpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 208 K, 600 MHz. The NOESY cross peaks between the Me signal at  $\delta$  2.16 ppm and the  $\text{H}^{\text{C}2+\text{C}4}$  signal at  $\delta$  7.58 ppm are clearly visible.

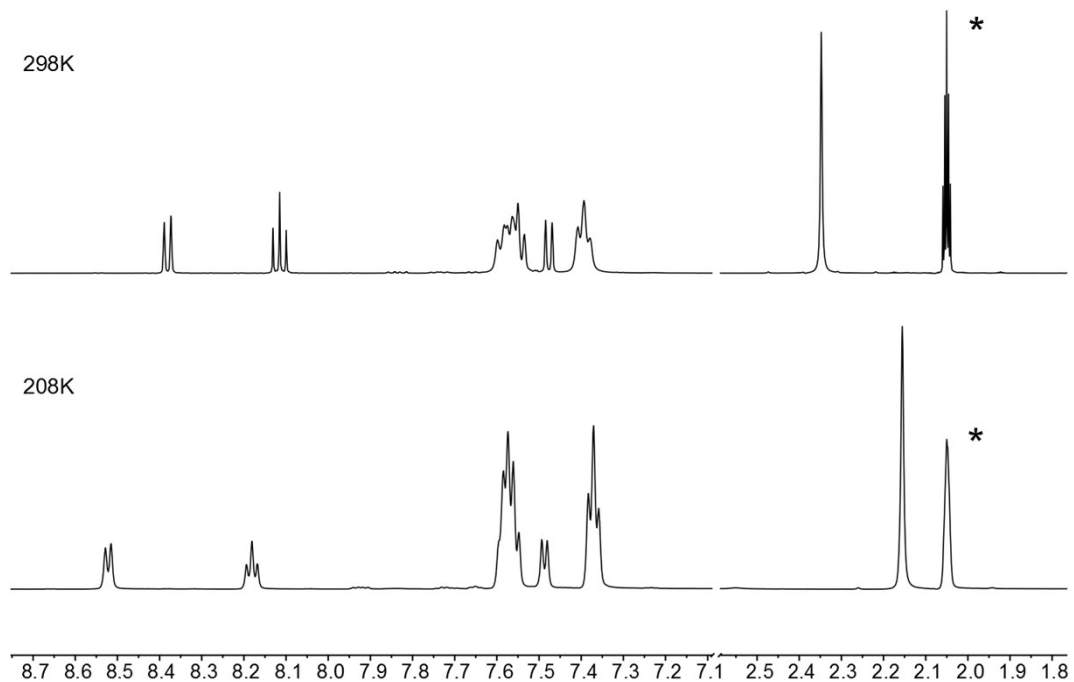


Fig. S3:  $^1\text{H}$  NMR spectra of  $[\text{Ag}_2(\text{dppa})_2(6,6'\text{-Me}_2\text{bpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz (top) and 208 K, 600 MHz (bottom). Signals marked with an asterisk indicate residual  $\text{CD}_3\text{CD}_2\text{HCO}$ .

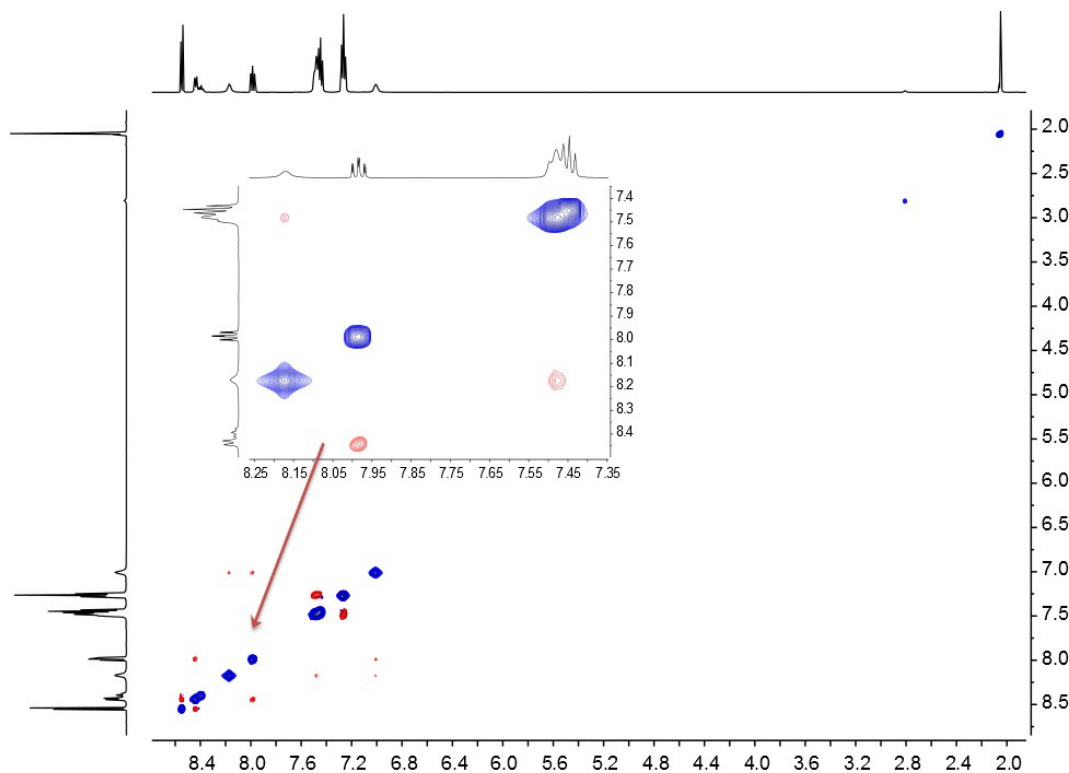


Fig. S4: NOESY spectrum of  $[\text{Ag}_2(\text{dppa})_2(\text{tpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz. The NOESY cross peaks between the  $\text{H}^{\text{A}6}$  signal at  $\delta$  8.17 ppm and the  $\text{H}^{\text{C}2}$  signal at  $\delta$  7.48 ppm are sufficiently visible.

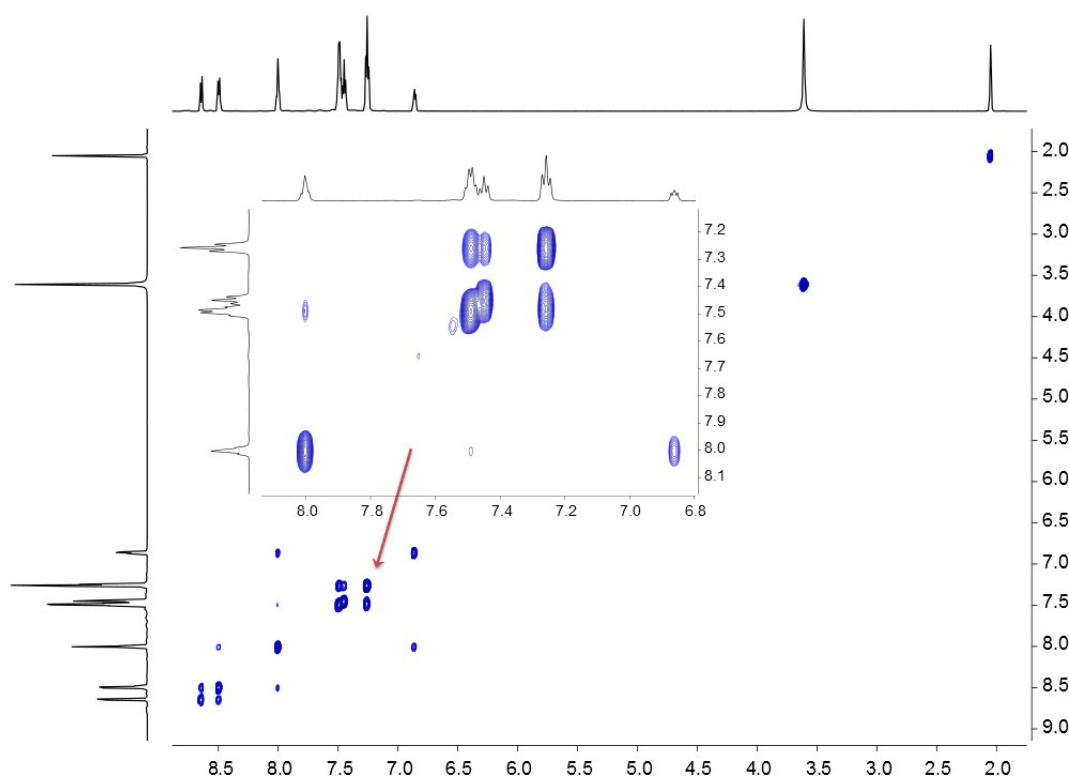


Fig. S5: NOESY spectrum of  $[\text{Ag}_2(\text{dppa})_2(\text{tpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 208 K, 600 MHz. The NOESY cross peaks between the  $\text{H}^{\text{A}6}$  signal at  $\delta$  8.00 ppm and the  $\text{H}^{\text{C}2}$  signal at  $\delta$  7.49 ppm are sufficiently visible.

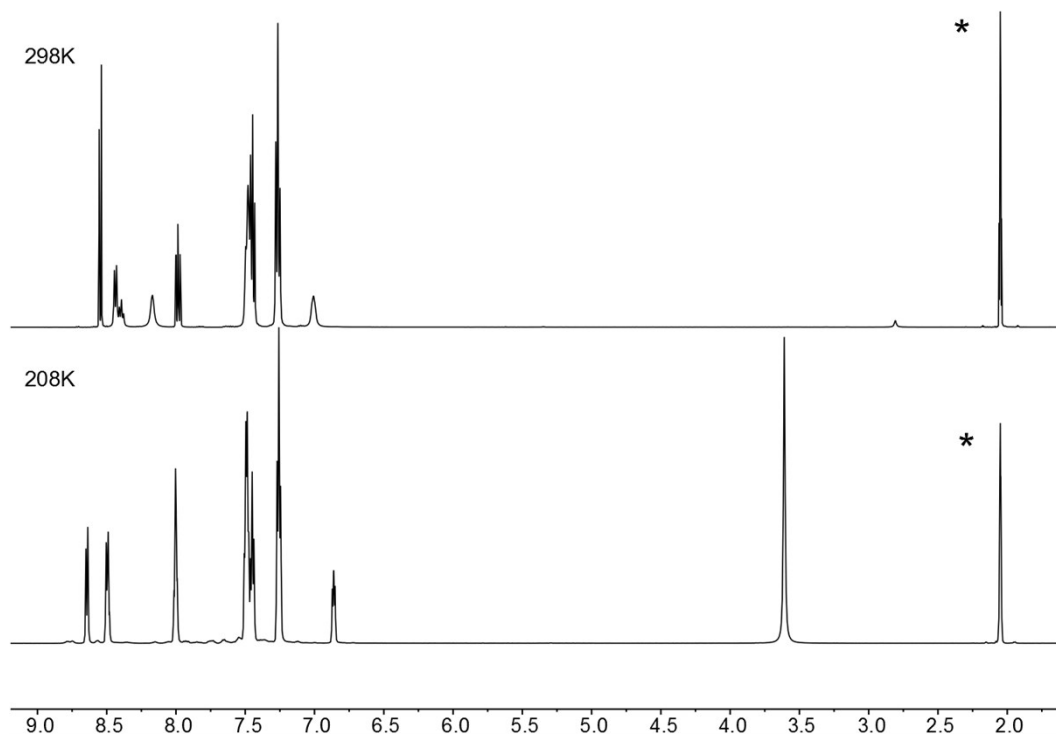


Fig. S6:  $^1\text{H}$  NMR spectra of  $[\text{Ag}_2(\text{dppa})_2(\text{tpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz (top) and 208 K, 600 MHz (bottom). Signals marked with an asterisk indicate residual  $\text{CD}_3\text{CD}_2\text{HCO}$ .

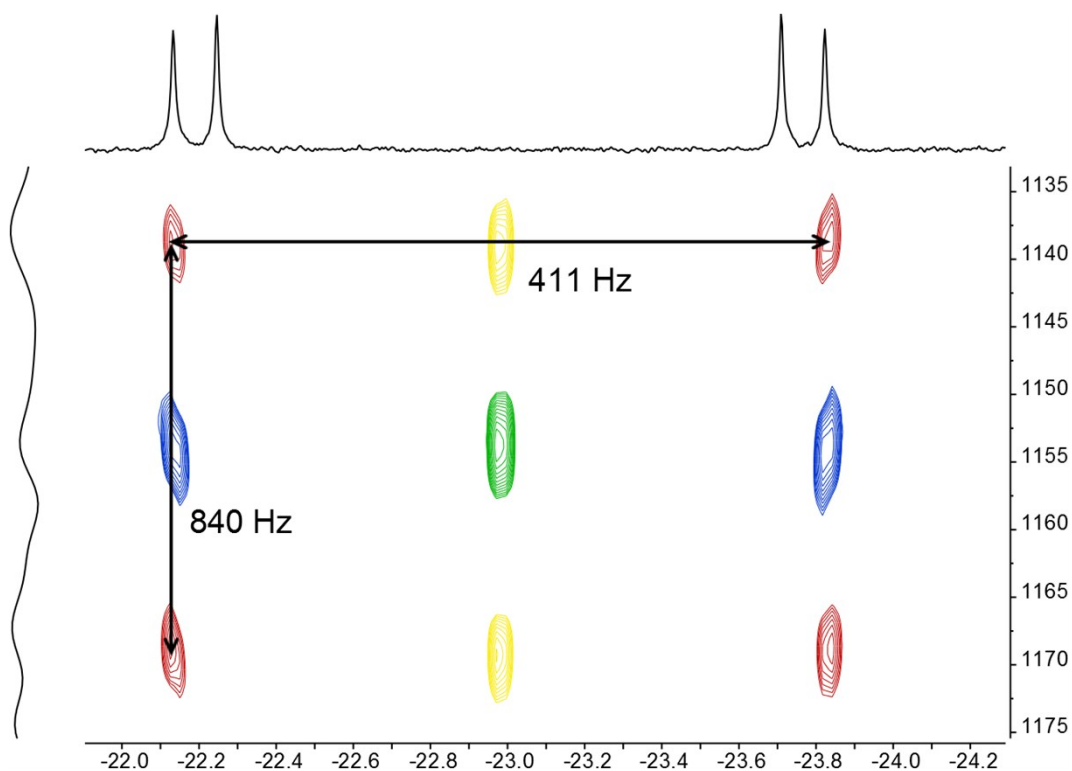


Fig. S7:  $^{31}\text{P}\{^1\text{H}\}\text{-}^{109}\text{Ag}$  HSQC spectrum of  $[\text{Ag}_2(\text{dppa})_2(\text{tpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 208 K, 14.1 T. Cross peaks without decoupling are coloured in red, with  $\{^{31}\text{P}\}$  decoupling in blue, with  $\{^{109}\text{Ag}\}$  decoupling in yellow and with both  $\{^{31}\text{P}\}$  and  $\{^{109}\text{Ag}\}$  decoupling green.

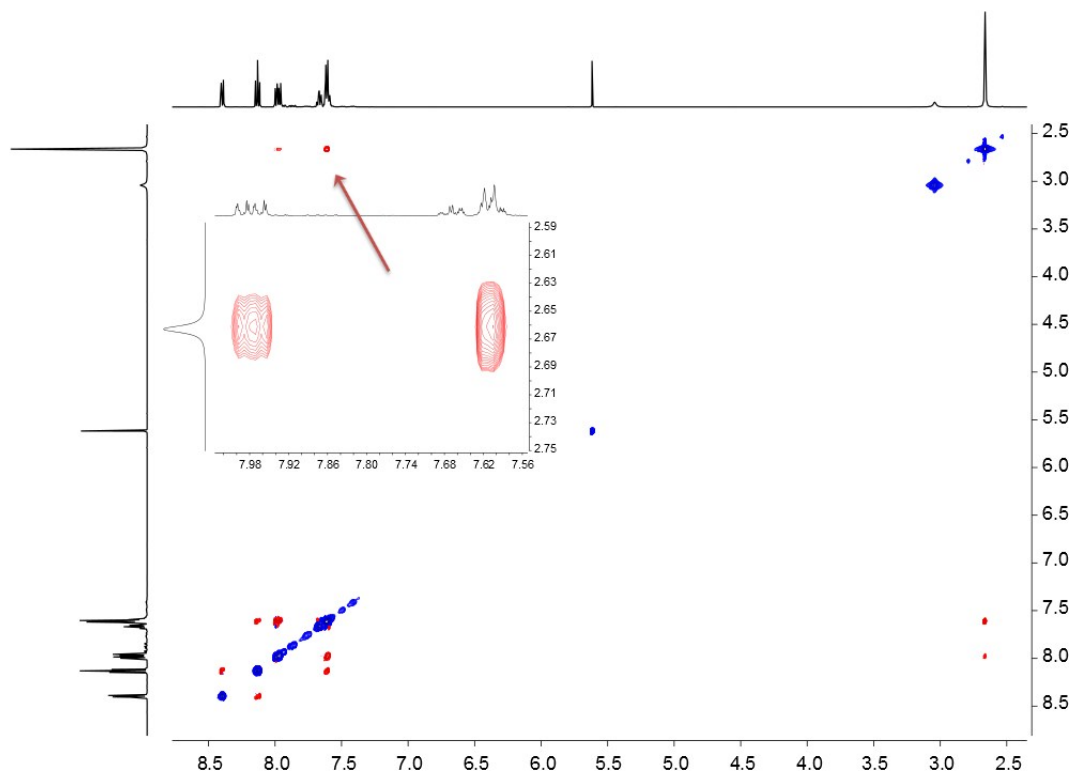


Fig. S8: NOESY spectrum of  $[\text{Ag}_2(\text{dppa})(6,6'\text{-Me}_2\text{bpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz. The NOESY cross peaks between the Me signal at  $\delta$  2.66 ppm and the  $\text{H}^{\text{C}2}$  signal at  $\delta$  7.98 ppm are clearly visible.

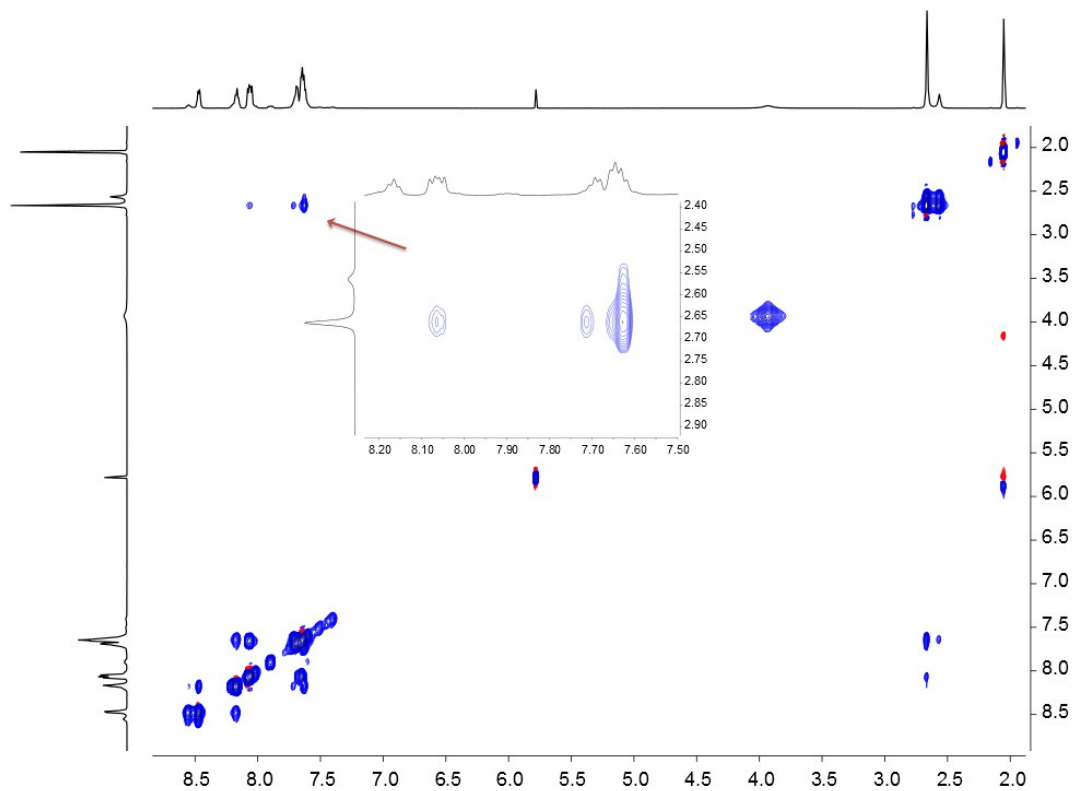


Fig. S9: NOESY spectrum of  $[\text{Ag}_2(\text{dppa})(6,6'\text{-Me}_2\text{bpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 208 K, 600 MHz. The NOESY cross peaks between the Me signal at  $\delta$  2.66 ppm and the  $\text{H}^{\text{C}2}$  signal at  $\delta$  8.06 ppm are clearly visible.

visible. Also we see an exchange between the main Me signal at  $\delta$  2.66 ppm and the additional Me signal at  $\delta$  2.56 ppm.

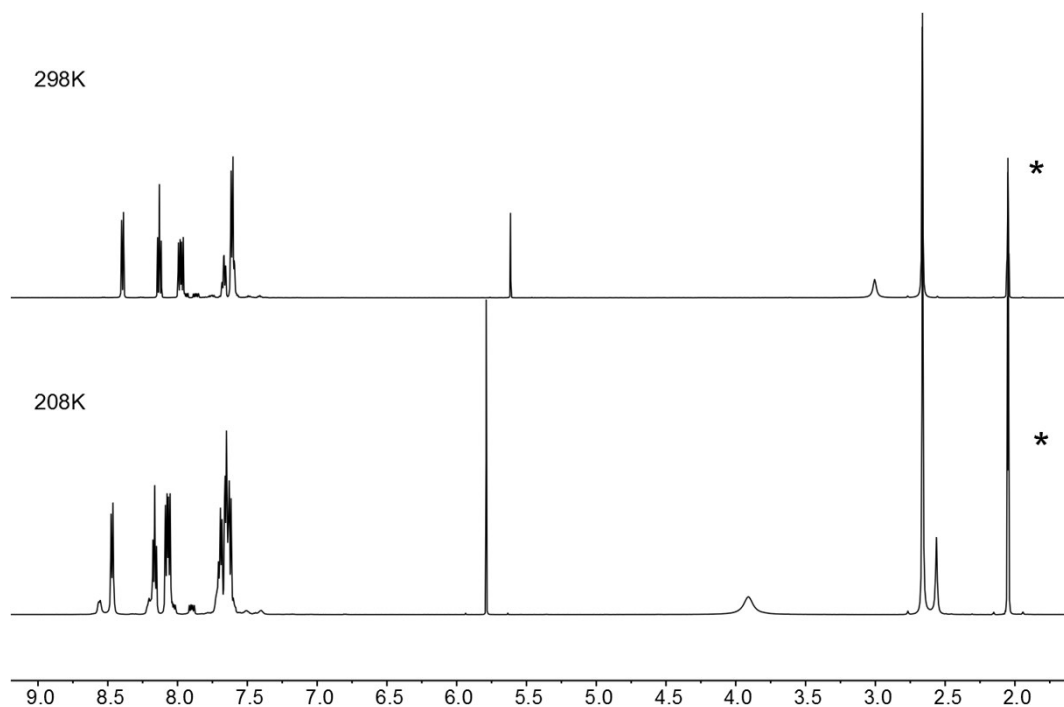


Fig. S10:  $^1\text{H}$  NMR spectra of  $[\text{Ag}_2(\text{dppa})(6,6'\text{-Me}_2\text{bpy})_2][\text{PF}_6]_2$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz (top) and 208 K, 600 MHz (bottom). Signals marked with an asterisk indicate residual  $\text{CD}_3\text{CD}_2\text{HCO}$ .

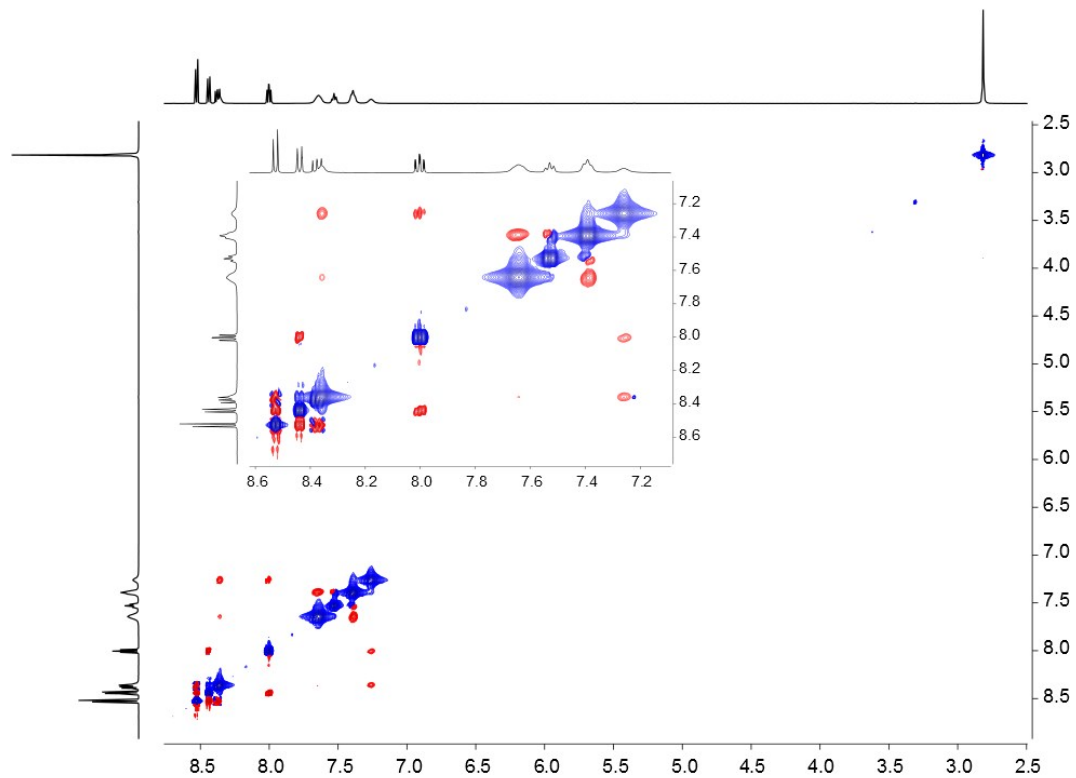


Fig. S11: NOESY spectrum of a 2:2:1 mixture of  $[\text{Ag}][\text{PF}_6]$ , tpy and dppa in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz. The NOESY cross peaks between the  $\text{H}^{\text{A}6}$  signal at  $\delta$  8.36 ppm and the  $\text{H}^{\text{C}2}$  signal at  $\delta$  7.65 ppm are clearly visible.

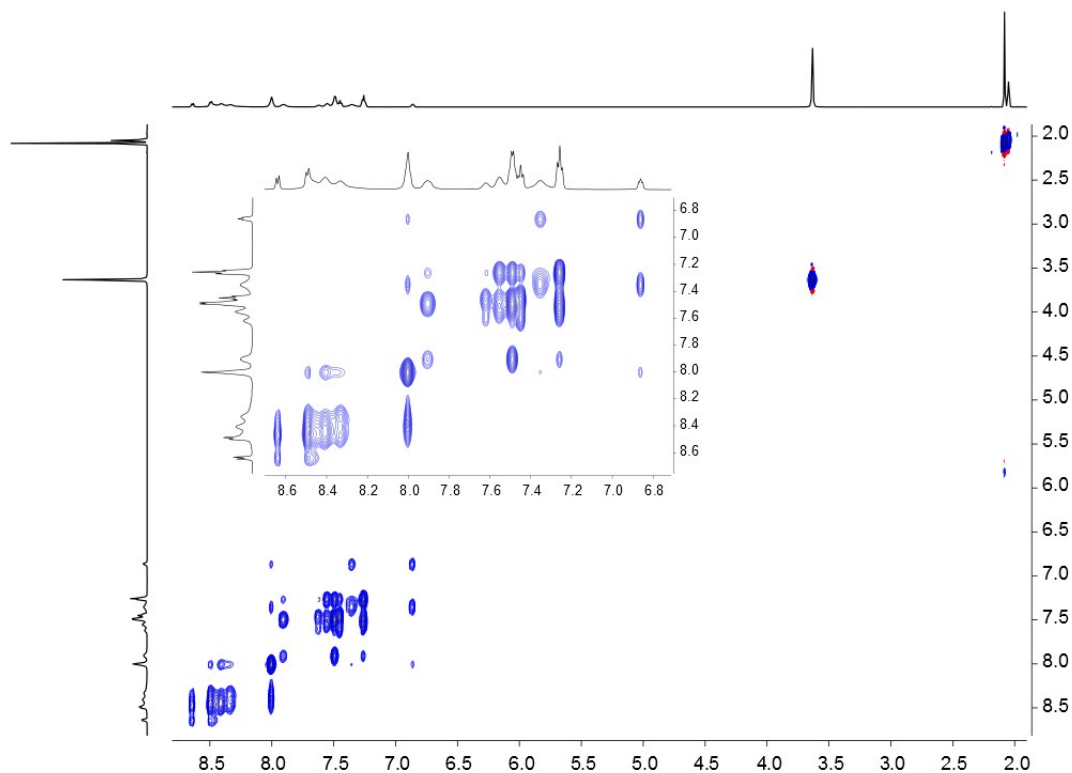


Fig. S12: NOESY spectrum of a 2:2:1 mixture of  $[\text{Ag}][\text{PF}_6]$ , tpy and dppa in  $(\text{CD}_3)_2\text{CO}$  at 208 K, 600 MHz.

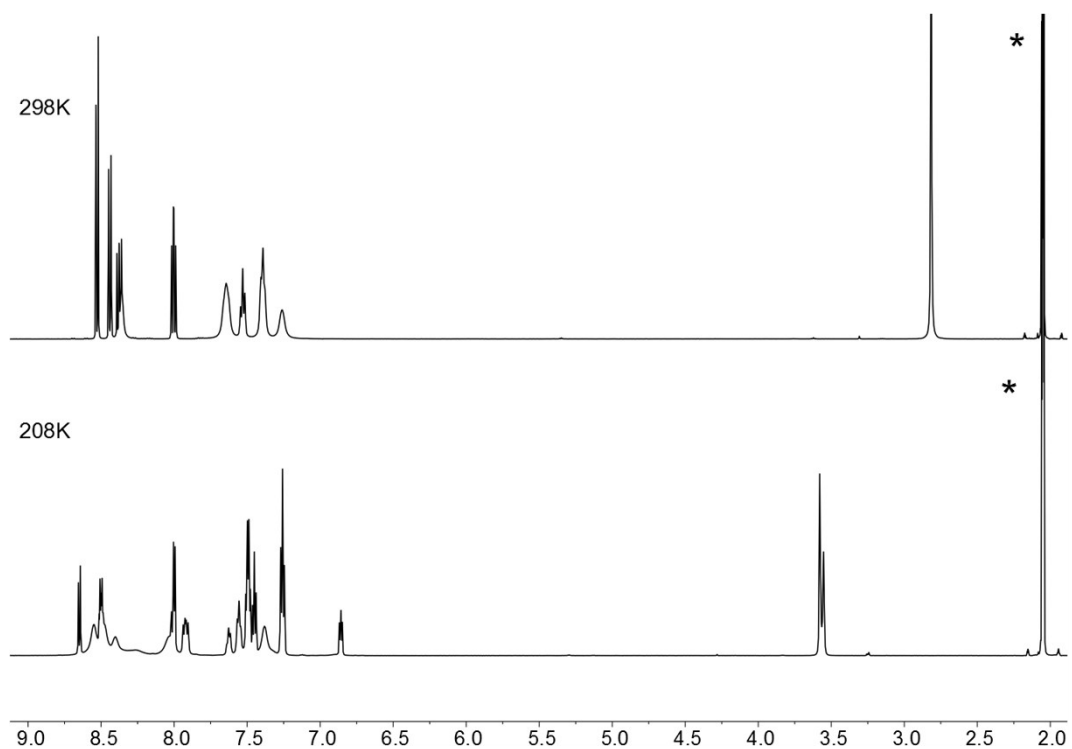


Fig. S13:  $^1\text{H}$  NMR spectra of a 2:2:1 mixture of  $[\text{Ag}][\text{PF}_6]$ , tpy and dppa in  $(\text{CD}_3)_2\text{CO}$  at 298 K, 500 MHz (top) and 208 K, 600 MHz (bottom). Signals marked with an asterisk indicate residual  $\text{CD}_3\text{CD}_2\text{HCO}$ .

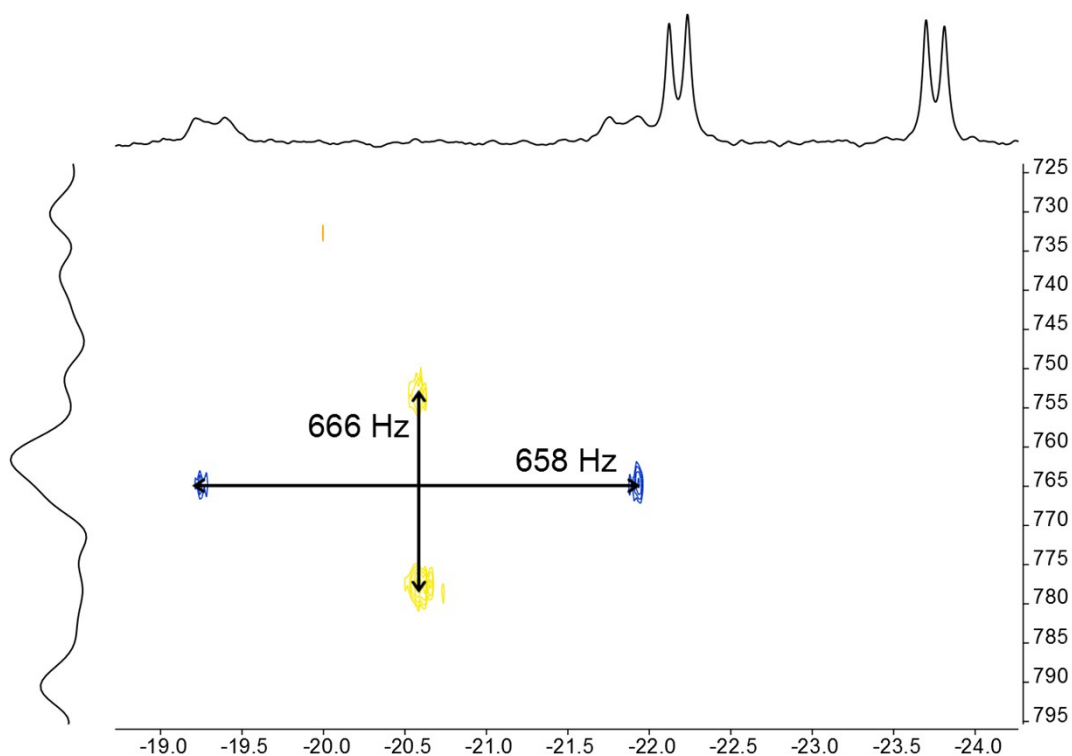


Fig. S14:  $^{31}\text{P}\{^1\text{H}\}\text{-}^{109}\text{Ag}$  HSQC spectrum of a 2:2:1 mixture of  $\text{Ag}[\text{PF}_6]$ , tpy and dppa in  $(\text{CD}_3)_2\text{CO}$  at 208 K, 14.1 T. Cross peaks with  $\{^{31}\text{P}\}$  decoupling are coloured in blue and with  $\{^{109}\text{Ag}\}$  decoupling in yellow. The spectra without decoupling and with both  $\{^{31}\text{P}\}$  and  $\{^{109}\text{Ag}\}$  decoupling are not shown due to weak signal to noise ratio.