

Coordination Polymers *via* Self-assembly of Silver(I) and *cis*-Bis-nitrile-oxa-bowl Derivatives[†]

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Supporting information

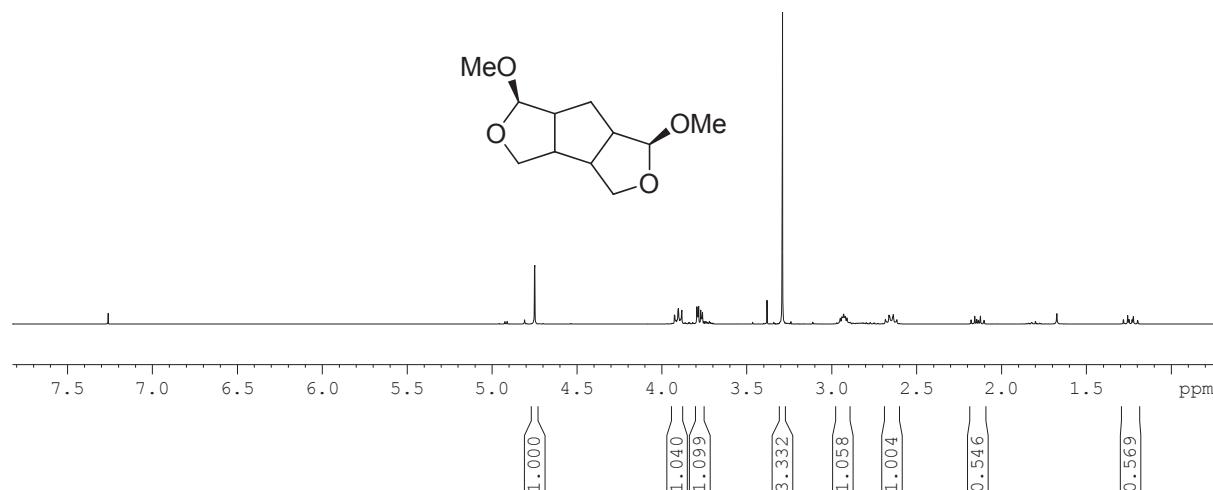


Figure S-1. 400 MHz ^1H NMR spectrum of acetal-1 in CDCl_3 .

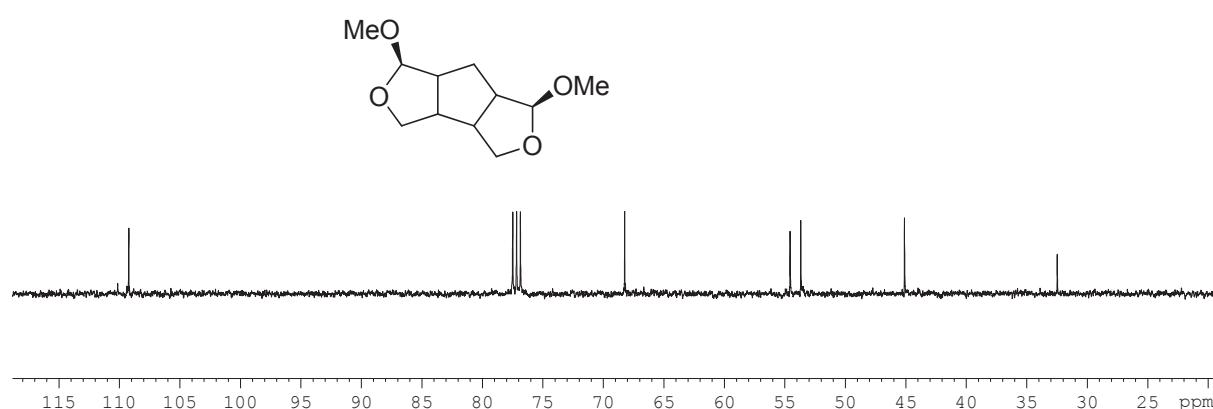


Figure S-2. 100 MHz ^{13}C NMR spectrum of acetal-1 in CDCl_3 .

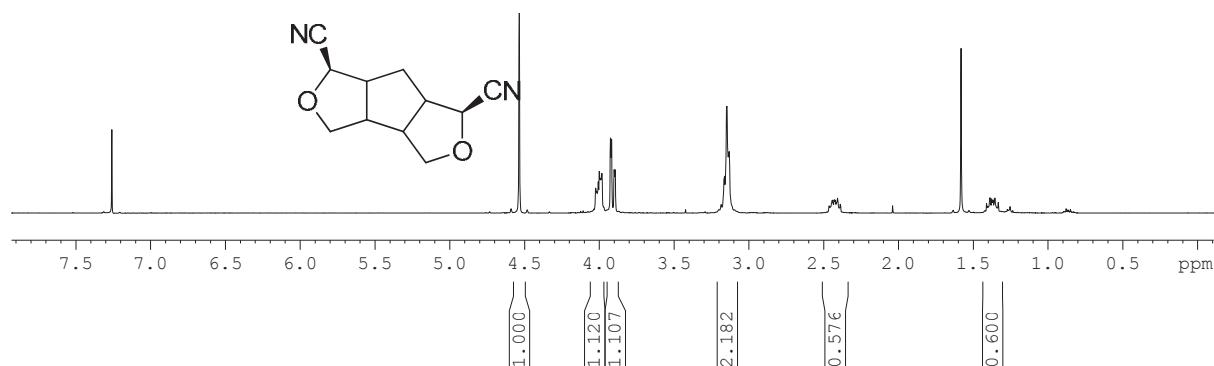


Figure S-3. 400 MHz ^1H NMR spectrum of **L1** in CDCl_3 .

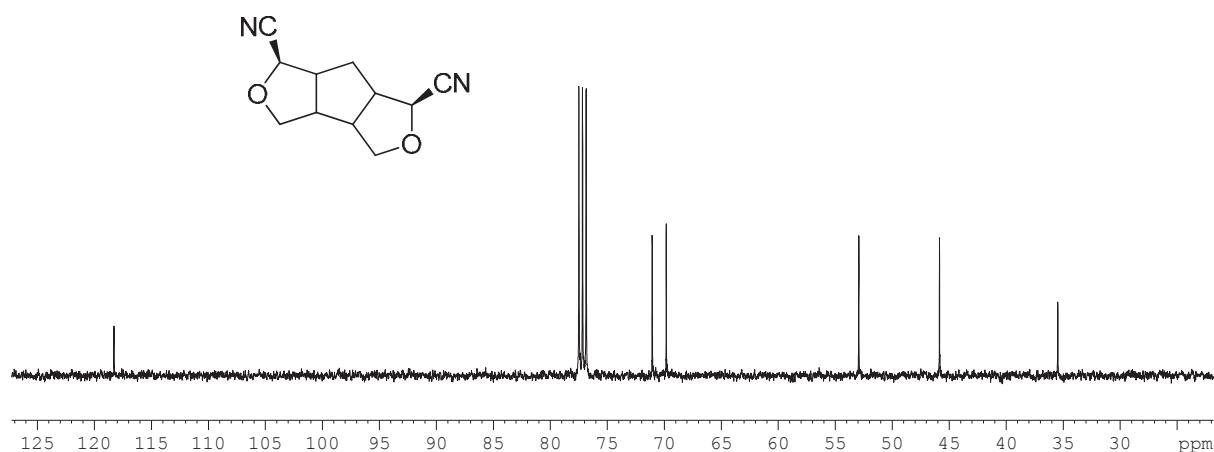


Figure S-4. 100 MHz ^{13}C NMR spectrum of **L1** in CDCl_3 .

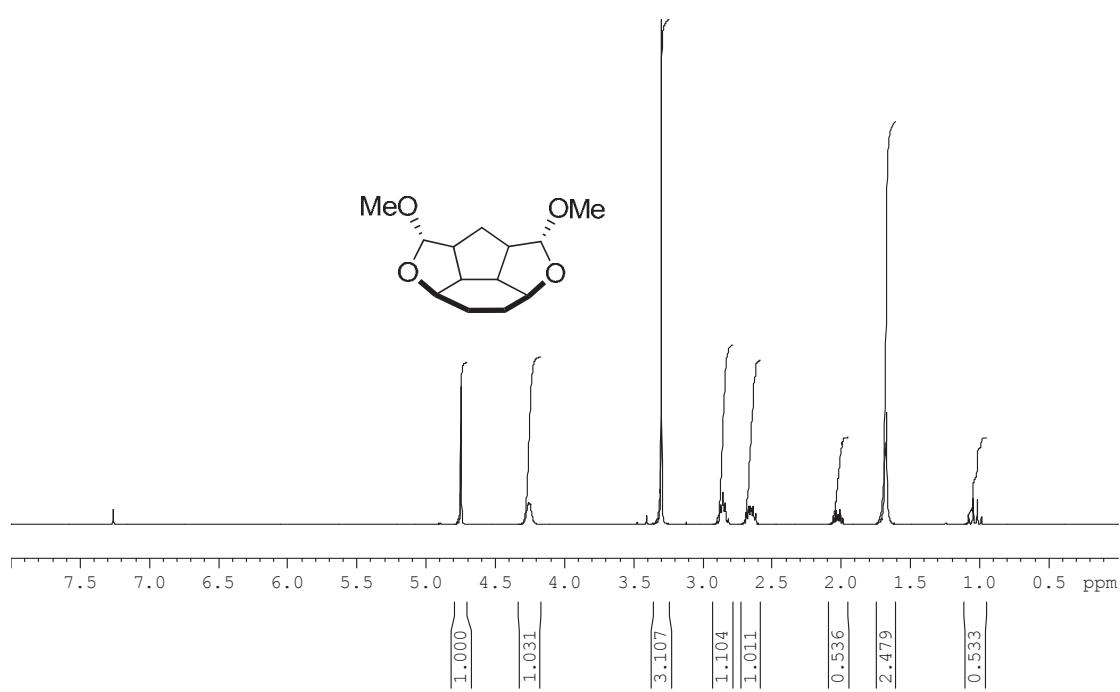


Figure S-5. 400 MHz ^1H NMR spectrum of acetal-2 in CDCl_3 .

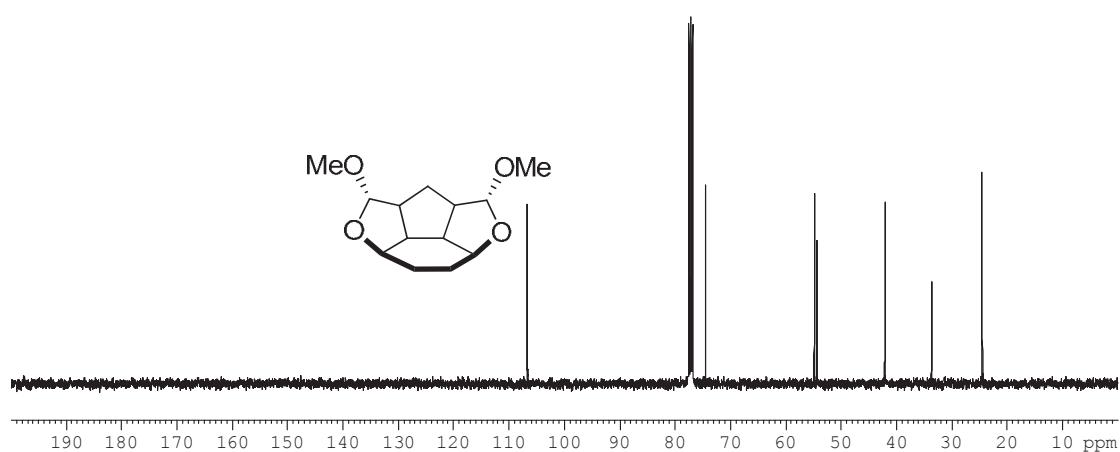


Figure S-6. 100 MHz ^{13}C NMR spectrum of acetal-2 in CDCl_3 .

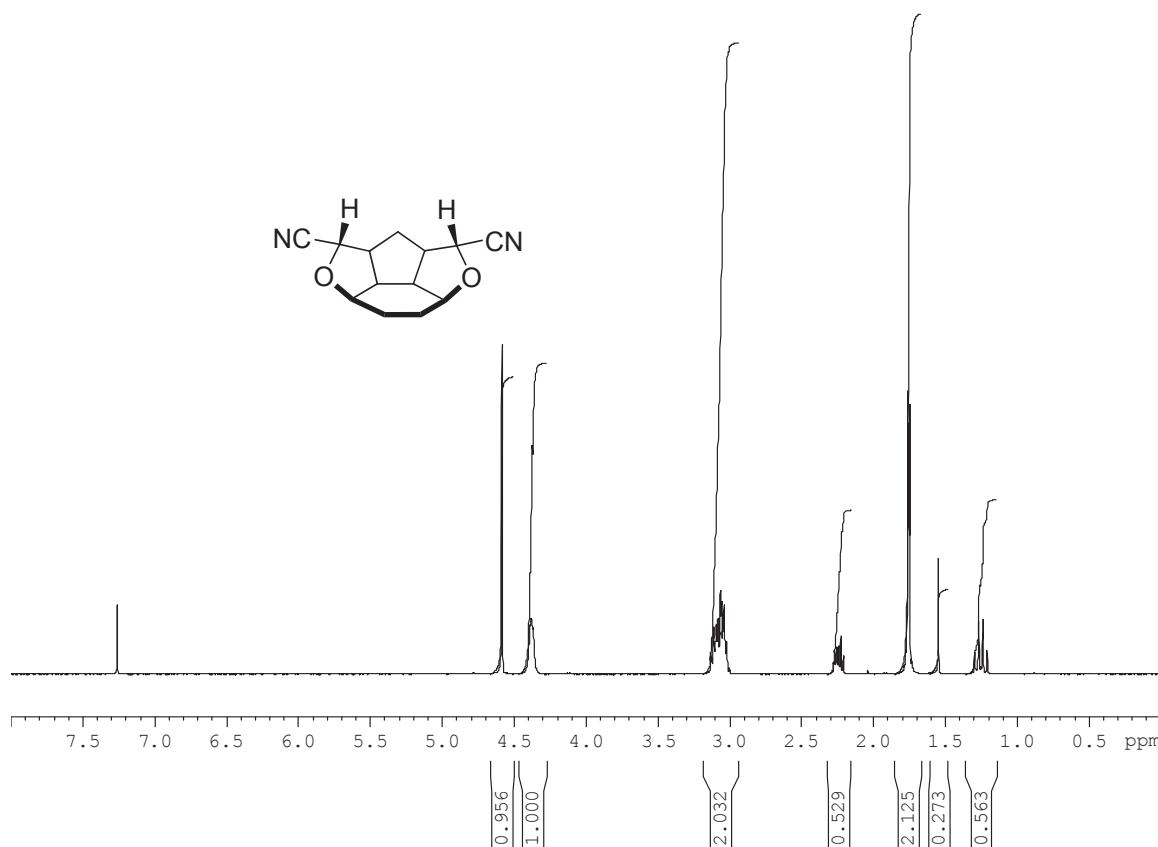


Figure S-7. 400 MHz ^1H NMR spectrum of **L2** in CDCl_3 .

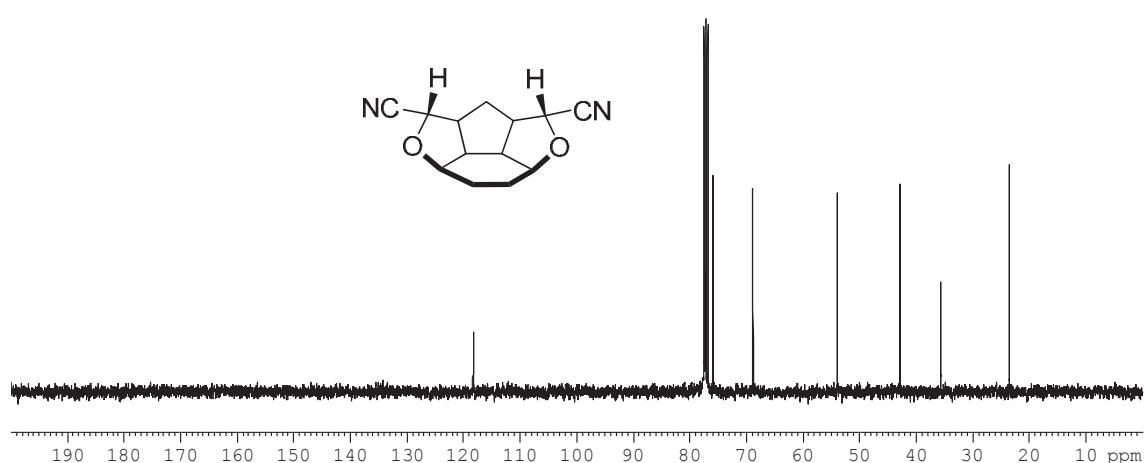


Figure S-8. 100 MHz ^{13}C NMR spectrum of **L2** in CDCl_3 .

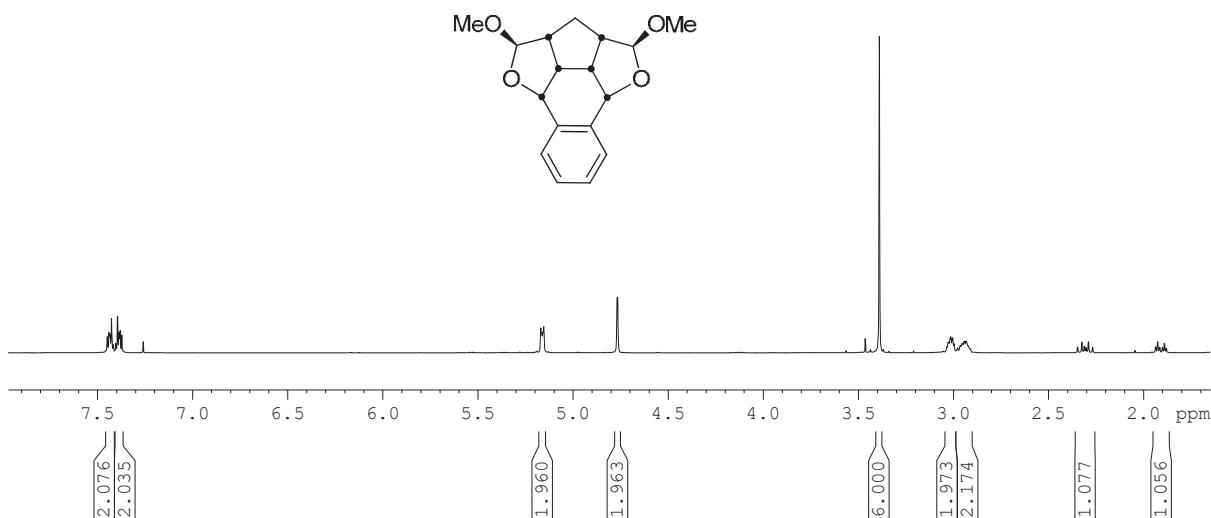


Figure S-9. 400 MHz ^1H NMR spectrum of acetal-3 in CDCl_3 .

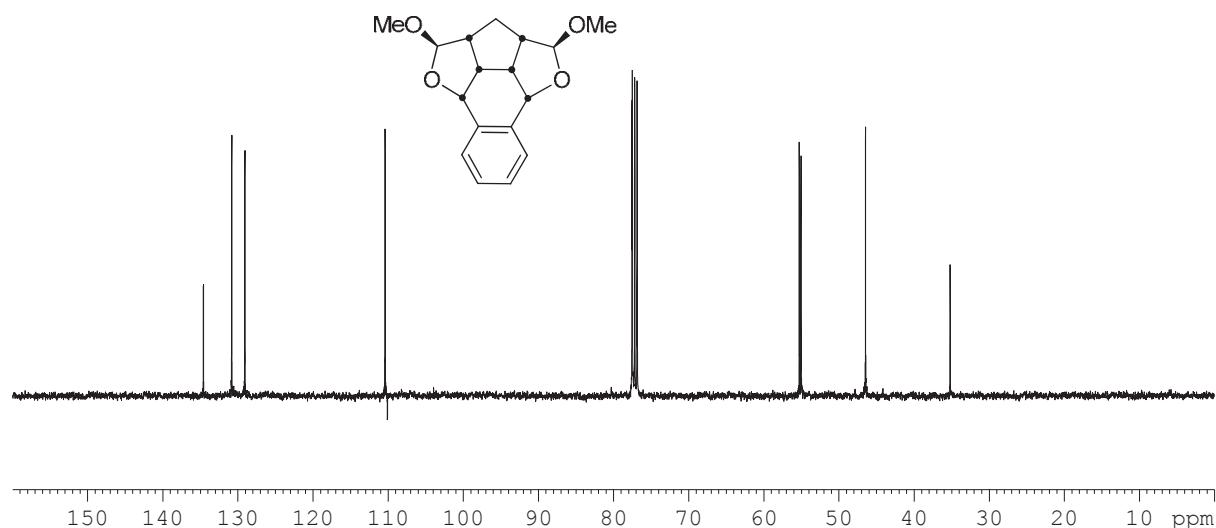


Figure S-10. 100 MHz ^{13}C NMR spectrum of acetal-3 in CDCl_3 .

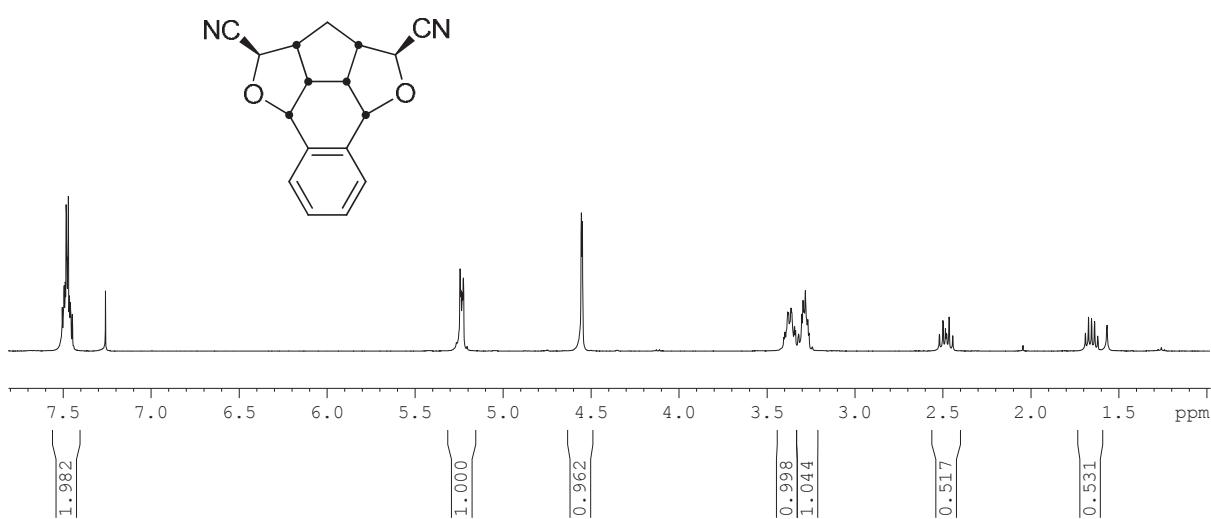


Figure S-11. 400 MHz ^1H NMR spectrum of **L3** in CDCl_3 .

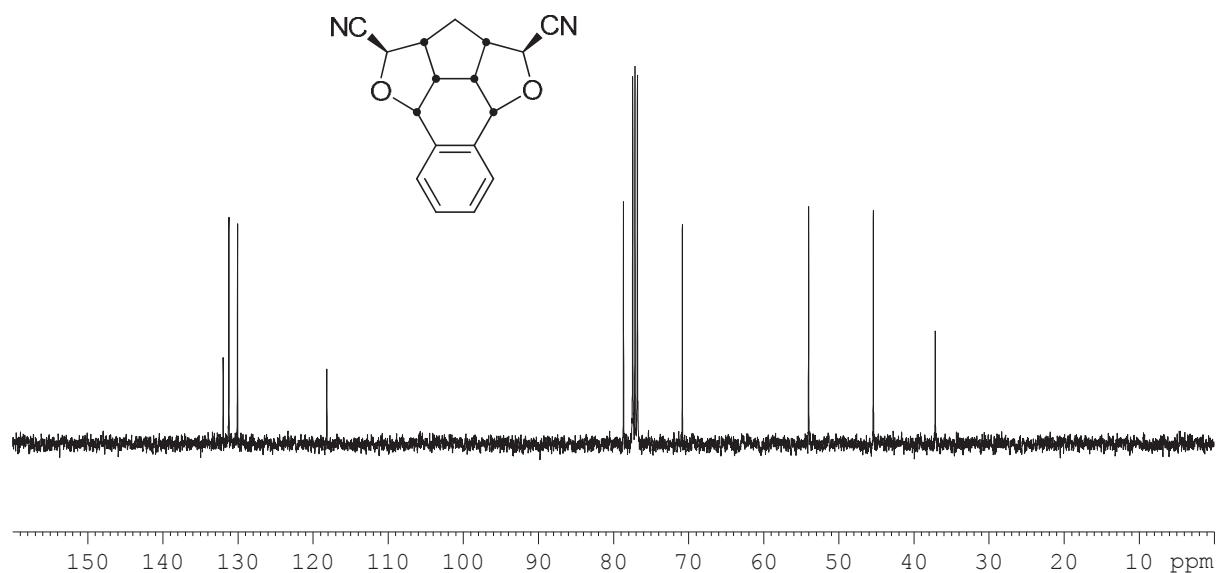


Figure S-12. 100 MHz ^{13}C NMR spectrum of **L3** in CDCl_3 .

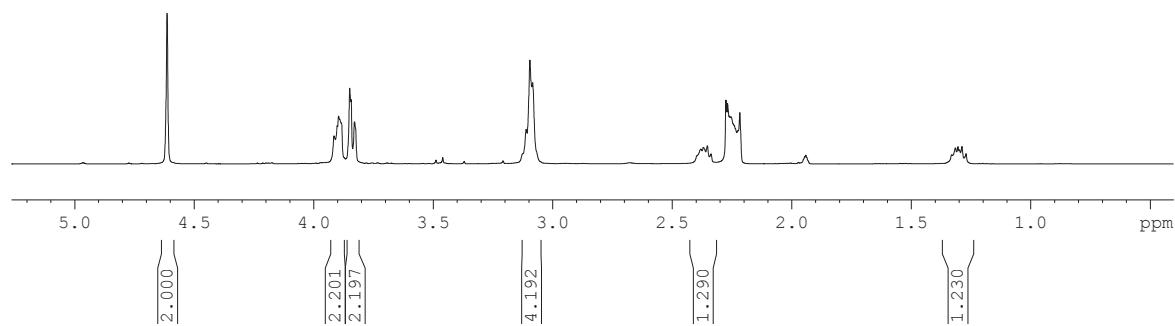


Figure S-13. 500 MHz ^1H NMR spectrum of **L1** in CD_3CN .

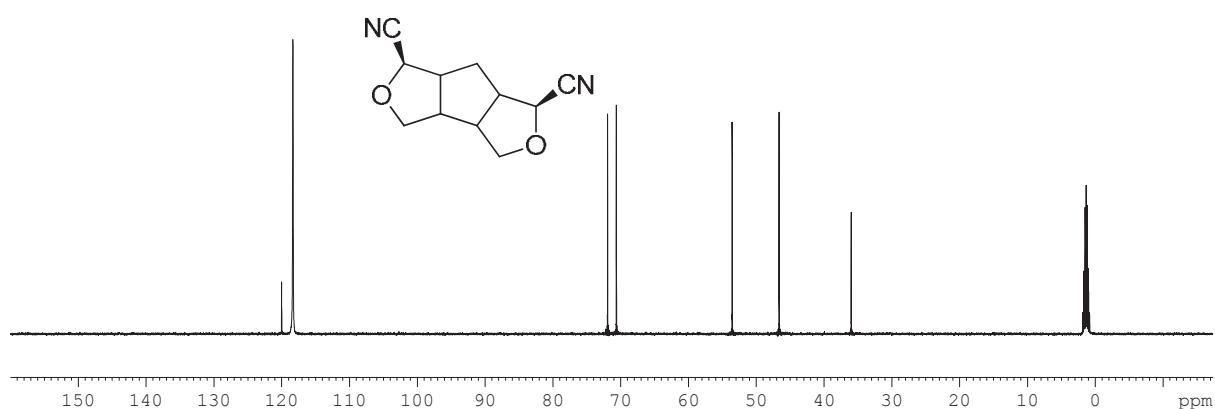


Figure S-14. 125 MHz ^{13}C NMR spectrum of **L1** in CD_3CN .

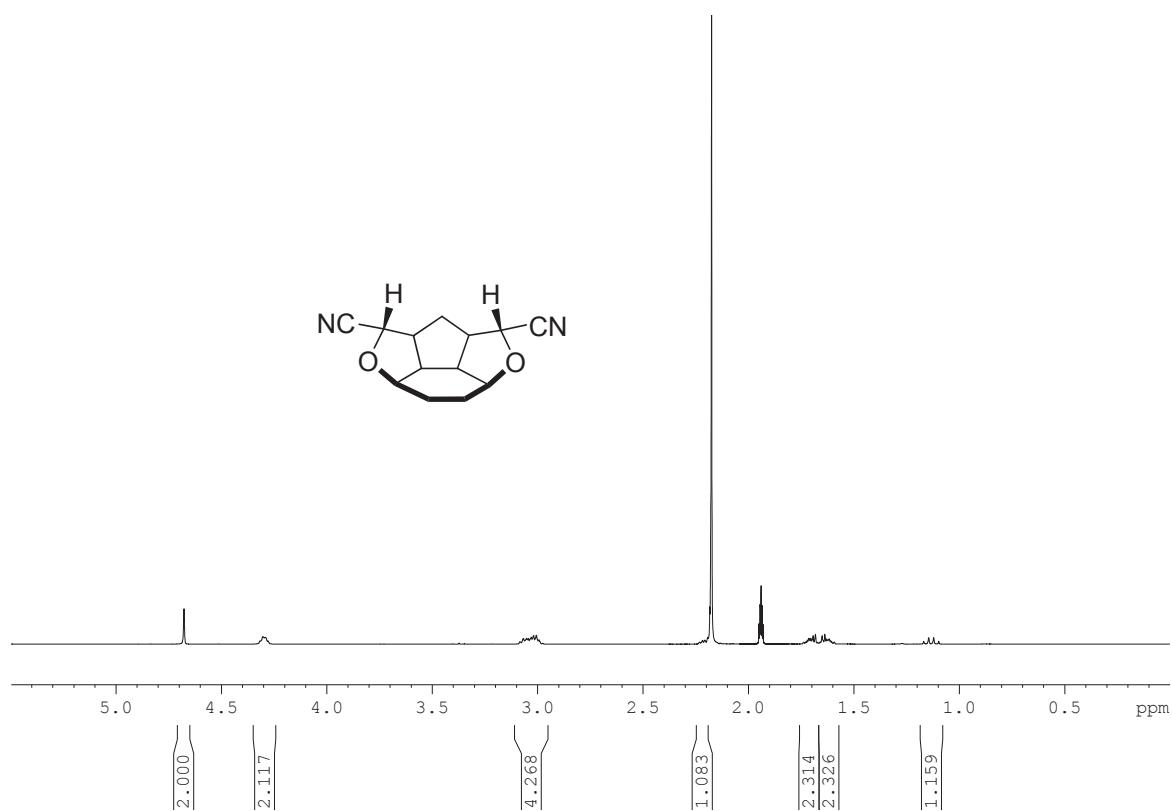


Figure S-15. 500 MHz ^1H NMR spectrum of **L2** in CD_3CN .

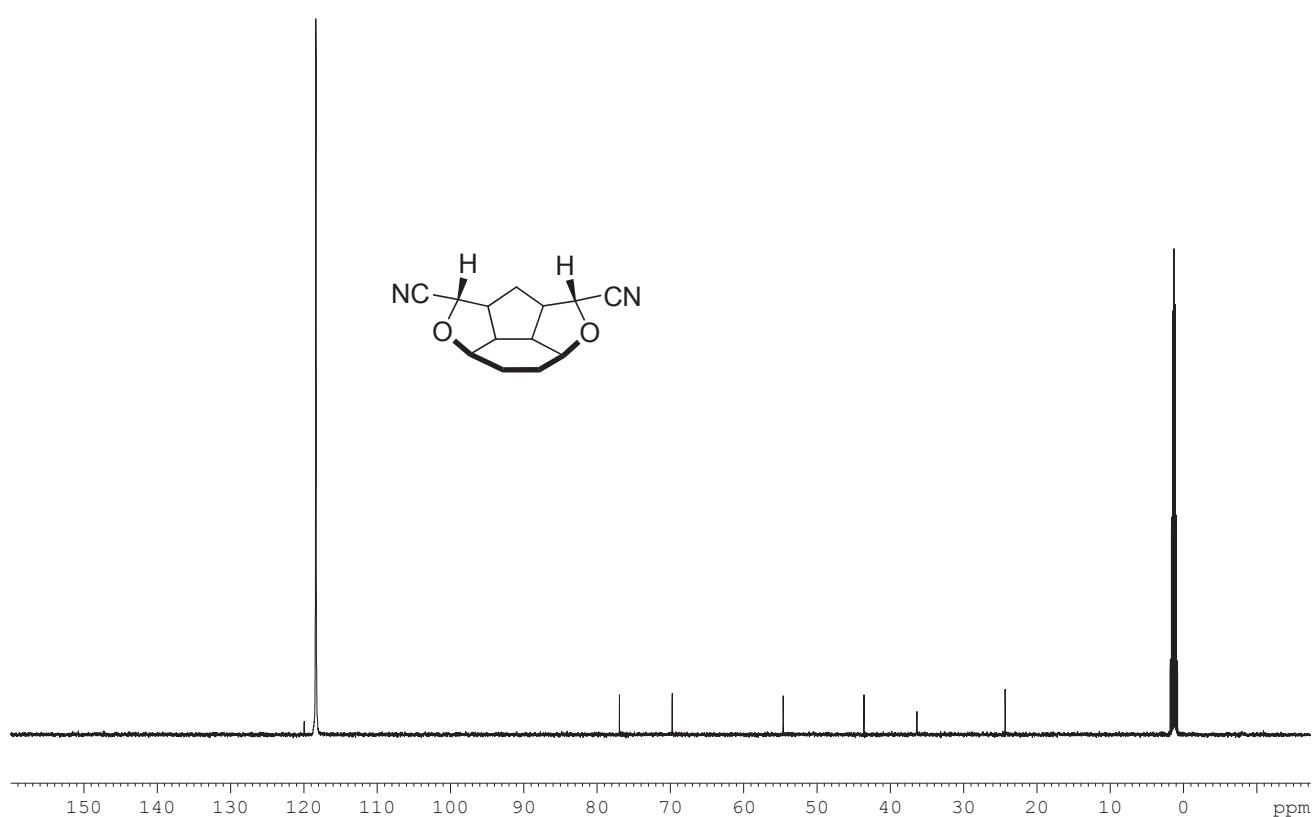


Figure S-16. 125 MHz ^{13}C NMR spectrum of **L2** in CD_3CN .

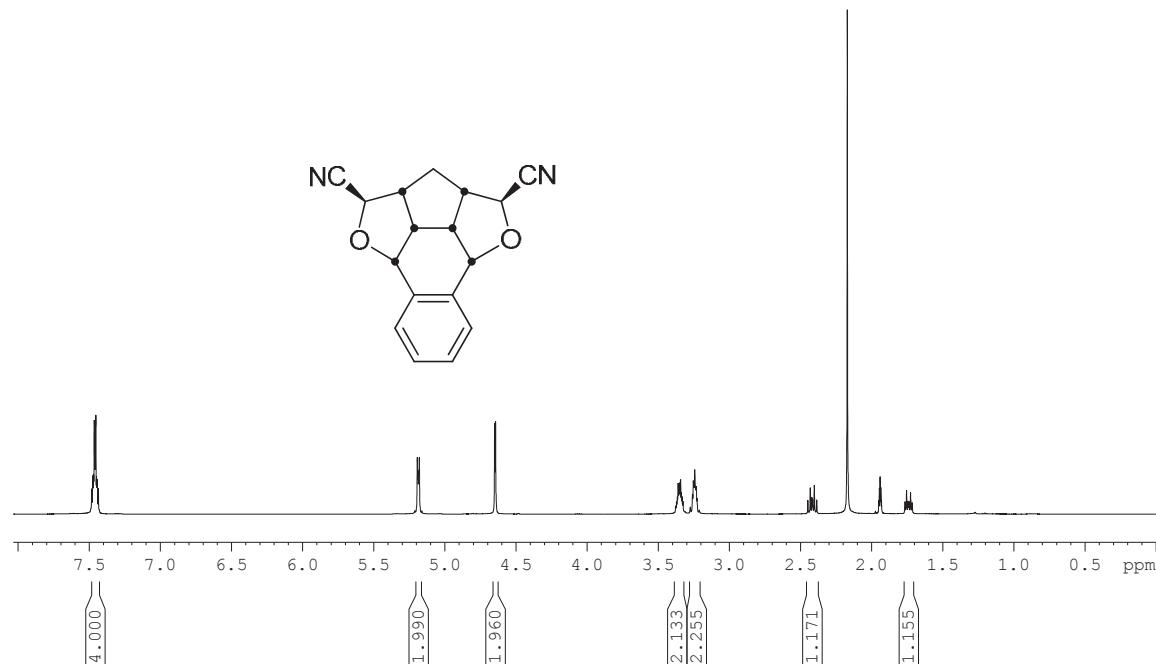


Figure S-17. 500 MHz ^1H NMR spectrum of **L3** in CD_3CN .

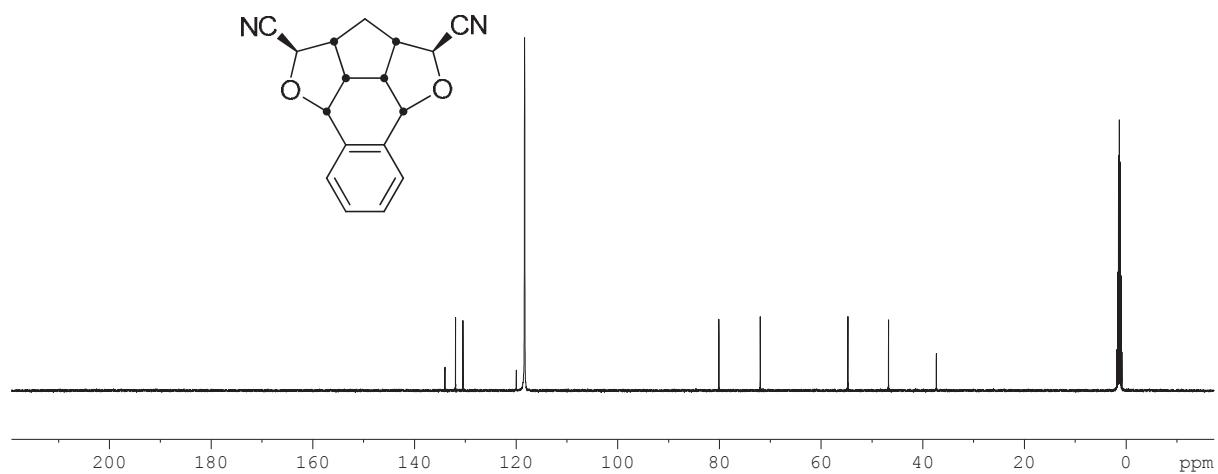


Figure S-18. 125 MHz ^{13}C NMR spectrum of **L3** in CD_3CN .

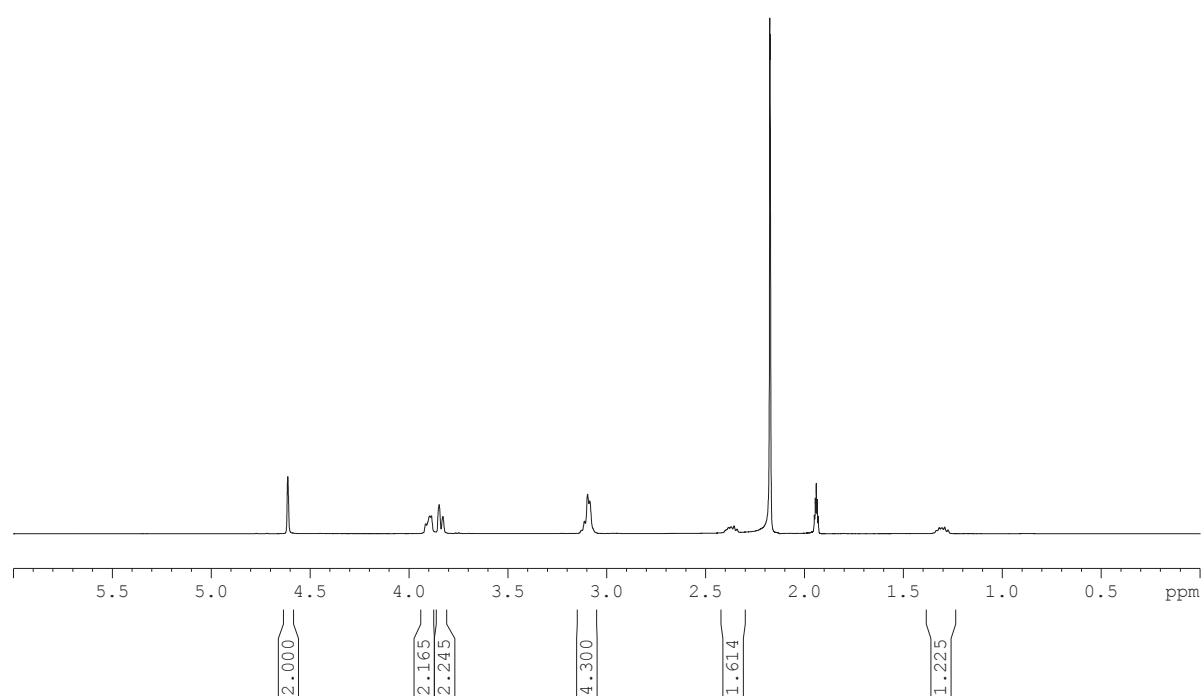


Figure S-19. 500 MHz ^1H NMR spectrum of **1a** in CD_3CN .

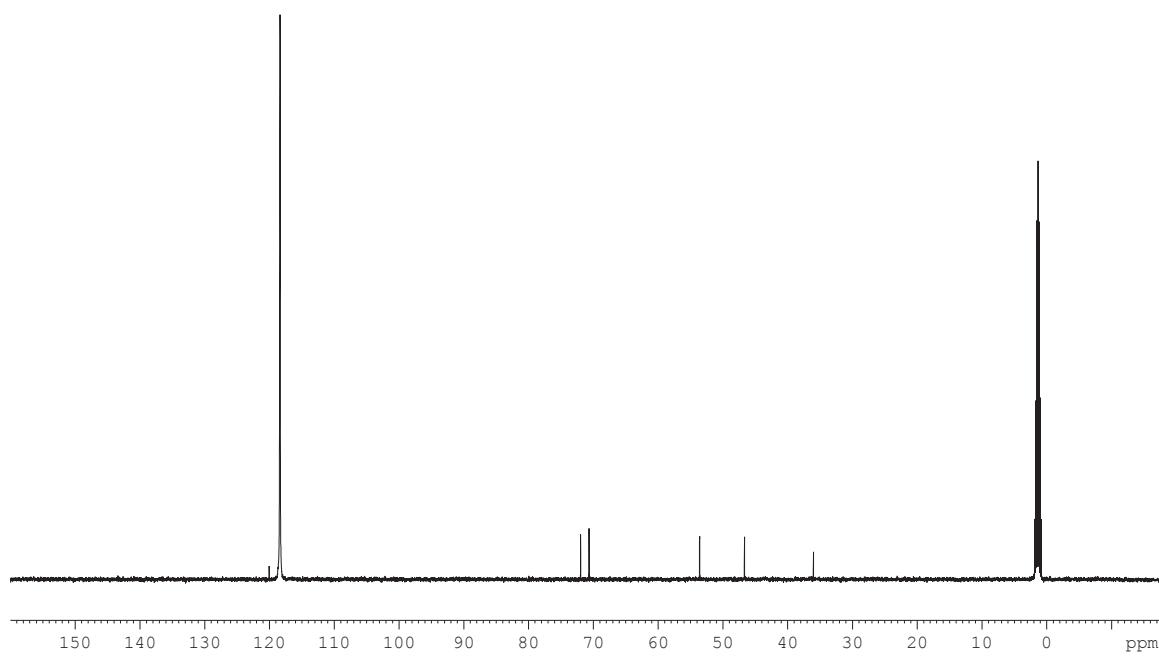


Figure S-20. 125 MHz ^{13}C NMR spectrum of **1a** in CD_3CN .

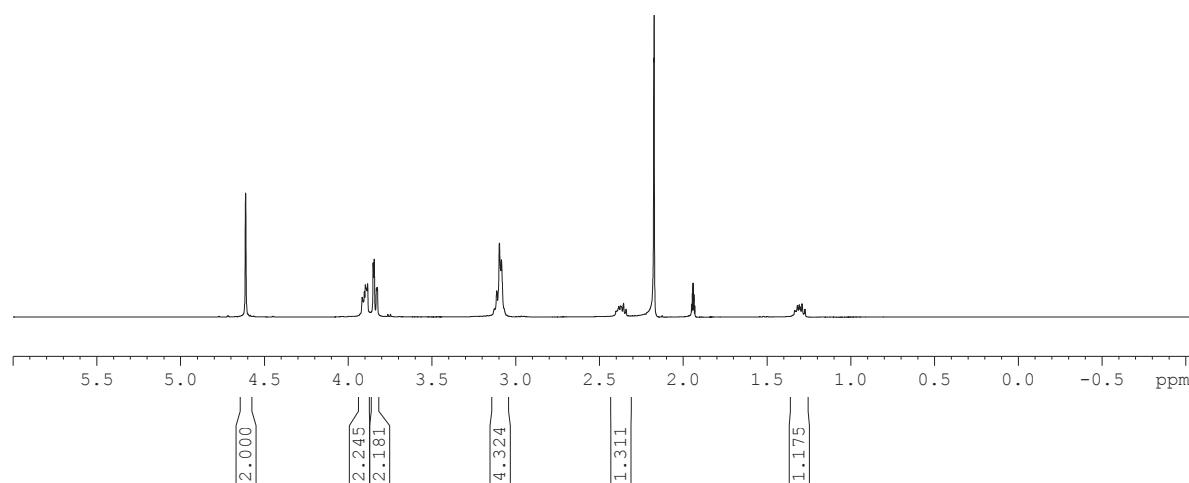


Figure S-21. 500 MHz ^1H NMR spectrum of **1b** in CD_3CN .

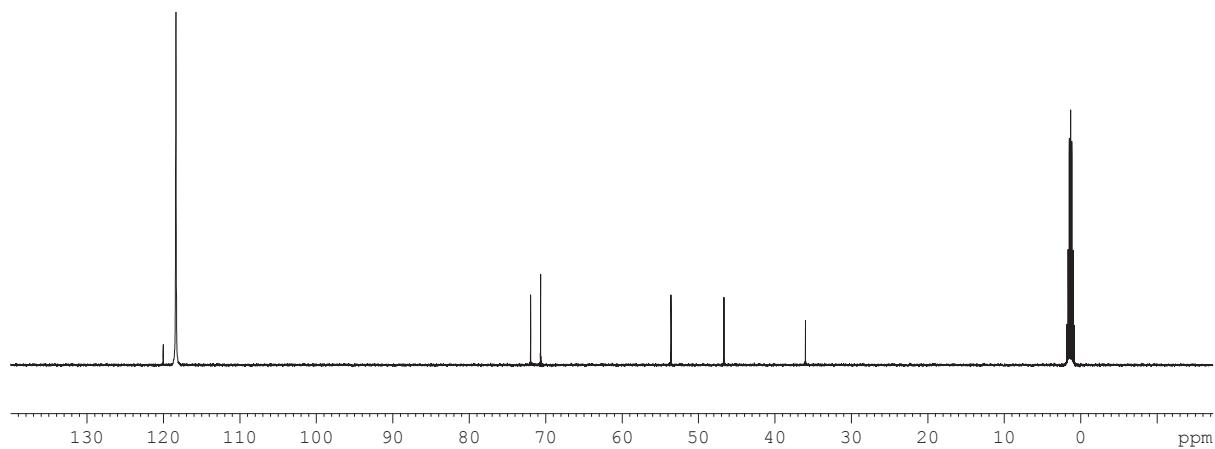


Figure S-22. 125 MHz ^{13}C NMR spectrum of **1b** in CD_3CN .

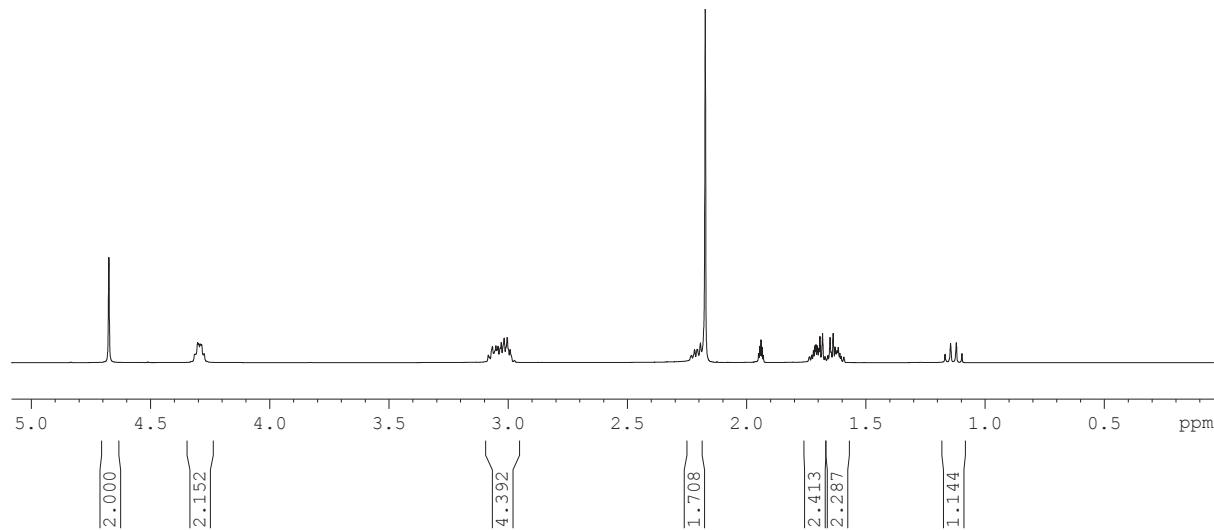


Figure S-23. 500 MHz ^1H NMR spectrum of **2a** in CD_3CN .

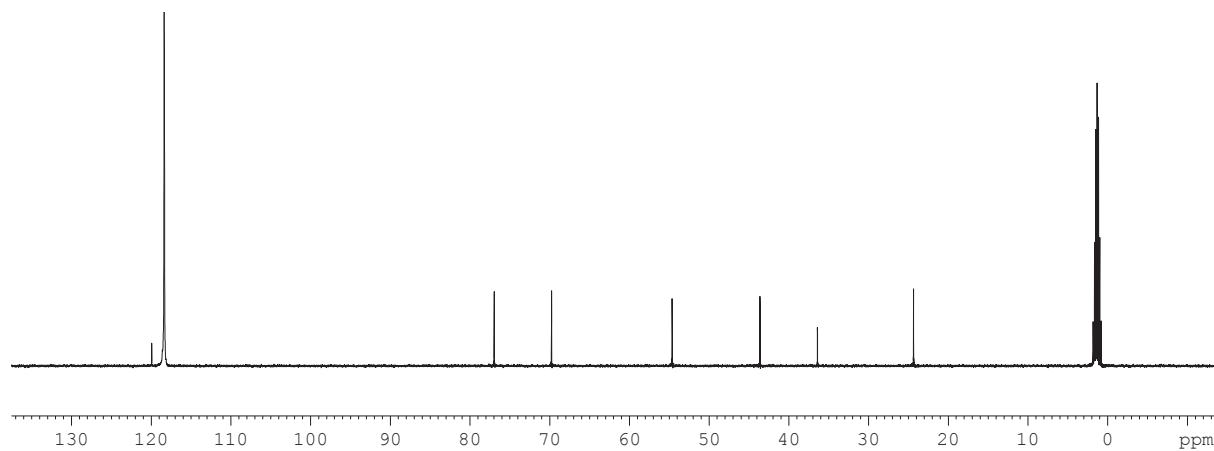


Figure S.24. 125 MHz ^{13}C NMR spectrum of **2a** in CD_3CN .

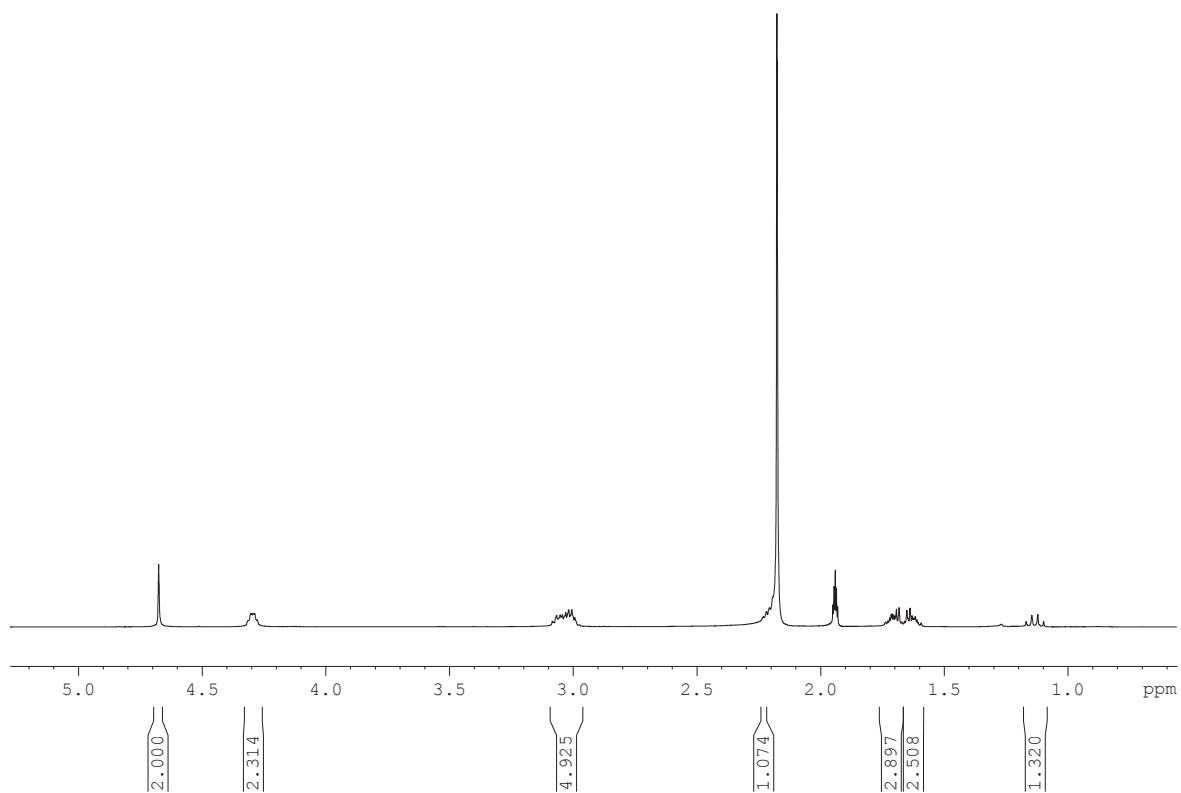


Figure S-25. 500 MHz ¹H NMR spectrum of **2b** in CD₃CN.

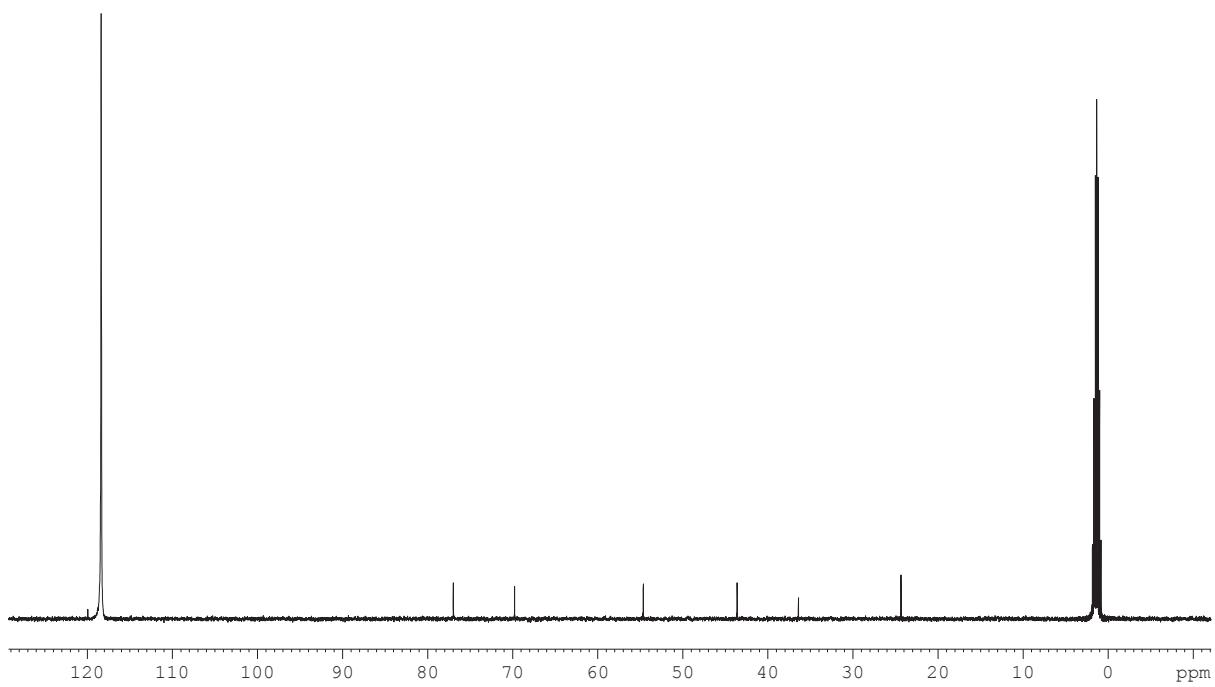


Figure S.26. 125 MHz ¹³C NMR spectrum of **2b** in CD₃CN.

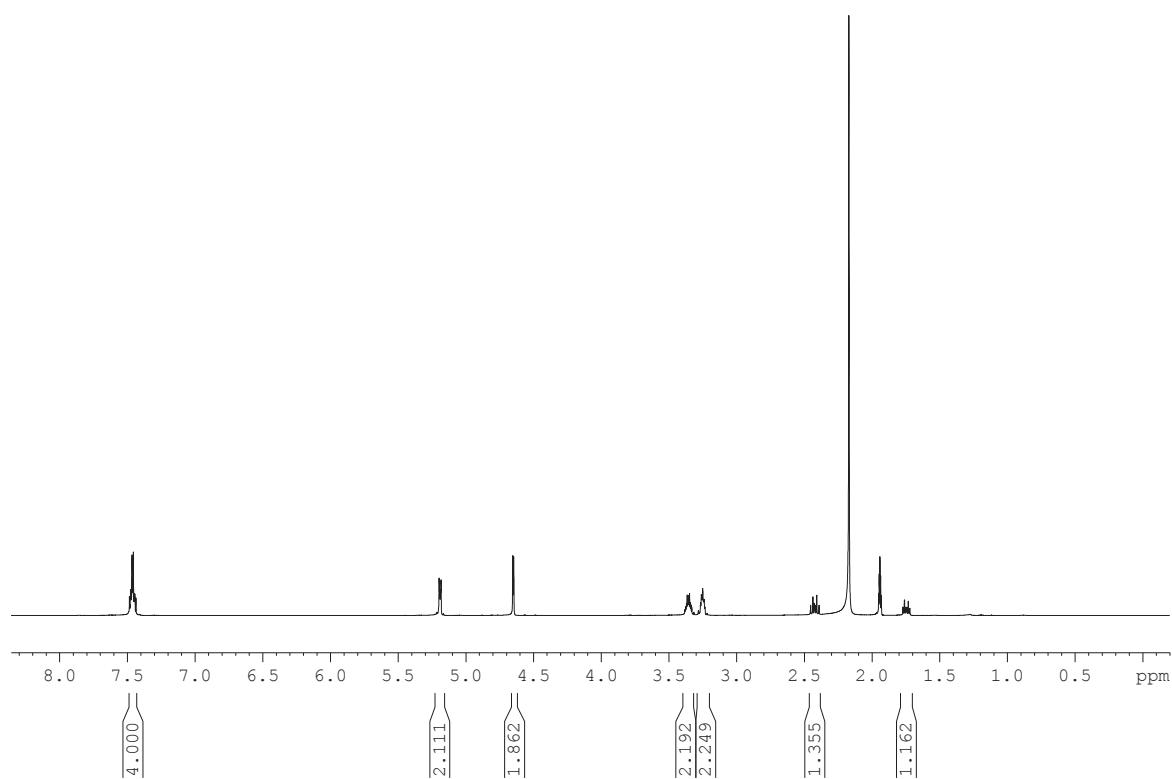


Figure S-27. 500 MHz ^1H NMR spectrum of **3a** in CD_3CN .

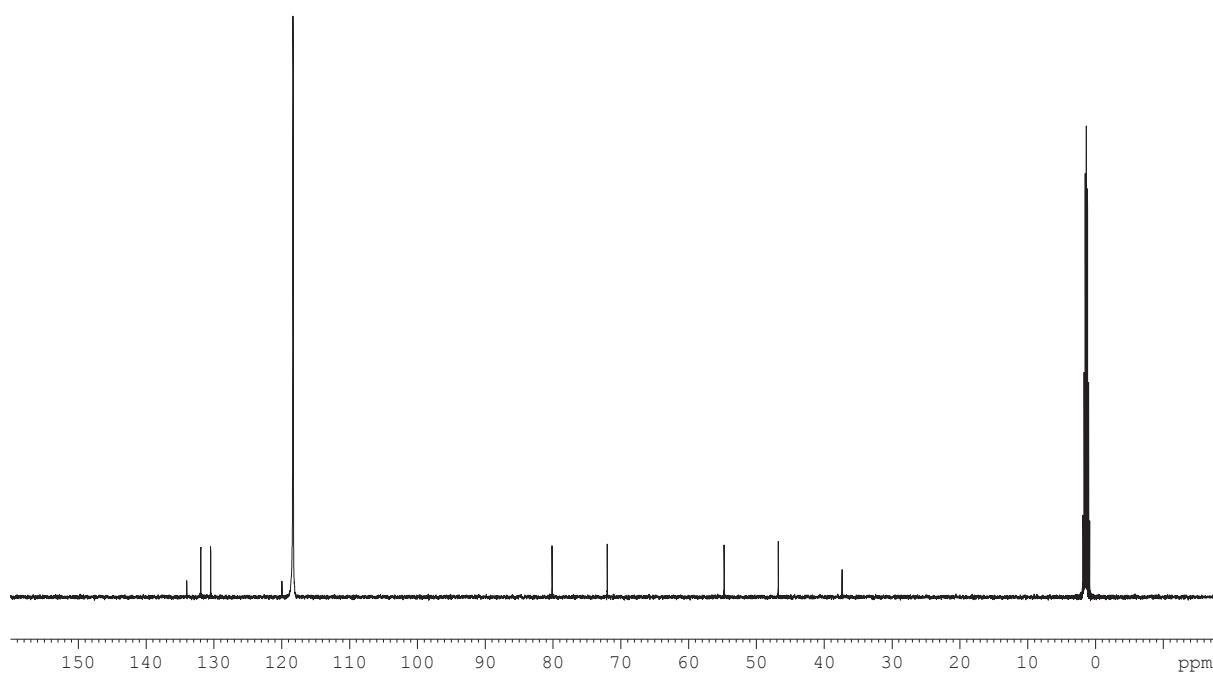


Figure S.28. 125 MHz ^{13}C NMR spectrum of **3a** in CD_3CN .

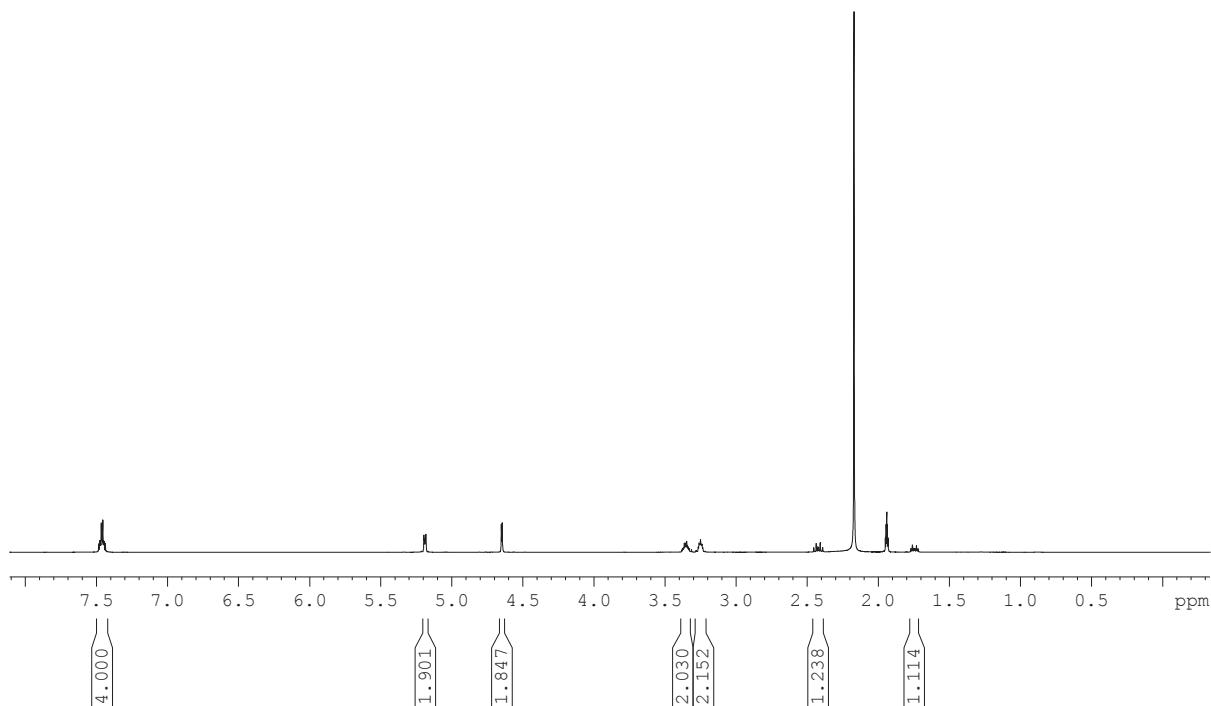


Figure S-29. 500 MHz ^1H NMR spectrum of **3b** in CD_3CN .

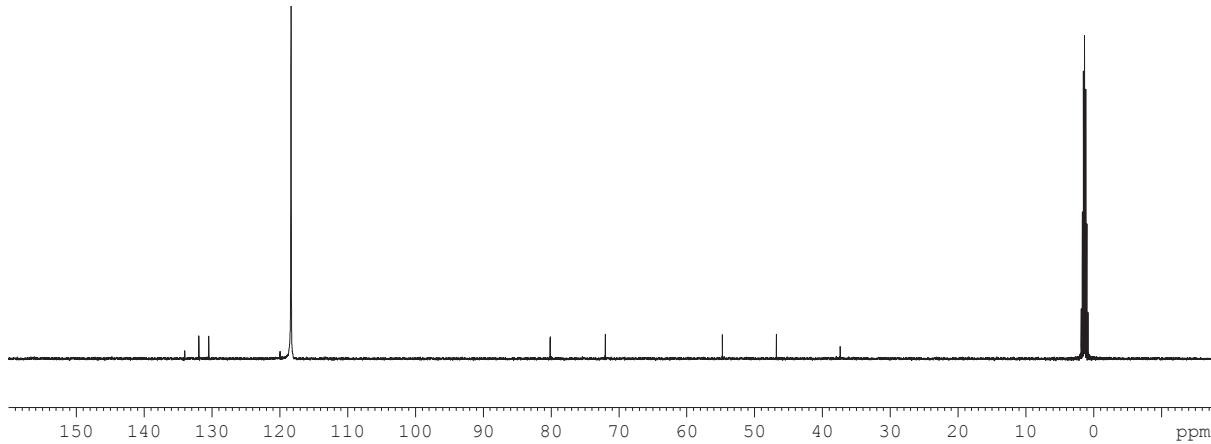


Figure S-30. 125 MHz ^{13}C NMR spectrum of **3b** in CD_3CN .

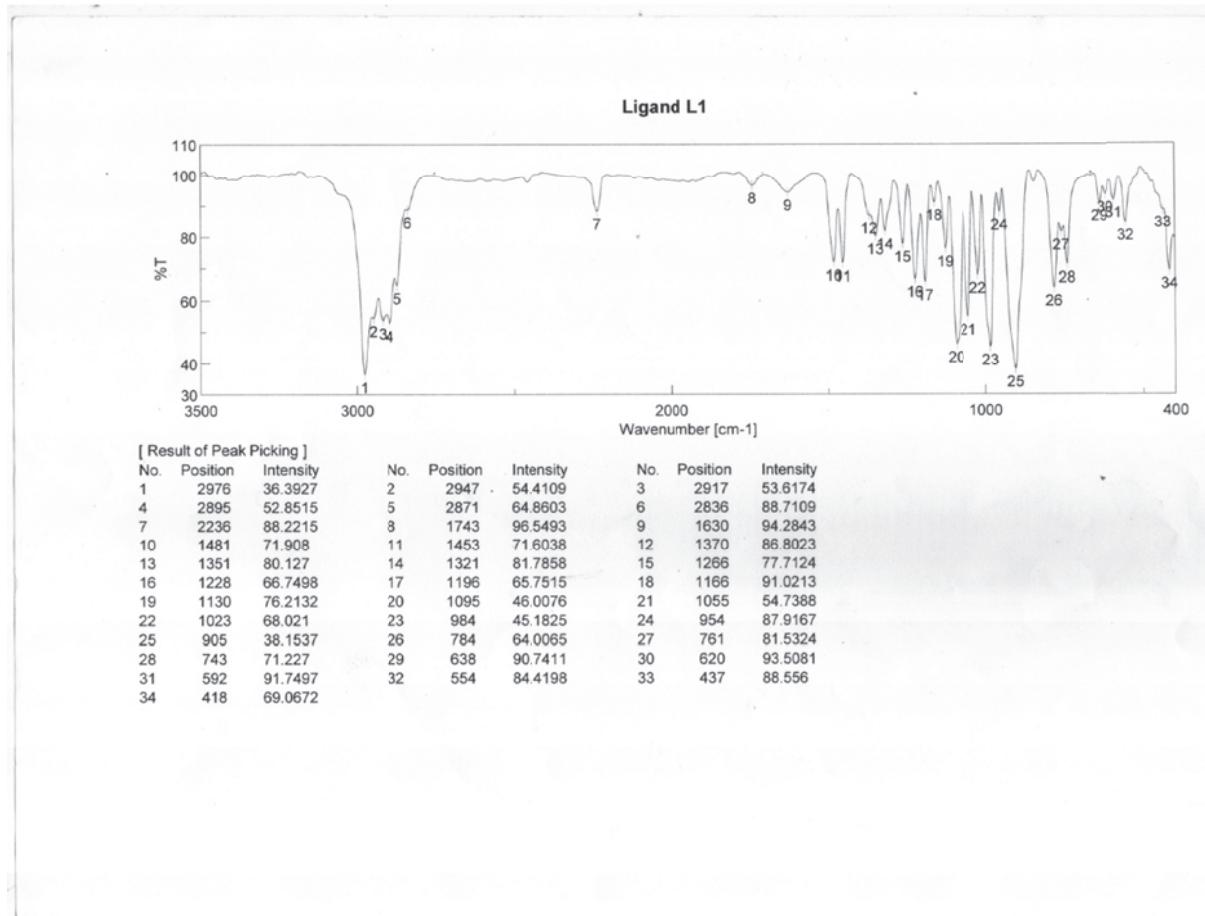


Figure S-31. IR spectrum of L1.

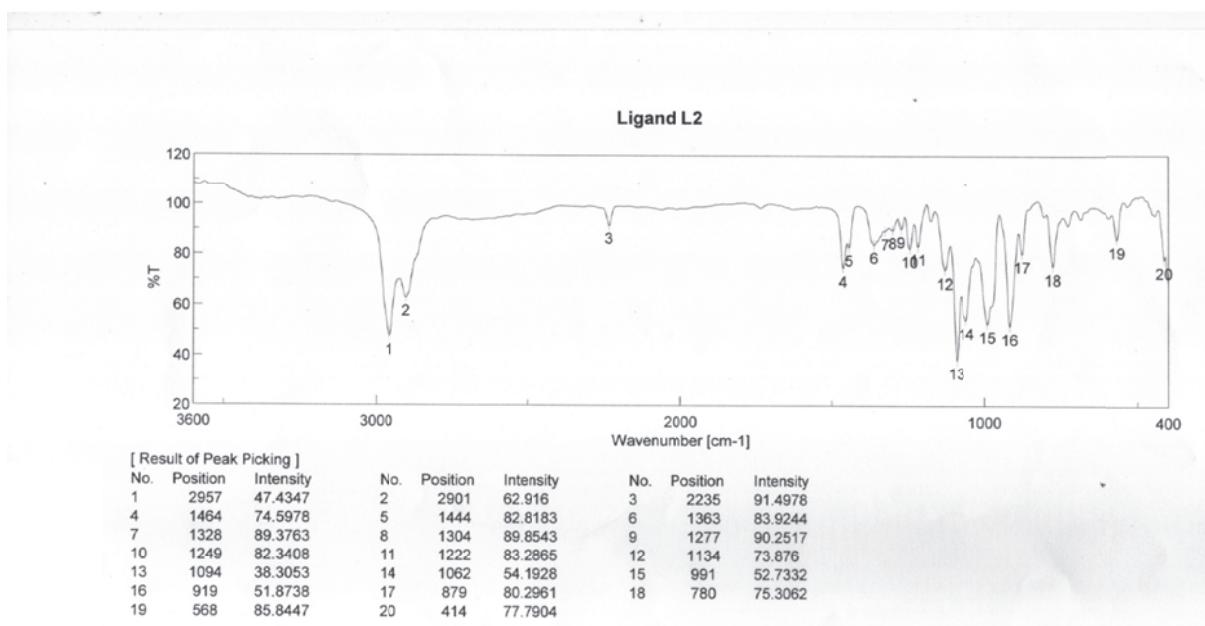


Figure S-32. IR spectrum of L2.

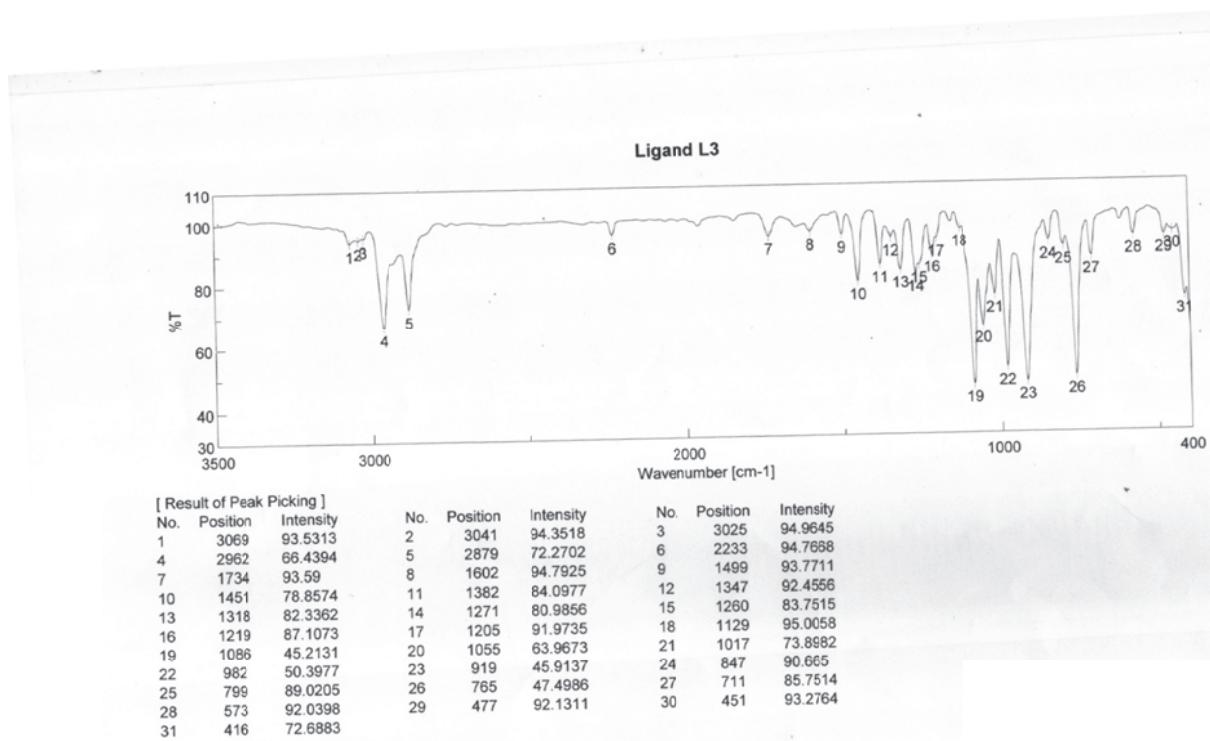


Figure S-33. IR spectrum of L3.

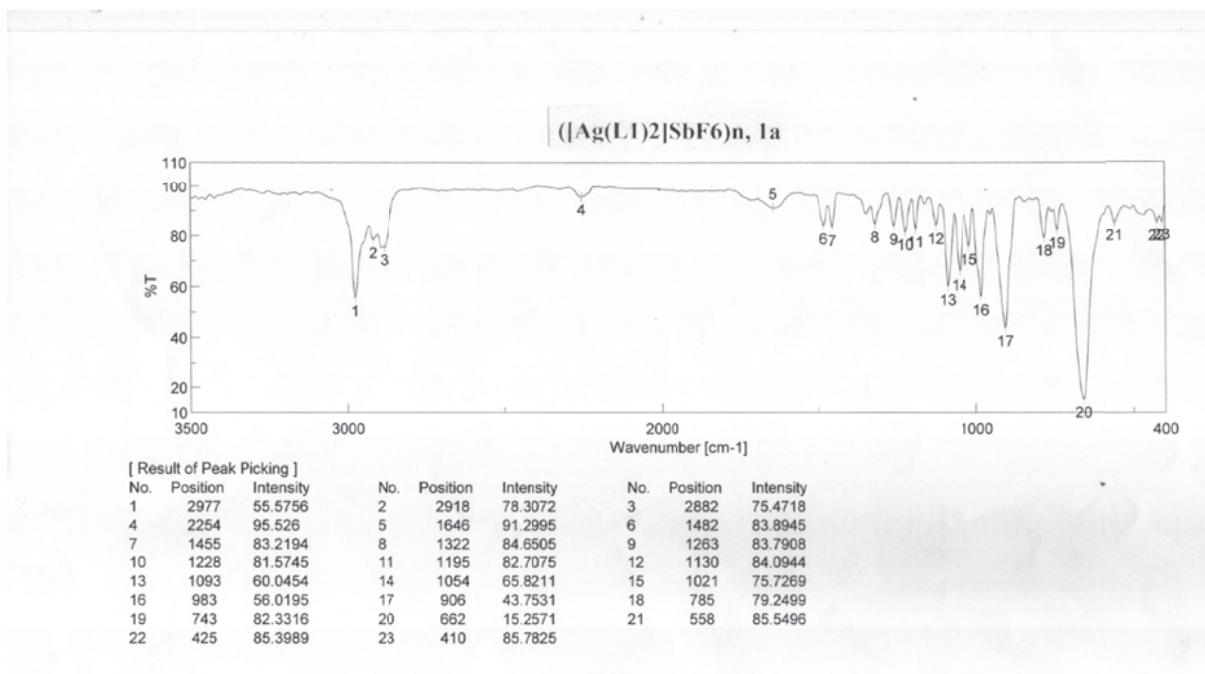


Figure S-34. IR spectrum of **1a**.

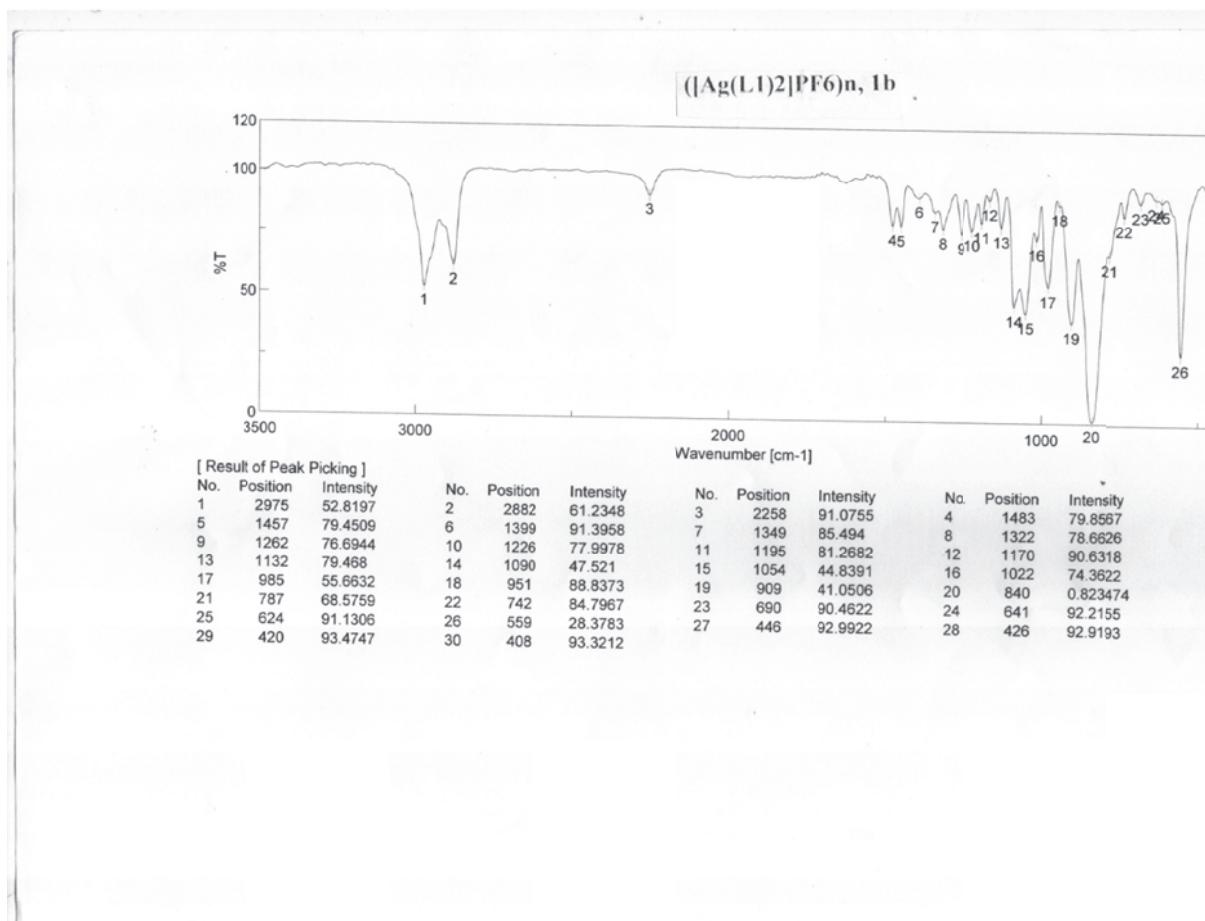


Figure S-35. IR spectrum of **1b**.

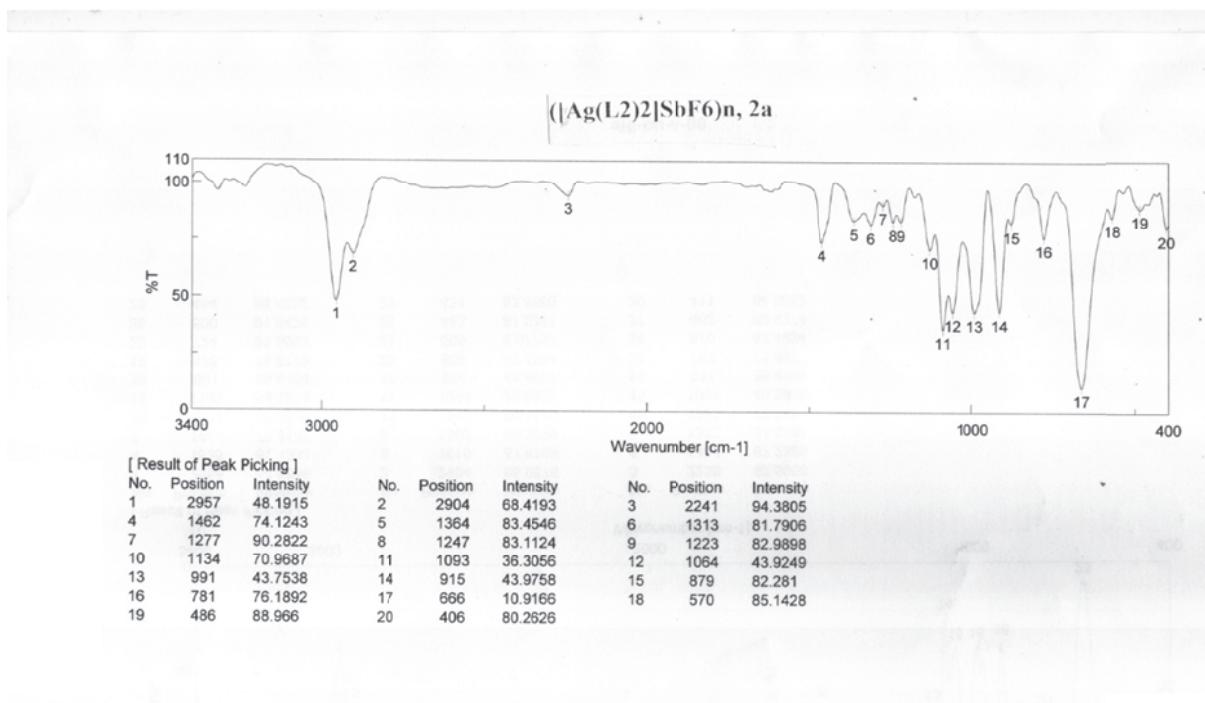


Figure S-36. IR spectrum of 2a.

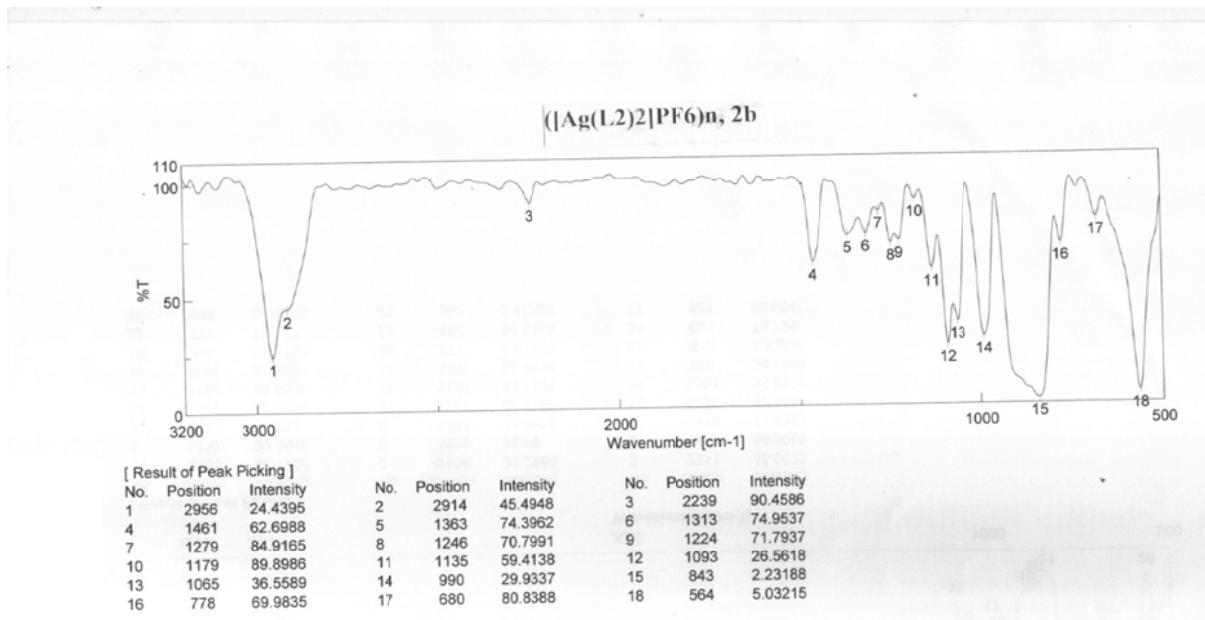


Figure S-37. IR spectrum of **2b**.

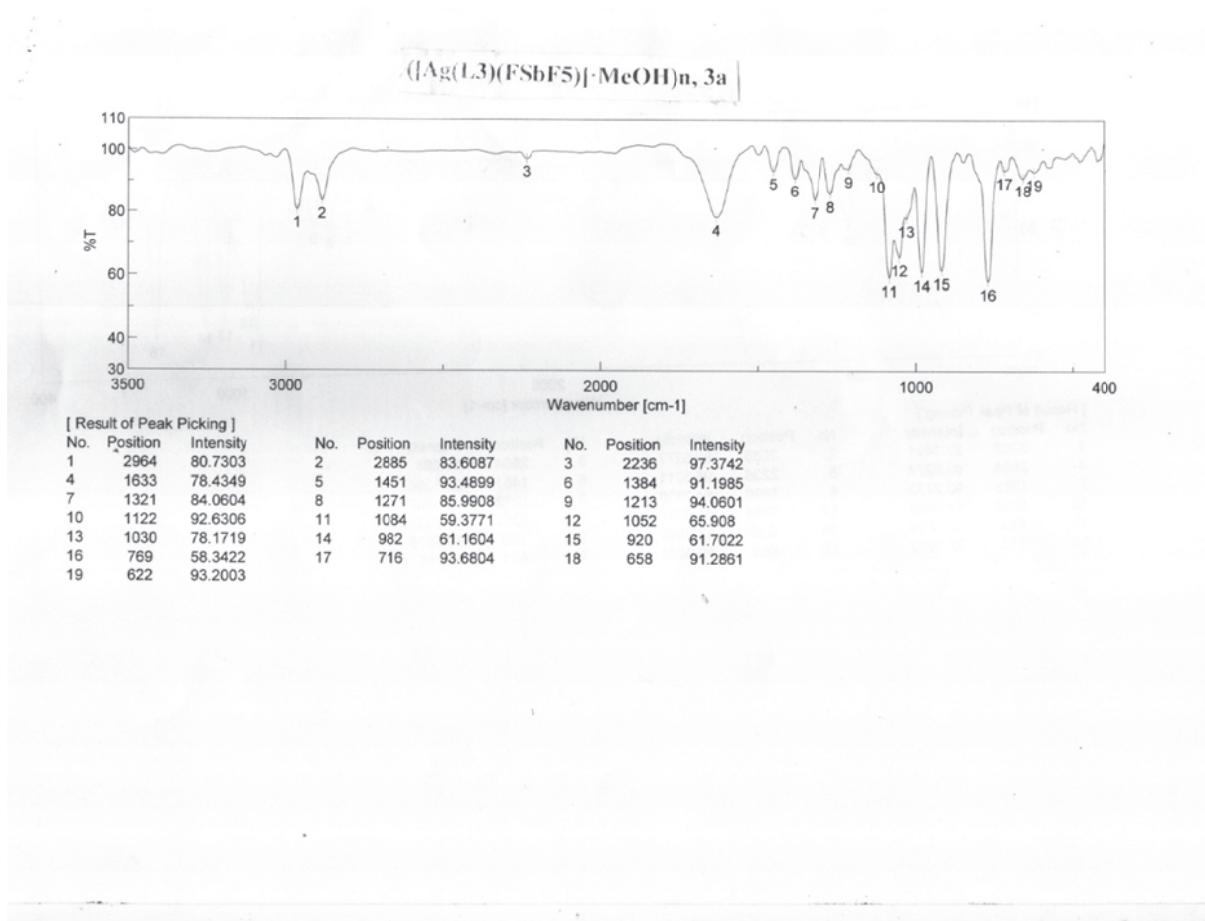


Figure S-38. IR spectrum of 3a.

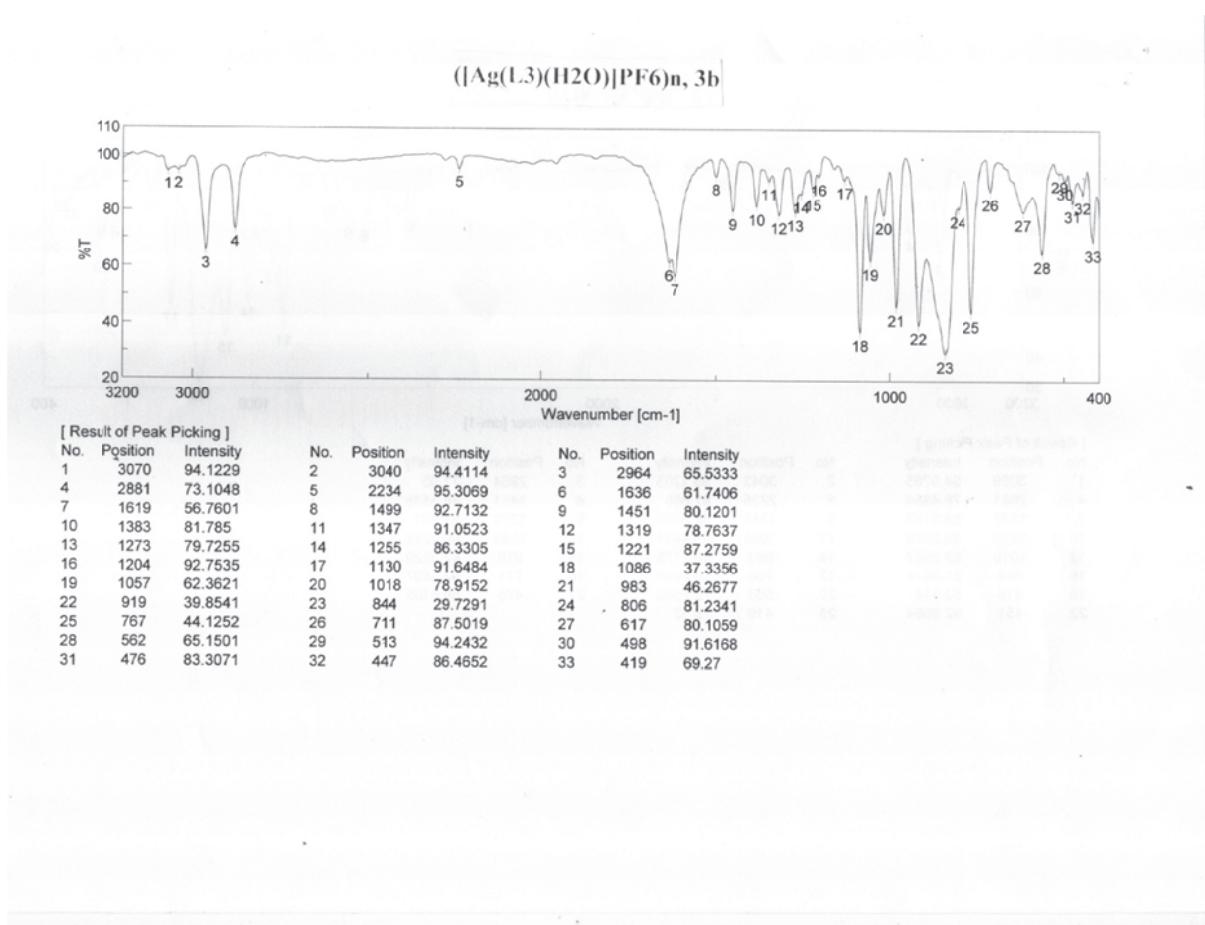


Figure S-39. IR spectrum of **3b**.

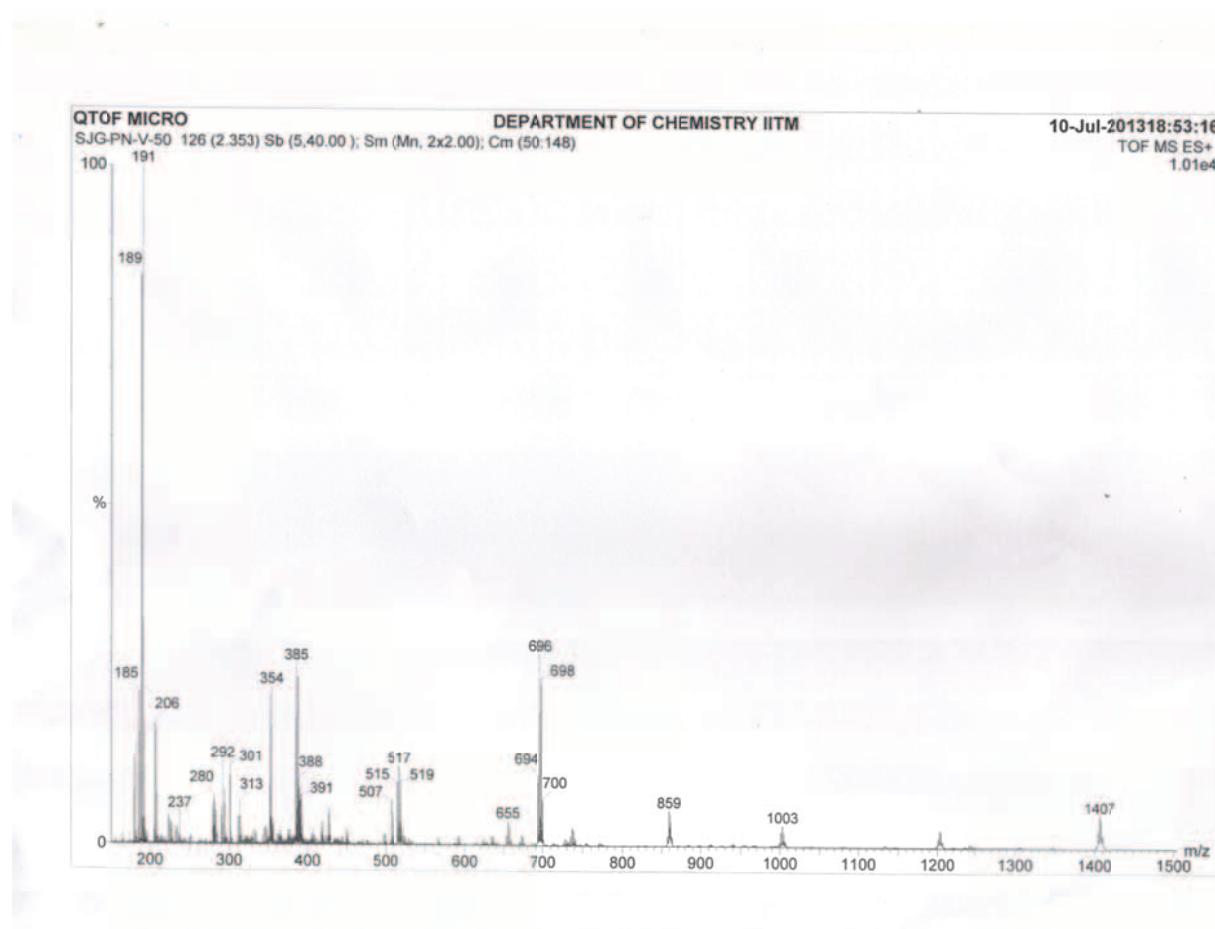


Figure S-40. ESI-MS spectrum of **1a**.

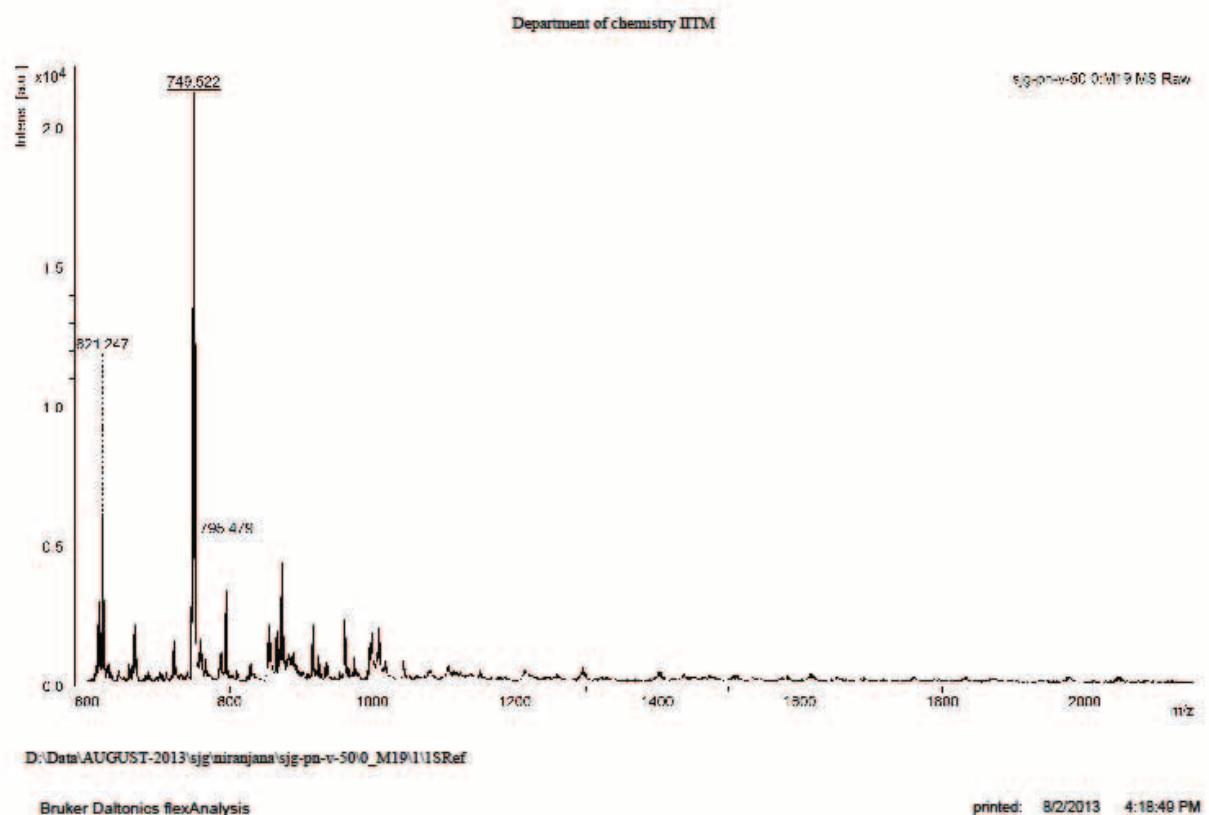


Figure S-41: MALDI-TOFMS spectrum of **1a**.

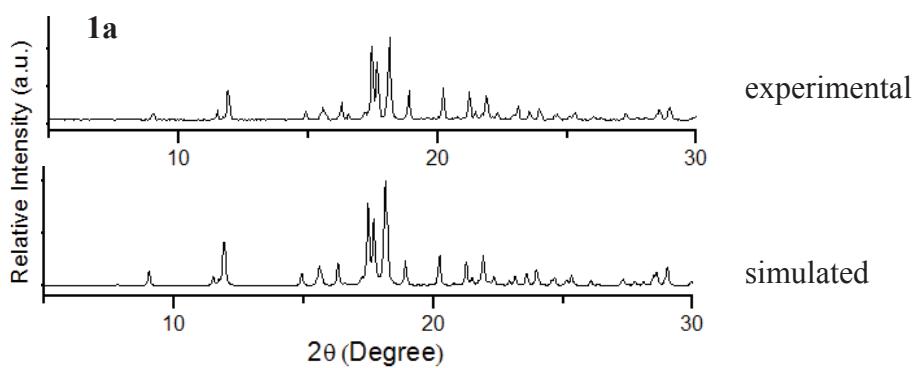


Figure S-42. Experimental and simulated PXRD pattern of **1a**.

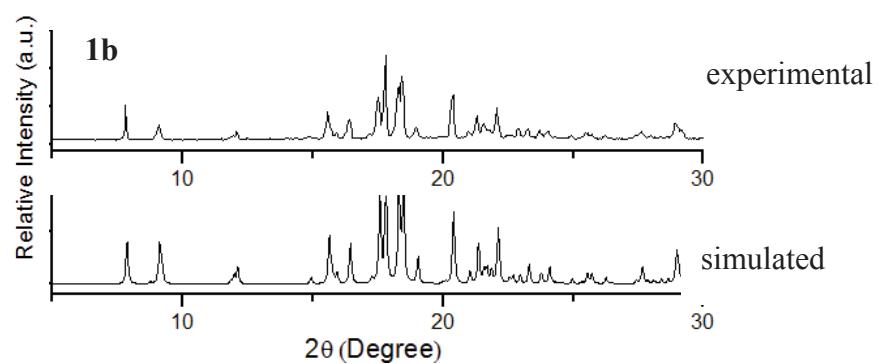


Figure S-43. Experimental and simulated PXRD pattern of **1b**.

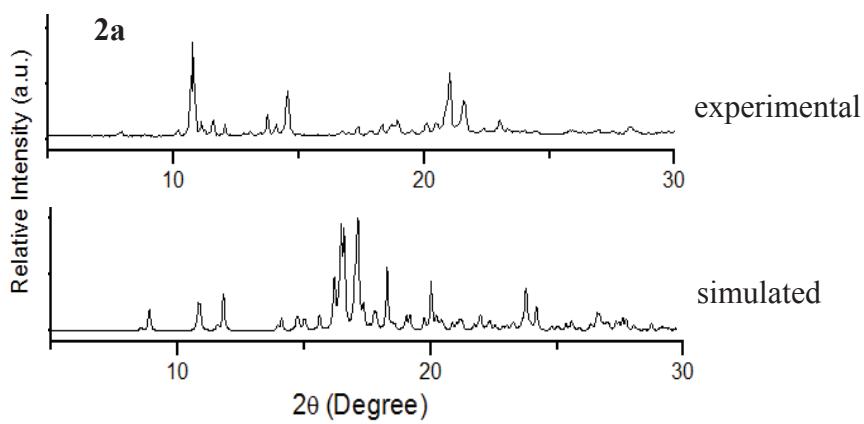


Figure S-44. Experimental and simulated PXRD pattern of **2a**.

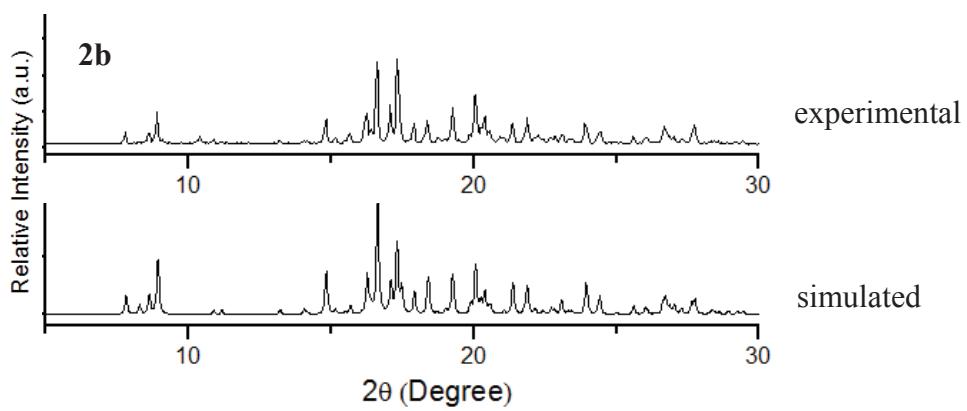


Figure S-45. Experimental and simulated PXRD pattern of **2b**.

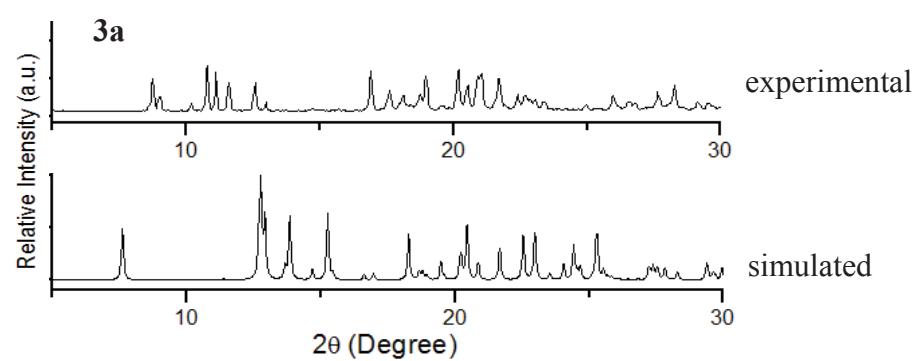


Figure S-46. Experimental and simulated PXRD pattern of **3a**.

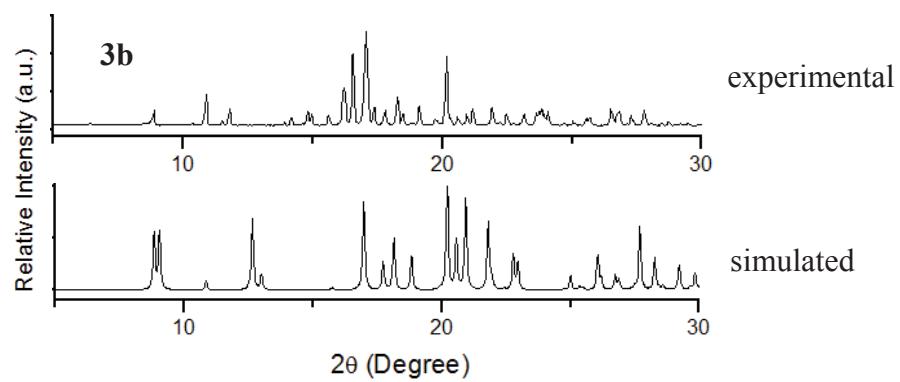


Figure S-47. Experimental and simulated PXRD pattern of **3b**.

Table S-1. Crystal data and structure refinement parameters for the ligands **L1**, **L2** and **L3**

Compounds	L1	L2	L3
Empirical formula	C ₁₁ H ₁₂ N ₂ O ₂	C ₁₃ H ₁₄ N ₂ O ₂	C ₁₇ H ₁₄ N ₂ O ₂
Formula weight	204.23	230.26	278.30
Crystal system	Monoclinic	Triclinic	Triclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	7.1344 (2)	8.8137 (7)	9.3570(6)
<i>b</i> (Å)	9.0828 (3)	11.8850 (4)	9.7318(10)
<i>c</i> (Å)	16.2936 (6)	12.8820 (4)	9.7501(5)
α (°)	90°	115.1300 (10)°	103.814(4)
β (°)	102.446 (2)°	102.974 (10)°	117.360(3)
γ (°)	90°	95.330 (2)°	104.070(4)
Volume (Å) ³	1031.02 (6)	1163.07 (11)	698.71(9)
Z	4	2	2
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature (K)	298 (2)	275 (2)	297(2)
Calculated density (g/cm ³)	1.316	1.315	1.323
Absorption coefficient (mm ⁻¹)	0.092	0.090	0.088
F(000)	432	488	292
Crystal dimensions (mm) ³	0.25 x 0.18 x 0.12	0.45 x 0.25 x 0.15	0.45 x 0.20 x 0.18
θ range for data collection (°)	2.56 to 28.45	1.83 to 32.71	2.36 to 32.50
Limiting indices	-9≤ <i>h</i> ≤6, -12≤ <i>k</i> ≤12, -19≤ <i>l</i> ≤21	-10≤ <i>h</i> ≤13, -17≤ <i>k</i> ≤10, -16≤ <i>l</i> ≤19	-13≤ <i>h</i> ≤14 -14≤ <i>k</i> ≤10 -14≤ <i>l</i> ≤14
Reflections collected / unique	7467 / 2314	15330 / 6562	10370 / 4400
Data / restraints / parameter	2314 / 0 / 136	6562 / 0 / 307	4400 / 0 / 190
GOF	0.660	1.047	1.040
Final ^a <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1 = 0.0372 <i>wR</i> 2 = 0.1035	<i>R</i> 1 = 0.0524, <i>wR</i> 2 = 0.1342	<i>R</i> 1 = 0.0462 <i>wR</i> 2 = 0.1128
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0507 <i>wR</i> 2 = 0.1250	<i>R</i> 1 = 0.0790, <i>wR</i> 2 = 0.1524	<i>R</i> 1 = 0.0717 <i>wR</i> 2 = 0.1274
CCDC	942151	942152	942153

Table S-2. Crystal data and structure refinement parameters for the complexes **1a**, **2a** and **3a**.

Compounds	1a	2a	3a
Empirical formula	C ₂₂ H ₂₃ AgF ₆ N ₄ O ₄ Sb	C ₅₂ H ₅₅ Ag ₂ F ₁₄ N ₈ O ₈ Sb ₂	C ₃₅ H ₃₂ Ag ₂ F ₁₂ N ₄ O ₅ Sb ₂
Formula weight	751.06	1645.28	1275.91
Crystal system	Monoclinic	Triclinic	Monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	11.3040 (2)	11.403 (3)	7.4347(4)
<i>b</i> (Å)	19.54360 (4)	12.604 (4)	18.1183(10)
<i>c</i> (Å)	11.8709 (2)	20.686 (5)	15.1884(9)
α (°)	90°	89.498 (15)°	90
β (°)	92.3040 (10)°	89.662 (15)°	95.864
γ (°)	90°	84.312 (16)°	90
Volume (Å) ³	2620.41 (8)	2958.5 (13)	2035.2(2)
<i>Z</i>	4	2	2
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature(K)	298 (2)	298 (2)	298(2)
Calculated density(g/cm ³)	1.904	1.847	2.082
Absorption coefficient (mm ⁻¹)	1.857	1.658	2.363
F(000)	1468	1618	1228
Crystal dimensions (mm) ³	0.25 x 0.20 x 0.15	0.25 x 0.20 x 0.15	0.35 x 0.25 x 0.18
θ range for data collection (°)	2.01 to 30.39	0.98 to 29.06	2.25 to 25.00
Limiting indices	-16≤ <i>h</i> ≤15, -26≤ <i>k</i> ≤17, -14≤ <i>l</i> ≤16	-14≤ <i>h</i> ≤15, -12≤ <i>k</i> ≤15, -25≤ <i>l</i> ≤25	-8≤ <i>h</i> ≤8 -21≤ <i>k</i> ≤20 -17≤ <i>l</i> ≤17
Reflections collected / unique	20288 / 6903	19280 / 10836	12463 / 3550
Data / restraints / parameter	6903 / 0 / 344	10836 / 0 / 775	3550 / 0 / 282
GOF	1.002	1.125	1.063
Final ^a <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1 = 0.0468, <i>wR</i> 2 = 0.1402	<i>R</i> 1 = 0.0600, <i>wR</i> 2 = 0.1652	<i>R</i> 1 = 0.0395 <i>wR</i> 2 = 0.1003
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0796, <i>wR</i> 2 = 0.1634	<i>R</i> 1 = 0.1045, <i>wR</i> 2 = 0.1956	<i>R</i> 1 = 0.0453 <i>wR</i> 2 = 0.1051
CCDC	942145	942147	942149

Table S-3. Crystal data and structure refinement parameters for the complexes **1b**, **2b** and **3b**.

Compounds	1b	2b	3b
Empirical formula	C ₂₂ H ₂₃ Ag F ₆ N ₄ O ₄ P	C ₂₆ H ₂₈ Ag F ₆ N ₄ O ₄ P	C ₁₇ H ₁₆ Ag F ₆ N ₂ O ₃ P
Formula weight	660.28	731.36	549.16
Crystal system	Monoclinic	Monoclinic	Orthorhombic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	Pmna
<i>a</i> (Å)	11.2301 (6)	11.3548 (5)	13.5994(5)
<i>b</i> (Å)	19.1920 (11)	20.4728 (7)	9.9972(5)
<i>c</i> (Å)	11.8597 (6)	12.5381 (4)	14.0444(7)
α (°)	90°	90°	90
β (°)	92.214 (2)°	95.9590 (10)°	90
γ (°)	90°	90°	90
Volume (Å) ³	2554.2 (2)	2898.91 (19)	1909.42(15)
Z	4	4	4
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature (K)	293 (2)	298 (2)	298(2)
Calculated density (g/cm ³)	1.717	1.635	1.910
Absorption coefficient (mm ⁻¹)	0.933	0.828	1.219
F(000)	1324	1440	1088
Crystal dimensions (mm) ³	0.20 x 0.15 x 0.12	0.35 x 0.25 x 0.20	0.25 x 0.20 x 0.15
θ range for data collection (°)	1.81 to 28.36	1.80 to 28.42	2.08 to 28.46
Limiting indices	-14≤ <i>h</i> ≤13, -15≤ <i>k</i> ≤25, -15≤ <i>l</i> ≤11	-15≤ <i>h</i> ≤14, -27≤ <i>k</i> ≤27, -15≤ <i>l</i> ≤16	-15≤ <i>h</i> ≤17 -13≤ <i>k</i> ≤10 -18≤ <i>l</i> ≤13
Reflections collected / unique	17078 / 5359	22780 / 7005	7551 / 2348
Data / restraints / parameter	5359 / 2 / 343	7005 / 0 / 379	2348 / 0 / 146
GOF	1.038	1.058	1.110
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> 1 = 0.0660 <i>wR</i> 2 = 0.1901	<i>R</i> 1 = 0.0604, <i>wR</i> 2 = 0.1916	<i>R</i> 1 = 0.0505 <i>wR</i> 2 = 0.1682
<i>R</i> indices (all data)	<i>R</i> 1= 0.0989 <i>wR</i> 2 = 0.2190	<i>R</i> 1=0.0888, <i>wR</i> 2 = 0.2156	<i>R</i> 1 = 0.0572 <i>wR</i> 2 = 0.1744
CCDC	942146	942148	942150

Description of the structure of $([Ag(L1)_2]PF_6)_n$, **1b**

The overall crystal structure of **1b** is very much comparable to that of **1a**. The Ag-N bond distances in the complex are noted in the range of 2.233–2.414 Å.²² The nitrile nitrogens of the two ligand strands of the asymmetric units are separated by 9.307 Å (N2---N4) and 8.382 Å (N1---N3). The short contact interactions of silver(I) with oxygen of neighbouring sheets are 2.713 and 3.229 Å.²³ The packing of the sheets in the superstructure is also comparable to **1a**. The packing diagram of the stacked sheets is shown in Figure S-48.

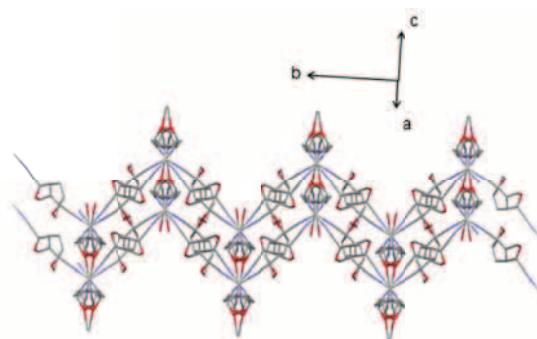


Figure S-48. Packing of the two-dimensional “zig-zag sheets” in the crystal structure of **1b**. The inter-sheet connection using one of the short contact types is also shown.

$([Ag(L2)_2]PF_6)_n$, **2b**

The asymmetric unit in the structure of **2b** is composed of one silver(I), two ligands and one PF_6^- moieties. The coordination geometry around the silver(I) is distorted-bisphenoidal that is derived from four units of **L2**. The relevant bond lengths and angles around the metal centre are noted in Table S-6. The Ag-N bond distances in the complex are found to be in the range of 2.200–2.515 Å.²² The nitrile nitrogens of the two strands of the asymmetric units are separated by 9.272 (N1---N4), 9.073 (N2---N3), as compared to 9.334 Å (i.e average of 9.302 and 9.366 Å) for **L2**. The overall crystal structure of **2b** is very much comparable to that of **2a**. The silver centres are found to be pseudo-pentacoordinated due to additional short contact interactions with oxygen atoms of ligand strands belonging to the neighbouring sheets. These distances for the two silver centres of the asymmetric units are 2.837 (Ag1-O3) Å.²³ The packing of the sheets in the superstructure is also comparable to **1a**. The packing diagram of the stacking of sheets is shown in Figure S-49.

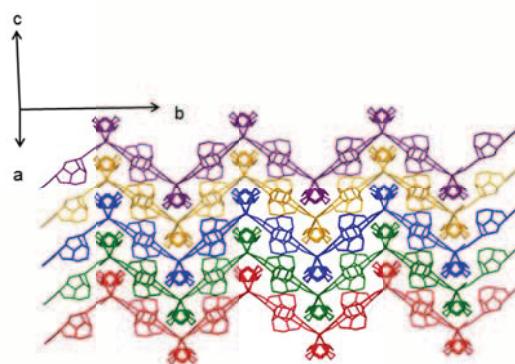


Figure S-49. Packing of the two-dimensional “zig-zag sheets” in the crystal structure of **2b**. The sheets are shown in different colours.

Table S-4. Selected interatomic distances (\AA) and angles ($^\circ$) for **1a**

Ag(2)-N(1)	2.237(4)
Ag(2)-N(2)	2.292(5)
Ag(2)-N(4)	2.369(5)
Ag(2)-N(3)	2.423(6)
N(1)-Ag(2)-N(2)	145.9(2)
N(1)-Ag(2)-N(4)	110.85(19)
N(2)-Ag(2)-N(4)	96.14(19)
N(1)-Ag(2)-N(3)	101.51(17)
N(2)-Ag(2)-N(3)	91.5(2)
N(4)-Ag(2)-N(3)	103.6(2)

Table S-5 . Selected interatomic distances (\AA) and angles ($^\circ$) for **2a**

Ag(1)-N(1)	2.211(7)
Ag(1)-N(3)	2.247(8)
Ag(1)-N(2)	2.288(7)
Ag(1)-N(4)	2.507(8)
Ag(2)-N(8)	2.228(7)
Ag(2)-N(5)	2.252(7)
Ag(2)-N(7)	2.269(9)
Ag(2)-N(6)	2.489(8)
N(1)-Ag(1)-N(3)	153.0(3)
N(1)-Ag(1)-N(2)	102.8(3)
N(3)-Ag(1)-N(2)	100.7(4)
N(1)-Ag(1)-N(4)	99.4(3)
N(3)-Ag(1)-N(4)	84.3(3)
N(2)-Ag(1)-N(4)	111.2(3)
N(8)-Ag(2)-N(5)	153.1(3)
N(8)-Ag(2)-N(7)	103.2(3)
N(5)-Ag(2)-N(7)	100.3(4)
N(8)-Ag(2)-N(6)	98.7(3)
N(5)-Ag(2)-N(6)	85.1(3)
N(7)-Ag(2)-N(6)	110.1(3)

Table S-6. Selected interatomic distances (\AA) and angles ($^\circ$) for **2b**.

Ag(1)-N(1)	2.200(4)
Ag(1)-N(3)	2.250(5)
Ag(1)-N(2)	2.292(5)
Ag(1)-N(4)	2.515(5)
N(1)-Ag(1)-N(3)	154.1(2)
N(1)-Ag(1)-N(2)	100.7(2)
N(3)-Ag(1)-N(2)	102.4(2)
N(1)-Ag(1)-N(4)	97.35(18)
N(3)-Ag(1)-N(4)	83.9(2)
N(2)-Ag(1)-N(4)	113.7(2)

Table S-7. Selected interatomic distances (\AA) and angles ($^\circ$) for **3a**.

Ag(1)-N(4)	2.172(4)
Ag(1)-N(5)	2.231(4)
Ag(1)-F(6)	2.512(5)
Ag(1)-O(1)	2.595(3)
N(4)-Ag(1)-N(5)	141.00(15)
N(4)-Ag(1)-F(6)	102.97(18)
N(5)-Ag(1)-F(6)	99.27(16)
N(4)-Ag(1)-O(1)	129.30(12)
N(5)-Ag(1)-O(1)	79.59(11)
F(6)-Ag(1)-O(1)	94.54(19)

Table S-8. Selected interatomic distances (\AA) and angles ($^\circ$) for **3b**.

Ag(01)-N(1)#1	2.156(4)
Ag(01)-N(1)	2.156(4)
Ag(01)-O(2)	2.450(6)
N(1)#1-Ag(01)-N(1)	151.3(2)
N(1)#1-Ag(01)-O(2)	104.30(12)
N(1)-Ag(01)-O(2)	104.30(12)