Electronic Supplementary Information for Dalton Transactions

Supporting information

A multicomponent CuAAC "click" approach to a library of hybrid polydentate 2-pyridyl-1,2,3-triazole ligands: New building blocks for the generation of metallosupramolecular architectures.

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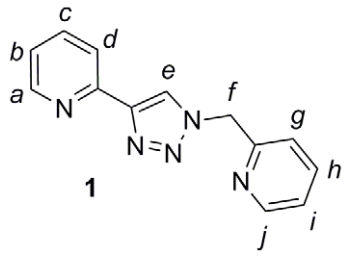
1. General Experimental Section

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Dry CH_2Cl_2 and CH_3CN were obtained by passing the solvents through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). 2,6-Diethynylpyridine,[1] 4,4'-diiododiphenylmethane,[2] were prepared according to literature procedures. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. Flash column chromatography was carried out using Kiesegel C60 (Fisher) as the stationary phase. Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60F254, Merck, Germany) and observed under UV light. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz Varian UNITY INOVA INOVA or 400 MHz Varian 400 MR spectrometer at 298 K. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer using KBr discs. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. ESI Mass Spectra were collected on a Bruker micro-TOF-Q spectrometer.

Safety Note: Sodium azide is toxic and appropriate precautions should be taken. As low molecular weight organic azides are potential explosives, care must be taken during their handling.[3] Generally, when the total number of carbon (C) plus oxygen (O) atoms is less than the total number of nitrogen atoms (N) by a ratio of three, i.e., (C + O) / N < 3, the compound is considered as an

explosive hazard. A standard PVC blast shield was used when necessary. Additionally, copper azides and acetylides are explosive when dry, and their traces should be removed before the CuAAC reaction products are dried. This is achieved by pouring the crude reaction mixture into 100 mL of aqueous EDTA/NH_4OH.

2. Experimental Procedures

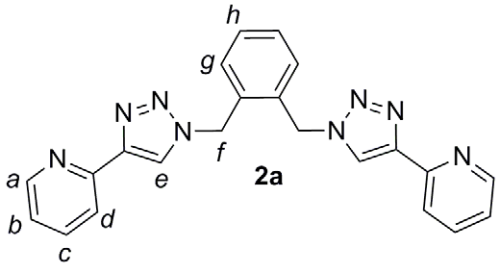


2-[1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazol-4-yl]pyridine (1). To a stirred solution of 2-(bromomethyl)pyridine hydrobromide (0.554 g, 2.2 mmol, 1.1 eq.) in DMF/H_2O (10 mL, 4:1) was added NaN_3 (0.156 g, 2.4 mmol, 1.2 eq.), Na_2CO_3 (0.312 g, 3.0 mmol, 3.00 eq.), $CuSO_4$•$5H_20$ (0.246 g, 1.2 mmol, 0.40 eq.) and ascorbic acid (0.42 g, 2.4 mmol, 0.80 eq). 2-ethynylpyridine (0.206 g, 2.0 mmol, 1.0 eq.) was added and the reaction mixture was stirred at room temperature for 20 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (200 mL) and EtOAc (200 ml) and the layers separated. The organic phase was washed with H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (gradient CH_2Cl_2/acetone to 7:3 ratio) gave the product as a colourless solid. Yield: 0.43 g, 91%. Mp 71-73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, J = 4.8, 1H, H_j), 8.57 (dd, J = 0.8, 4.1, 1H, H_a), 8.27 (s, 1H, H_e), 8.18 (d, J = 8.0, 1H, H_d), 7.77 (td, J = 1.8, 7.8, 1H, H_c), 7.68 (td, J = 1.8, 7.7, 1H, H_h), 7.30–7.18 (m, 3H, $H_{b,i,g}$), 5.73 (s, 2H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 150.1, 149.8,

149.3, 148.7, 137.3, 136.9, 123.4, 122.9, 122.7, 122.4, 120.3, 55.7; I. R. (KBr): υ (cm^{-1}) 3500-3200 (sb), 3109, 3077, 2925, 1606, 1598, 1569, 1551, 1416, 1314, 1223, 1197, 1152, 1075, 1040, 995, 953, 917, 847, 782, 723. HRESI-MS ($CDCl_3$/MeOH): *m/z* = 238.1028 $[\mathbf{1}+H]^+$ (calc. for $C_{13}H_{12}N_8$ 238.1092), 260.0897 $[\mathbf{1}+Na]^+$ (calc. for $C_{13}H_{11}N_5Na$ 260.0907); Anal. calcd for $C_{13}H_{11}N_5 \bullet 0.25H_2O$: C, 64.58; H, 4.79; N, 28.97. Found: C, 64.23; H, 4.78; N, 29.25.

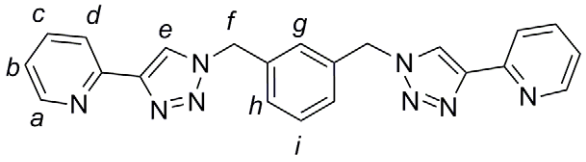
2.1 General CuAAC Experimental Procedure for Benzyl Spacer Ligands.

To a stirred solution of either dibromide (3.0 mmol, 1.00 eq.) or tribromide (2.0 mmol, 1.00 eq.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.41 g, 6.2 mmol, either 2.1 eq. or 3.1 eq.), Na_2CO_3 (0.312 g, 3.0 mmol, 1.00 eq.), $CuSO_4$ (0.246 g, 1.2 mmol, 0.40 eq.) and ascorbic acid (0.42 g, 2.4 mmol, 0.80 eq). 2-ethynylpyridine (0.64 g, 6.0 mmol, either 2.05 eq. or 3.10 eq.) was added and the reaction mixture was stirred at room temperature for 16 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (200 mL) and EtOAc (200 ml) and the layers separated. The organic phase was washed with H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (gradient CH_2Cl_2/acetone) gave the products as colourless solids.



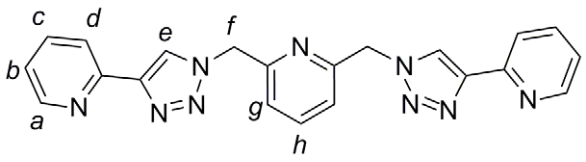
Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product **2a** as a colourless solid. Yield: 1.03 g, 88%. Mp 207-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (ddd, *J* = 0.9, 1.7, 4.9, 2H, H_a), 8.14 (dt, *J* = 0.9, 7.9, 2H, H_g), 8.04 (s, 2H, H_e),

7.75 (td, J = 1.8, 7.8, 2H, H_c), 7.45–7.29 (m, 4H, $H_{b,h}$), 7.20 (ddd, J = 1.2, 4.9, 7.5, 2H, H_d), 5.73 (s, 4H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.4, 148.9, 137.2, 133.3, 130.9, 130.2, 123.1, 122.3, 120.5, 51.6; I. R. (KBr): υ (cm^{-1}) 3109, 3077, 2925, 1606, 1597, 1570, 1551, 1421, 1314, 1228, 1154, 1074, 1051, 996, 861, 786, 727. HRESI-MS (MeOH): *m/z* = 395.1707 [**2a**+H]$^+$ (calc. for $C_{22}H_{19}N_8$ 395.1733), 417.1523 [**2a**+Na]$^+$ (calc. for $C_{22}H_{18}N_8Na$ 417.1552); Anal. calcd for $C_{22}H_{18}N_8$: C, 66.99; H, 4.60; N, 28.41. Found: C, 66.60; H, 4.58; N, 28.73.



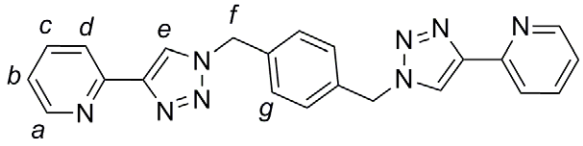
2b

Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product **2b** as a colourless solid. Yield: 0.99 g, 85%. Mp 171-172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 4.6, 2H, H_a), 8.24 – 8.12 (m, 4H, $H_{e,h}$), 7.80 (td, J = 1.7, 7.8, 2H, H_c), 7.43–7.20 (m, 6H, $H_{b,d,g}$), 5.58 (s, 4H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 149.5, 149.0, 137.2, 135.8, 130.4, 128.8, 128.1, 123.1, 122.2, 120.5, 54.1; I.R. (KBr): υ (cm^{-1}) 3108, 3089, 2925, 1603, 1597, 1570, 1547, 1420, 1314, 1248, 1228, 1148, 1083, 1046, 997, 896, 861, 843, 787, 738; HRESI-MS (MeOH): *m/z* = 395.1721 [**2b**+H]$^+$ (calc. for $C_{22}H_{19}N_8$ 395.1733), 417.1539 [**2b**+Na]$^+$ (calc. for $C_{22}H_{18}N_8Na$ 417.1552); Anal. calcd for $C_{22}H_{18}N_8$: C, 66.99; H, 4.60; N, 28.41. Found: C, 66.75; H, 4.57; N, 28.62.



2c

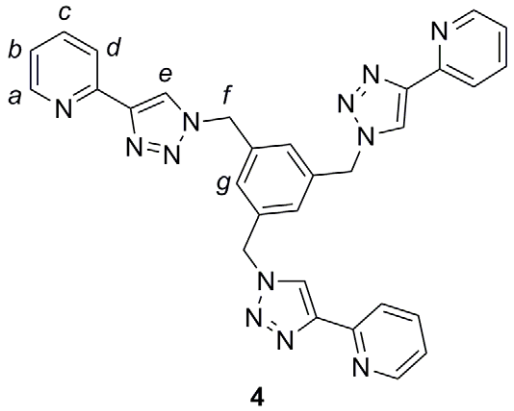
Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product **2c** as a colourless solid. Yield: 1.10 g, 94%. Mp 170-171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.4, 2H, H_a), 8.26 (s, 2H, H_e), 8.17 (d, *J* = 7.9, 2H, H_d), 7.77 (td, J = 1.8, 7.8, 2H, H_c), 7.68 (t, J = 7.8, 1H, H_h), 7.26–7.18 (m, 4H, $H_{b,g}$), 5.72 (s, 4H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 150.3, 149.6, 149.1, 138.9, 137.1, 123.1, 122.8, 122.1, 120.5, 55.7; I. R. (KBr): υ (cm^{-1}) 3500-3200 (br), 3145, 3124, 2925, 1605, 1597, 1574, 1548, 1418, 1341, 1306, 1247, 1227, 1193, 1155, 1088, 1074, 1043, 997, 841, 785, 771. HRESI-MS (MeOH): *m/z* = 396.1704 [**2c**+H]$^+$ (calc. for $C_{21}H_{18}N_9$ 396.1685), 418.1515 [**2c**+Na]$^+$ (calc. for $C_{21}H_{18}N_9Na$ 418.1505); Anal. calcd for $C_{21}H_{17}N_9$: C, 63.79; H, 4.33; N, 31.88. Found: C, 63.65; H, 4.39; N, 31.60.



2d

Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product as a colourless solid. X-ray quality colourless crystals were obtained by vapour diffusion of a chloroform solution of **2d** with petrol. Yield: 0.98 g, 85%. Mp 234-235 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.5, 2H, H_a), 8.16 (d, 2H, H_d), 8.06 (s, *J* = 7.5, 2H, H_e), 7.77 (td, *J* = 8.5, 2H, H_c), 7.34 (s, 4H, H_g), 7.20 (m, 2H, H_b), 5.58 (s, 4H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 149.4, 149.0, 137.2, 135.4, 129.2, 123.1, 122.2, 120.5, 54.0; I.R. (KBr): υ (cm^{-1}) 3400-3200 (br), 3119, 3087, 2925, 1606, 1597, 1570, 1546, 1418, 1347, 1315, 1257, 1248, 1223, 1149, 1082, 1046, 1022, 996, 899, 865, 840, 791, 741; HRESI-MS (MeOH): *m/z* = 395.1740 [**2d**+H]$^+$ (calc. for $C_{22}H_{19}N_8$

395.1733), 417.1558 [**2d**+Na]$^+$ (calc. for $C_{22}H_{18}N_8Na$ 417.1552); Anal. calcd for $C_{22}H_{18}N_8$•0.33(H_2O): C, 66.00; H, 4.70; N, 27.99. Found: C, 66.22; H, 4.60; N, 28.27.



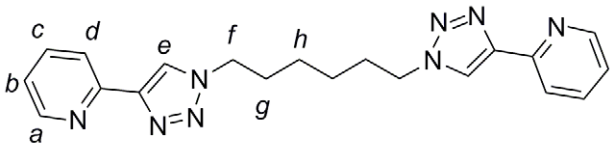
4

Chromatography (gradient CH_2Cl_2/acetone to a ratio 1:1) gave the product as a colourless solid. Yield: 0.89 g, 82%. Mp 209-210 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (ddd, J = 0.9, 1.7, 4.8, 3H, H_a), 8.16 (dt, J = 1.0, 8.0, 3H, H_d), 8.09 (s, 3H, H_e), 7.77 (td, J = 1.8, 6.0, 7.8, 3H, H_c), 7.26 (s, 3H, H_g), 7.20 (m, 3H, H_b), 5.58 (s, 6H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.5, 149.1, 137.2, 137.1, 128.1, 123.2, 122.4, 120.5, 53.7; I.R. (KBr): υ (cm^{-1}) 3400-3200 (br), 3103, 3087, 2924, 1596, 1569, 1544, 1420, 1344, 1311, 1226, 1199, 1168, 1156, 1080, 1045, 996, 977, 890, 846, 826, 791, 775, 755, 741; HRESI-MS (MeOH): *m/z* = 553.2322 [**4**+H]$^+$ (calc. for $C_{30}H_{25}N_{12}$ 553.2325), 575.2138 [**4**+Na]$^+$ (calc. for $C_{30}H_{25}N_{12}Na$ 575.2145); Anal. calcd for $C_{30}H_{24}N_{12}$•(H_2O): C, 63.15; H, 4.59; N, 29.46. Found: C, 63.44; H, 4.36; N, 29.37.

2.2 General CuAAC Experimental Procedure for Alkyl Spacers

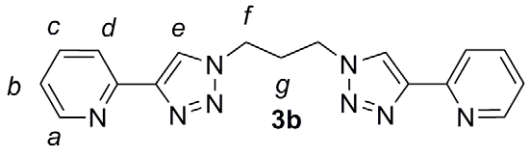
To a stirred solution of dibromide (1.5 mmol, 1.00 eq.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.410 g, 6.2 mmol, 2.10 eq.), Na_2CO_3 (0.13 g, 1.2 mmol, 0.8 eq.), $CuSO_4$ (0.150 g, 0.6 mmol, 0.40 eq.) and ascorbic acid (0.21 g, 1.2 mmol, 0.80 eq). 2-ethynylpyridine (0.32 g, 3.1 mmol, 2.05 eq.) was added and the reaction mixture was stirred at room temperature for 24 h. The suspension was then partitioned between

aqueous NH_4OH/EDTA (200 mL) and EtOAc (200 ml) and the layers separated. The organic phase was washed with H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography gave the ligands as colourless solids.



3a

Chromatography through a short pad of silica (gradient CH_2Cl_2/acetone to a ratio 1:1) gave the product as a colourless solid. Yield: 0.47 g, 82 %. Mp 181-183 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J = 4.3, 2H, H_a), 8.18 (d, J = 7.9, 2H, H_d), 8.12 (s, 2H, H_e), 7.78 (td, J = 1.8, 7.8, 2H, H_c), 7.23 (ddd, J = 1.1, 4.9, 7.5, 2H, H_b), 4.42 (t, J = 7.0, 4H, H_f), 2.05 – 1.89 (m, 4H, H_h), 1.49 – 1.33 (m, 4H, H_g); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.3, 149.4, 148.5, 136.9, 122.8, 121.8, 120.2, 50.2, 30.0, 25.9; I.R. (KBr): υ (cm^{-1}) 3500-3200 (br), 3128, 2724, 1596, 1568, 1544, 1417, 1306, 1264, 1222, 1155, 1137, 1090, 1075, 1047, 1010, 997, 971, 895, 846, 786, 764; HRESI-MS (MeOH): *m/z* = 375.2019 [**3a**+H]$^+$ (calc. for $C_{20}H_{23}N_8$ 375.2045), 397.1860 [**3a**+Na]$^+$ (calc. for $C_{20}H_{23}N_8Na$ 397.1865); Anal. calcd for $C_{20}H_{23}N_8$•(H_2O): C, 63.15; H, 4.59; N, 29.46. Found: C, 63.44; H, 4.36; N, 29.37.



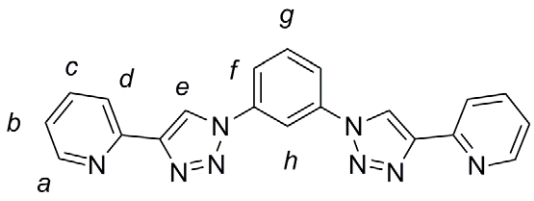
3b

Chromatography through a short pad of silica (gradient CH_2Cl_2/acetone to a ratio 1:1) gave the product as a colourless solid. X-ray quality colorless crystals were obtained

by vapour diffusion of chloroform solution of **3b** with petrol. Yield: 0.42 g, 82 %. Mp 184 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61–8.59 (m, 2H, H_a), 8.23 (s, 2H, H_e), 8.16 (d, *J* = 7.9, 2H, H_b), 7.78 (td, *J* = 1.8, 7.8, 2H, H_c), 7.24 (ddd, *J* = 1.2, 4.9, 7.5, 2H, H_b), 4.51 (t, *J* = 6.5, 4H, H_g), 2.67 (p, *J* = 6.5, 2H, H_f); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.1, 149.6, 148.8, 137.0, 123.1, 122.7, 120.3, 47.0, 30.7; I.R. (KBr): υ (cm^{-1}) 3500-3200 br, 3120, 3057, 2997, 2947, 1701, 1639, 1595, 1568, 1545, 1463, 1437, 1416, 1363, 1319, 1295, 1276, 1252, 1202, 1188, 1137, 1092, 1080, 1044, 996, 976, 895, 854, 786, 768, 710, 663, 517; HRESI-MS ($CDCl_3$/MeOH): *m/z* = 333.1551 [**3b**+H]$^{+}$ (calc. for $C_{17}H_{17}N_8$ 333.1571), 355.1376 [**3b**+Na]$^{+}$ (calc. for $C_{17}H_{16}N_8Na$ 355.1390); Anal. calcd for $C_{17}H_{16}N_8$: C, 61.43; H, 4.85; N, 33.71. Found: C, 61.41; H, 4.97; N, 33.80.

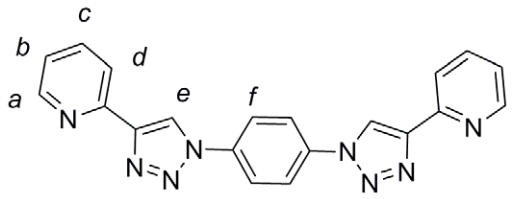
2.3 General CuAAC Experimental Procedure for Aryl Spacers

To a stirred degassed solution (EtOH/H_2O, 10 mL, 7:3) of diiodide (1.5 mmol, 1.0 eq.) or triiodide (1.0 mmol, 1.0 eq.) was added NaN_3 (0.21 g, 3.1 mmol, 2.2 or 3.1 eq.), CuI (0.06 g, 0.3 mmol, 0.2 or 0.3 eq.), N,N'-dimethylethylenediamine (0.04 g, 0.4 mmol, 0.3 or 0.45 eq.) and sodium ascorbate (0.15 g, 0.75 mmol, 0.5 eq.). The reaction was then heated to reflux under a nitrogen atmosphere for 2 h. After this time had elapsed the reaction mixture was cooled to room temperature and 2-ethynylpyridine (0.31 g, 3.0 mmol, 1 eq.), $CuSO_4$ (0.10 g, 0.40 mmol, 0.2 or 0.4 eq.), and sodium ascorbate (0.15 g, 0.75 mmol, 0.5 eq.) were added to the reaction mixture and the resulting suspension was stirred at room temperature for 20 h. The reaction mixture was then poured into aqueous NH_4OH/EDTA (100 mL). The resulting precipitate was isolated by filtration and washed well with H_2O then vacuum dried.



5a

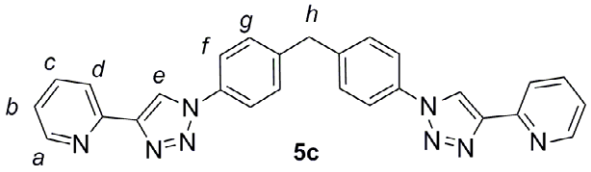
5a was a pale yellow solid. Yield: 0.46 g, 89%. Mp 241-242°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.58 (s, 2H, H_e), 8.73 (t, J = 2.0, 1H, H_h), 8.69 (s, 2H, H_a), 8.22 (dd, J = 2.0, J = 8.2, 2H, H_f), 8.16 (m, 2H, H_d), 7.97 (td, J = 1.5, 7.8, 2H, H_g), 7.87 (t, J = 8.2, 1H, H_c), 7.43 (dd, J = 5.3, 6.5, 2H, H_b); ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.4, 150.0, 149.1, 138.2, 138.1, 132.4, 124.2, 122.3, 120.5, 120.4, 112.1; I. R. (KBr): υ (cm^{-1}) 3117, 3049, 2725, 1599, 1592, 1567, 1543, 1411, 1353, 1273, 1237, 1146, 1090, 1073, 1036, 993, 842, 794, 758; HRESI-MS (DMSO): m/z = 367.1407 [**5a**+H]$^+$ (calc. for $C_{20}H_{15}N_8$ 367.1414); Anal. calcd for $C_{20}H_{14}N_8$•($0.25H_2O$): C, 64.77; H, 3.94; N, 30.21. Found: C, 64.57; H, 3.87; N, 29.99.



5b

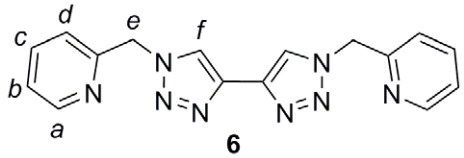
5b was a yellow solid. Yield: 0.45 g, 85%. Mp 266°C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.47 (s, 2H, H_e), 8.68 (dd, J = 1.9, J = 2.8, 2H, H_a), 8.30 (s, 4H, H_f), 8.19–8.13 (m, 2H, H_d), 7.97 (td, J = 1.7, J = 7.7, 2H, H_c), 7.42 (ddd, J = 1.2, J =4.9, J = 7.5, 2H, H_b); ^{13}C NMR (75 MHz, DMSO-d_6) δ too insoluble to obtain; I. R. (KBr): υ (cm^{-1}) 3500-3200 (sb), 3117, 2725, 1504, 1596, 1571, 1523, 1407, 1305, 1277, 1238, 1153, 1025, 846, 820, 781; HRESI-MS (DMSO): m/z = 367.1412 [**5b**+H]$^+$ (calc. for $C_{20}H_{15}N_8$ 367.1414), 389.1232 [**5b**+Na]$^+$ (calc. for $C_{20}H_{14}N_8Na$

389.1234); Anal. calcd for $C_{20}H_{14}N_8$•($0.5H_2O$): C, 63.99; H, 4.03; N, 29.85. Found: C, 63.81; H, 4.21; N, 29.98.



5c

5c was obtained as a yellow solid. Yield: 0.49 g, 72%. Mp 223-224°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.28 (s, 2H, H_e), 8.64 (ddd, J = 0.9, J = 1.7, J = 4.8, 2H, H_a), 8.11 (dt, J = 1.0, 7.9, 2H, H_c), 8.03 – 7.88 (m, 6H, $H_{d,f}$), 7.53 (d, J = 8.6, 4H, H_g), 7.39 (ddd, J = 1.2, J = 4.9, J = 7.5, 2H, H_b), 4.15 (s, 2H, H_i); ^{13}C NMR (75 MHz, DMSO-d_6) δ 149.6, 149.5, 148.1, 141.7, 137.3, 134.9, 130.1, 123.3, 121.2, 120.4, 119.8, 79.2; I. R. (KBr): υ (cm^{-1}) 3500-3200 (sb), 3049, 2725, 1602, 1592, 1570, 1549, 1405, 1305, 1237, 1150, 1088, 1030, 995, 854, 812, 776; HRESI-MS (CH_2Cl_2/MeOH): *m/z* = 457.1898 [**5c**+H]$^+$ (calc. for $C_{27}H_{21}N_8$ 457.1884); Anal. calcd for $C_{27}H_{21}N_8$•($5H_2O$): C, 59.33; H, 5.53; N, 20.50. Found: C, 59.42; H, 5.17; N, 20.00.



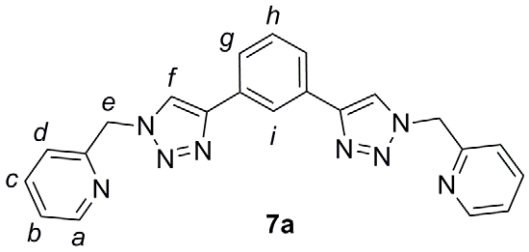
6

To a stirred solution of 2-(bromomethyl)pyridine hydrobromide (1.6 g, 6.1 mmol, 2.05 eq.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.41 g, 6.2 mmol, 2.10 or 3.15 eq.), Na_2CO_3 (0.31 g, 3.0 mmol, 1.00 eq.), $CuSO_4$ (0.30 g, 1.2 mmol, 0.40 eq.), ascorbic acid (0.42 g, 2.4 mmol, 0.80 eq) and $AgPF_6$ (0.22 g, 0.6 mmol, 0.20 eq). Then 1,4-Bis(trimethylsilyl)-1,3-butadiyne (0.583 g, 3.0 mmol, 1.0 eq.) was added to the reaction mixture and the resulting suspension was stirred at 40 ˚C for 24 h. The

suspension was then partitioned between aqueous NH_4OH/EDTA (200 mL) and EtOAc (200 ml) and the layers separated. The organic phase was washed with H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product as a colourless solid. Yield: 0.75 g, 80%. Mp 161-163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62-8.60 (m, 2H, H_a), 8.18 (s, 2H, H_f), 7.68 (td, J = 1.8, 7.7, 2H, H_c), 7.30–7.24 (m, 2H, H_b), 7.19 (d, J = 7.8, 2H, H_d), 5.71 (s, 4H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 150.1, 140.6, 137.5, 123.6, 122.5, 121.5, 55.9; I. R. (KBr): υ (cm^{-1}) 3109, 3077, 2725, 1606, 1597, 1570, 1551, 1421, 1314, 1228, 1154, 1074, 1051, 996, 861, 786, 727; HRESI-MS (MeOH): *m/z* = 341.1254 [**6**+Na]$^+$ (calc. for $C_{16}H_{14}N_8Na$ 341.1239); Anal. calcd for $C_{16}H_{14}N_8$: C, 60.37; H, 4.43; N, 35.20. Found: C, 60.35; H, 4.43; N, 35.41.

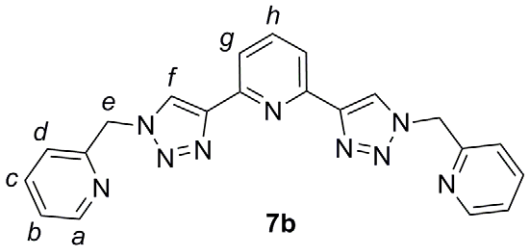
2.4 General CuAAC Experimental Procedure for methylene bridged ligands.

To a stirred solution of 2-(bromomethyl)pyridine hydrobromide (1.55 g, 6.1 mmol, 2.05 or 3.1 eq.) in DMF/H_2O (15 mL, 4:1) was added NaN_3 (0.41 g, 6.2 mmol, 2.10 or 3.15 eq.), Na_2CO_3 (0.31 g, 3.0 mmol, 1.00 eq.), $CuSO_4$ (0.30 g, 1.2 mmol, 0.40 eq.) and ascorbic acid (0.42 g, 2.4 mmol, 0.80 eq). Then either a dialkyne (3.0 mmol, 1.0 eq.) or trialkyne (2.0 mmol, 1.0 eq.) was added to the reaction mixture and the resulting suspension was stirred at room temperature for 20 h. The suspension was then partitioned between aqueous NH_4OH/EDTA (200 mL) and EtOAc (200 ml) and the layers separated. The organic phase was washed with H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (gradient CH_2Cl_2/acetone) gave the product as a colourless solid.



7a

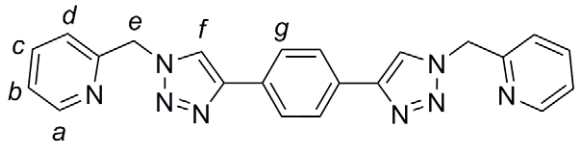
Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product as a colourless solid. Yield: 0.97 g, 82%. Mp 164-166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64-8.62 (m, 2H, H_a), 8.25 (t, J = 1.7, 1H, H_i), 8.02 (s, 2H, H_f), 7.83 (dd, J = 1.7, 7.8, 2H, H_g), 7.70 (td, J = 1.8, 7.7, 2H, H_c), 7.46 (t, J = 7.7, 1H, H_h), 7.35-7.20 (m, 4H, $H_{b,d}$), 5.75 (s, 4H, H_h); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 150.0, 148.1, 137.7, 131.3, 131.3, 129.6, 125.6, 123.7, 123.1, 122.7, 120.8, 55.9; I. R. (KBr): υ (cm^{-1}) 3109, 3077, 2725, 1606, 1597, 1570, 1551, 1421, 1314, 1228, 1154, 1074, 1051, 996, 861, 786, 727. HRESI-MS (MeOH): *m/z* = 395.1707 [**7a**+H]$^+$ (calc. for $C_{22}H_{19}N_8$ 395.1733), 417.1523 [**7a**+Na]$^+$ (calc. for $C_{22}H_{18}N_8Na$ 417.1552); Anal. calcd for $C_{22}H_{18}N_8$•(0.66H_2O): C, 65.03; H, 4.79; N, 27.58. Found: C, 65.08; H, 4.54; N, 27.80.



7b

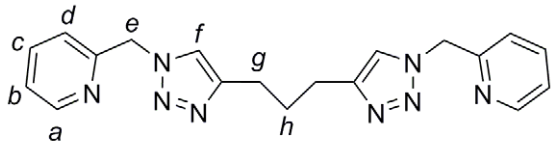
Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product as a colourless solid. Yield: 1.05 g, 89%. Mp 173-175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65–8.61 (m, 2H, H_a), 8.30 (s, 2H, H_f), 8.11 (d, J = 7.8, 2H, H_g), 7.86 (t, J = 7.6, 1H, H_h), 7.70 (td, J = 1.8, 7.7, 2H, H_c), 7.30–7.23 (m, 4H, $H_{b,d}$), 5.73 (s, 4H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 149.9, 149.8, 148.8, 137.7, 137.4, 123.5, 122.7, 122.4, 119.3, 55.8; I. R. (KBr): υ (cm^{-1}) 3109, 3077, 2725, 1606, 1597, 1570, 1551, 1421, 1314, 1228, 1154, 1074, 1051, 996, 861, 786, 727; HRESI-MS (MeOH): *m/z* =

418.1503 [**7b**+Na]$^+$ (calc. for $C_{21}H_{17}N_9Na$ 418.1504); Anal. calcd for $C_{21}H_{17}N_9$•(1.5H_2O): C, 59.71; H, 4.77; N, 29.84. Found: C, 59.61; H, 4.30; N, 29.93.



7c

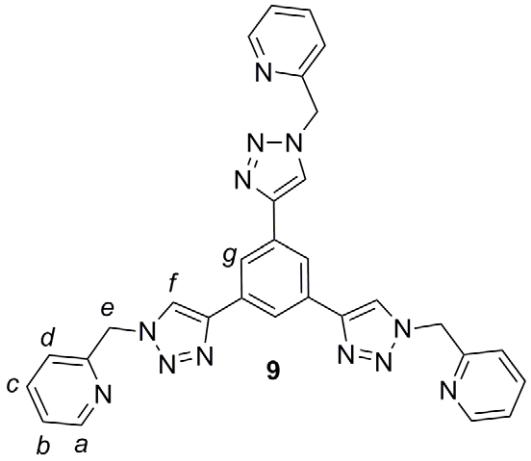
Chromatography (gradient CH_2Cl_2/acetone to a ratio 6:4) gave the product as a colourless solid. Yield: 0.99 g, 84%. Mp 207-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.4 Hz, 2H, H_a), 7.98 (s, 2H, H_f), 7.90 (s, 4H, H_g), 7.71 (td, *J* = 7.7, 1.7 Hz, 2H, H_c), 7.31-7.25 (m, 4H, $H_{b,d}$), 5.72 (s, 2H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 150.0, 137.6, 136.8, 130.5, 126.3, 123.7, 122.7, 120.4, 56.0; I. R. (KBr): υ (cm^{-1}) 3109, 3077, 2725, 1606, 1597, 1570, 1551, 1421, 1314, 1228, 1154, 1074, 1051, 996, 861, 786, 727. HRESI-MS (MeOH): *m/z* = 395.1707 [**7c**+H]$^+$ (calc. for $C_{22}H_{19}N_8$ 395.1733), 417.1523 [**7c**+Na]$^+$ (calc. for $C_{22}H_{18}N_8Na$ 417.1552); Anal. calcd for $C_{22}H_{18}N_8$: C, 66.99; H, 4.60; N, 28.41. Found: C, 66.72; H, 4.61; N, 28.27.



8

Chromatography (gradient CH_2Cl_2/acetone to a ratio 1:1) gave the product as a colourless solid. Yield: 0.84 g, 78%. Mp 94-95 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 4.4, 2H, H_a), 7.68 (td, *J* = 1.8, 7.7, 2H, H_c), 7.47 (s, 2H, H_f), 7.26 (dt, *J* = 3.3, 5.6, 2H, H_b), 7.15 (d, *J* = 7.8, 2H, H_d), 5.62 (s, 4H, H_e), 2.78 (t, *J* = 7.6, 4H, H_g), 2.18 – 1.93 (m, 2H, H_h); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.7, 149.7, 148.0, 137.3, 123.3, 122.3, 121.5, 55.5, 28.9, 25.0; I. R. (KBr): υ (cm^{-1}) 3500-3200 (sb), 3136, 3117, 2725, 1654, 1588, 1570, 1551, 1321, 1290, 1214, 1170, 1151, 1122, 1090, 1048, 996, 827, 762, 753. HRESI-MS (MeOH): *m/z* = 361.1894 [**8**+H]$^+$ (calc. for $C_{19}H_{21}N_8$

361.1889), 383.1723 [**8**+Na]$^+$ (calc. for $C_{19}H_{20}N_8Na$ 383.1709); Anal. calcd for $C_{19}H_{20}N_8$: C, 63.32; H, 5.59; N, 31.09; Found: C, 63.13; H, 5.59; N, 30.75.



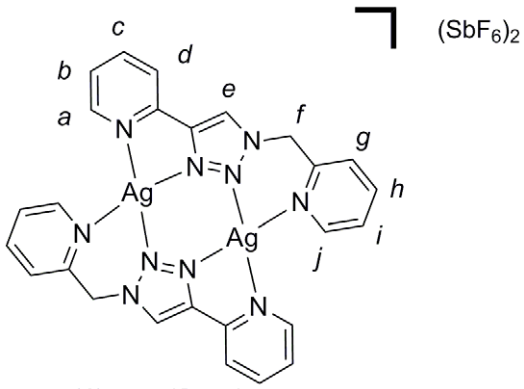
9

The suspension was then poured into aqueous NH_4OH/EDTA (200 mL) and stirred for 1 h. A tan solid was isolated by filtration and was washed well with H_2O then vaccum dried. Yield: 0.96 g, 84%. Mp 224-225 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.80 (s, 3H, H_f), 8.56 (dd, J = 0.9, J = 4.7, 3H, H_a), 8.35 (s, 3H, H_g), 7.84 (td, J = 1.5, J = 7.6, 3H, H_c), 7.36 (m, 6H, $H_{b,d}$), 5.79 (s, 6H, H_e); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.5, 150.2, 146.8, 138.1, 132.6, 124.0, 123.5, 123.0, 121.9, 55.4; I. R. (KBr): υ (cm^{-1}) 3300-3200 (sb) 3109, 3077, 2725, 1606, 1597, 1588, 1570, 1306, 1229, 1153, 1093, 1049, 995, 886, 848, 804; HRESI-MS (DMSO/MeOH): *m/z* = 553.2279 [**9**+H]$^+$ (calc. for $C_{30}H_{25}N_{12}$ 553.2320); Anal. calcd for $C_{30}H_{24}N_{12}$•(0.75H_2O): C, 65.65; H, 4.54; N, 29.69. Found: C, 63.89; H, 4.58; N, 29.31.

3. Synthesis of silver(I) complexes:

General: All the silver reactions were carried out in the absence of light.

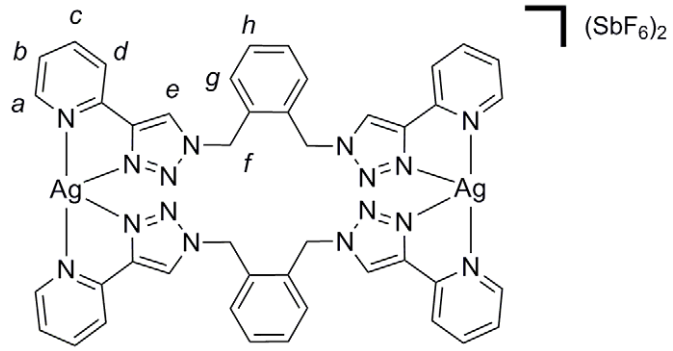
3.1 Synthesis of silver(I) complexes of the 2-pyridyl-1,2,3-triazole ligands.



$[(\mathbf{1})_2Ag_2](SbF_6)_2$

A solution (acetone, 2.5 mL) of anhydrous $AgSbF_6$ (0.034 g, 0.1 mmol, 1 eq.) was added dropwise slowly to an acetone (2.5 mL) solution of the ligand **1** (0.023 g, 0.1 mmol, 1 eq.). The resulting clear solution was vapour diffused with MeOH leading to colourless X-ray quality crystals of $[(\mathbf{1})_2Ag_2](SbF_6)_2$, The crystals were isolated by filtration and were washed with MeOH (10 mL), Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.05 g, 86%). Mp 229-230 °C; ^{1}H NMR (300 MHz, d_6-acetone) δ 9.16 (s, 1H, H_e), 8.98 (dd, J = 0.8, 5.1, 1H, H_j), 8.84 (d, J = 4.9, 1H, H_a), 8.26 (td, J = 1.7, 7.7, 1H, H_c), 8.18 – 8.08 (m, 2H, $H_{h,g}$), 8.03 (d, J = 8.0, 1H, H_d), 7.72 (ddd, J = 1.3, 5.2, 7.6, 1H, H_i), 7.62 – 7.58 (m, 1H, H_b), 6.26 (s, 2H, H_f); ^{13}C NMR (100 MHz, d_6-acetone) δ 154.1, 153.8, 152.3, 147.5, 146.9, 141.57, 140.7, 127.5, 126.6, 126.3, 126.0, 123.4, 57.4; I.R. (KBr): υ (cm^{-1}) 3500-3200 br, 3144, 2924, 1601, 1573, 1476, 1451, 1366, 1330, 1293, 1231, 1203, 1158, 1112, 1089, 1062, 1049, 997, 990, 891, 834, 788, 695, 513; HRESI-MS (CH_3CN): m/z = 924.9131 $[Ag_2(\mathbf{1})_2](SbF_6)^+$) (calc. for $C_{26}H_{22}Ag_2F_6N_{10}Sb$ 924.9068), 581.1148 $[Ag(\mathbf{1})_2]^+$ (calc. for $C_{26}H_{22}AgN_{10}$ 581.1074), 344.0150 $[Ag(\mathbf{1})]^+$ (calc. for $C_{13}H_{11}AgN_5$ 344.0065), 260.0898 $[\mathbf{1}+Na]^+$,

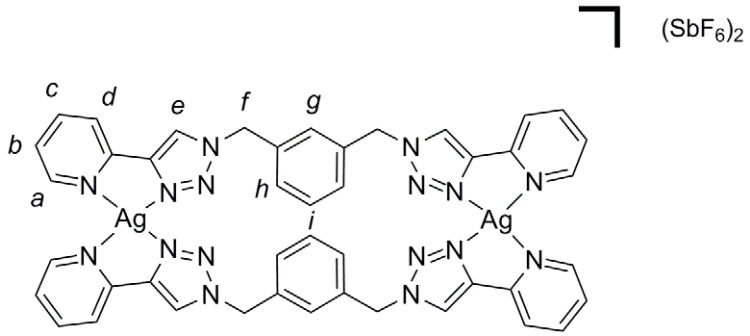
(calc. for $C_{13}H_{11}N_5Na$ 260.0907); Anal. calcd for $C_{44}H_{36}Ag_2F_{12}N_{16}Sb_2$: C, 35.80; H, 2.46; N, 15.18. Found: C, 36.05; H, 2.42; N, 15.18



$[(\mathbf{2a})_2Ag_2](SbF_6)_2$

A solution (acetonitrile, 5 mL) of anhydrous $AgSbF_6$ (0.034 g, 0.1 mmol, 1 eq.) was added dropwise slowly to an acetonitrile (5 mL) solution of the ligand **2a** (0.039 g, 0.1 mmol, 1 eq.). The resulting suspension was stirred at room temperature for 1 h then warmed with a heat gun until all the solids dissolved. The resulting solution was hot filtered through cotton wool then vapour diffused with MeOH leading to X-ray quality colourless crystals. The crystals were isolated by filtration and were washed with MeOH (10 mL), Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.061 g, 82%). Mp < 300 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 8.53 (d, J = 4.2, 4H, H_a), 7.76 (dd, J = 8.1, 12.5, 12H, $H_{e,g,h}$), 7.62 (t, J = 7.6, 4H, H_c), 7.41 (d, J = 7.9, 4H, H_d), 7.32–7.16 (m, 4H, H_b), 5.86 (s, 8H, H_f); ^{13}C NMR (75 MHz, CD_3CN) δ 150.9, 147.1, 145.2, 138.9, 133.8, 133.3, 131.4, 124.8, 123.4, 121.9, 53.2; I.R. (KBr): υ (cm^{-1}) 3143, 2924, 1603, 1571, 1467, 1432, 1345, 1287, 1237, 1206, 1163, 1105, 1086, 1059, 1049, 1015, 987, 830, 783, 743, 659, 512; HRESI-MS (DMSO/CH_3CN): m/z = 1239.0403 $[Ag_2(\mathbf{2a})_2](SbF_6)^+$ (calc. for $C_{44}H_{36}Ag_2F_6N_{16}Sb$ 1239.0349), 897.2376 $[Ag(\mathbf{2a})_2]^+$ (calc. for $C_{44}H_{36}AgN_{16}$ 897.2359), 503.0860 $[Ag_2(\mathbf{2a})_2]^{2+}$ (calc. for

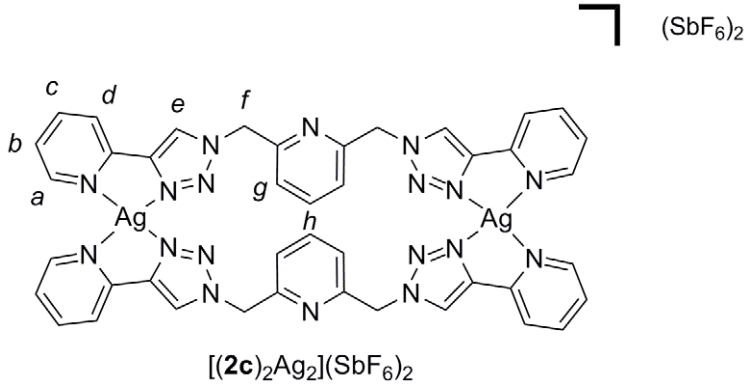
$C_{44}H_{36}Ag_2N_{16}$ 503.0772), 501.0721 $[Ag(\mathbf{2a})]^+$ (calc. for $C_{22}H_{18}AgN_8$ 501.0700), 395.1717 $[\mathbf{2a}+H]^+$, (calc. for $C_{22}H_{19}N_8$ 395.1733). Anal. calcd for $C_{44}H_{36}Ag_2F_{12}N_{16}Sb_2$: C, 35.80; H, 2.46; N, 15.18. Found: C, 36.04; H, 2.37; N, 15.11



$[(\mathbf{2b})_2Ag_2](SbF_6)_2$

A solution (acetonitrile, 5 mL) of anhydrous $AgSbF_6$ (0.068 g, 0.2 mmol, 1 eq.) was added dropwise slowly to an acetonitrile (5 mL) solution of the ligand **2b** (0.078 g, 0.2 mmol, 1 eq.). The resulting suspension was stirred at room temperature for 1 h then warmed with a heat gun until all the solids dissolved. The resulting solution was hot filtered through cotton wool then vapour diffused with MeOH. A colourless solid slowly precipitated over one day. The solid was isolated by filtration and was washed with MeOH (10 mL), Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.120 g, 85%). Mp < 300 °C; ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ 8.79 (s, 4H, H_e), 8.63 (sb, 4H, H_a), 8.06–7.89 (m, 8H, $H_{c,d}$), 7.53–7.33 (m, 10H, $H_{b,g,h}$), 7.28 (s, 2H, H_i), 5.72 (s, 8H, H_f); ^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 150.9, 148.8, 146.7, 139.1, 137.1, 130.1, 128.6, 127.8, 125.1, 124.7, 121.7, 53.8; I.R. (KBr): υ (cm^{-1}) 3140, 2926, 1602, 1571, 1474, 1449, 1431, 1342, 1319, 1255, 1238, 1206, 1158, 1107, 1090, 1059, 1049, 1008, 986, 899, 844, 816, 786, 746, 668, 571; HRESI-MS (DMSO/CH_3CN): m/z = 1239.0425 $[Ag_2(\mathbf{2b})_2](SbF_6)^+$ (calc. for $C_{44}H_{36}Ag_2F_6N_{16}Sb$ 1239.0349), 502.0715 $[Ag_2(\mathbf{2b})_2]^{2+}$ (calc. for $C_{44}H_{36}Ag_2N_{16}$ 502.0700), 501.0839 $[Ag(\mathbf{1})]^+$ (calc. for $C_{22}H_{18}AgN_8$

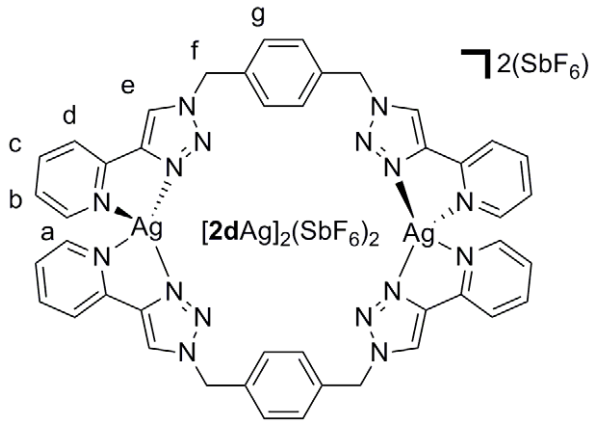
501.0700), 395.1730 [**2b**+H]$^+$, (calc. for $C_{22}H_{19}N_8$ 395.1733). Anal. calcd for $C_{44}H_{36}Ag_2F_{12}N_{16}Sb_2$: C, 35.80; H, 2.46; N, 15.18. Found: C, 35.63; H, 2.51; N, 14.94



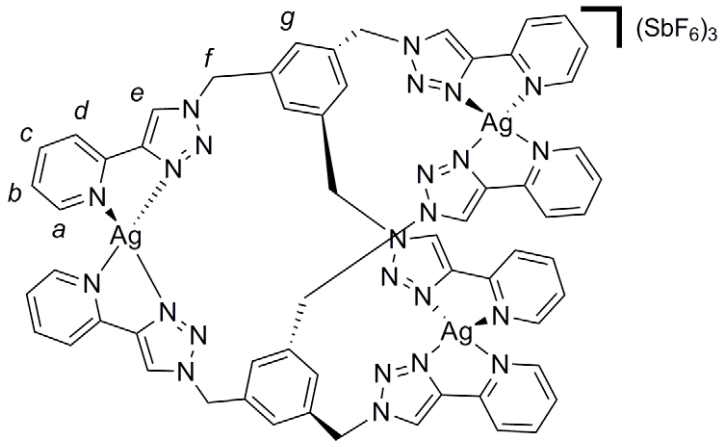
[(**2c**)$_2$Ag$_2$](SbF$_6$)$_2$

A solution (acetone, 5 mL) of $AgSbF_6$ (0.069 g, 0.2 mmol, 1 eq.) was added dropwise slowly to an acetone (5 mL) solution of the ligand **2c** (0.080 g, 0.2 mmol, 1 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and was washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.086 g, 58%). Mp 190-192 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 8.59 (d, J = 4.9, 4H, H_a), 8.24 (s, 4H, H_e), 7.89 (t, J = 7.8, 2H, H_h), 7.80 (dd, J = 10.9, 4.6, 4H, H_c), 7.70 (d, J = 7.9, 4H, H_d), 7.42 (d, J = 7.7, 4H, H_g), 7.39–7.30 (m, 4H, H_b), 5.72 (s, 8H, H_f); ^{13}C NMR (100 MHz, CD_3CN) δ 156.6, 154.6, 150.8, 148.4, 146.0, 138.7, 138.5, 124.6, 124.3, 121.6, 54.8; I.R. (KBr): υ (cm^{-1}) 3500-3200 br, 3148, 2925, 1598, 1581, 1477, 1456, 1351, 1315, 1253, 1241, 1163, 1114, 1095, 1065, 1054, 1018, 994, 834, 775, 757, 662, 538; HRESI-MS (CH_3CN): m/z = 1241.0354 [Ag_2(**2c**)$_2$](SbF$_6$)$^+$ (calc. for $C_{42}H_{34}Ag_2F_6N_{18}Sb$ 1241.0349), 895.2380 [Ag(**2c**)$_2$]$^+$ (calc. for $C_{44}H_{36}AgN_{16}$ 895.2354), 504.0750 [Ag_2(**2c**)$_2$]$^{2+}$ (calc. for $C_{42}H_{34}Ag_2N_{18}$ 502.0700), 501.0768 [Ag(**2c**)]$^+$ (calc. for $C_{21}H_{17}AgN_9$ 501.0700), 396.1738 [**2c**+H]$^+$, (calc. for $C_{21}H_{18}N_9$ 396.1733). Anal. calcd for

$C_{42}H_{34}Ag_2F_{12}N_{18}Sb_2\cdot(H_2O)$: C, 34.13; H, 2.32; N, 17.08. Found: C, 34.45; H, 2.45; N, 16.83



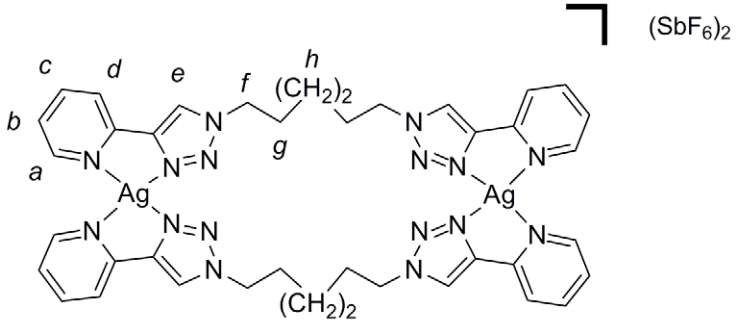
A solution (acetone, 5 mL) of $AgSbF_6$ (0.117 g, 0.34 mmol, 1 eq.) was added dropwise slowly to a CH_2Cl_2 (5 mL) solution of the ligand **2d** (0.134 g, 0.34 mmol, 1 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.240 g, 90%). Mp 293°C (decomp.); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ 8.91 (s, 4H, H_e), 8.60 (d, *J* = 4.8, 4H, H_a), 8.06–7.90 (m, 8H, $H_{c,d}$), 7.49 – 7.37 (m, 12H, $H_{b,g}$), 5.71 (s, 8H, H_f); ^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 150.7, 148.9, 146.7, 138.9, 136.3, 129.3, 124.9, 124.5, 121.4, 53.7; I.R. (KBr): υ (cm^{-1}) 3141, 2925, 1705, 1601, 1571, 1301, 1257, 1239, 1201, 1157, 1104, 1088, 1059, 989, 836, 786, 770, 748, 721. HRESI-MS (DMSO/CH_3CN): m/z = 1239.0383 $[Ag_2(\mathbf{2d})_2](SbF_6)^+$ (calc. for $C_{44}H_{36}Ag_2F_6N_{16}Sb$ 1239.0349), 895.2380 $[Ag(\mathbf{2d})_2]^+$ (calc. for $C_{44}H_{36}AgN_{16}$ 895.2354), 502.0750 $[Ag_2(\mathbf{2d})_2]^{2+}$ (calc. for $C_{44}H_{36}Ag_2N_{16}$ 502.0700), 501.0768 $[Ag(\mathbf{2d})]^+$ (calc. for $C_{22}H_{18}AgN_8$ 501.0700), 395.1738 $[\mathbf{2d}+H]^+$, (calc. for $C_{22}H_{19}N_8$ 395.1733). Anal. calcd for $C_{44}H_{36}Ag_2F_{12}N_{16}Sb_2$: C, 35.80; H, 2.46; N, 15.18. Found: C, 35.77; H, 2.82; N, 15.17



$[(\mathbf{4})_2Ag_3](SbF_6)_3$

The ligand **4** (0.055 g, 0.1 mmol, 2 eq.) was added as a solid to a solution (acetonitrile, 8 mL) of $AgSbF_6$ (0.053 g, 0.15 mmol, 3 eq.). All the solids dissolved and a colourless solid precipitated slowly over ten minutes. The resulting suspension was stirred at room temperature for 1 h then was warmed with a heat gun until all the solids dissolved and hot filtered through cotton wool. The resulting colourless acetonitrile solution was vapour diffused with MeOH. The colourless solid which slowly precipitated over one day was isolated by filtration and was washed with MeOH (10 mL), Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.080 g, 80%). Mp 274°C (decomp.); ^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ 8.84 (s, 6H, H_e), 8.66 (d, J = 4.9, 6H, H_a), 7.97 (d, J = 3.6, 12H, $H_{c,d}$), 7.46 (dd, J = 4.6, 9.1, 6H, H_b), 7.18 (s, 6H, H_f), 5.73 (s, 12H, H_g); ^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 150.2, 148.5, 146.4, 138.2, 137.2, 126.5, 124.4, 123.8, 120.8, 52.7; I.R. (KBr): υ (cm^{-1}) 3144, 2928, 1602, 157, 1452, 1424, 1355, 1319, 1275, 1255, 1236, 1205, 1160, 1106, 1089, 1058, 1048, 1007, 989, 890, 835, 786, 758, 744, 662, 512; HRESI-MS (DMSO/CH_3CN): m/z = 1898.9519 $[Ag_3(\mathbf{4})_2](SbF_6)_2^+$ (calc. for $C_{60}H_{48}Ag_3F_{12}N_{24}Sb_2$ 1898.9532), 1002.9299 $[Ag_2(\mathbf{4})](SbF_6)^+$ (calc. for $C_{30}H_{24}Ag_2F_6N_{12}Sb$ 1002.9988), 659.1389 $[Ag(\mathbf{4})]^+$ (calc.

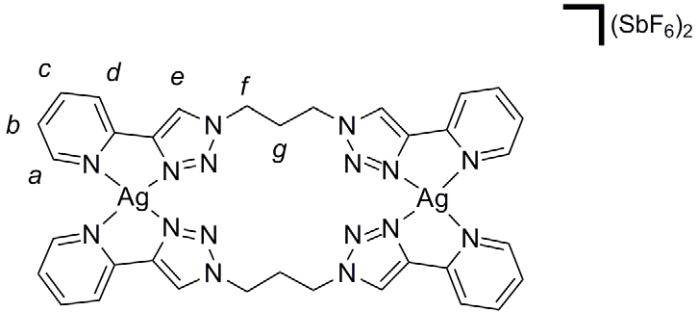
for $C_{30}H_{24}AgN_{12}$ 659.1298). Anal. calcd for $C_{60}H_{48}Ag_3F_{18}N_{24}Sb_3$: C, 33.74; H, 2.26; N, 15.74. Found: C, 33.89; H, 2.62; N, 15.70.



$[(\mathbf{3a})_2Ag_2](SbF_6)_2$

A solution (acetonitrile, 5 mL) of $AgSbF_6$ (0.034 g, 0.1 mmol, 1 eq.) was added dropwise slowly to an acetonitrile (2.5 mL) solution of the ligand **3a** (0.037 g, 0.1 mmol, 1 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.044 g, 62%). Mp 252-253 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 8.66 (d, J = 4.6, 4H, H_a), 8.36 (s, 4H, H_e), 7.95 (td, J = 1.7, 7.8, 4H, H_c), 7.86 (d, J = 7.9, 4H, H_d), 7.50–7.40 (m, 4H, H_b), 4.40 (t, J = 6.5, 8H, H_f), 1.98–1.86 (m, 8H, H_g), 1.22 (d, J = 3.1, 8H, H_h); ^{13}C NMR (75 MHz, CD_3CN) δ 150.9, 148.8, 146.3, 139.1, 124.6, 123.7, 122.0, 50.8, 29.6, 25.4; I.R. (KBr): υ (cm^{-1}) 3146, 2920, 2860, 1599, 1569, 1522, 1446, 1422, 1373, 1254, 1233, 1198, 1157, 1106, 1089, 1060, 1008, 996, 831, 783, 744, 707, 658, 515; HRESI-MS (CH_3CN): m/z = 1199.0946 $[Ag_2(\mathbf{3a})_2](SbF_6)^+$ (calc. for $C_{40}H_{44}Ag_2F_6N_{16}Sb$ 1199.0976), 855.2946 $[Ag(\mathbf{3a})_2]^+$ (calc. for $C_{40}H_{44}AgN_{16}$ 855.2986), 481.1042 $[Ag(\mathbf{3a})]^+$ (calc. for $C_{20}H_{22}AgN_8$ 481.1018), 375.2057 $[\mathbf{3a}+H]^+$, (calc. for $C_{20}H_{22}N_8$

375.1967). Anal. calcd for $C_{40}H_{44}Ag_2F_{12}N_{16}Sb_2 \bullet (C_2H_6O)$: C, 34.03; H, 3.40; N, 15.12. Found: C, 34.33; H, 3.29; N, 15.49.

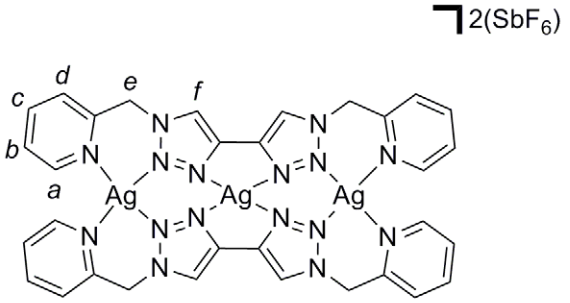


$[(\mathbf{3b})_2Ag_2](SbF_6)_2$

A solution (acetonitrile, 5 mL) of $AgSbF_6$ (0.072 g, 0.2 mmol, 1 eq.) was added dropwise slowly to an acetonitrile (5 mL) solution of the ligand **3b** (0.069 g, 0.2 mmol, 1 eq.). The resulting solution was stirred at room temperature for 1 h then was filtered through cotton wool and vapour diffused with MeOH. A colourless solid slowly precipitated over one day. This solid was isolated by filtration and was washed with MeOH (10 mL), Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.090 g, 64%). Mp 283°C (decomp.); ^{1}H NMR (300 MHz, CD_3CN) δ 8.52 (d, J = 4.4, 4H, H_a), 8.25 (s, 4H, H_e), 7.75 (td, J = 7.8, 1.7, 4H, H_c), 7.61 (dd, J = 7.0, 1.0, 4H, H_d), 7.31 (ddd, J = 7.5, 5.0, 1.2, 4H, H_b), 4.83–4.64 (m, 8H, H_f), 2.84–2.66 (m, 4H, H_g); ^{13}C NMR (75 MHz, CD_3CN) δ 150.9, 148.8, 146.1, 139.0, 124.7, 124.0, 121.7, 49.8, 29.2; I.R. (KBr): υ (cm^{-1}) 3143, 3089, 2958, 1603, 1570, 1473, 1446, 1422, 1365, 1350, 1257, 1231, 1213, 1159, 1111, 1090, 1080, 1044, 1008, 997, 988, 833, 785, 742, 723, 659, 514; HRESI-MS (CH_3CN): m/z = 1115.0046 $[Ag_2(\mathbf{3b})_2](SbF_6)^+$ (calc. for $C_{34}H_{32}Ag_2F_6N_{16}Sb$ 1115.0037), 964.1234 $[Ag_2(\mathbf{3b})_2](CH_3CN)(CO_2H)^+$ (calc. for $C_{37}H_{36}Ag_2N_{17}O_2$ 964.1340), 439.0672 $[Ag(\mathbf{3a})]^+$ (calc. for $C_{17}H_{16}AgN_8$ 439.0549);

Anal. calcd for $C_{34}H_{32}Ag_2F_{12}N_{16}Sb_2$•3($CH_3CN$): C, 32.57; H, 2.80; N, 18.04. Found: C, 32.61; H, 2.69; N, 17.68.

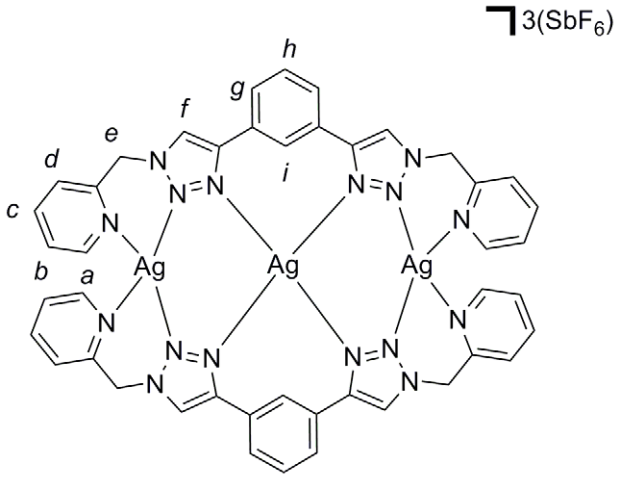
3.2 Synthesis of silver(I) complexes of the methylene bridged 2-pyridyl-1,2,3-triazole ligands.



$[(\mathbf{6})_2Ag_3](SbF_6)_3$

A solution (acetone, 5 mL) of anhydrous $AgSbF_6$ (0.102 g, 0.3 mmol, 3 eq.) was added dropwise slowly to an acetone (5 mL) solution of the ligand **6** (0.064 g, 0.2 mmol, 2 eq.). The resulting solution was stirred at room temperature for 1 h then was filtered through cotton wool and vapour diffused with MeOH. A colourless solid slowly precipitated over one day. The solid was isolated by filtration and was washed with MeOH (10 mL), Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.100 g, 60%). Mp 280 °C (decomp.); ^{1}H NMR (300 MHz, CD_3CN) δ 8.55 (d, J = 4.2, 4H, H_a), 8.27 (s, 4H, H_f), 7.82 (td, J = 7.7, 1.8, 4H, H_c), 7.44 – 7.32 (m, 8H, $H_{b,d}$), 5.73 (s, 8H, H_e); ^{13}C NMR (75 MHz, CD_3CN) δ 154.6, 150.7, 139.3, 138.4, 124.3, 123.6, 123.2, 56.0; I.R. (KBr): υ (cm^{-1}) 3136, 3103, 2926, 2106, 1596, 1569, 1477, 1436, 1356, 1321, 1278, 1256, 1236, 1223, 1150, 1083, 1047, 1011, 952, 844, 802, 756, 706, 659, 512; HRESI-MS (CH_3CN): m/z = 1430.7821 $[Ag_3(\mathbf{6})_2](SbF_6)^+$ (calc. for $C_{32}H_{28}Ag_3F_{12}N_{16}Sb_2$ 1430.7716), 1324.8825 $[Ag_2(\mathbf{6})_2](SbF_6)_2+H^+$ (calc. for $C_{32}H_{29}Ag_3F_{12}N_{16}Sb_2$ 1324.8748), 1086.9722 $[Ag_2(\mathbf{6})_2](SbF_6)^+$ (calc. for $C_{32}H_{29}Ag_3F_6N_{16}Sb$ 1086.9787), 743.1779 $[Ag(\mathbf{6})_2]^+$ (calc. for $C_{32}H_{29}AgN_{16}$

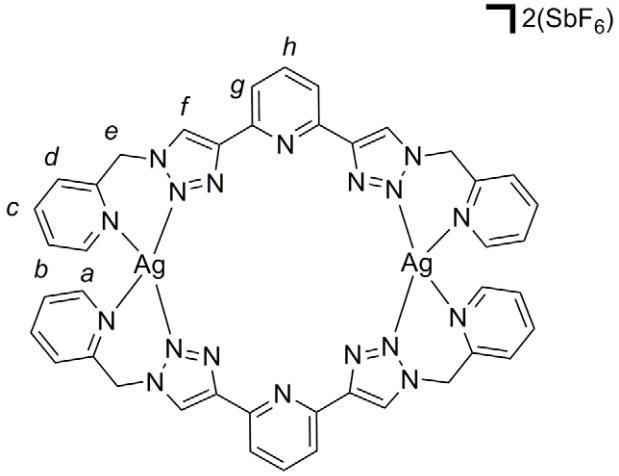
743.1728), 425.0392 $[Ag(\mathbf{6})]^+$ (calc. for $C_{16}H_{14}AgN_8$ 425.0392); Anal. calcd for $C_{34}H_{28}Ag_3F_{18}N_{16}Sb_3$•$(CH_3CN)$: C, 23.90; H, 1.83; N, 13.94. Found: C, 23.91; H, 1.78; N, 13.62



$[(\mathbf{7a})_2Ag_3](SbF_6)_3$

A solution (acetonitrile, 5 mL) of anhydrous $AgSbF_6$ (0.102 g, 0.3 mmol, 3 eq.) was added dropwise slowly to an acetonitrile (5 mL) solution of the ligand **7a** (0.078 g, 0.2 mmol, 2 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.081 g, 86%). Mp 181 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 8.55 (dd, J = 4.9, 0.7, 4H, H_a), 8.24 (d, J = 2.7, 8H, $H_{f,i}$), 7.83 (td, J = 7.7, 1.7, 4H, H_c), 7.73 (dd, J = 7.8, 1.7, 4H, H_g), 7.45 (d, J = 7.7, 2H, H_h), 7.41 (d, J = 7.9, 4H, H_d), 7.39–7.32 (m, 4H, H_b), 5.70 (s, 8H, H_e); ^{13}C NMR (100 MHz, CD_3CN) δ 155.6, 151.7, 148.5, 139.5, 132.5, 130.9, 126.8, 125.2, 124.6, 124.1, 123.6, 56.8; I.R. (KBr): υ (cm^{-1}) 3145, 2924, 2101, 1601, 1573, 1558, 1479, 1443, 1347, 1315, 1226, 1158, 1096, 1056, 1013, 976, 899, 800, 766, 696, 660, 511; HRESI-MS (CH_3CN): m/z = 1582.8453 $[Ag_3(\mathbf{7a})_2](SbF_6)_2^+$ (calc. for

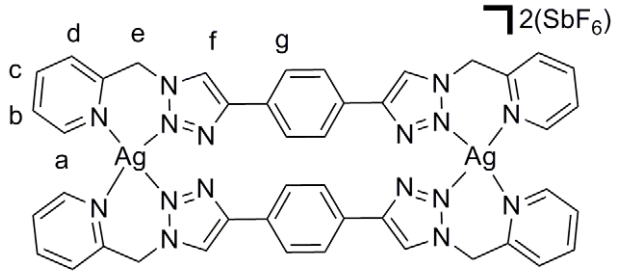
$C_{44}H_{36}Ag_3F_{12}N_{18}Sb_2$ 1584.8248), 1239.0418 $[Ag_2(\mathbf{7a})_2](SbF_6)^+$ (calc. for $C_{44}H_{36}Ag_2F_6N_{16}Sb$ 1239.0349), 897.2393 $[Ag(\mathbf{7a})_2]^+$ (calc. for $C_{44}H_{36}AgN_{16}$ 897.2359), 502.0741 $[Ag_2(\mathbf{7a})_2]^{2+}$ (calc. for $C_{44}H_{36}Ag_2N_{16}$ 502.0700), 501.0743 $[Ag(\mathbf{7a})]^+$ (calc. for $C_{22}H_{18}AgN_8$ 501.0700); Anal. calcd for $C_{44}H_{36}Ag_2F_{12}N_{16}Sb_2\cdot(2CH_3CN)$: C, 30.31; H, 2.23; N, 13.26. Found: C, 30.39; H, 2.18; N, 13.07.



$[(\mathbf{7b})_2Ag_2](SbF_6)_2$

A solution (acetone, 5 mL) of anhydrous $AgSbF_6$ (0.051 g, 0.15 mmol, 3 eq.) was added dropwise slowly to a CH_2Cl_2 (5 mL) solution of the ligand **7b** (0.040 g, 0.1 mmol, 2 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.060 g, 65%). Mp 282 °C (decomp.); ^{1}H NMR (300 MHz, d_6-DMSO) δ 9.09 (s, 4H, H_f), 8.55 (d, J = 4.0, 4H, H_a), 8.13 (t, J = 7.6, 2H, H_h), 7.99 (d, J = 7.7, 4H, H_g), 7.88 (t, J = 7.3, 4H, H_c), 7.51 – 7.33 (m, 8H, $H_{b,d}$), 5.88 (s, 8H, H_e); ^{13}C NMR (75 MHz, d_6-DMSO) δ 154.2, 149.7, 147.0, 144.6, 139.9, 137.6, 125.6, 123.6, 122.7, 120.7, 55.0; I.R. (KBr): υ (cm^{-1})

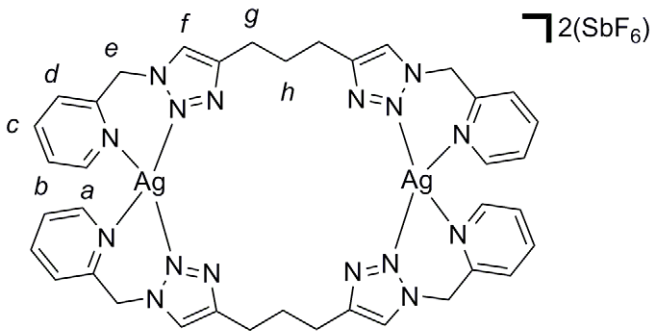
3148, 3106, 2924, 1598, 1581, 1477, 1456, 1440, 1351, 1315, 1253, 1241, 1198, 1163, 1095, 1065, 1054, 1018, 994, 834, 813, 775, 757, 662, 538; HRESI-MS (CH_3CN): m/z = 1584.8274 $[Ag_3(\mathbf{7b})_2](SbF_6)_2^+$ (calc. for $C_{42}H_{34}Ag_3F_{12}N_{18}Sb_2$ 1584.8248), 1241.0250 $[Ag_2(\mathbf{7b})_2](SbF_6)^+$ (calc. for $C_{42}H_{34}Ag_2F_6N_{18}Sb$ 1241.0254), 899.2243 $[Ag_2(\mathbf{7b})_2](SbF_6)^+$ (calc. for $C_{42}H_{34}AgN_{18}$ 899.2261), 502.0737 $[Ag(\mathbf{7b})]^+$ (calc. for $C_{21}H_{17}AgN_{18}$ 502.0652), 396.1717 $[\mathbf{7b}+H]^+$, (calc. for $C_{21}H_{18}N_8$ 396.1685). Anal. calcd for $C_{42}H_{34}Ag_2F_{12}N_{18}Sb_2$: C, 34.13; H, 2.33; N, 16.78. Found: C, 34.08; H, 2.33; N, 16.78.



$[\mathbf{7c}Ag]_2(SbF_6)_2$

A solution (acetone, 5 mL) of anhydrous $AgSbF_6$ (0.117 g, 0.34 mmol, 1 eq.) was added dropwise slowly to a CH_2Cl_2 (5 mL) solution of the ligand **7c** (0.135 g, 0.34 mmol, 1 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.245 g, 97%). Mp 270-271°C; ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.71 (s, 4H, H_f), 8.62–8.53 (m, 4H, H_a), 7.94 (s, 8H, H_g), 7.86 (td, J = 7.7, 1.8, 4H, H_d), 7.41–7.37 (m, 8H, $H_{b,c}$), 5.79 (s, 8H, H_e); ^{13}C NMR (75 MHz, d_6-DMSO) δ 155.4, 150.4, 146.9, 138.4, 130.7, 126.4, 124.2, 123.2, 123.1, 55.4; I.R. (KBr): υ (cm^{-1}) 3142, 2924, 1502, 1571, 1472, 1423, 1346, 1322, 1297, 1237, 1213, 1201, 1159, 1104, 1088, 1058, 1048, 1009, 988, 834, 785, 771,

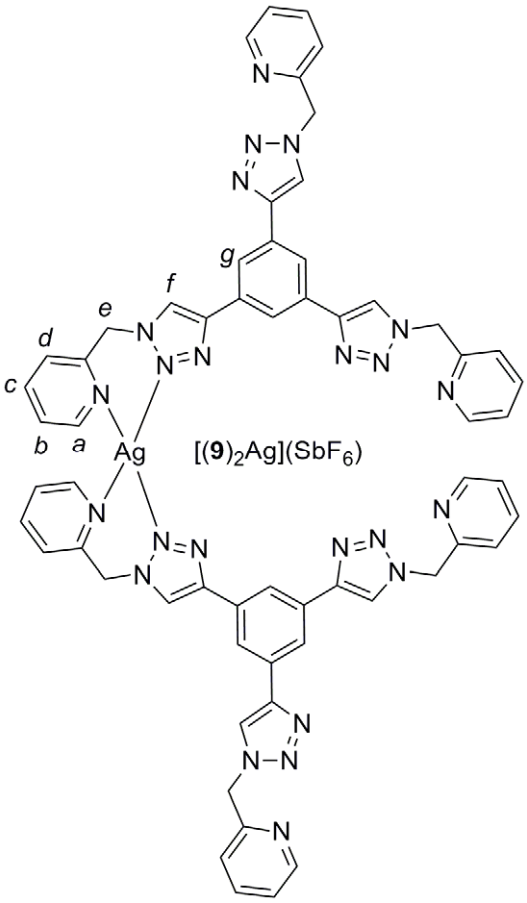
748, 659, 511; HRESI-MS (DMSO/CH_3CN): m/z = 1239.0291 $[Ag_2(\mathbf{7c})_2](SbF_6)^+$ (calc. for $C_{44}H_{36}Ag_2F_6N_{16}Sb$ 1239.0349), 897.2317 $[Ag(\mathbf{7c})_2]^+$ (calc. for $C_{44}H_{36}AgN_{16}$ 897.2359), 502.0725 $[Ag_2(\mathbf{7c})_2]^{2+}$ (calc. for $C_{44}H_{36}Ag_2N_{16}$ 502.0700), 501.0721 $[Ag(\mathbf{7c})]^+$ (calc. for $C_{22}H_{18}AgN_8$ 501.0700), 395.1717 $[\mathbf{7c}+H]^+$, (calc. for $C_{22}H_{19}N_8$ 395.1733); Anal. calcd for $C_{44}H_{36}Ag_2F_{12}N_{16}Sb_2$: C, 35.80; H, 2.46; N, 15.18. Found: C, 36.05; H, 2.42; N, 15.18



$[(\mathbf{8})_2Ag_2](SbF_6)_2$

A solution (acetonitrile, 5 mL) of anhydrous $AgSbF_6$ (0.034 g, 0.1 mmol, 1 eq.) was added dropwise slowly to an acetonitrile (5 mL) solution of the ligand **8** (0.036 g, 0.1 mmol, 1 eq.) and the resulting solution was stirred at room temperature for 1 h. The solution was filtered through a plug of cotton wool and vapour diffused with methanol to yield colourless crystals. The colourless crystals were isolated by filtration and were washed with Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.058 g, 82%). Mp 183 °C (decomp.); ^1H NMR (400 MHz, CD_3CN) δ 8.49 (d, J = 4.7, 4H, H_a), 7.82 (m, 8H, $H_{d,f}$), 7.39 (d, J = 7.8, 4H, H_c), 7.34 (dd, J = 7.2, 5.3, 4H, H_b), 5.64 (s, 8H, H_e), 2.63 (t, J = 6.8, 8H, H_g), 1.91–1.81 (m, 4H, H_h); ^{13}C NMR (100 MHz, CD_3CN) δ 154.2, 150.6, 148.6, 138.3, 124.2, 124.2, 123.6, 55.9, 30.4, 23.6; I.R. (KBr): υ (cm^{-1}) 3142, 2946, 2924, 1595, 1572, 1525, 1477, 1457, 1439, 1256, 1217,

1133, 1096, 1053, 997, 874, 759, 628; HRESI-MS (CH_3CN): m/z = 1171.0650 $[Ag_2(\mathbf{8})_2](SbF_6)^+$ (calc. for $C_{38}H_{40}Ag_2F_6N_{16}Sb$ 1171.0661), 897.2317 $[Ag(\mathbf{8})_2]^+$ (calc. for $C_{44}H_{36}AgN_{16}$ 897.2359), 829.2628 $[Ag(\mathbf{8})_2]^+$ (calc. for $C_{38}H_{40}AgN_{16}$ 829.2669), 467.0960 $[Ag(\mathbf{8})]^+$ (calc. for $C_{19}H_{20}AgN_8$ 467.0862), 383.1717 $[\mathbf{8}+Na]^+$, (calc. for $C_{19}H_{20}NaN_8$ 383.1709); Anal. calcd for $C_{38}H_{40}Ag_2F_{12}N_{16}Sb_2$: C, 32.41; H, 2.86; N, 15.92. Found: C, 32.31; H, 2.90; N, 15.67

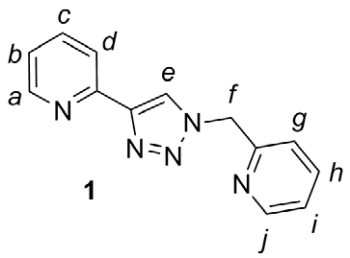


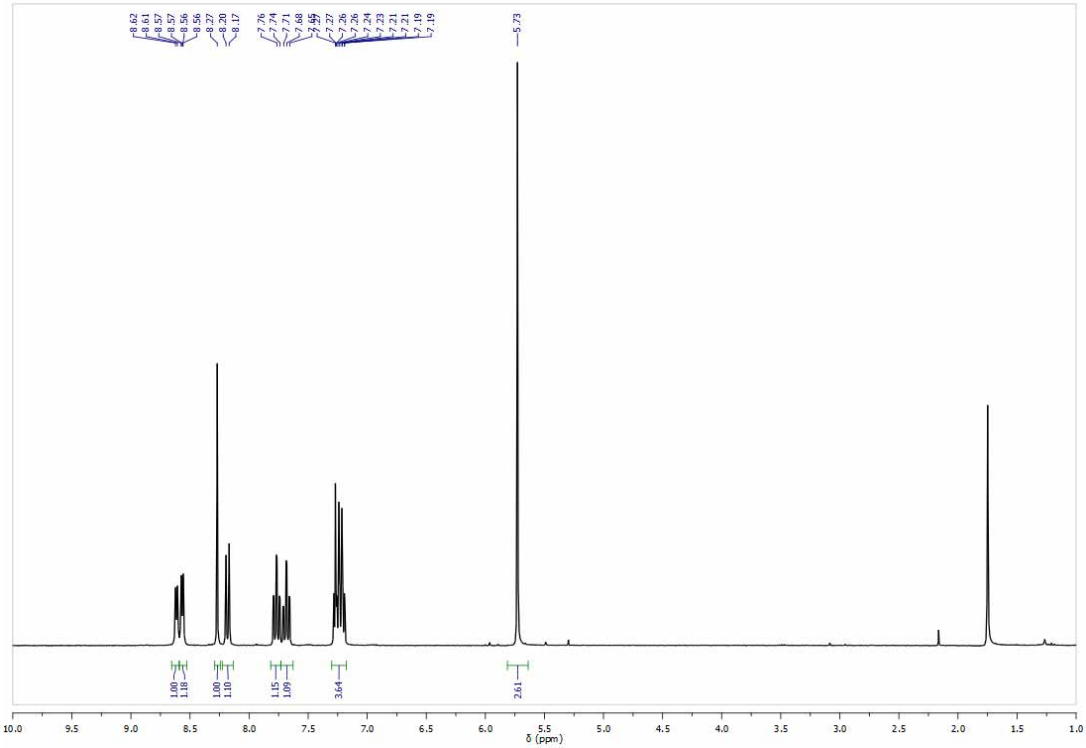
A solution (acetonitrile, 5 mL) of anhydrous $AgSbF_6$ (0.103 g, 0.3 mmol, 3 eq.) was added dropwise slowly to an acetonitrile (5 mL) solution of the ligand **9** (0.110 g, 0.2 mmol, 2 eq.). A colourless solid precipitated slowly over ten minutes and the resulting suspension was stirred at room temperature for 1 h. The volume of solvent was reduced by half and the colourless solid isolated by filtration and washed with

Et_2O (10 mL) and petrol (10 mL) then vacuum dried (0.093 g, 64%). Mp 160-161°C; ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ 8.82 (s, 6H, H_f), 8.58 (d, *J* = 4.2, 6H, H_a), 8.36 (s, 6H, H_g), 7.86 (td, *J* = 7.7, 1.7, 6H, H_c), 7.41-7.37 (m, 12H, $H_{b,d}$), 5.81 (s, 12H, H_e); ^{13}C NMR (100 MHz, *d*$_6$-DMSO) δ 155.2, 150.1, 146.6, 138.0, 132.4, 123.85, 123.3, 122.8, 121.7, 55.2; I.R. (KBr): υ (cm^{-1}) 3113, 3076, 2938, 2924, 1613, 1593, 1571, 1477, 1434, 1337, 1272, 1230, 1198, 1146, 1093, 1052, 1014, 996, 945, 886, 849, 825, 805, 760, 748, 690, 625, 594; HRESI-MS (DMSO/CH_3CN): m/z = 1213.3512 [Ag(**9**)$_2$](SbF_6)$^+$ (calc. for $C_{60}H_{48}AgN_{24}$ 1213.3541), 936.2417 [Ag(**9**)(CH_3CN)H](SbF_6)$^+$ (calc. for $C_{30}H_{24}AgF_6N_{13}Sb$ 936.0584), 553.2285 [**9**+H]$^+$ (calc. for $C_{30}H_{24}N_{12}$ 553.2235); Anal. calcd for $C_{60}H_{48}AgF_6N_{24}Sb$: C, 49.74; H, 3.34; N, 23.20. Found: C, 49.81; H, 3.41; N, 23.08

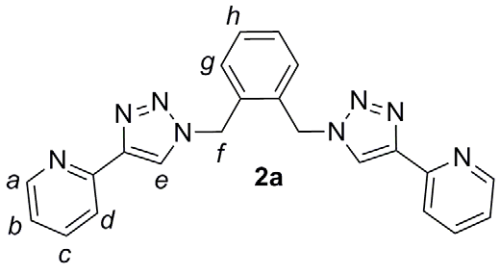
4. Selected ^{1}H NMR Spectra of synthesized compounds.

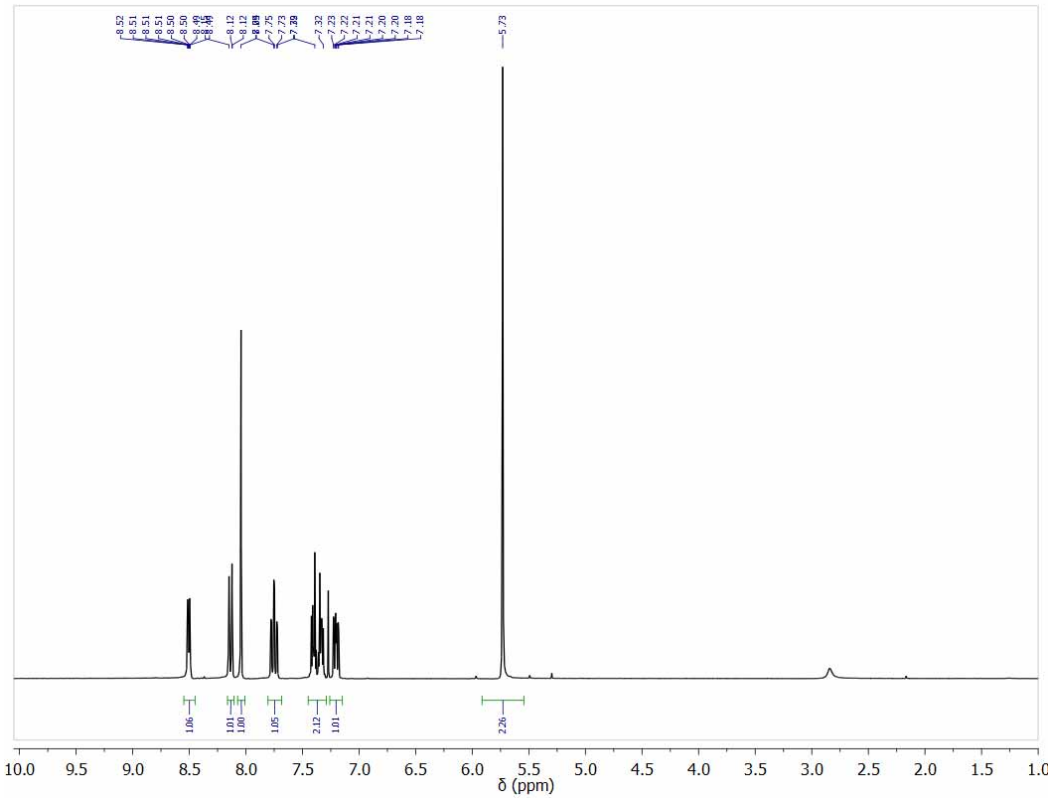
^{1}H NMR ($CDCl_3$, 300K) of **1.**



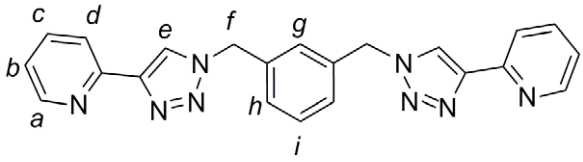


^{1}H NMR ($CDCl_3$, 300K) of **2a.**

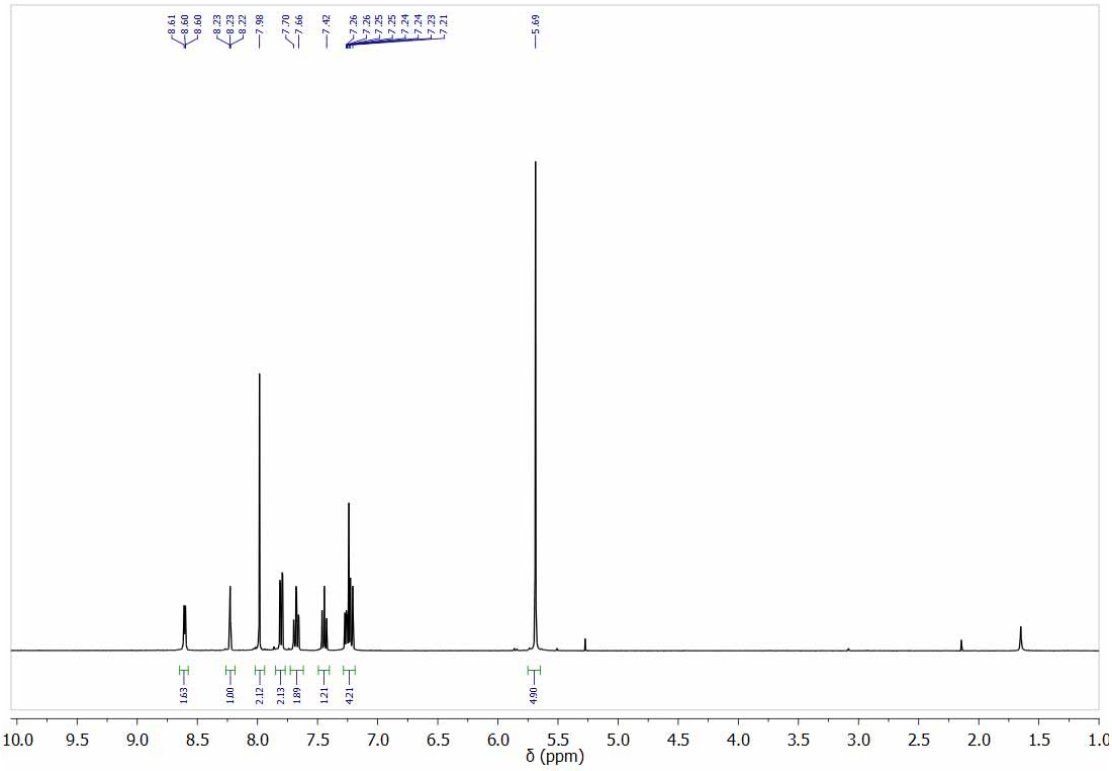




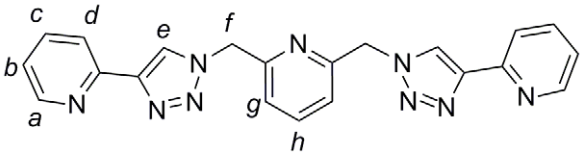
^{1}H NMR ($CDCl_3$, 300K) of **2b.**



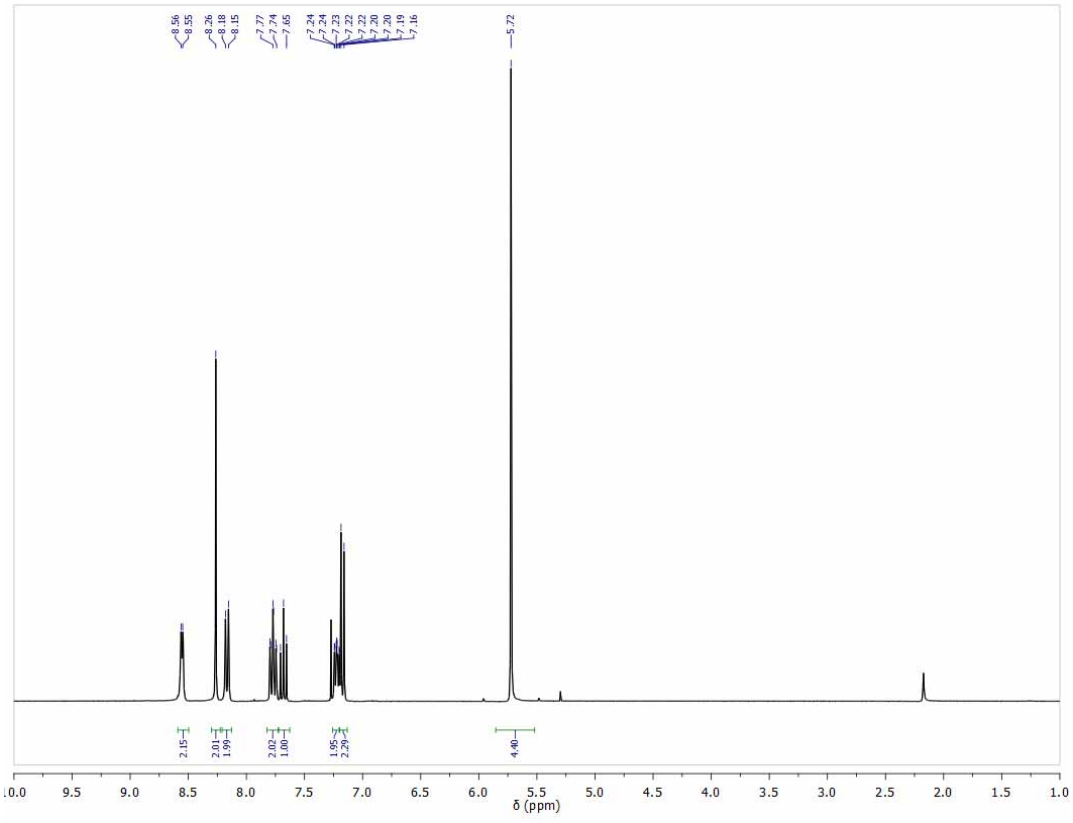
2b



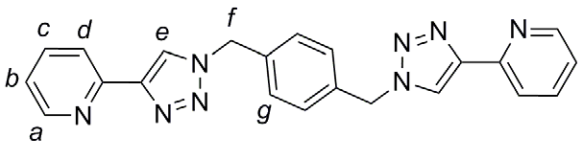
^{1}H NMR ($CDCl_3$, 300K) of **2c.**



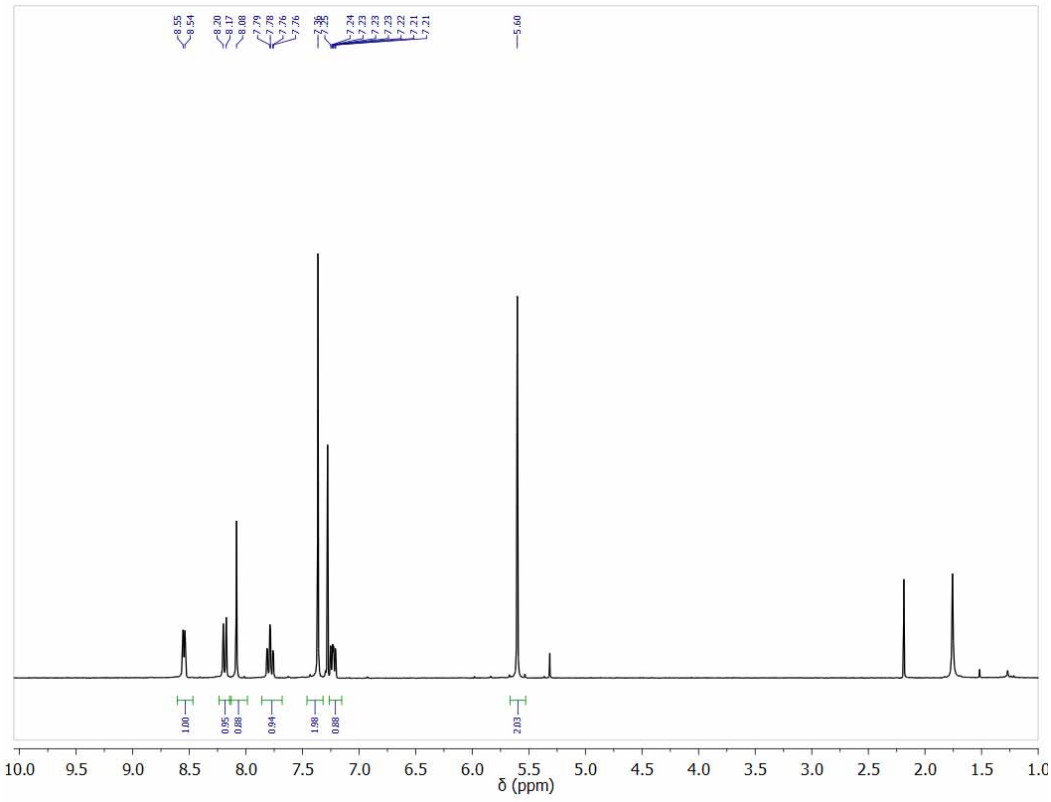
2c



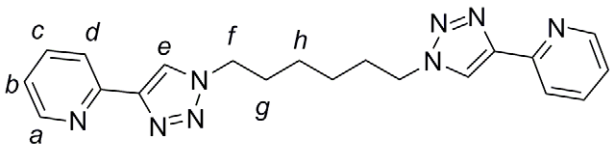
^{1}H NMR ($CDCl_3$, 300K) of **2d.**



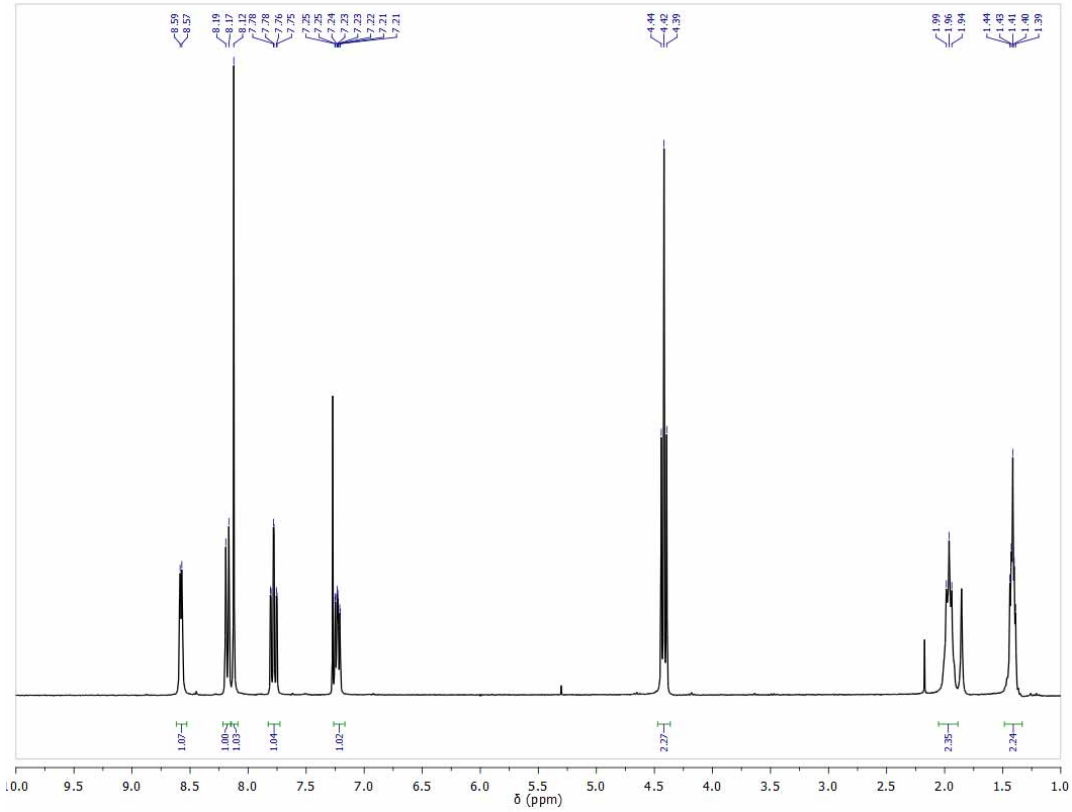
2d



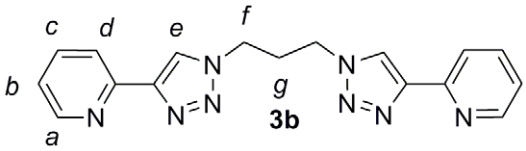
^{1}H NMR ($CDCl_3$, 300K) of **3a.**

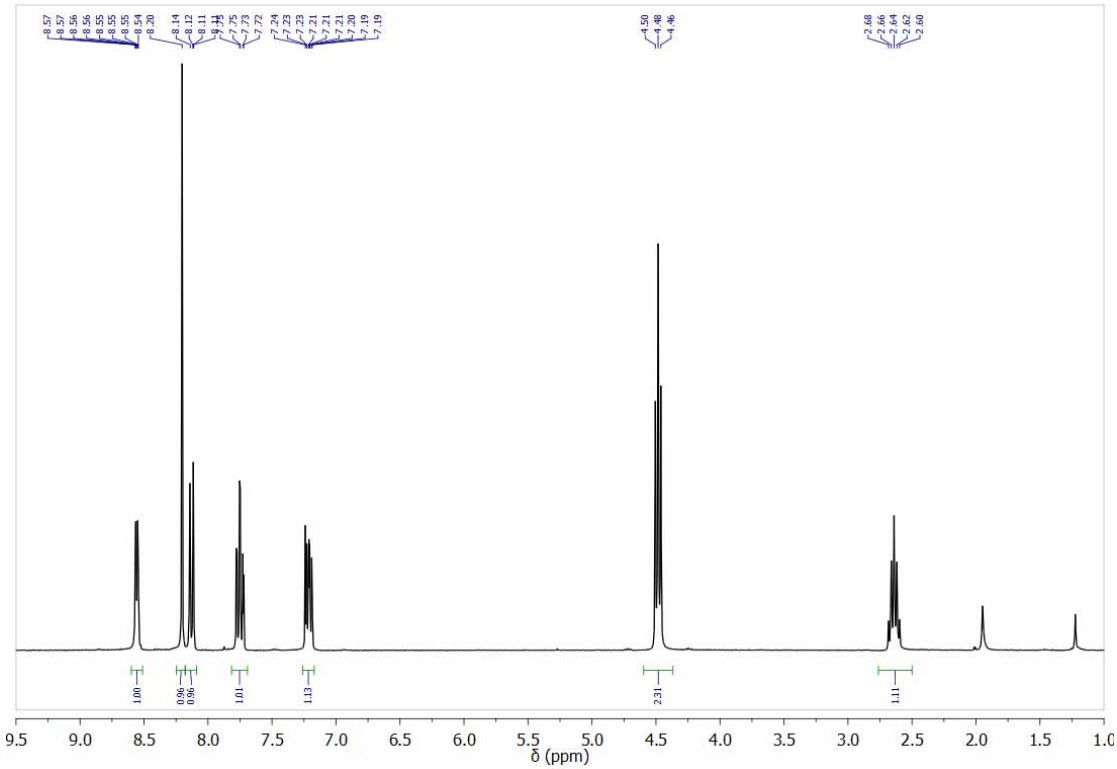


3a

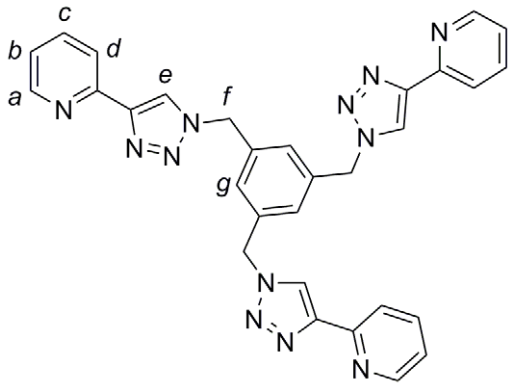


^{1}H NMR ($CDCl_3$, 300K) of **3b.**

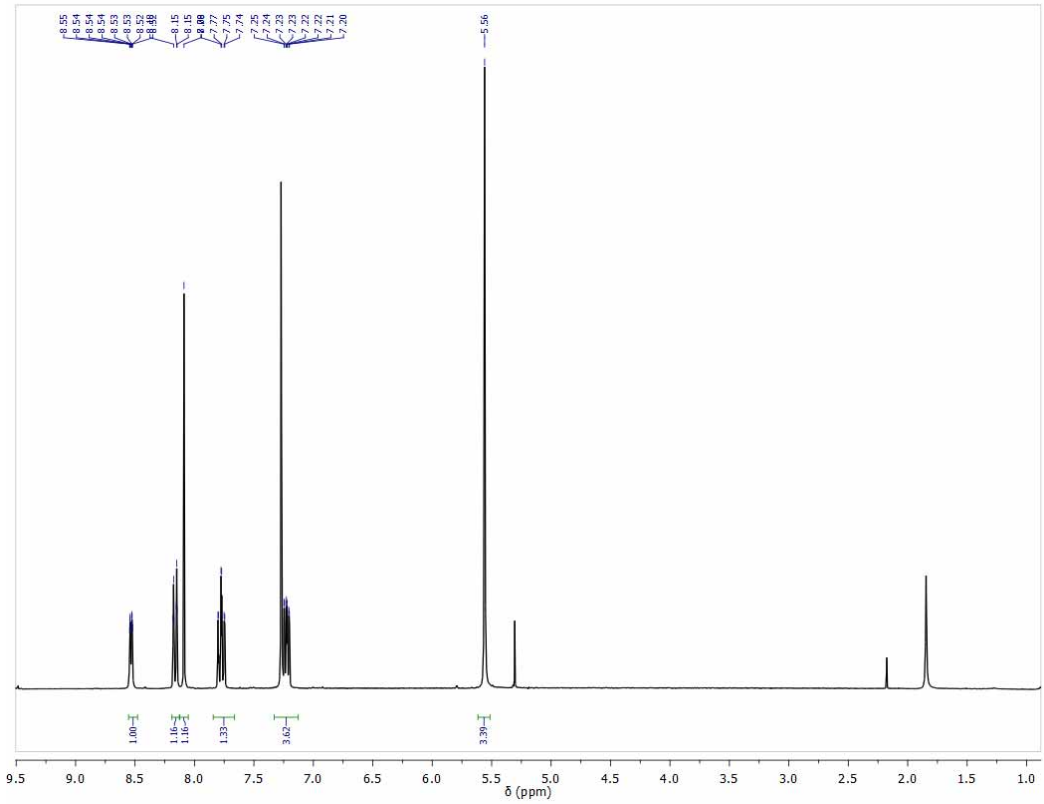




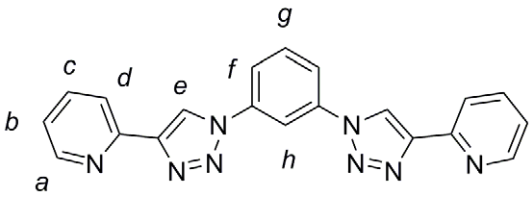
^{1}H NMR ($CDCl_3$, 300K) of **4.**



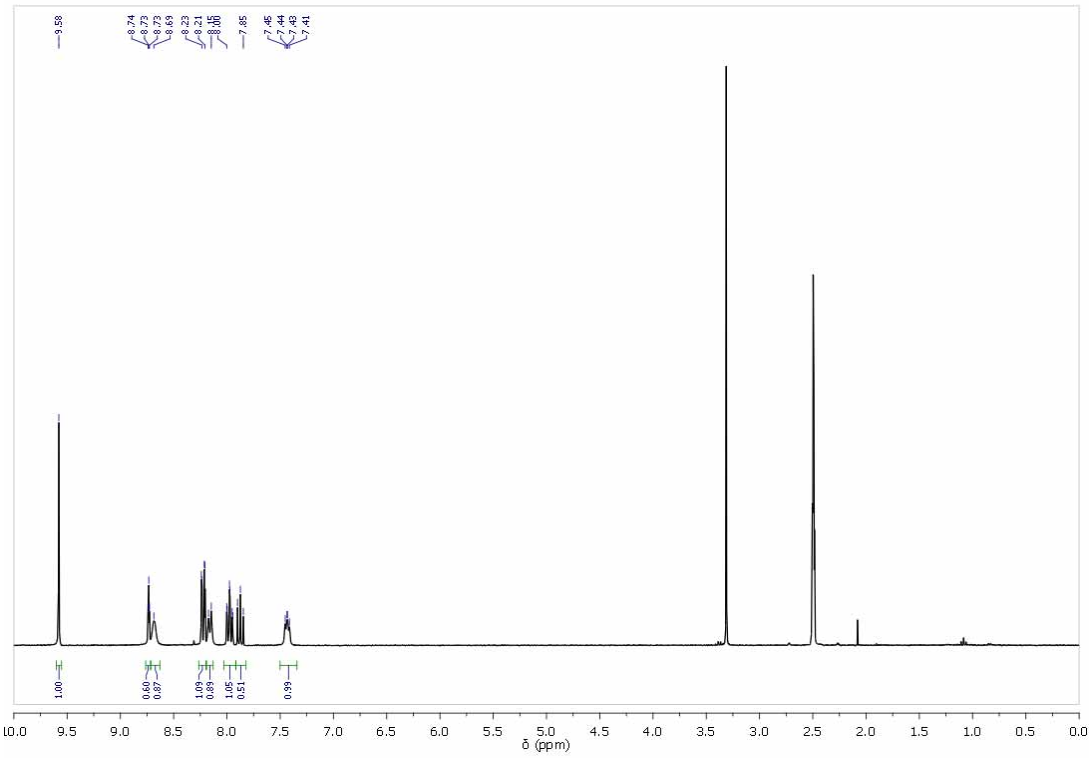
4



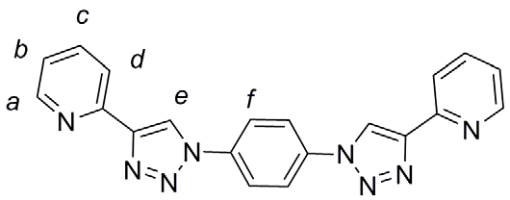
^{1}H NMR (D_6-DMSO, 300K) of **5a.**



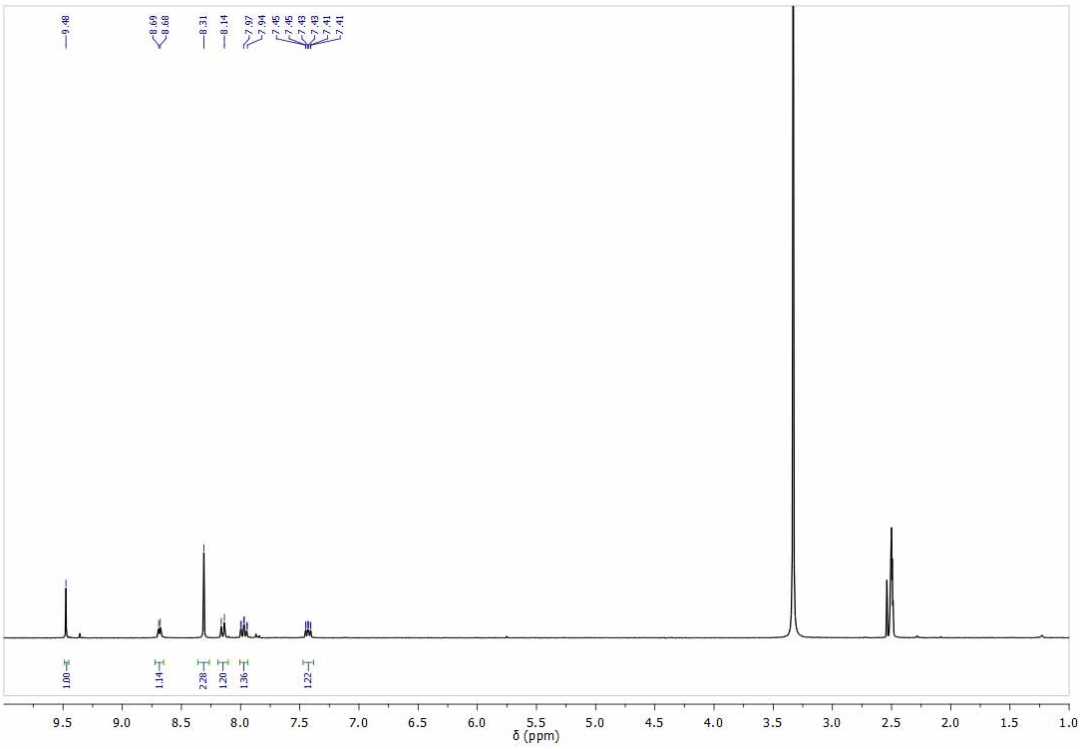
5a



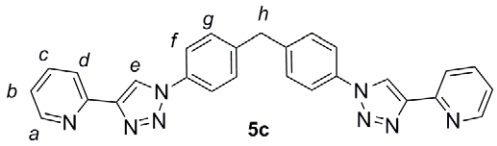
^{1}H NMR (D_6-DMSO, 300K) of **5b.**



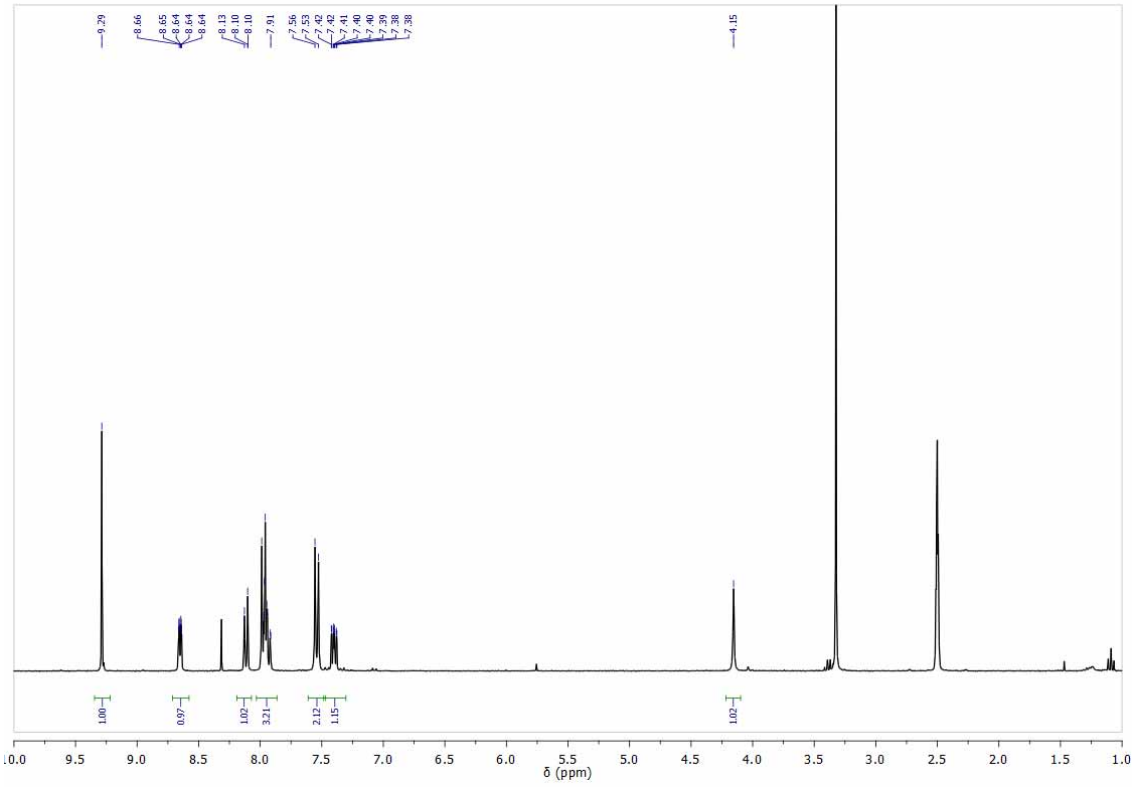
5b



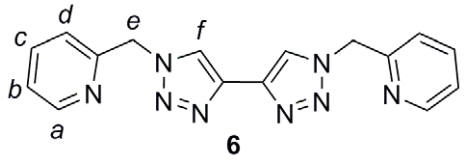
^{1}H NMR (D_6-DMSO, 300K) of **5c.**



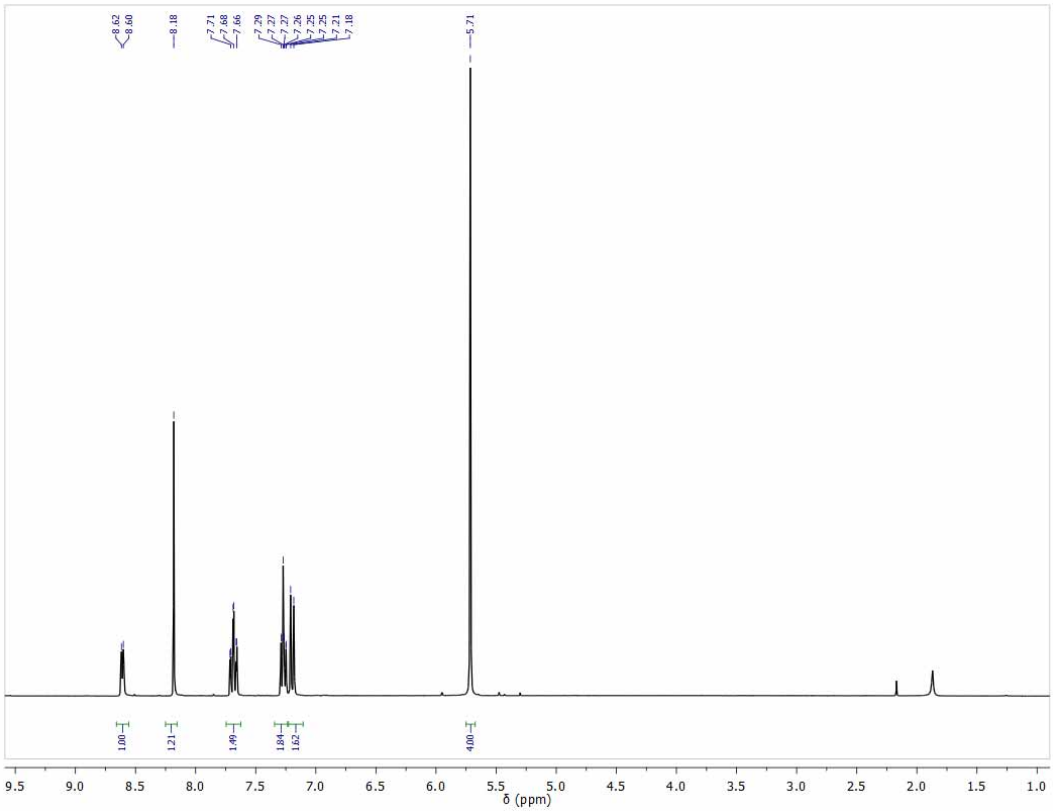
5c



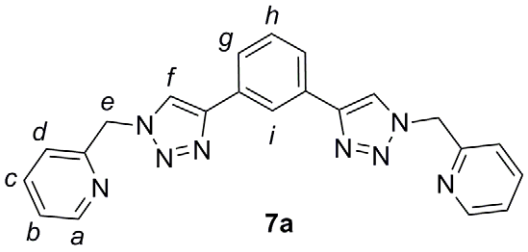
^{1}H NMR ($CDCl_3$, 300K) of **6.**



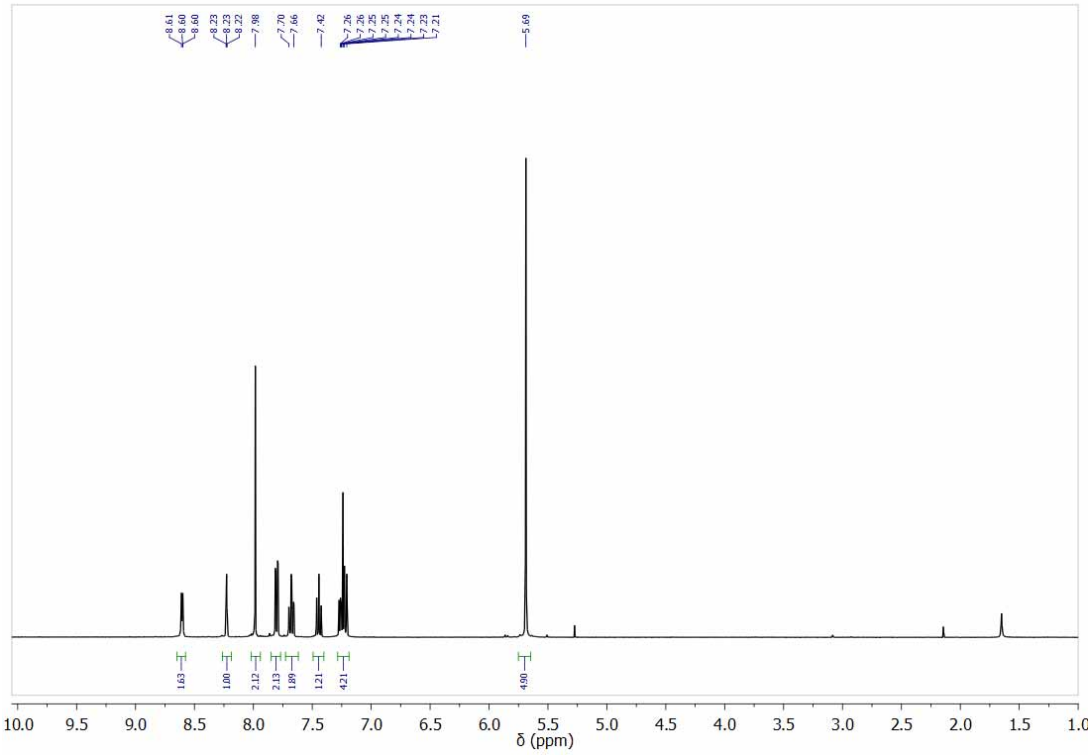
6



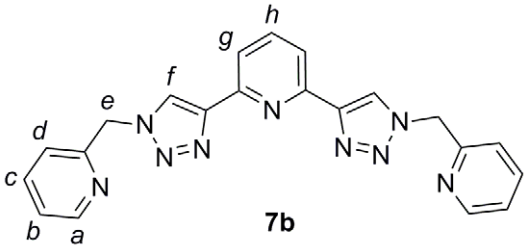
^{1}H NMR ($CDCl_3$, 300K) of **7a.**

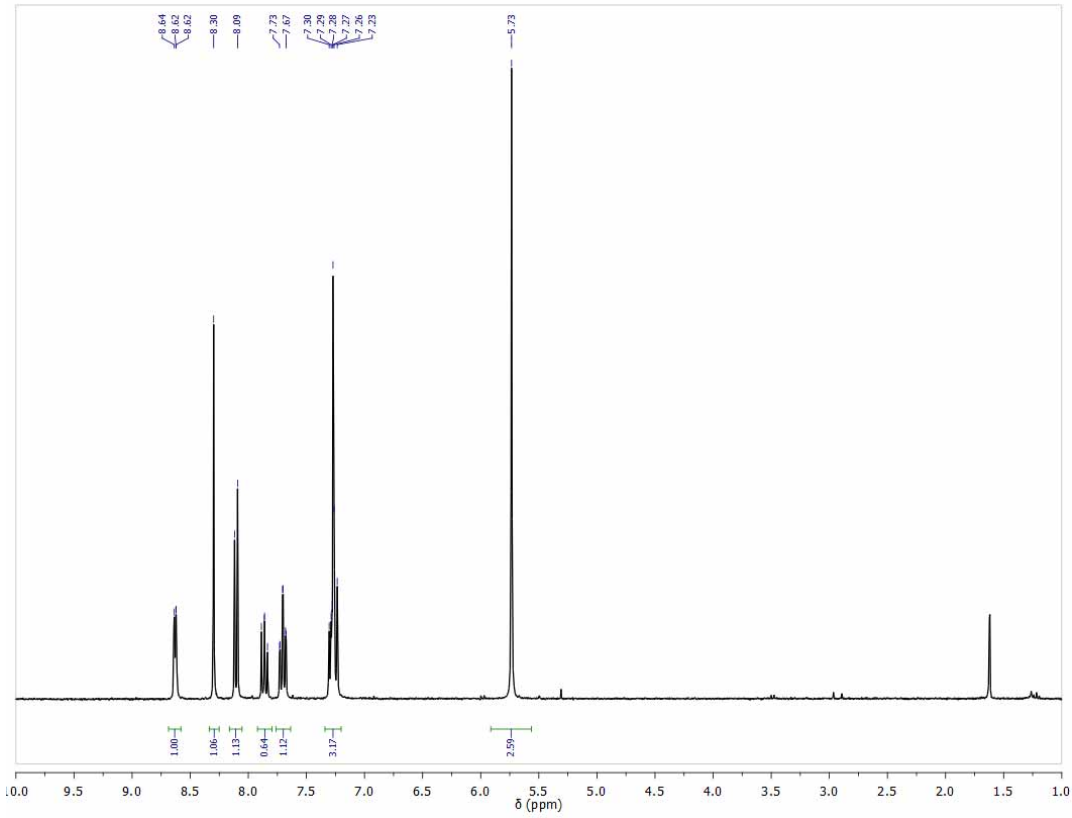


7a

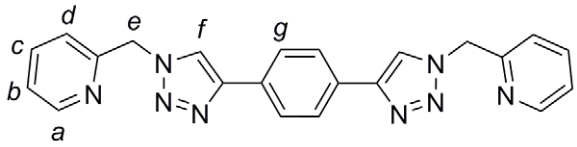


^{1}H NMR ($CDCl_3$, 300K) of **7b.**

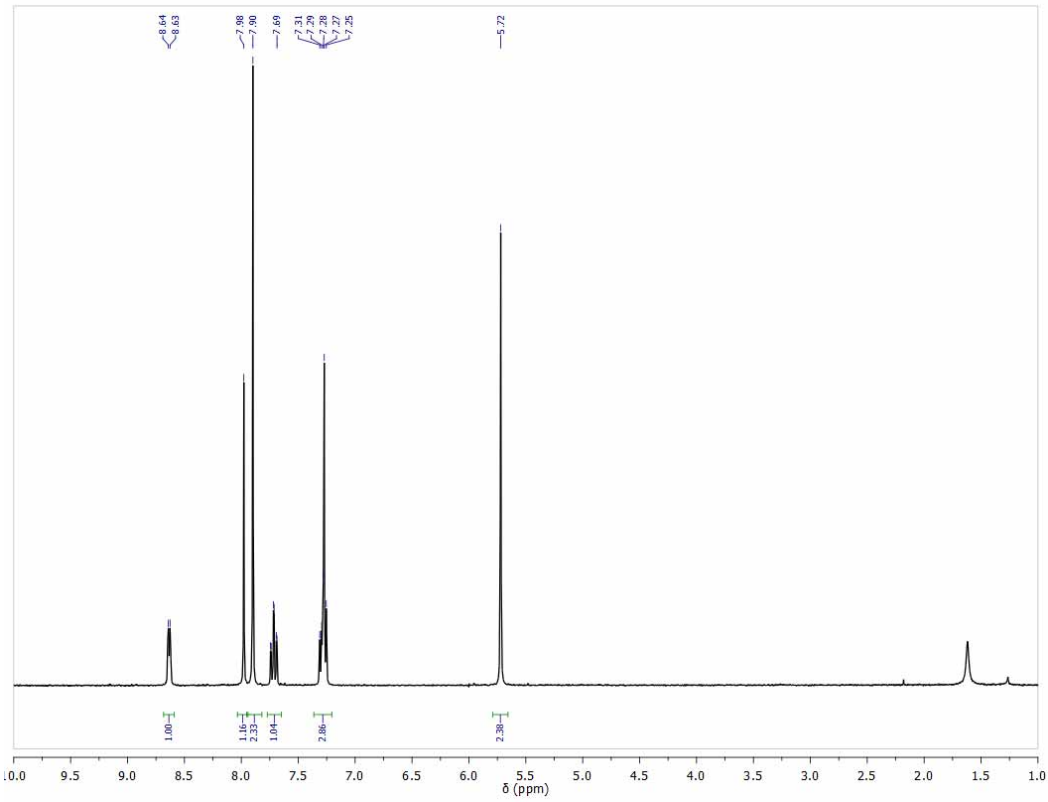




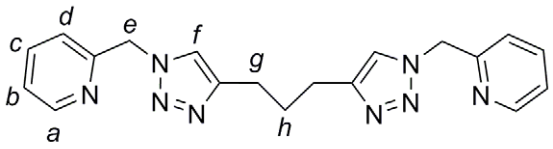
^{1}H NMR ($CDCl_3$, 300K) of **7c.**



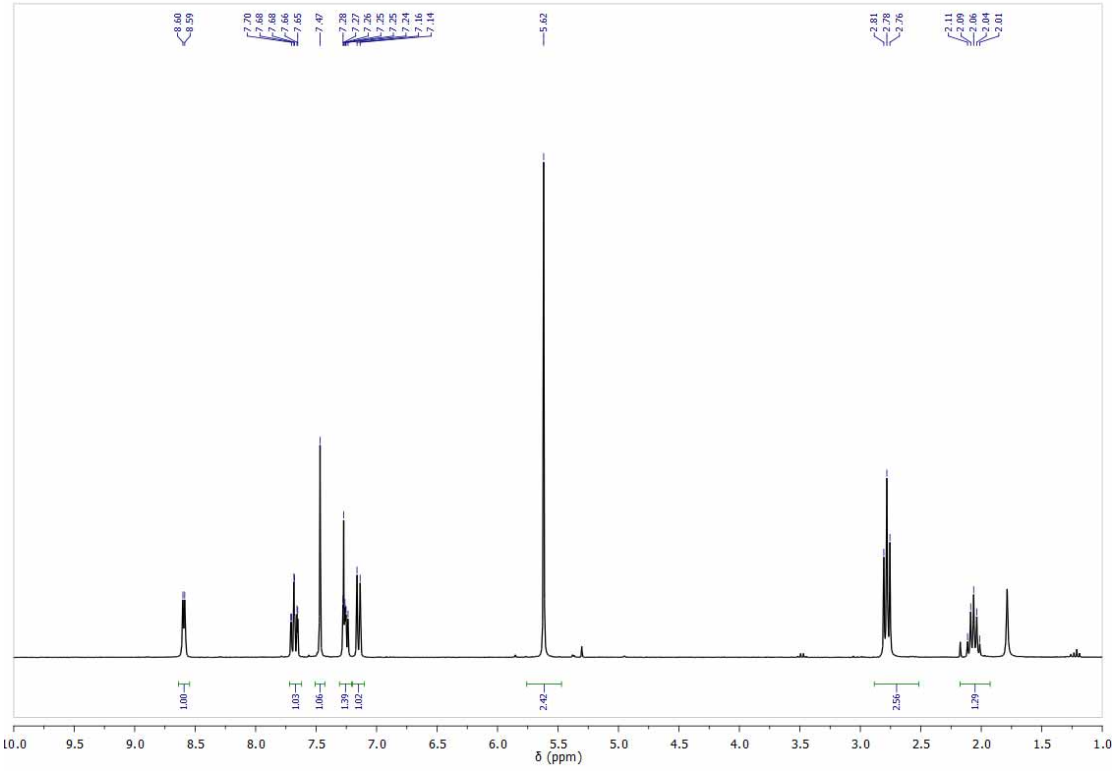
7c



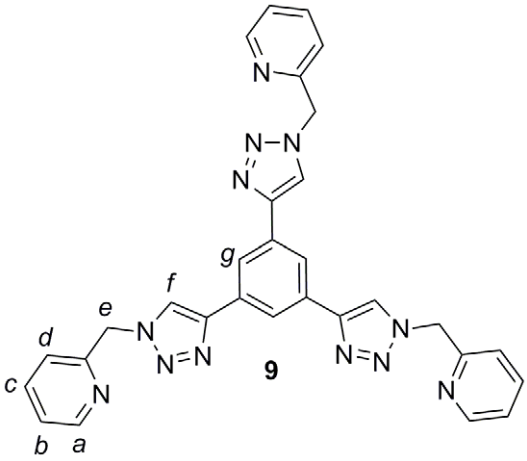
^{1}H NMR ($CDCl_3$, 300K) of **8.**

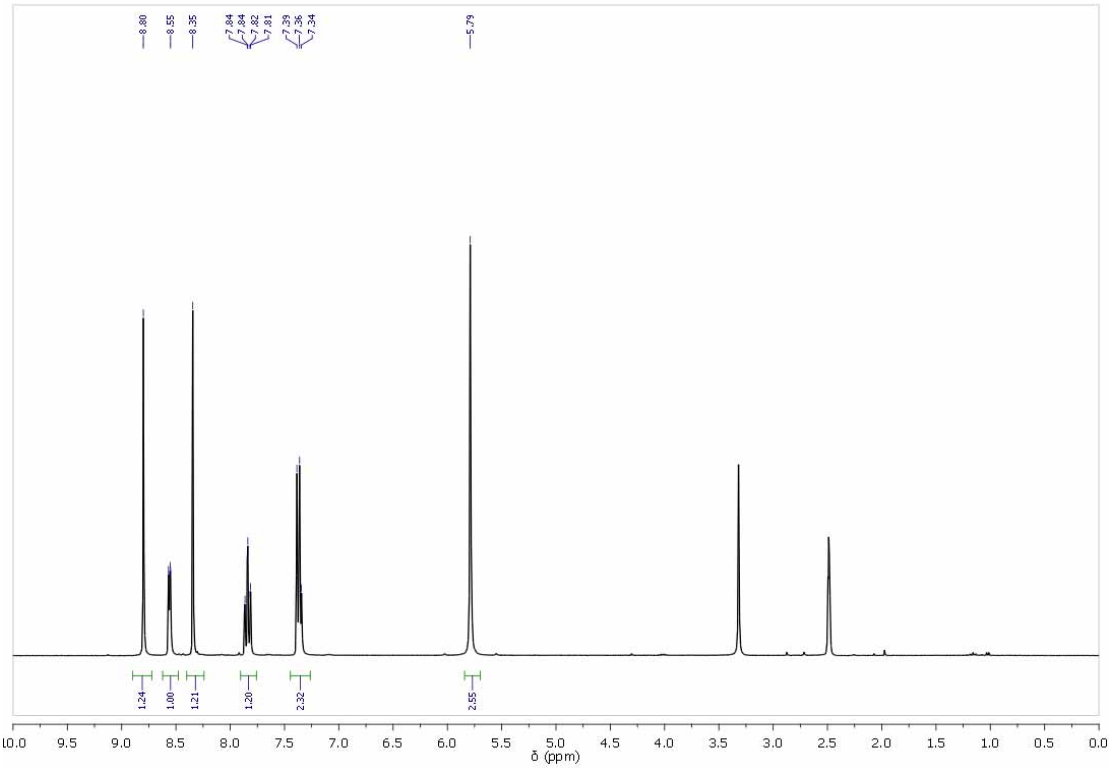


8

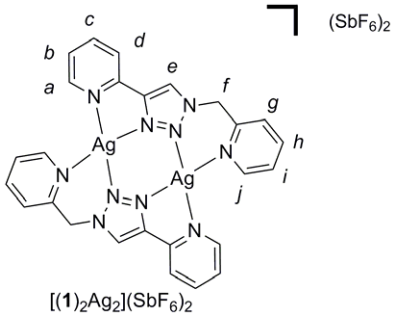


^{1}H NMR ($CDCl_3$, 300K) of **8.**

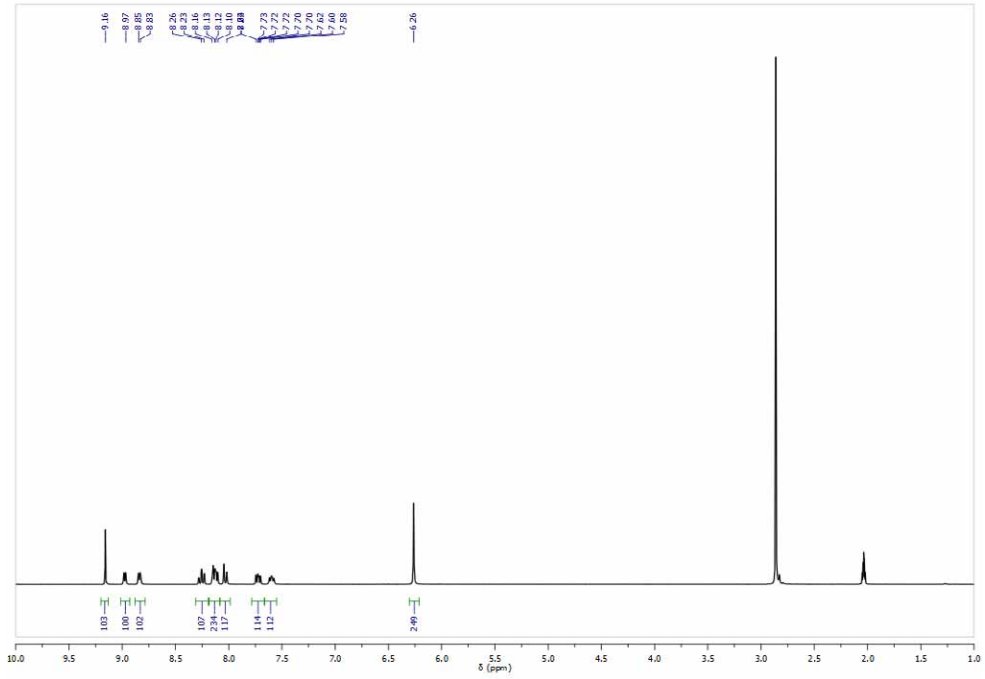




^{1}H NMR Spectra of selected silver complexes.



$[(\mathbf{1})_2Ag_2](SbF_6)_2$



^{1}H NMR (d_6-acetone, 300K) of $[Ag_2(\mathbf{1})_2](SbF_6)_2$.

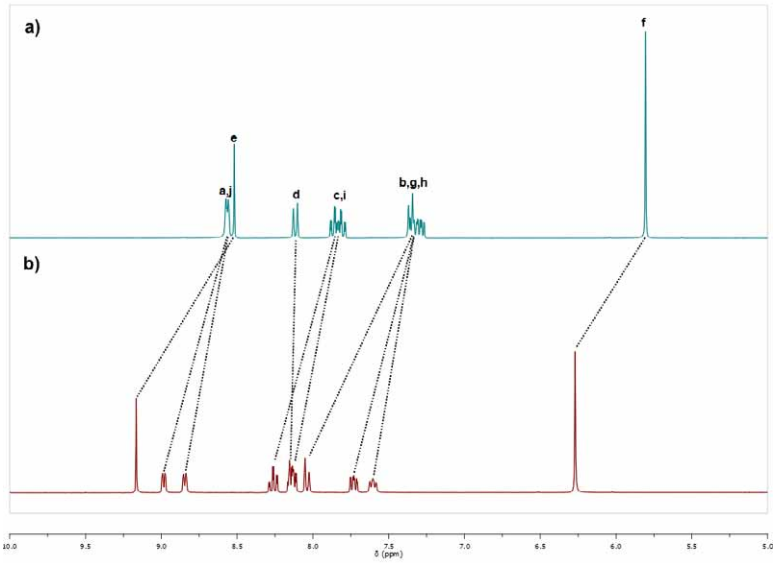
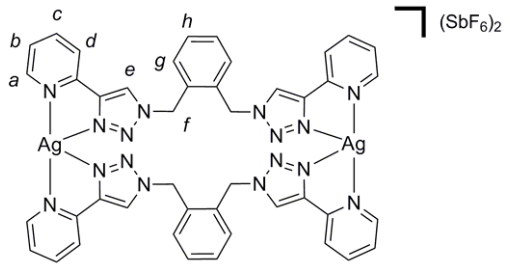
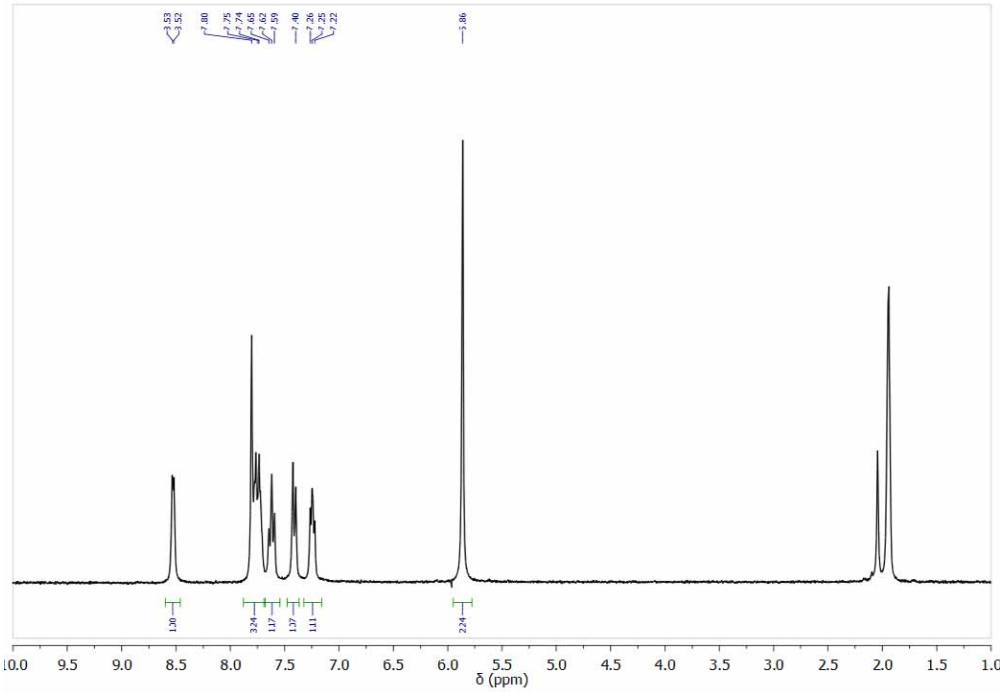


Figure 1. Partial ^{1}H NMR spectra (300 MHz, d_6-acetone, 300 K) of a) Ligand **1**, b) $[Ag_2(\mathbf{1})_2](SbF_6)_2$.



$[(\mathbf{2a})_2Ag_2](SbF_6)_2$



^{1}H NMR (CD_3CN, 300K) of $[Ag_2(\mathbf{2a})_2](SbF_6)_2$.

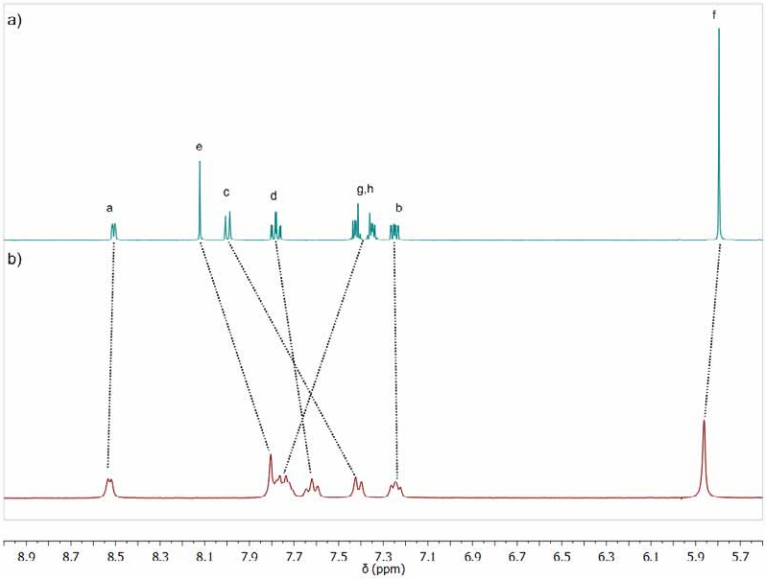
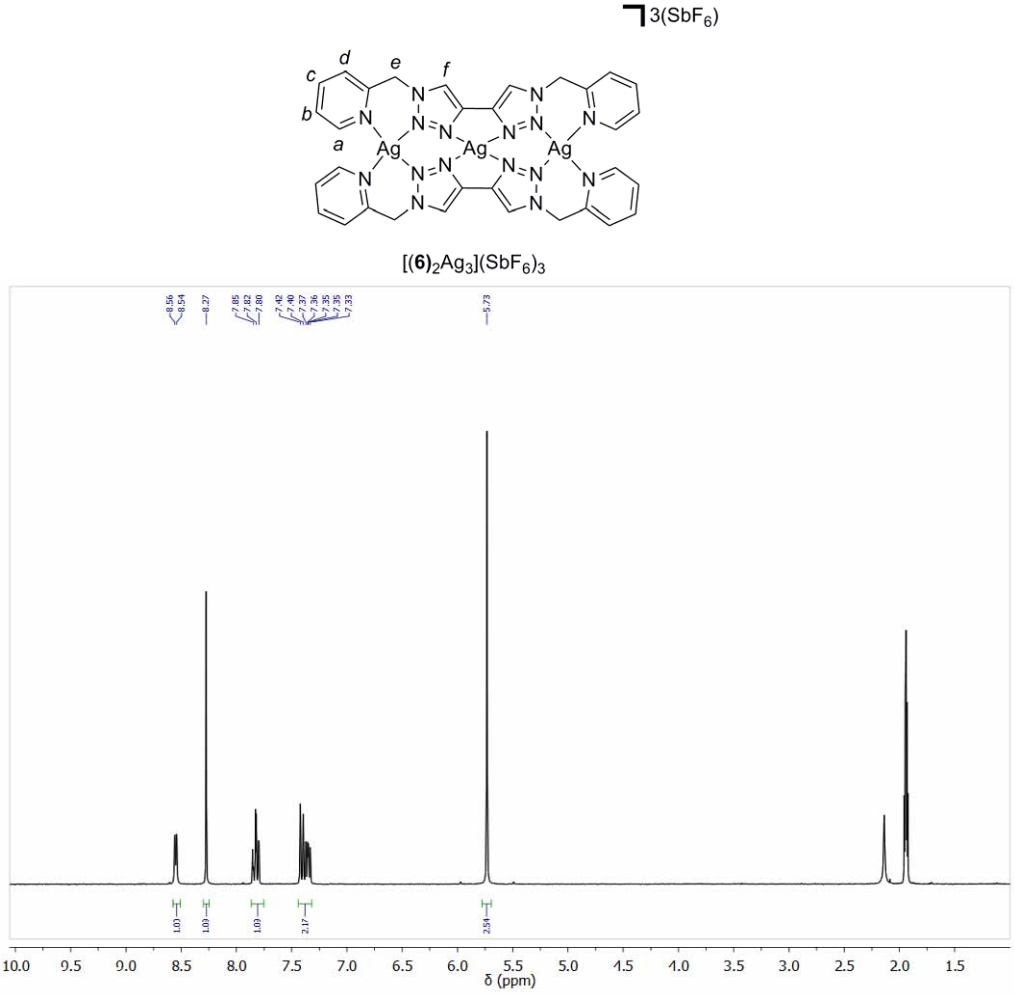


Figure 2. Partial ^{1}H NMR spectra (300 MHz, CD_3CN, 300 K) of a) Ligand **2a**, b) $[Ag_2(\mathbf{2a})_2](SbF_6)_2$.



^{1}H NMR (CD_3CN, 300K) of $[Ag_3(\mathbf{6})_2](SbF_6)_3$.

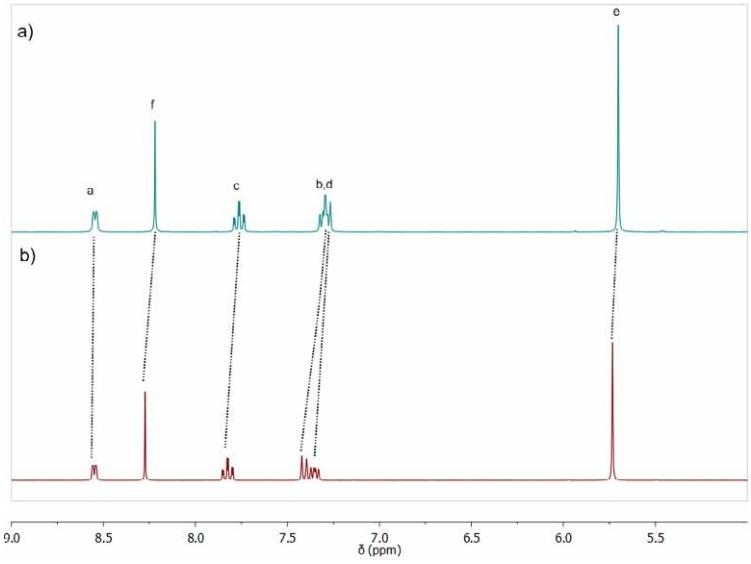
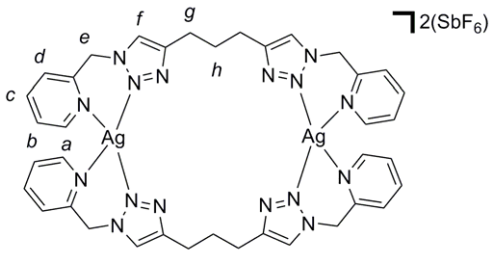
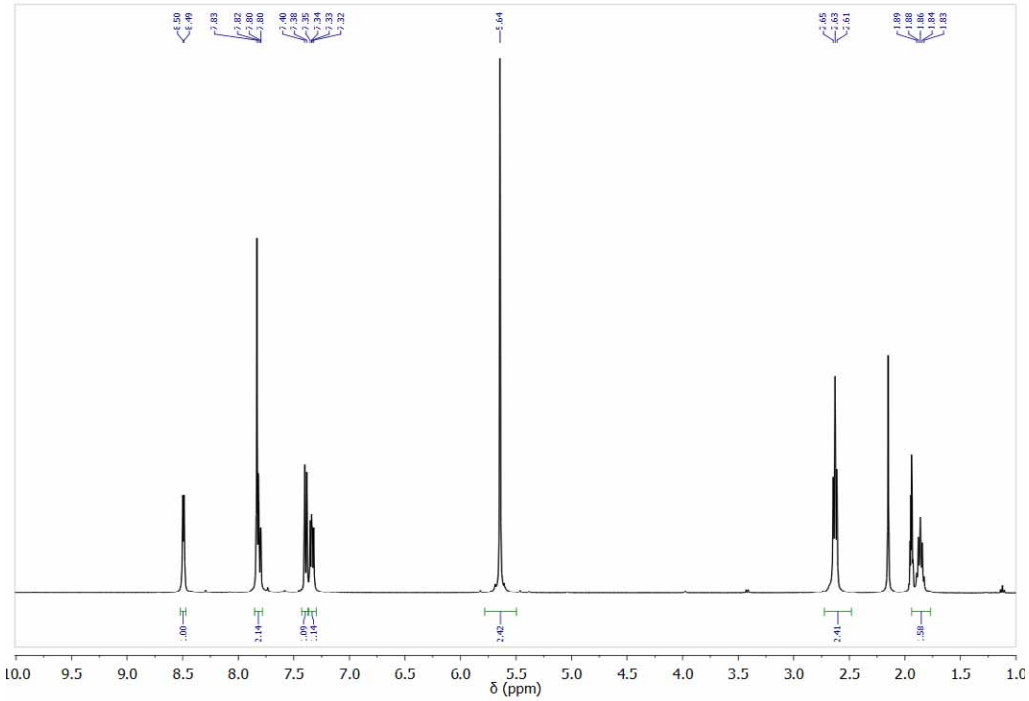


Figure 3. Partial ^{1}H NMR spectra (300 MHz, CD_3CN, 300 K) of a) Ligand **6**, b) $[Ag_3(\mathbf{6})_2](SbF_6)_3$.



$[(\mathbf{8})_2Ag_2](SbF_6)_2$



^{1}H NMR (CD_3CN, 300K) of $[Ag_2(\mathbf{8})_2](SbF_6)_2$.

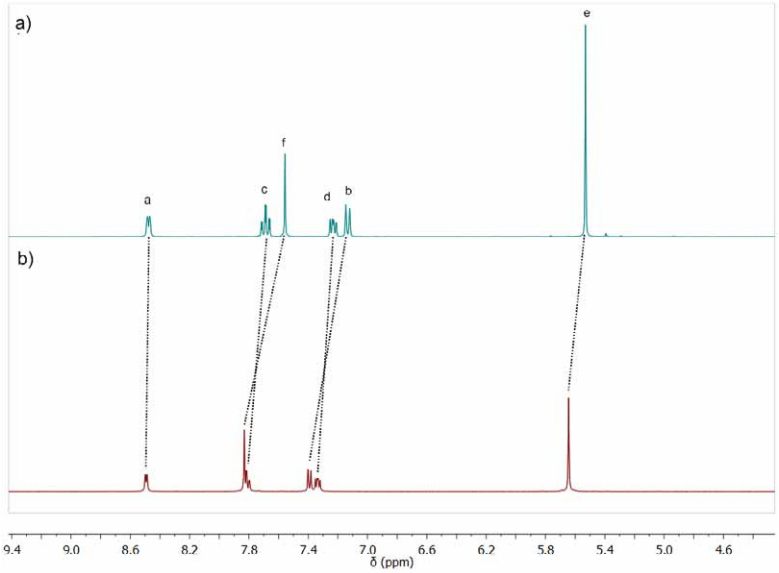
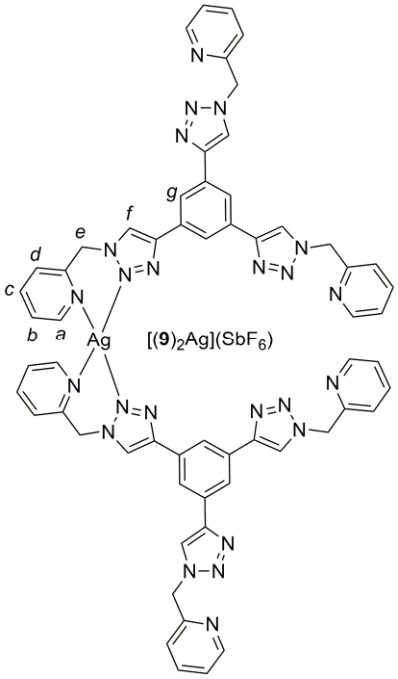
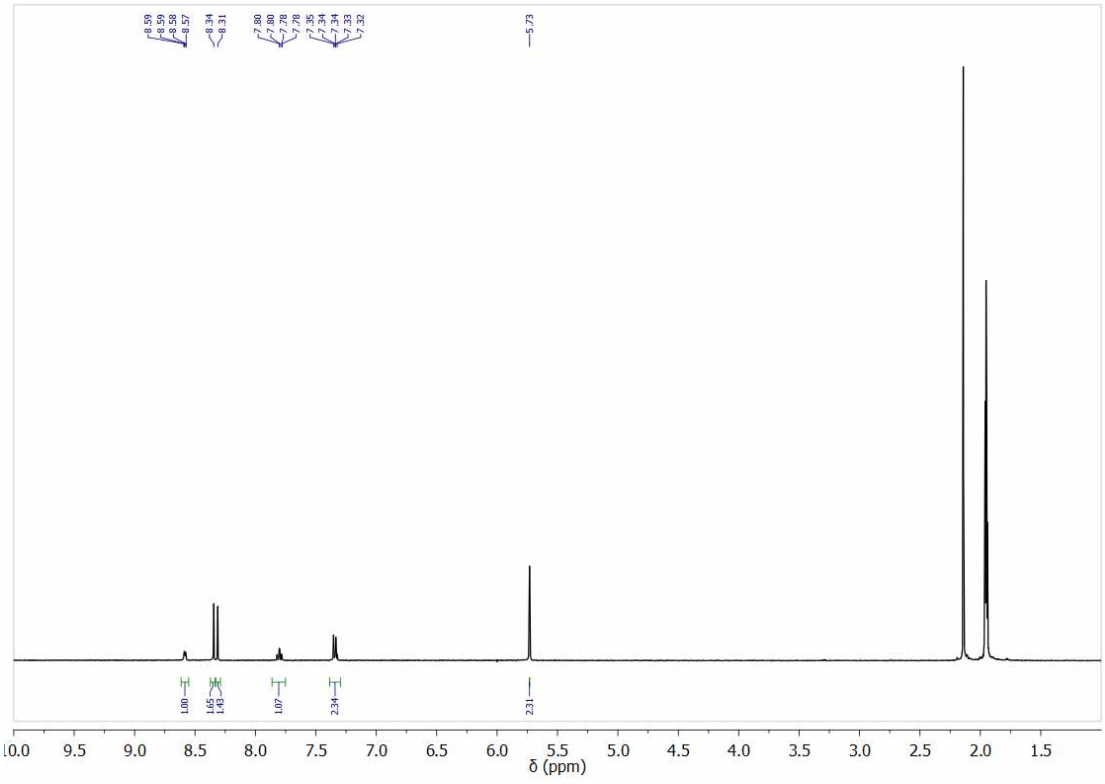


Figure 4. Partial ^{1}H NMR spectra (300 MHz, CD_3CN, 300 K) of a) Ligand **8**, b) $[Ag_2(\mathbf{8})_2](SbF_6)_2$.



^{1}H NMR (CD_3CN, 300K) of [Ag(**9**)$_2$](SbF_6).



5. Selected HR-ESMS Spectra of the silver complexes.

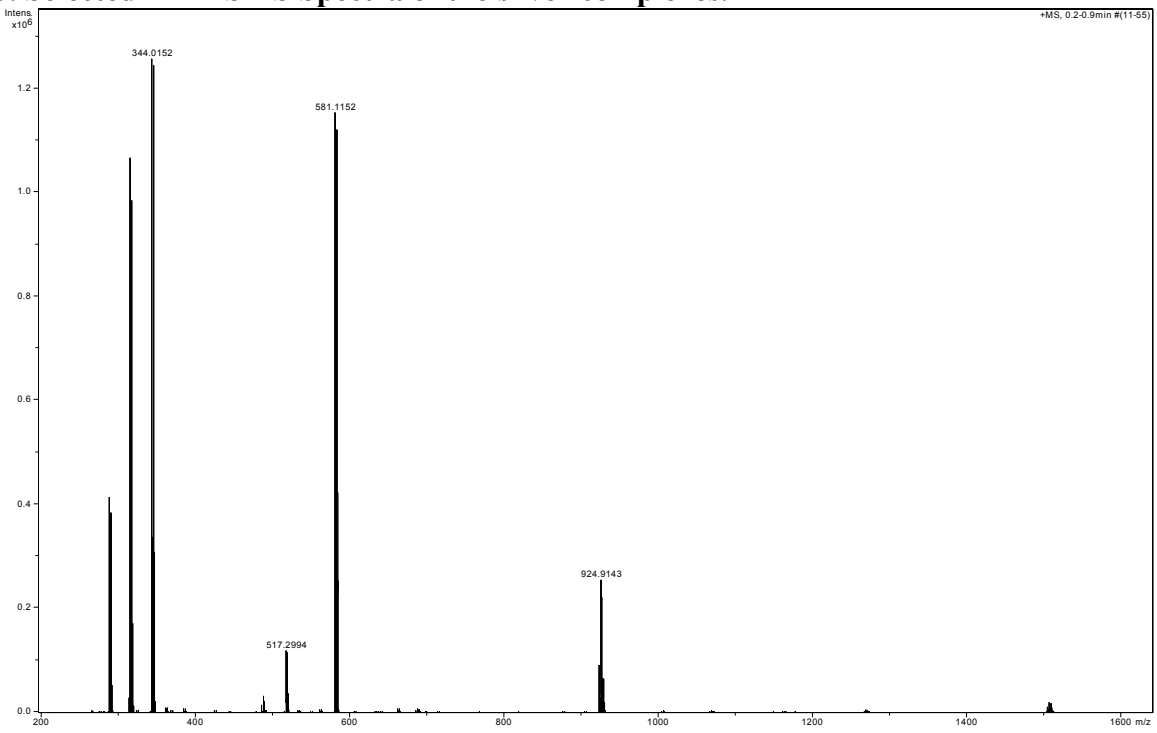


Figure 5. HR-ESMS (CH_3CN) of $[Ag_2(\mathbf{1})_2](SbF_6)_2$: *m/z* = 924.9131 $[Ag_2(\mathbf{1})_2](SbF_6)^+$ (calc. for $C_{26}H_{22}Ag_2F_6N_{10}Sb$ 924.9068), 581.1148 $[Ag(\mathbf{1})_2]^+$) (calc. for $C_{26}H_{22}AgN_{10}$ 581.1074), 344.0150 $[Ag(\mathbf{1})]^+$ (calc. for $C_{13}H_{11}AgN_5$ 344.0065).

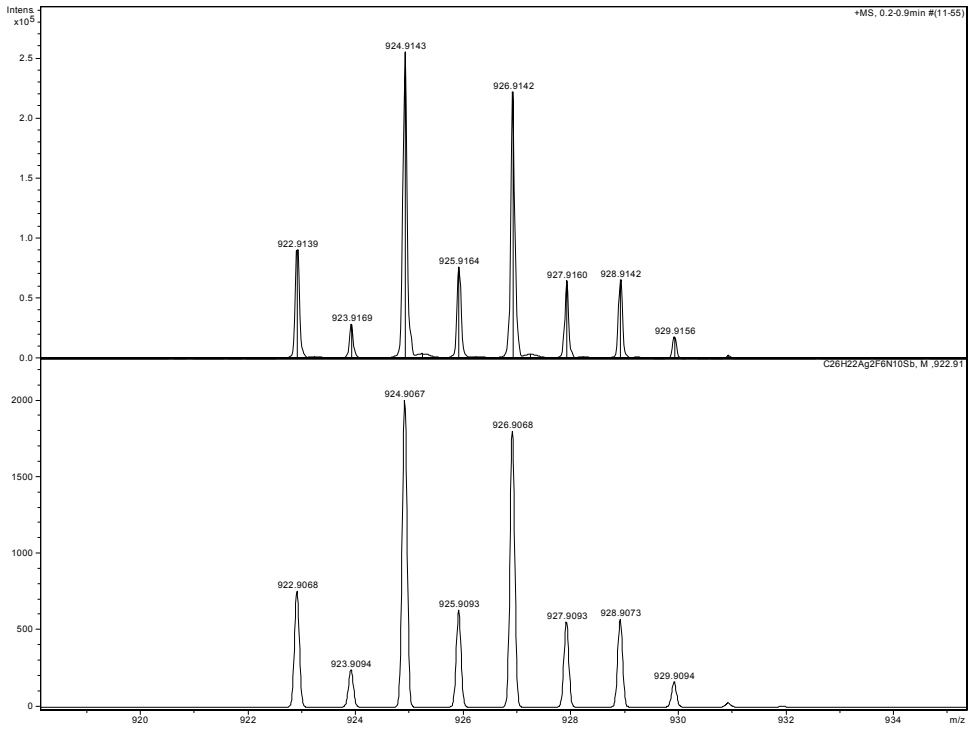


Figure 6. Observed and Calculated isotopic distribution for the $[Ag_2(\mathbf{1})_2](SbF_6)^+$ ion.

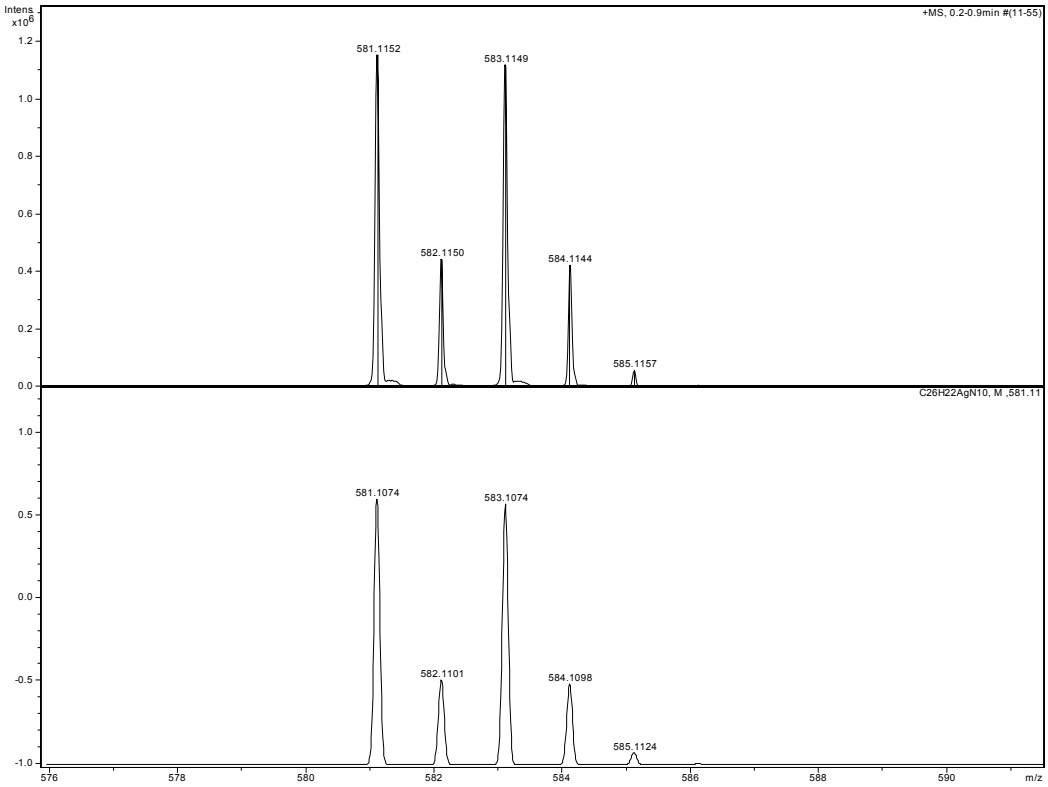


Figure 7. Observed and Calculated isotopic distribution for the [Ag(**1**)$_2$] ion.

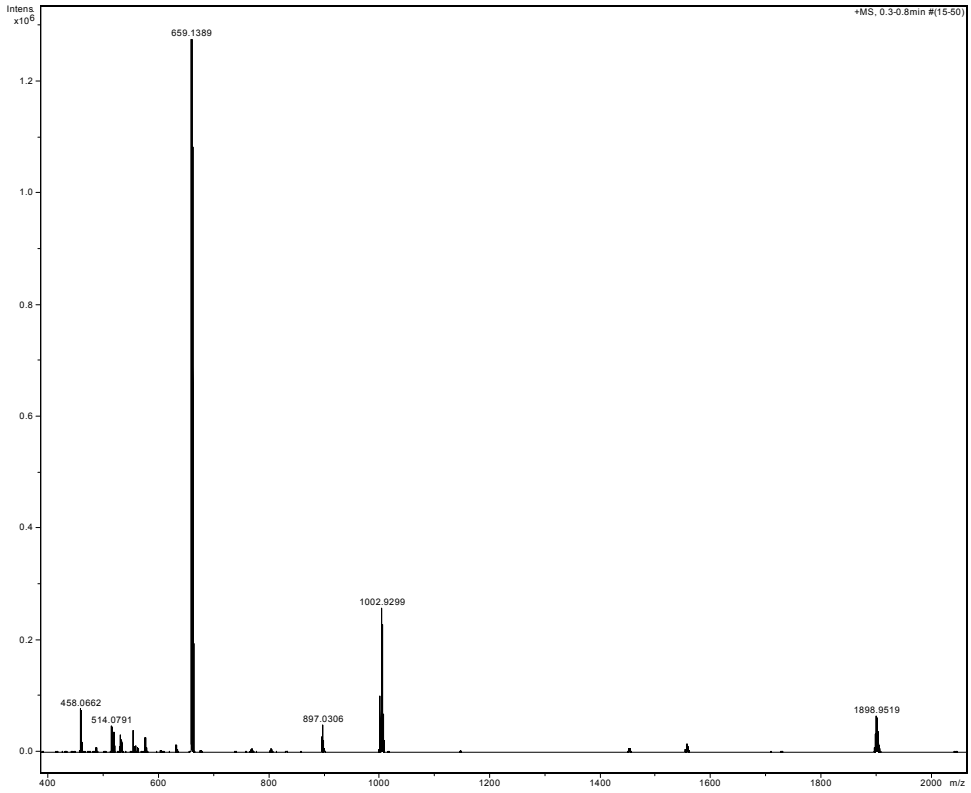


Figure 8. HR-ESMS (DMSO/CH_3CN): *m/z* = 1898.9519 $[Ag_3(\mathbf{4})_2](SbF_6)_2^+$ (calc. for $C_{60}H_{48}Ag_3F_{12}N_{24}Sb_2$ 1898.9532), 1002.9299 $[Ag_2(\mathbf{4})](SbF_6)^+$ (calc. for $C_{30}H_{24}Ag_2F_6N_{12}Sb$ 1002.9988), 659.1389 $[Ag(\mathbf{4})]^+$ (calc. for $C_{30}H_{24}AgN_{12}$ 659.1298).

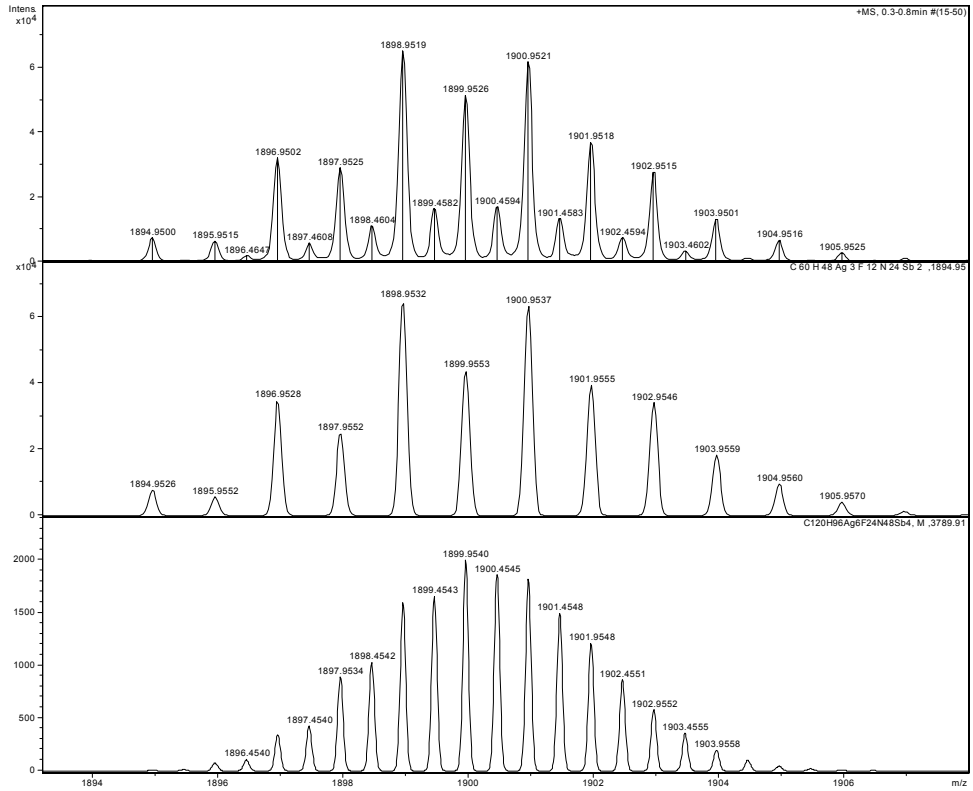


Figure 9. Observed and Calculated isotopic distribution for the $[Ag_3(\mathbf{4})_2](SbF_6)_2^+$ and $[Ag_6(\mathbf{4})_4](SbF_6)_4^{2+}$ ion.

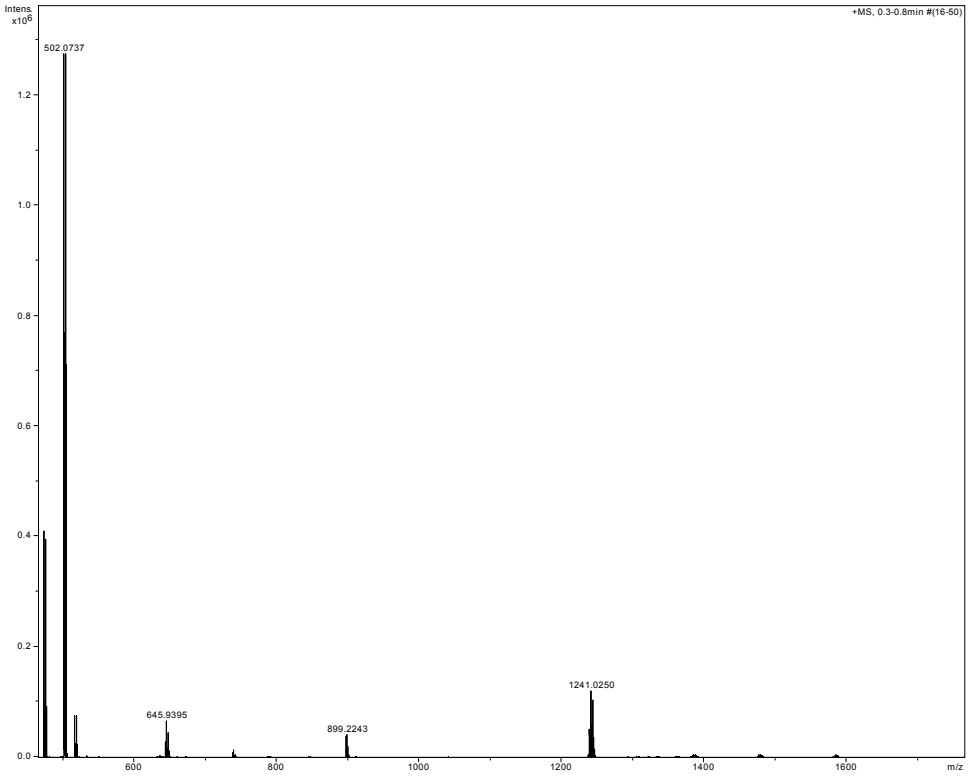


Figure 10. HR-ESMS (CH_3CN): *m/z* = 1584.8274 $[Ag_3(\mathbf{7b})_2](SbF_6)_2^+$ (calc. for $C_{42}H_{34}Ag_3F_{12}N_{18}Sb_2$ 1584.8248), 1241.0250 $[Ag_2(\mathbf{7b})_2](SbF_6)^+$ (calc. for $C_{42}H_{34}Ag_2F_6N_{18}Sb$ 1241.0254), 899.2243 $[Ag_2(\mathbf{7b})_2](SbF_6)^+$ (calc. for $C_{42}H_{34}AgN_{18}$ 899.2261), 502.0737 $[Ag(\mathbf{7b})]^+$ (calc. for $C_{21}H_{17}AgN_{18}$ 502.0652).

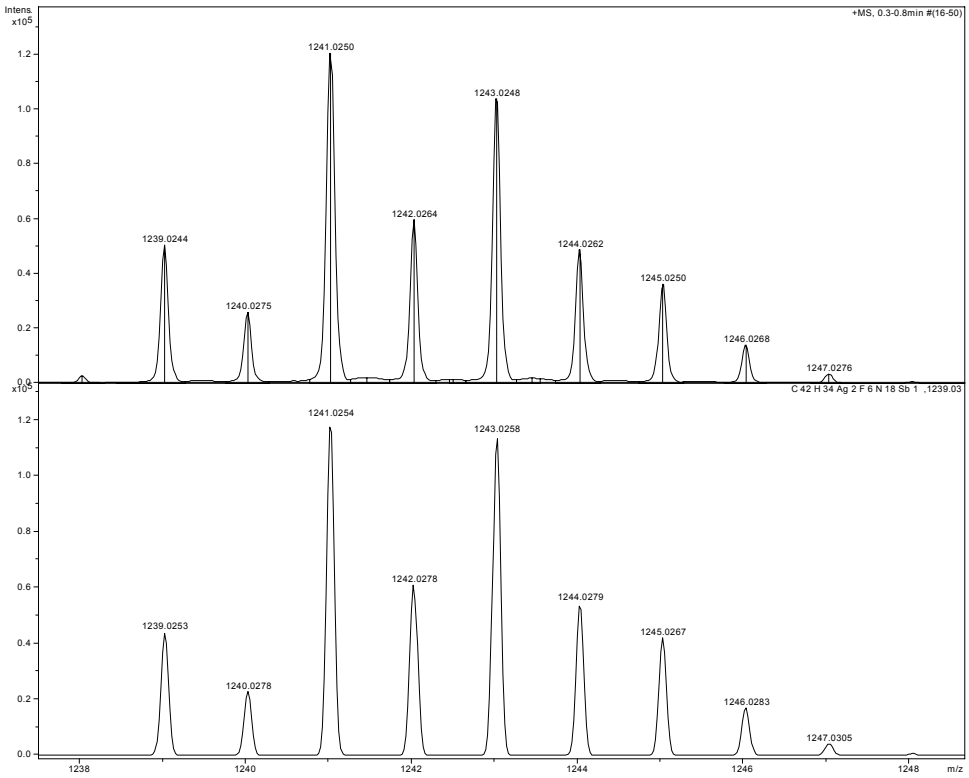


Figure 11. Observed and Calculated isotopic distribution for the $[Ag_2(\mathbf{7b})_2](SbF_6)^+$ ion.

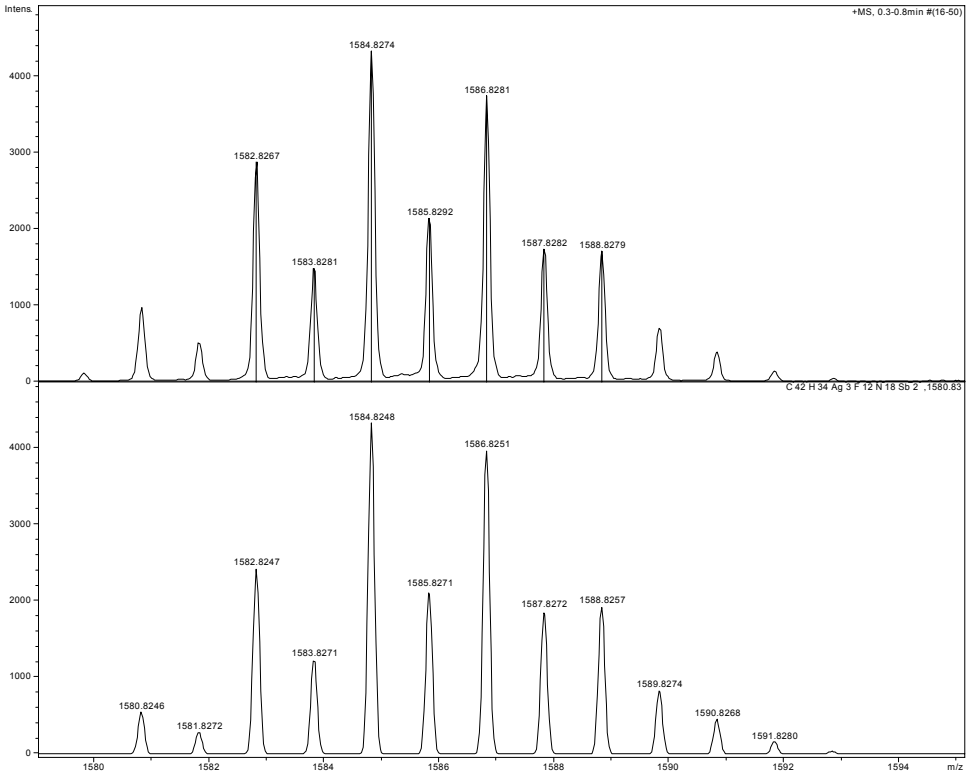


Figure 12. Observed and Calculated isotopic distribution for the $[Ag_3(\mathbf{7b})_2](SbF_6)_2^+$ ion.

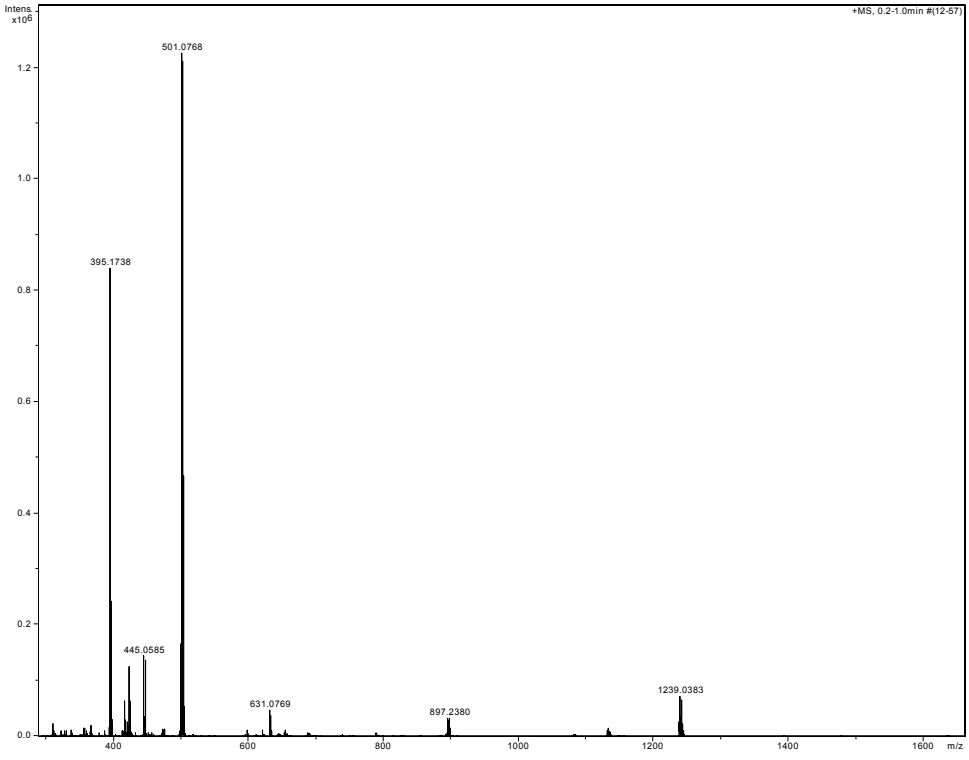


Figure 13. HR-ESMS (DMSO/CH_3CN): m/z = 1239.0291 $[Ag_2(\mathbf{7c})_2](SbF_6)^+$) (calc. for $C_{44}H_{36}Ag_2F_6N_{16}Sb$ 1239.0349), 897.2317 $[Ag(\mathbf{7c})_2]^+$) (calc. for $C_{44}H_{36}AgN_{16}$ 897.2359), 502.0725 $[Ag_2(\mathbf{7c})_2]^{2+}$ (calc. for $C_{44}H_{36}Ag_2N_{16}$ 502.0700), 501.0721 $[Ag(\mathbf{7c})]^+$ (calc. for $C_{22}H_{18}AgN_8$ 501.0700), 395.1717 $[L+H]^+$,

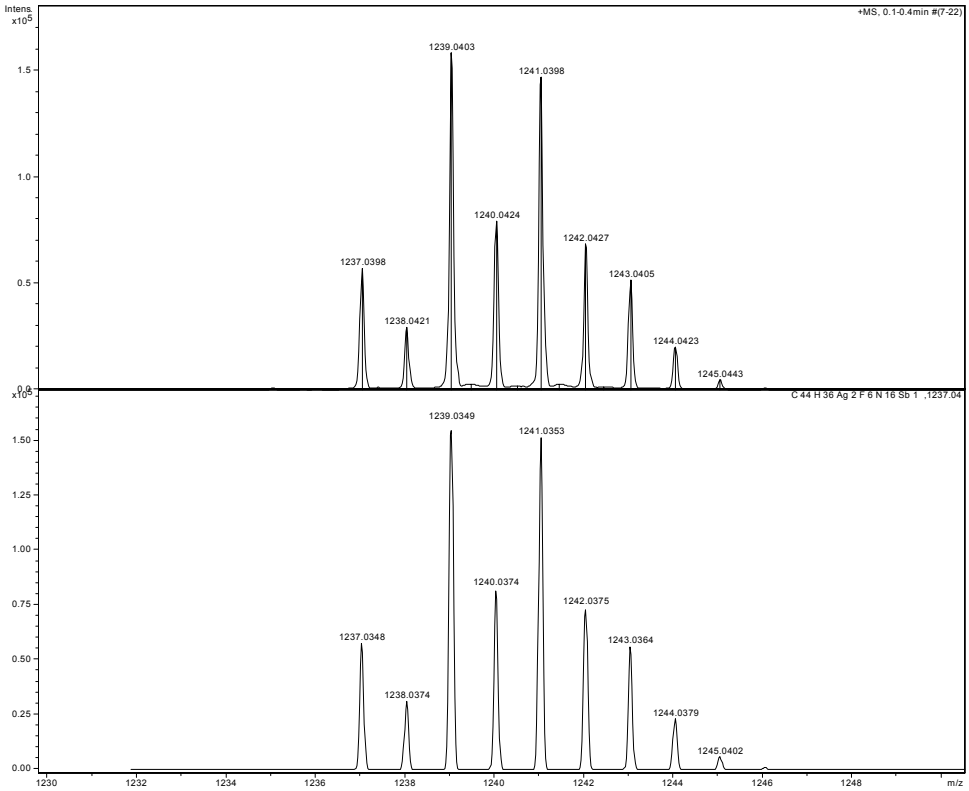


Figure 14. Observed and Calculated isotopic distribution for the $[Ag_3(\mathbf{7a})_2](SbF_6)_2^+$ ion.

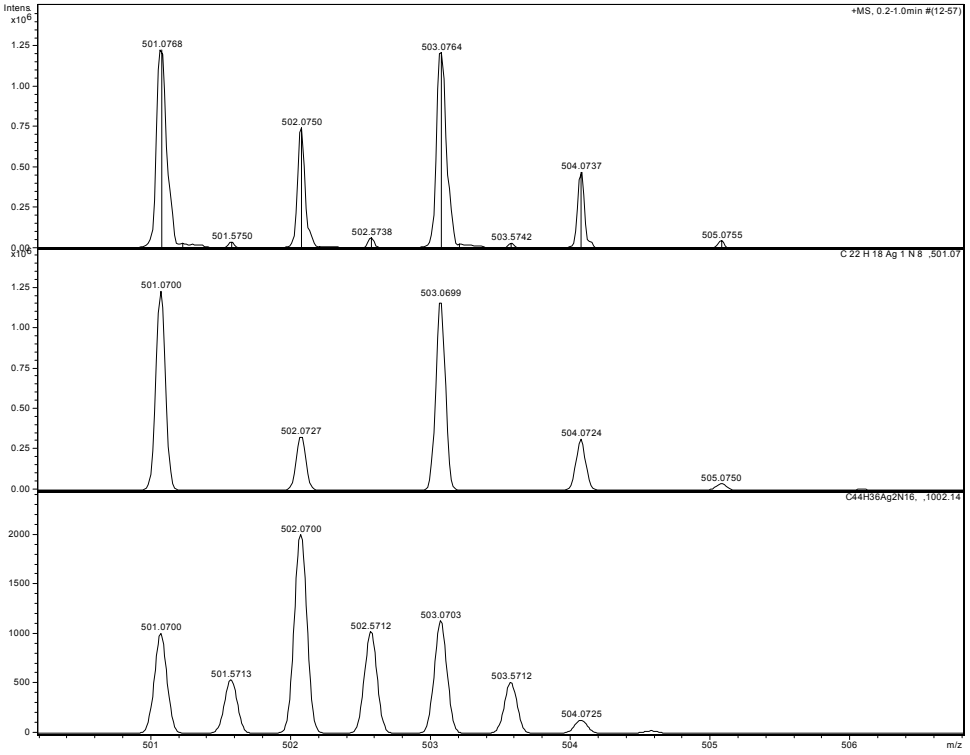


Figure 15. Observed and Calculated isotopic distribution for the $[Ag(\mathbf{7a})]^+$ and $[Ag_2(\mathbf{7a})_2]^{2+}$ ions.

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