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Supplementary Material

Facile synthesis and structures of silver formamidinates and pyrazolates

Zhifang Guo[A,B], *Nicole Wang*[A], *Victoria L. Blair*[A], *Ekaterina I. Izgorodina*[A], *Glen B. Deacon*[A] and *Peter C. Junk*[B,*]

[A]School of Chemistry, Monash University, Clayton, Vic. 3800, Australia

[B]College of Science and Engineering, James Cook University, Townsville, Qld 4811, Australia

*Correspondence to: Email: peter.junk@jcu.edu.au

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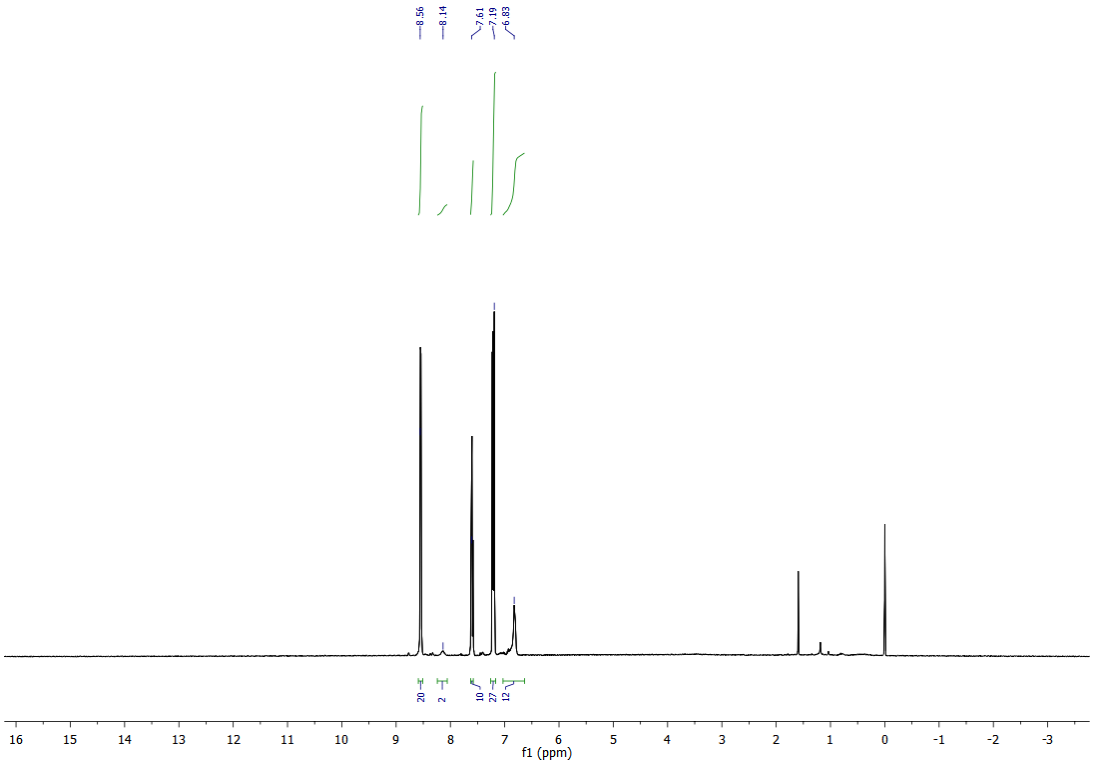

Fig. S1 ^{1}H NMR spectrum of $[Ag_2(DFForm)_2(py)_2]$ (**1**)

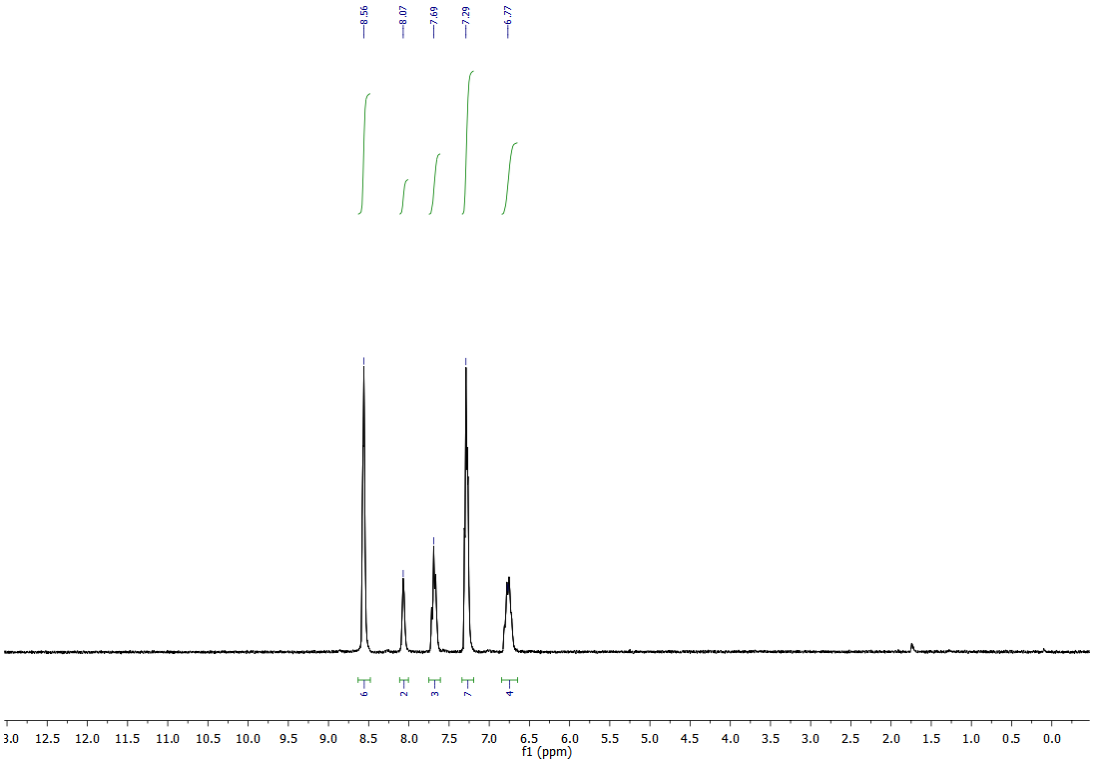

Fig. S2 ^{1}H NMR spectrum of $[Ag_2(2,3,4,6TFForm)_2(py)_3]$ (**2**)

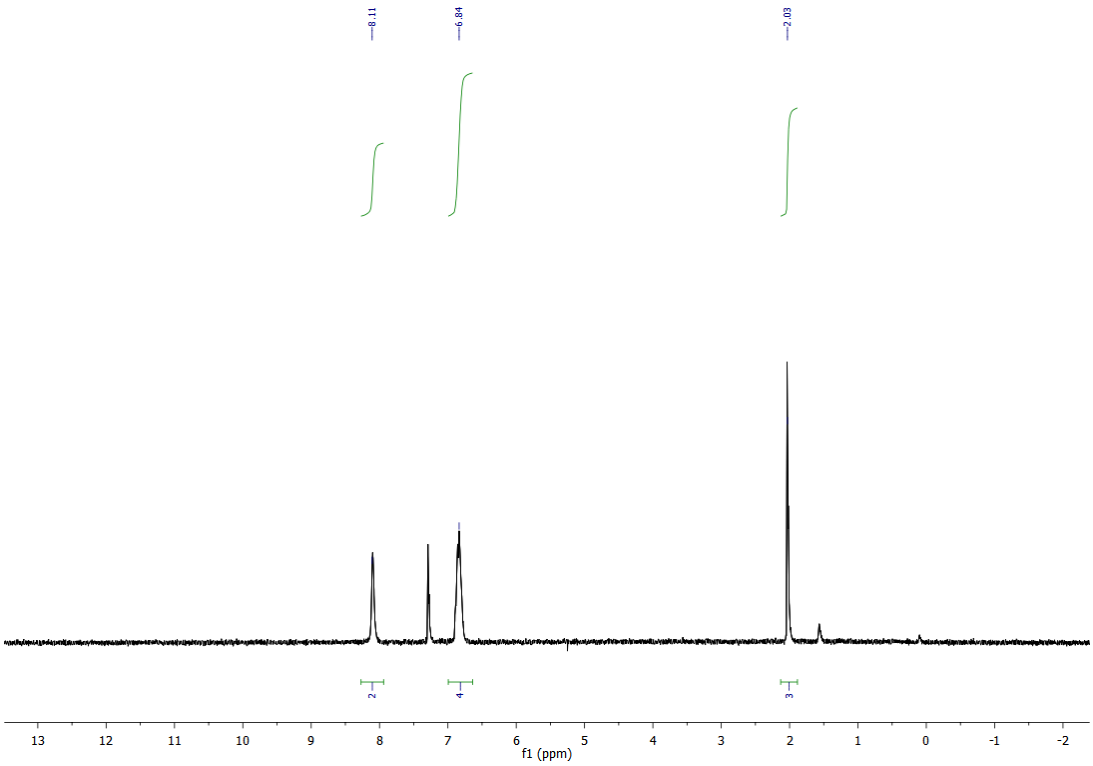

Fig. S3 ^{1}H NMR spectrum of $[Ag_2(2,3,4,6TFForm)_2(CH_3CN)_2]$ (**2a**)

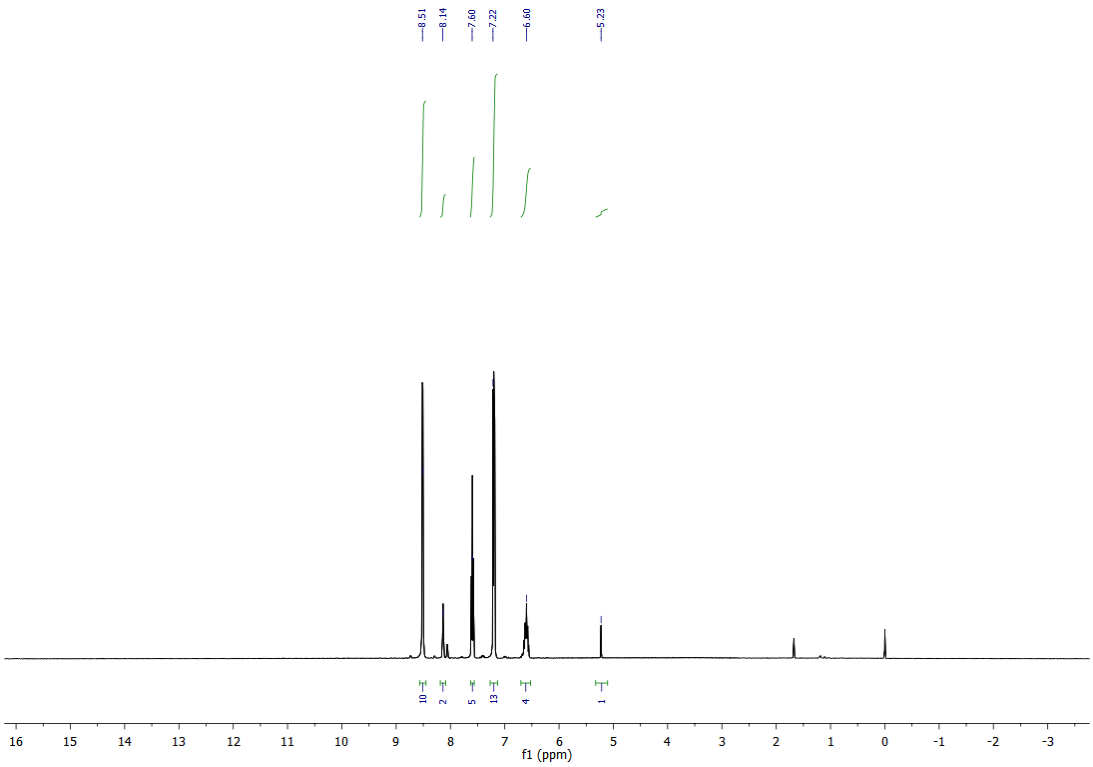

Fig. S4 ^{1}H NMR spectrum of [Ag_2(2,3,5,6TFForm)$_2$(py)$_3$] (**3**)

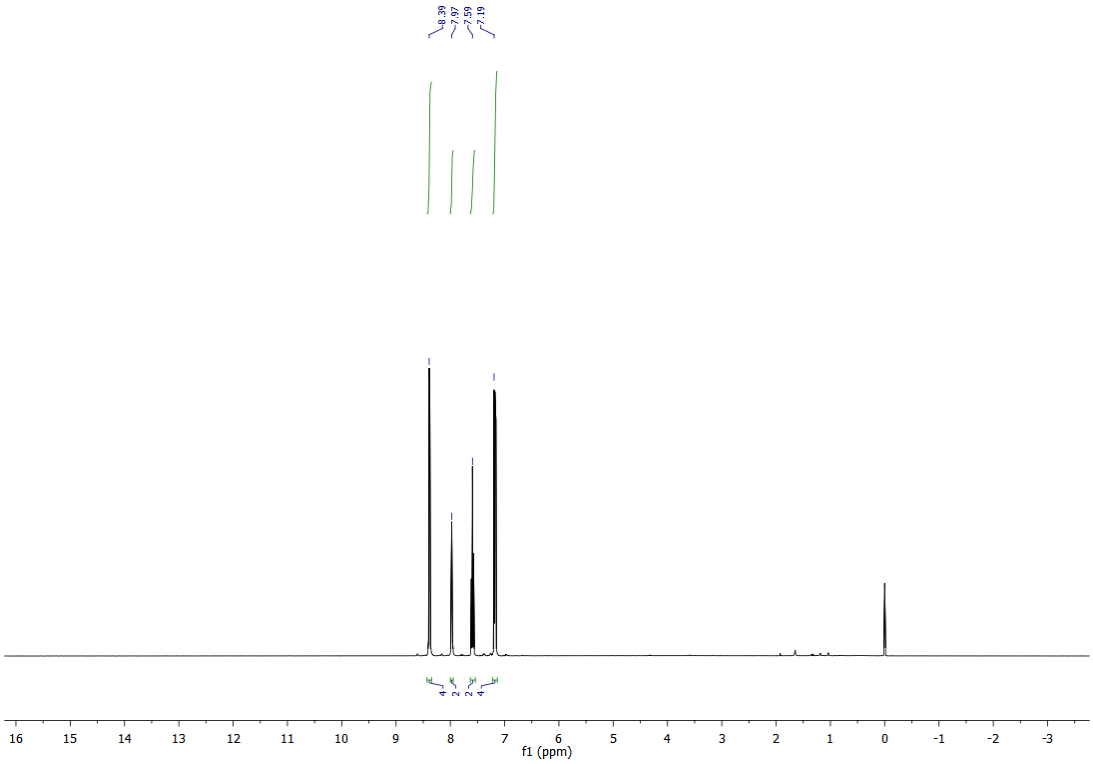

Fig. S5 ^{1}H NMR spectrum of [Ag_2(PFForm)$_2$(py)$_3$] (**4**)

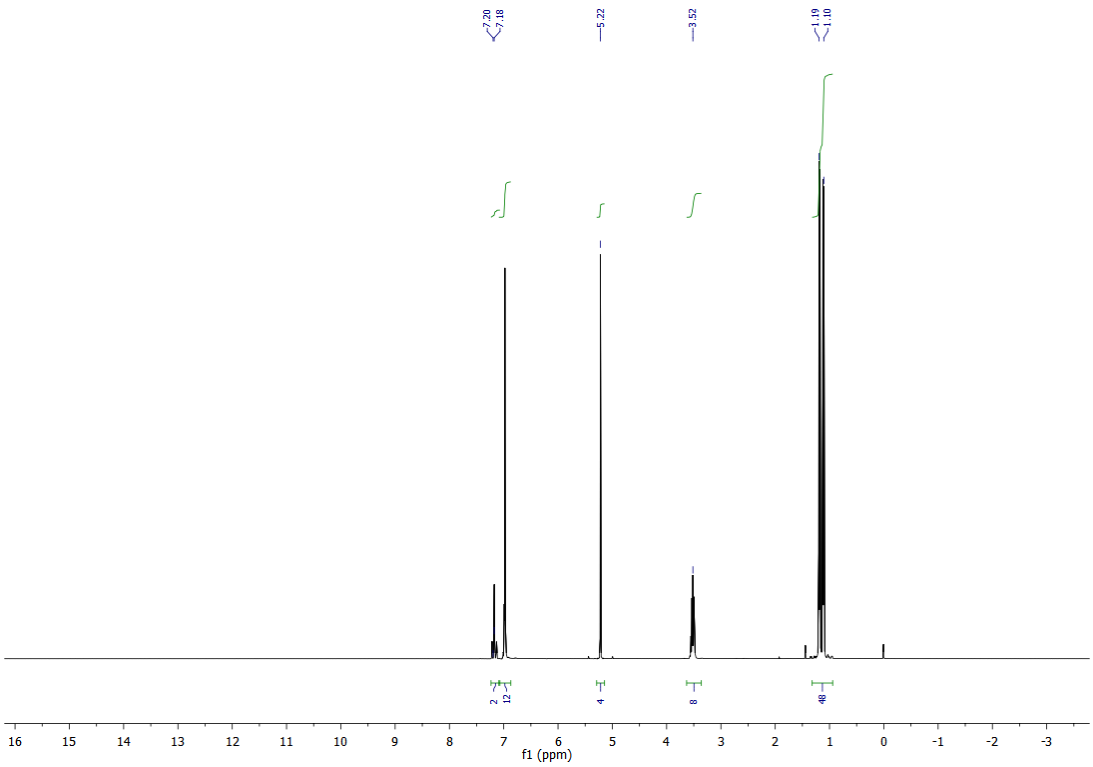

Fig. S6 ^{1}H NMR spectrum of $[Ag_2(DippForm)_2]\cdot 1.25CH_2Cl_2$ (**5**)

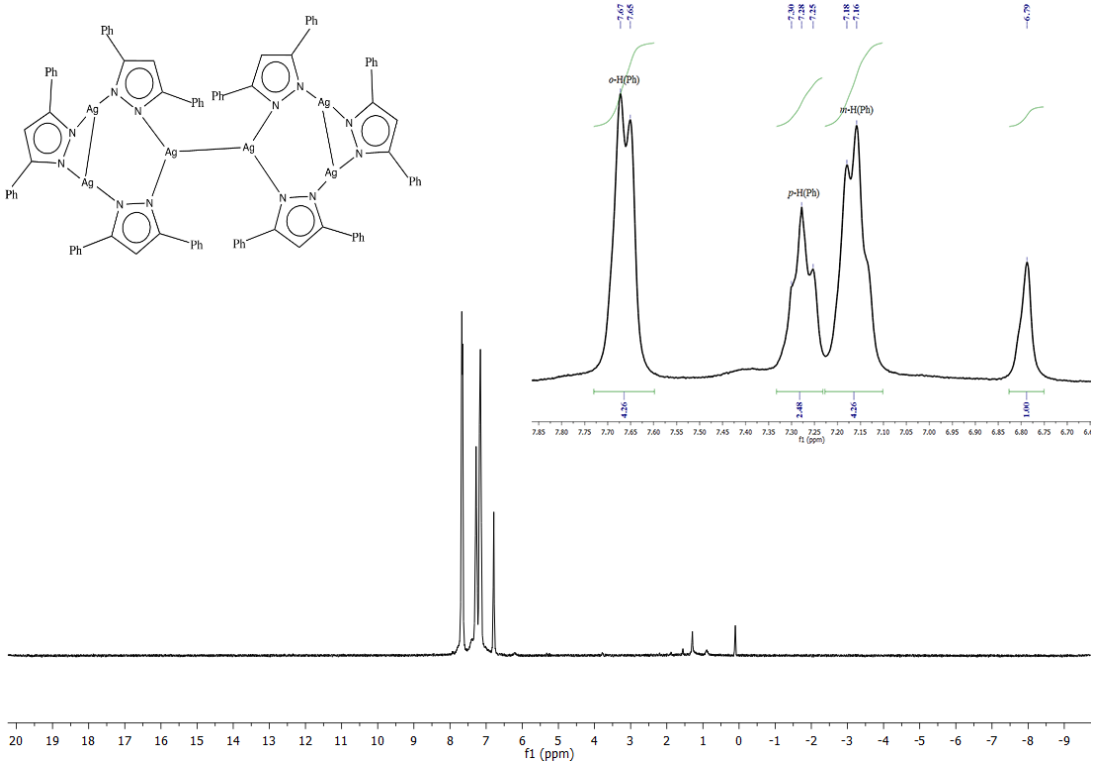

Fig. S7 ^{1}H NMR spectrum of $[\{Ag_3(Ph_2pz)_3\}_2]$ (**6**)

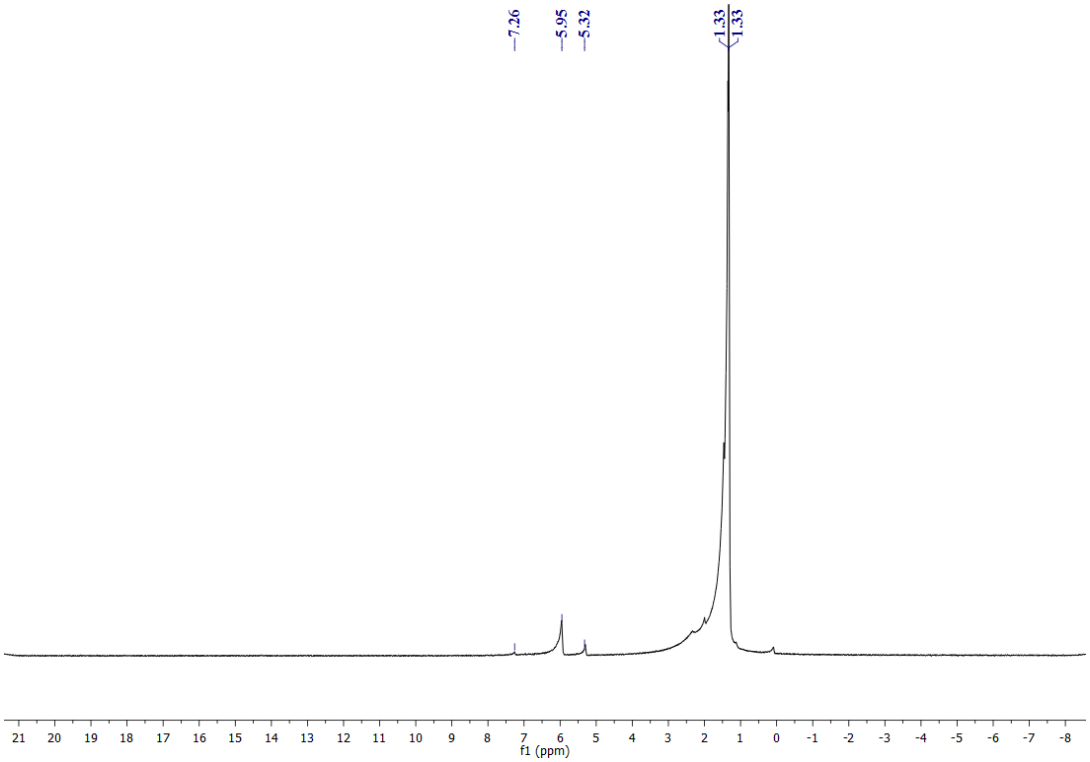

Fig. S8 ^{1}H NMR spectrum of [Ag(*t*Bu$_2$pz)]$_4$ (**7**)

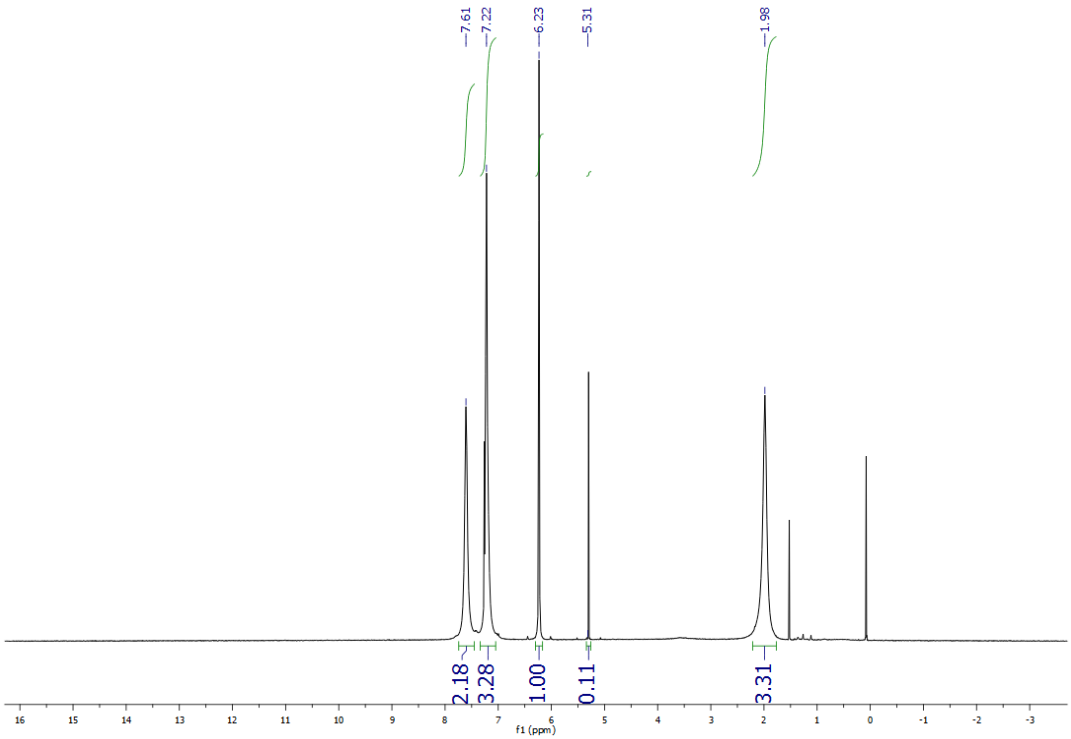

Fig. S9 ^{1}H NMR spectrum of [{Ag$_3$(PhMepz)$_3$}] (**8**)

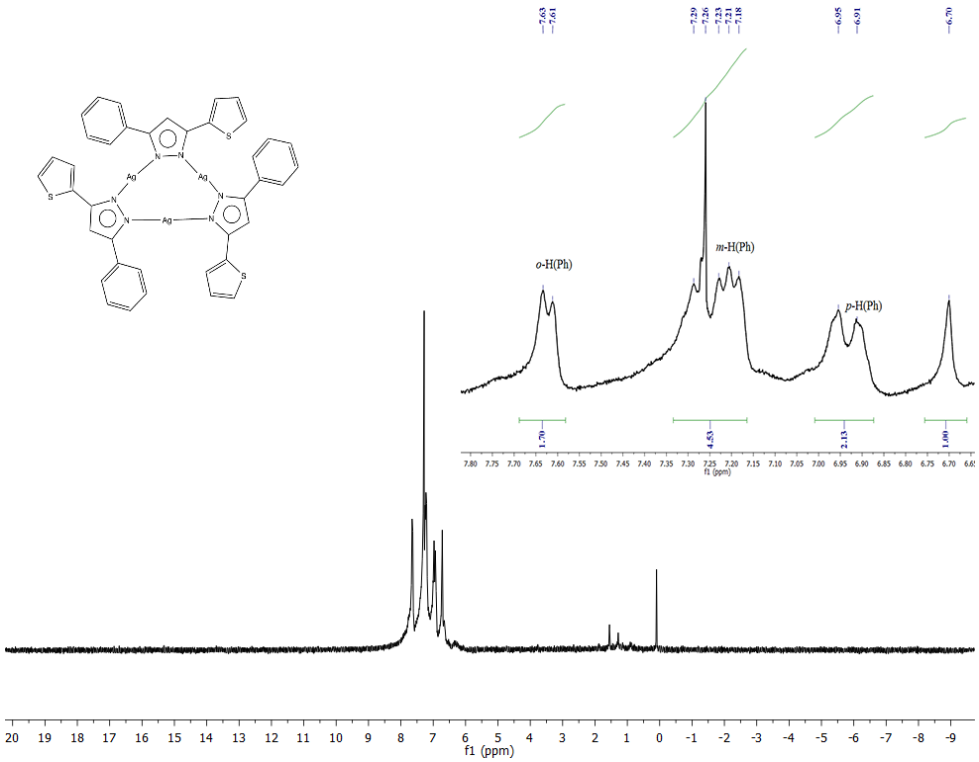

Fig. S10 ^{1}H NMR spectrum of [{$Ag_3(Phtpz)_3$}] (**9**)

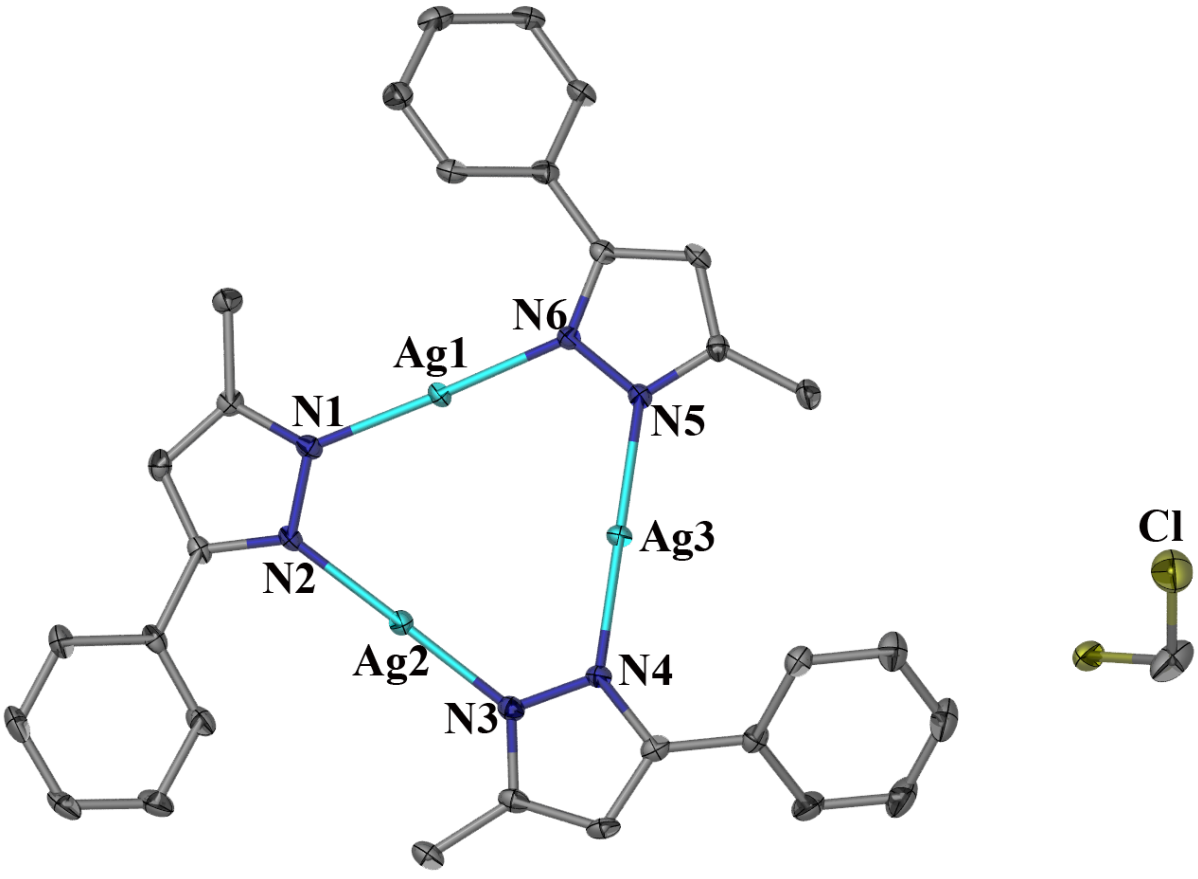

Figure S11. Molecular structure of **8** with non-hydrogen atoms represented by 50% probability thermal ellipsoids

X-ray crystallography:

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Complexes **2**, **2a**, **3** and **8** were measured on a "Bruker APEX-II CCD' diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 123 K, mounted on a fibre loop in crystallography oil. Absorption corrections were completed using Apex II program suite using SADABS.[1] Others (**1**, **4**, **9-11**) were measured at the Australian Synchrotron on the MX1 beamline, data integration was completed using Blue-ice[2] and XDS[3] software programs. Structural solutions were obtained by either direct methods[4] or charge flipping[5] methods and refined using full-matrix least-squares methods against F^2 using SHELX2018,[6] in conjunction with the Olex2[5] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. The disordered phenyl and thienyl groups in the crystal structure of [{Ag_3(Phtpz)$_3$}] **(9)** made it in low quality and low precision and it is just suitable for compound identification only. Crystal data and refinement details are given in **Table S1**.

Table S1. Crystal data and structural refinement for organosilver formamidinates **1-4** and **8-11**

	1	**2**	**2a**	**3**	**4**
Formula	$C_{36}H_{24}Ag_2F_8N_6$	$C_{41}H_{21}Ag_2F_{16}N_7$	$C_{30}H_{12}Ag_2F_{16}N_6$	$C_{41}H_{21}Ag_2F_{16}N_7$	$C_{41}H_{17}Ag_2F_{20}N_7$
M_r	908.35	1131.39	976.20	1131.39	1203.35
Space group	*P*-1	*C2/c*	$P2_1/n$	$P2_12_12$	$P2_12_12$
***a* (Å)**	8.2030(16)	22.698(5)	13.207(3)	13.9101(3)	14.369(3)
***b* (Å)**	11.086(2)	8.6380(17)	8.4560(17)	17.287(4)	17.302(4)
***c* (Å)**	11.255(2)	20.390(4)	15.508(3)	8.2383(16)	8.1860(16)
***α* (°)**	61.47(3)	90	90	90	90
***β* (°)**	73.09(3)	90.30(3)	111.35(3)	90	90
***γ* (°)**	70.49(3)	90	90	90	90
***V* (Å^3)**	836.9(4)	3997.7(14)	1613.1(6)	1981.0(7)	2035.1(7)
Z	1	4	2	2	2
ρ_{calc}, **g cm^{-3}**	1.803	1.880	2.010	1.897	1.964

μ, mm^{-1}	1.252	1.097	1.341	1.107	1.098
N_τ	16052	30082	22053	33675	30346
N (R_{int})	4722(0.0542)	4050(0.0630)	3820(0.0608)	4372(0.0555)	4771(0.0261)
R_1 ($I > 2\sigma(I)$)	0.0301	0.0360	0.0346	0.0346	0.0229
wR_2 (all data)	0.0813	0.0849	0.0895	0.0840	0.0571
GOF	1.121	1.074	1.059	1.064	1.126

	8	**9**	**10**	**11**
Formula	$C_{30.5}H_{28}Ag_3ClN_6$	$C_{39}H_{27}Ag_3N_6S_3$	$C_{24}H_{12}Ag_3F_9N_6S_3$	$C_{78}H_{69}Ag_2Cl_3N_2P_4$
M_r	837.65	999.45	975.19	1480.32
Space group	*P*-1	*P*-1	*C*2/*c*	$I4_1$
a (Å)	7.3723(2)	12.726(3)	27.160(5)	20.261(3)
b (Å)	14.0695(5)	15.974(3)	11.115(2)	20.261(3)
c (Å)	15.0692(5)	18.871(4)	23.475(5)	34.204(7)
α (°)	108.2680(10)	102.14(3)	90	90
β (°)	102.4750(10)	94.39(3)	124.83(3)	90
γ (°)	90.7980(10)	106.72(3)	90	90
V (Å^3)	1443.60(8)	3553.2(14)	5817(3)	14041(5)
Z	2	4	8	8
ρ_{calc}, g cm^{-3}	1.927	1.868	2.227	1.401
μ, mm^{-1}	2.140	1.853	2.302	0.808
N_τ	28902	62101	40842	62779
N (R_{int})	6644(0.0306)	12258(0.0288)	7134(0.0753)	16724(0.0425)
R_1 ($I > 2\sigma(I)$)	0.0213	0.0919	0.0830	0.0432
wR_2 (all data)	0.0481	0.2290	0.3009	0.1074
GOF	1.056	1.065	1.131	1.049

Theoretical Methodology

All geometry optimisations were performed with Gaussian 16[7] using M06-2X functional,[8] aug-cc-pVDZ Dunning's basis set[9] and a universal solvation model based on density (SMD),[10] with water as solvent. Frequency calculations were carried out to ensure the location of energy minima.[10] For each compound in its lowest energy conformation pKa values were calculated using the chemical reaction

$$BH = B^- + H^+ \quad (1)$$

Standard physical chemistry formulae were used to predict the pKa values:

$$pK_a = \frac{\Delta G}{2.303 \cdot RT} \quad (2)$$

$$\Delta G = \Delta E + \Delta ZPVE + TC - T\Delta S + \Delta(\Delta G_{solv}) \quad (3)$$

where ΔG is the Gibbs free energy of eq. 1, E is the electronic energy calculate with M06-2X/cc-pVTZ, ZPVE is zero-point vibrational energy taken from the geometry optimisation and ΔG_{solv}-is the solvation energy calculated as the difference between single points energies in solvent (water) and gas at M06-2X/cc-pVTZ level of theory for both the base (B) and its conjugated anion (B^-). The latter was suggested as an important correction by Ho and Coote (2010).[11] For more detail on the formulae for temperature correction (TC) and entropy (S), see elsewhere.[12,13] In this present study, Camaioni's and Schwerdtfeger's value[14] of -1112.52kJ/mol for $\Delta G_s(H^+)$ while the value of $G_{gas}(H^+)$ of -18.36kJ/mol was derived using the Sackur-Tetrode equation.[15]

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