$(C^{\wedge}N^{pz}{\wedge}C)Au^{III}$ complexes of acyclic carbene ligands decorated with amino esters: synthesis and anticancer properties

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Supporting Information

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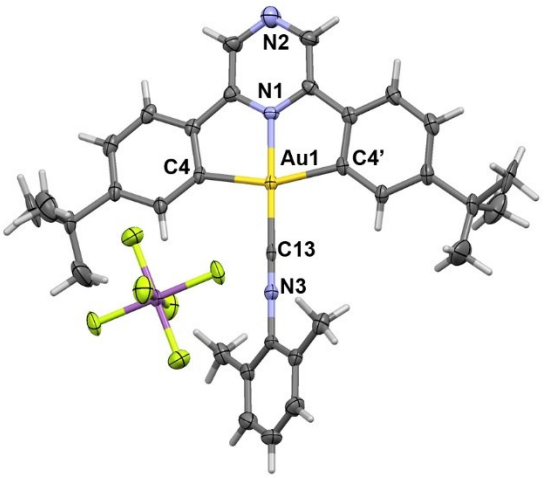

Figure S1a: Crystal structure of complex **2**. Ellipsoids set at 50% probability. Selected bond distances (Å) and angles (°): Au1-N1 1.975(4), Au1-C4 2.113(4), Au1-C13 1.992(6), C13-N3 1.124(7), C4-Au1-N3 80.31(11), C4-Au1-C13 99.69(11), Au1-C13-N3 180.

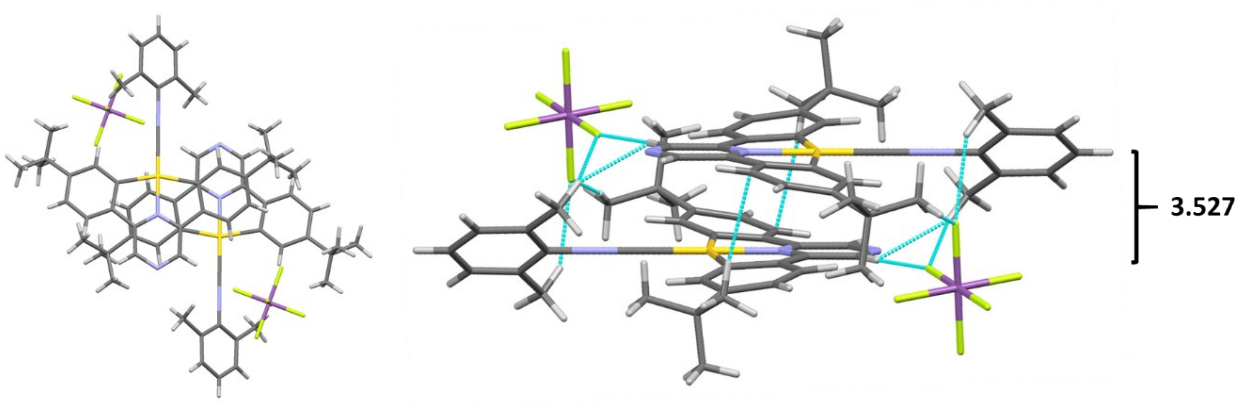

Figure S1b. Different views of the crystal packing of complex **2**. The packing shows the presence of dimers through the accommodation of π···π interactions between the pyrazine ring of the C^N^{pz}^C ligand of one molecule and one aryl ring of the neighboring molecule and *viceversa*. The SbF_6 anions form F···H interactions with both dimerized molecules contributing to stabilize the dimer.

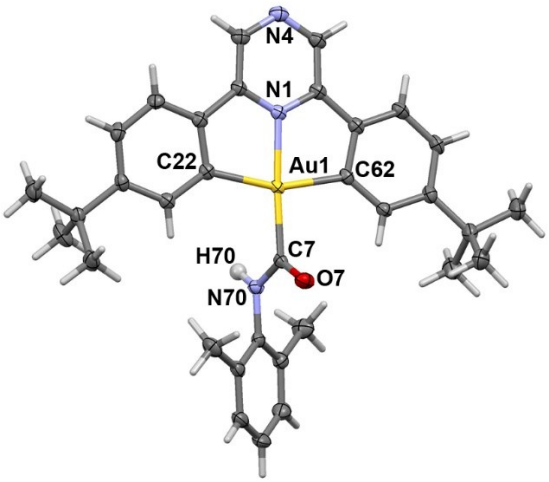

Figure S2a: Crystal structure of complex **3**. Ellipsoids set at 50% probability. Selected bond distances (Å) and angles (°):Au1-N1 2.0396(15), Au1-C7 2.0251(18), Au1-C22 2.0957(19), Au1-C62 2.0756(19), C7-N70 1.365(2), C7-Au1-N1 176.18(7), C7-Au-C62 97.15(7), N1-Au1-C62 80.21(7) , C7-Au1-C22 102.83(7), N1-Au1-C22 79.86(7), C62-Au-C22 160.01(7).

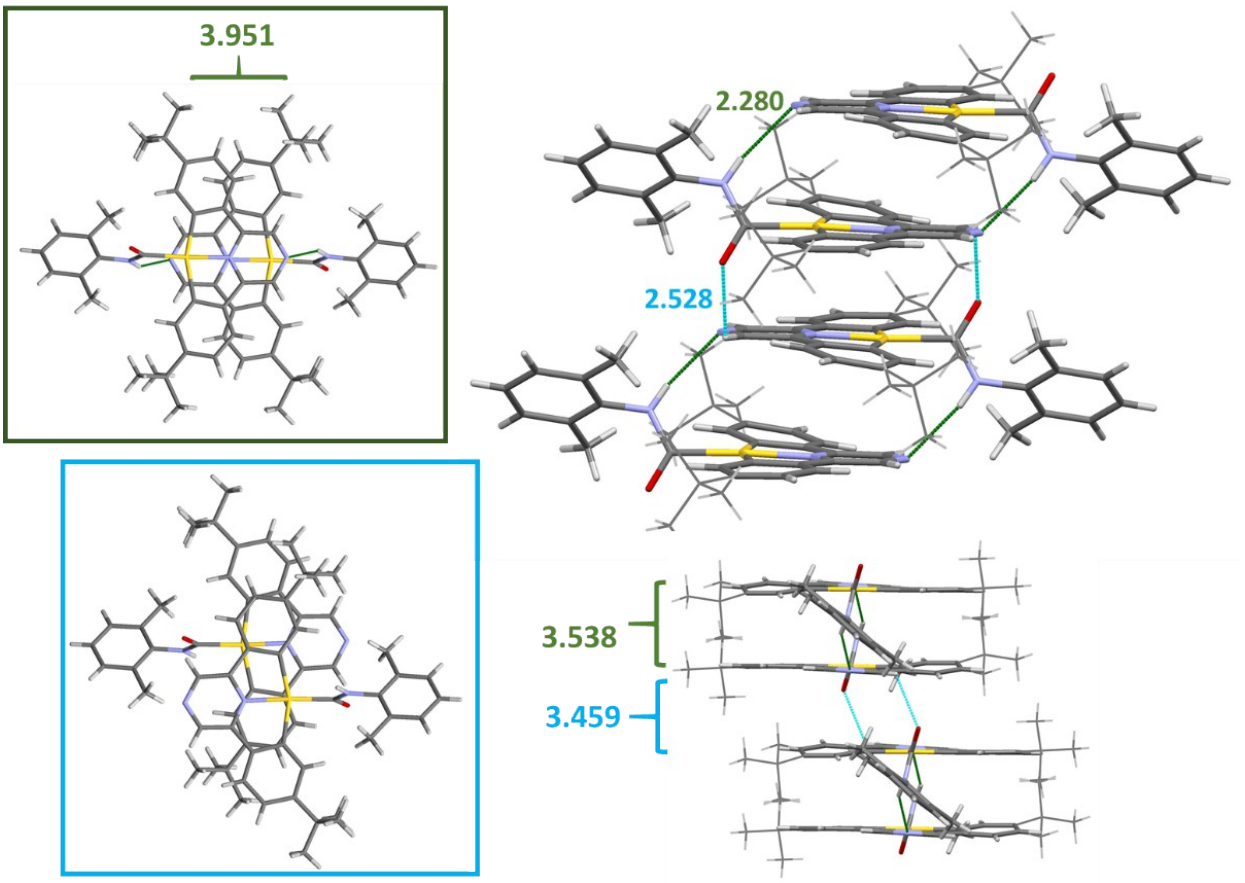

Figure S2b: Different views of the crystal packing of complex **3**. Each molecule interacts with one neighboring molecule through a double 2,6-diMePhNH···N^{pz} interaction (2.280 Å), and with another neighboring molecule through a double 2,6-diMePhNHCO···H(pyrazine) (2.528 Å) interaction. Two different intermolecular interactions are found in the rods thus formed: The molecules pack in a tail-to-tail disposition with average intermolecular distance of 3.538 Å and a displacement of 3.951 Å between Au centers to accommodate the 2,6-diMePhNH···N^{pz} interactions, while the 2,6-diMePhNHCO···H(pyrazine) interactions produce a closer accommodation of the molecules between them (3.459 Å) with the aryl ring of the C^N^{pz}^C ligand of one molecule on top of the 5 member Au$N^{pz}C_3$ metallacycle of the other, and *viceversa*.

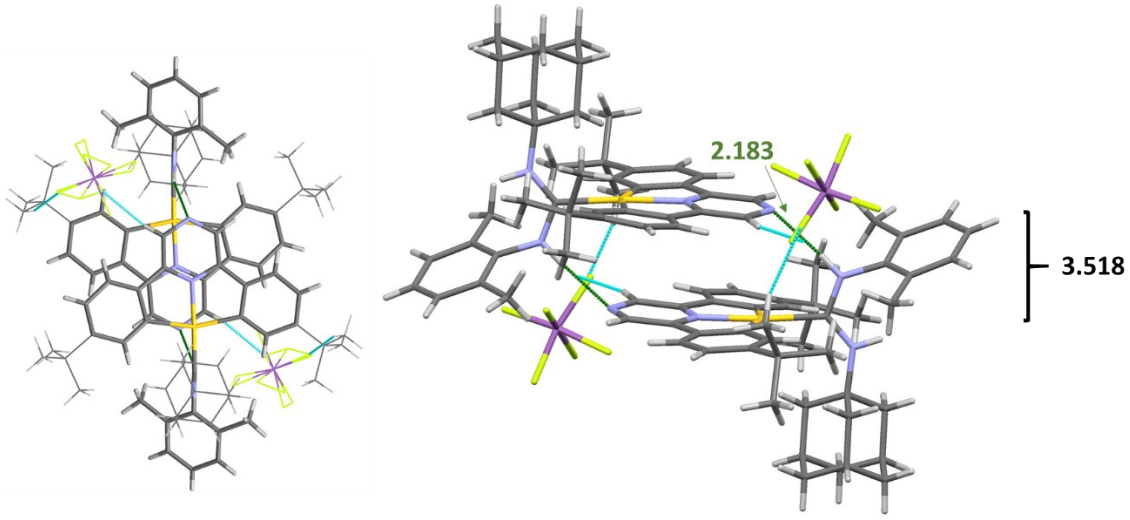

Figure S3: Different views of the crystal packing of complex **5**·1.5 C_7H_8. The packing shows the presence of dimers through the accommodation of two 2,6-diMePhNH···N^{pz} interactions (2.183 Å). The dimer is stabilized by the formation of F···H interactions with the SbF_6 anions.

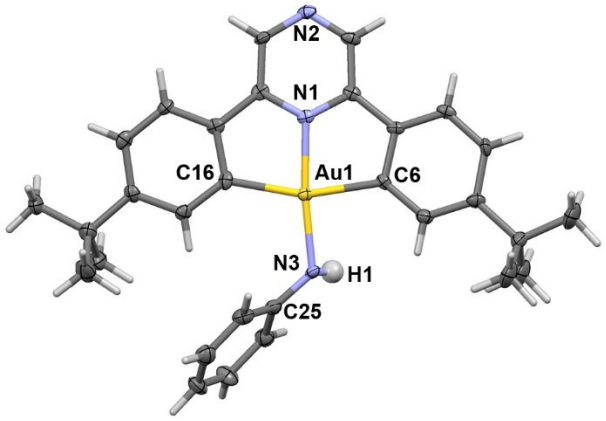

Figure S4a: Structure of **11a**. Ellipsoids set at 50% probability. Selected bond distances (Å) and angles (°): Au-N1 2.001(4), Au-C6 2.072(5), Au-C16 2.094(5), Au-N3 2.022(4), N1-Au-C6 80.43(17), N1-Au-C16 80.69(18), C6-Au-N3 93.54(18), C16-Au-N3 105.31(18), Au-N3-C25 126.1(3).

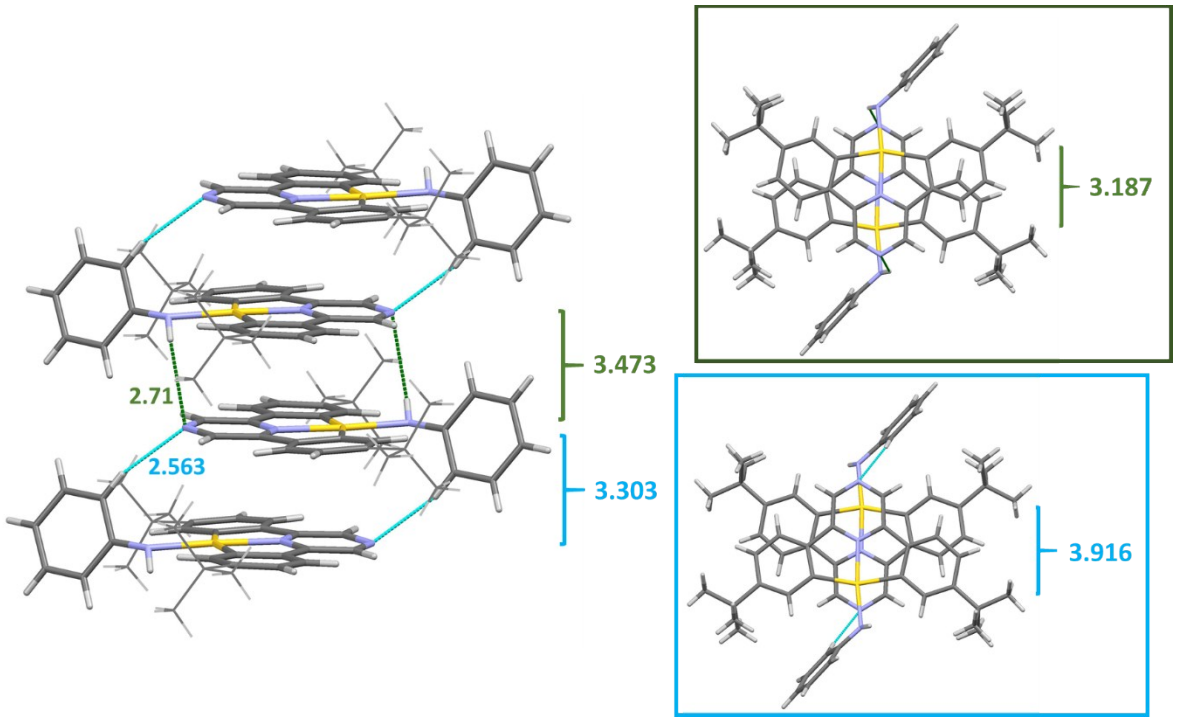

Figure S4b: Different views of the crystal packing of compound **11a**. The crystal shows the formation of rods due to the formation of H···N^{pz} bonds. Each molecule interacts with one neighboring molecule through a double PhNH···N^{pz} interaction (2.71 Å), and with other neighboring molecule through a double *o*-H (Ph ring of the aniline) ·· N^{pz} (2.563 Å) interaction. Due to the accommodation of these two types of interactions two different intermolecular distances (measured from a Au center to the coordination plane of the Au center of the neighboring molecule 3.303, 3.473 Å) are found, but the relative orientation of the molecules is in both cases tail-to-tail with the Au centers on top of the pyrazine ring of the C^N^{pz}^C of the neighboring molecule (displacement of 3.187 and 3.916 Å of the Au center with respect to the projection of the Au centers of the neighboring molecules).

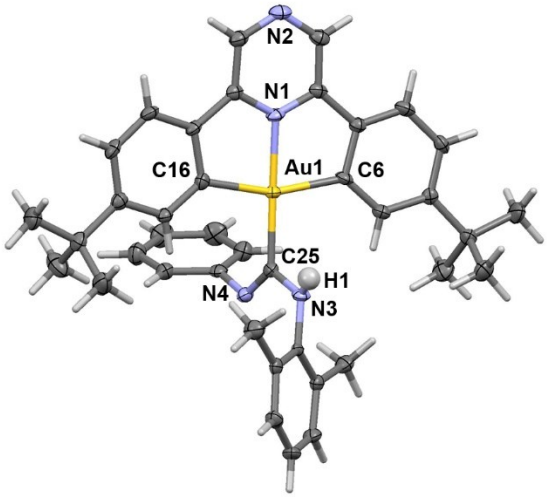

Figure S5a: Structure of **12**·C_7H_8 (Toluene molecules omitted for clarity). Ellipsoids set at 50% probability. Selected bond distances (Å) and angles (°): Au-N1 2.039(3), Au-C6 2.057(4), Au-C16 2.084(5), Au-C25 2.031(4), C25-N3 1.387(5), C25-N4 1.266(5), N1-Au-C6 80.2(1), N1-Au-C16 81.3(1), C6-Au-25 99.5(2), C16-Au-C25 99.0(2) Au-C25-N3 113.7(3), Au-C25-N4 126.1(3), N3-C25-N4 120.2(4).

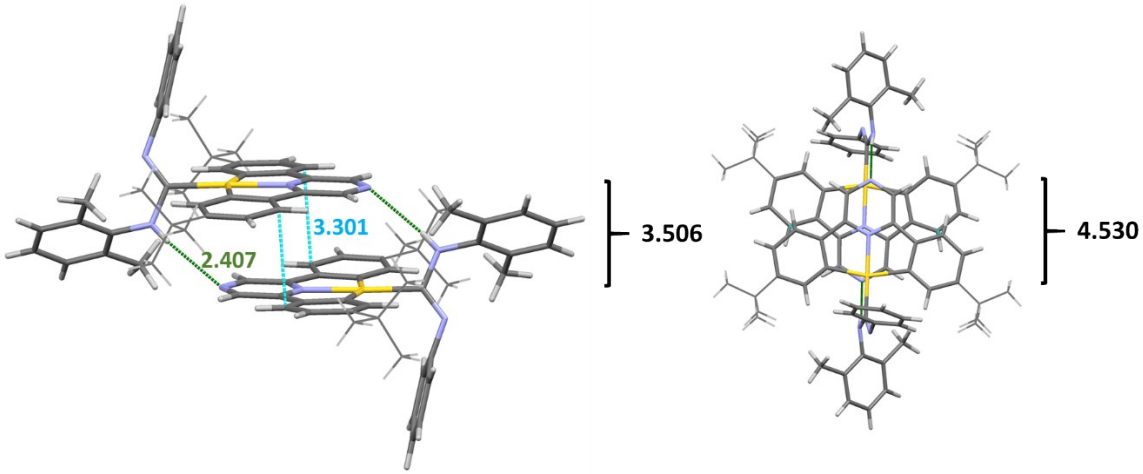

Figure S5b: Different views of the crystal packing of compound **12**·C_7H_8 (Toluene molecules omitted for clarity). The packing shows the formation of dimers in a tail-to-tail disposition, with a displacement of 4.530 Å between the Au centers. The most relevant interactions in these dimers are a double 2,6-diMePhNH···N^{pz} interaction (2.407 Å) and a π···π double interaction between carbon atoms of the cyclometallated ligand (3.301 Å).

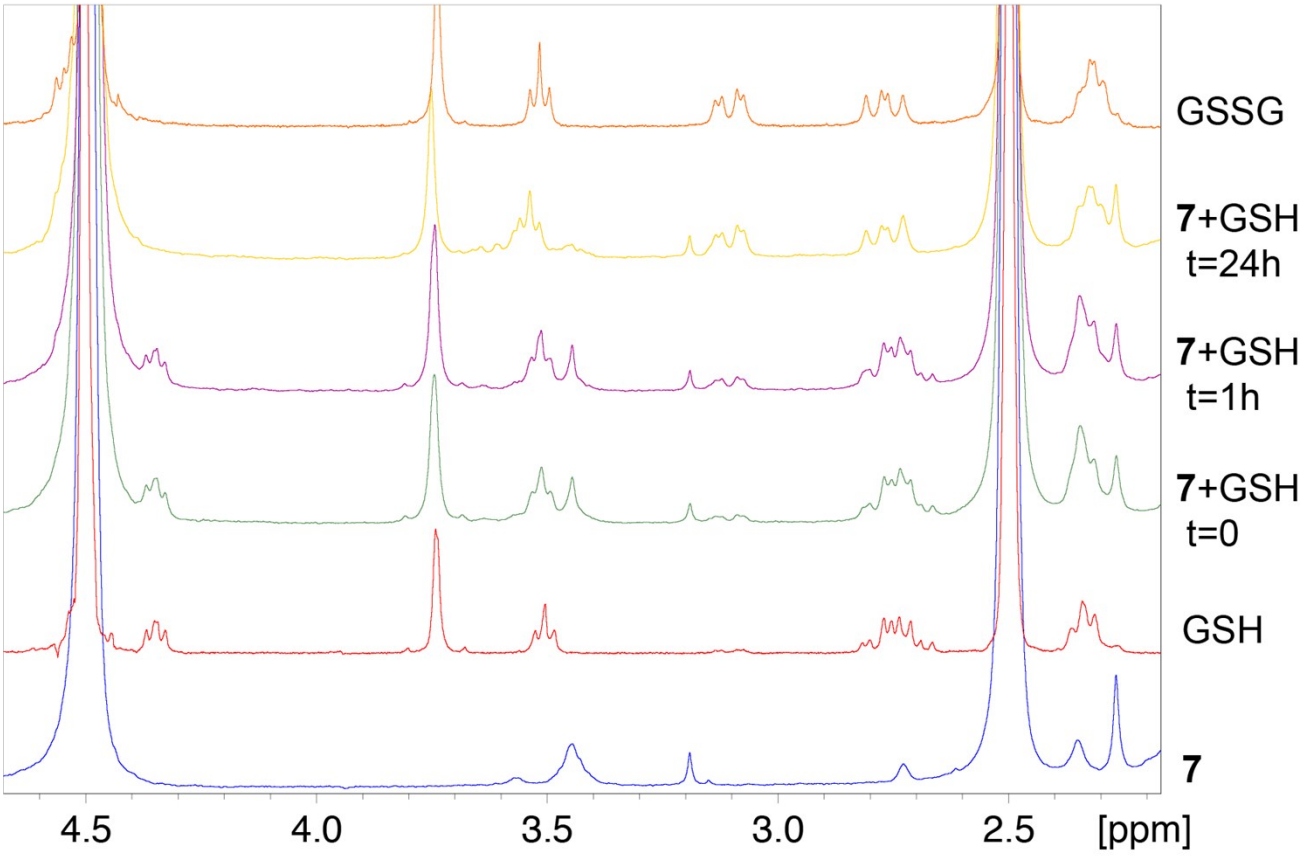

Figure S6: ^{1}H NMR spectra in deuterated DMSO/D_2O (1/1) of a 1/1 mixture of compound **7** with GSH after different reaction times at room temperature and compared with the starting materials **7** and GSH and GSSG.

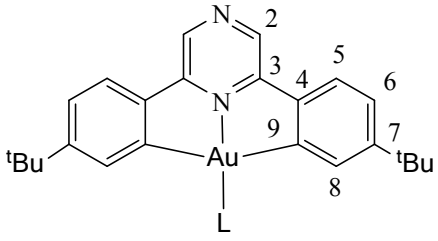

Figure S7: Numbering of the positions for NMR assignment.

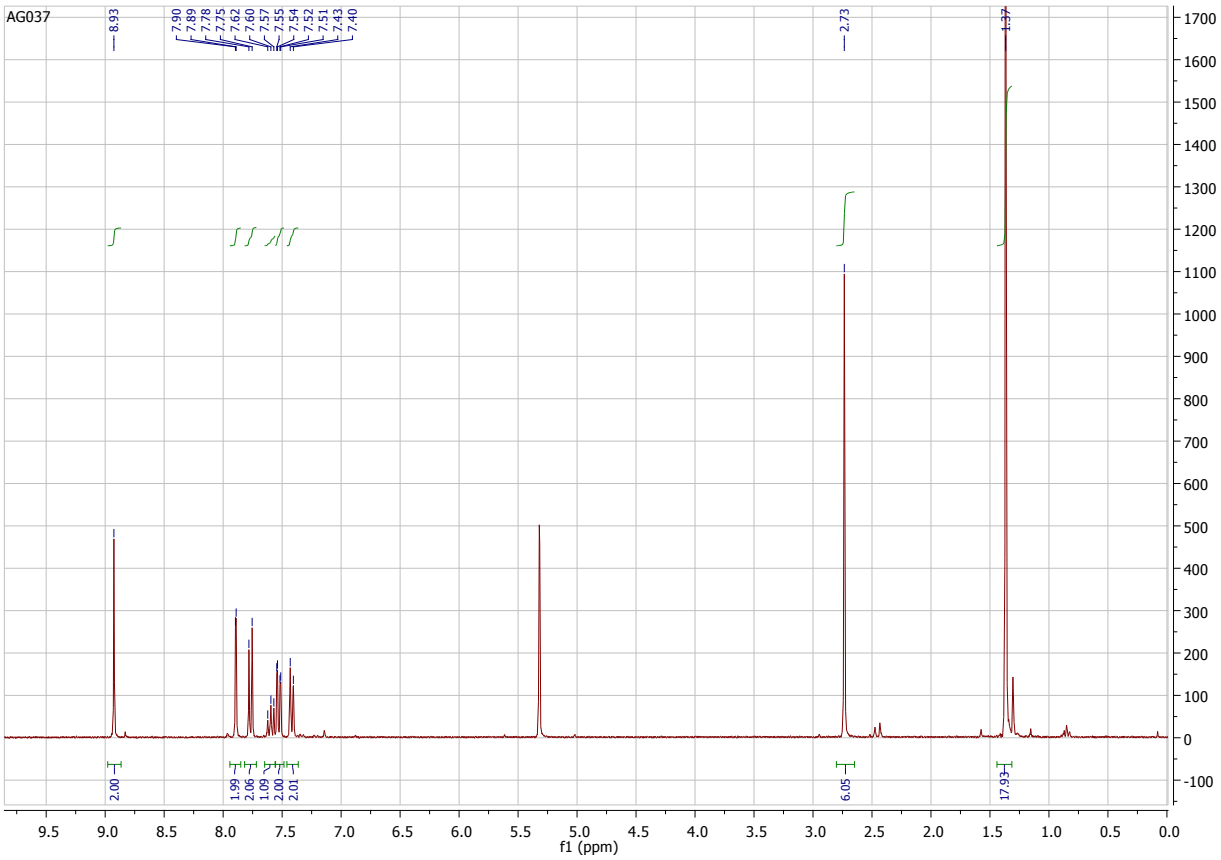

Figure S8: ^{1}H NMR spectrum of compound **2** in CD_2Cl_2

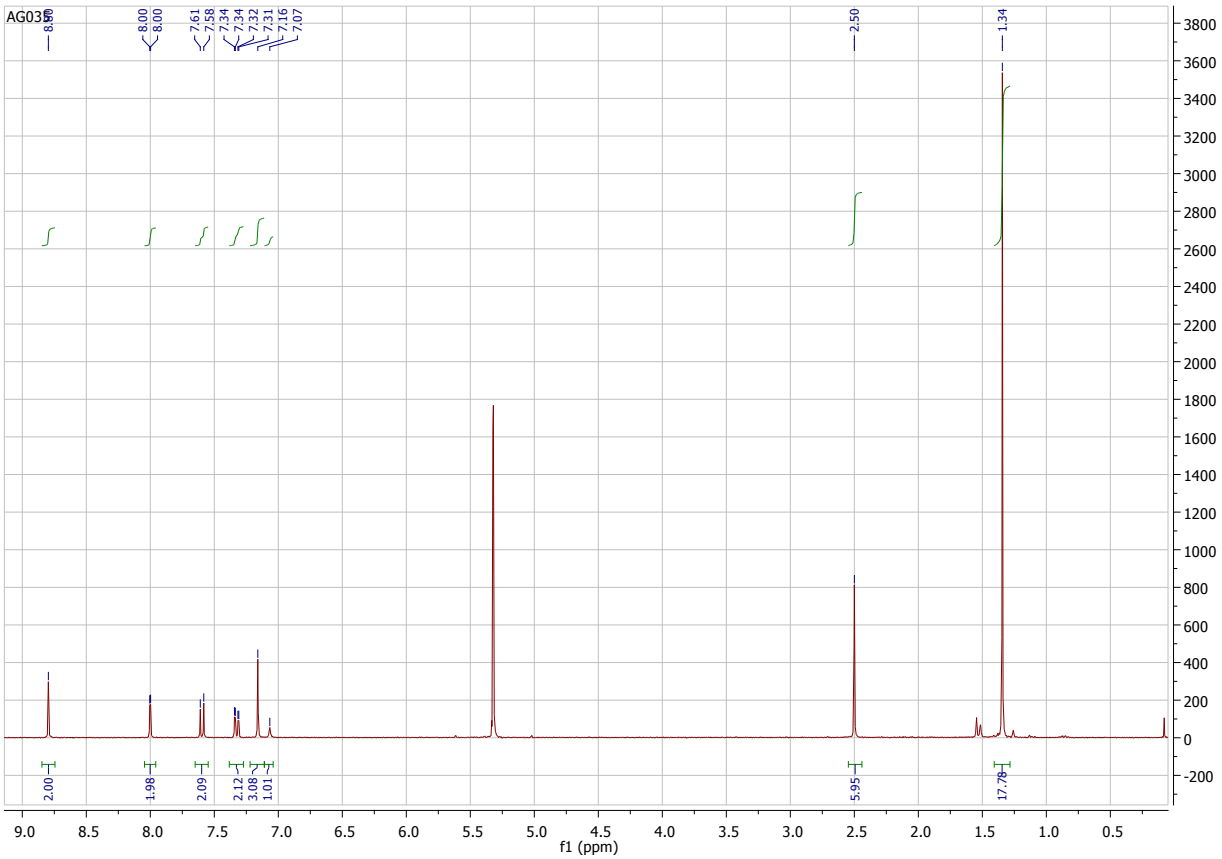

Figure S9: ^{1}H NMR spectrum of compound **3** in CD_2Cl_2

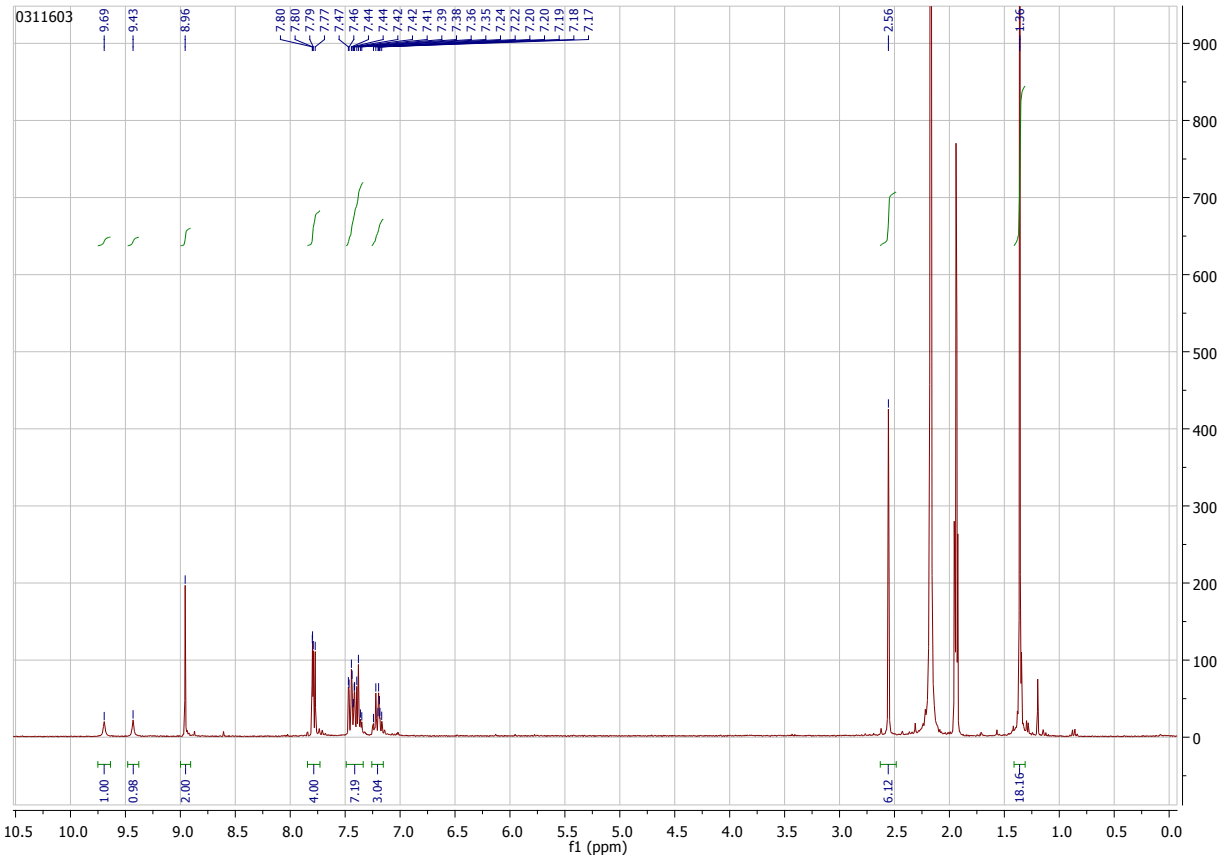

Figure S10: ^{1}H NMR spectrum of compound **4.SbF$_6$** in CD_3CN

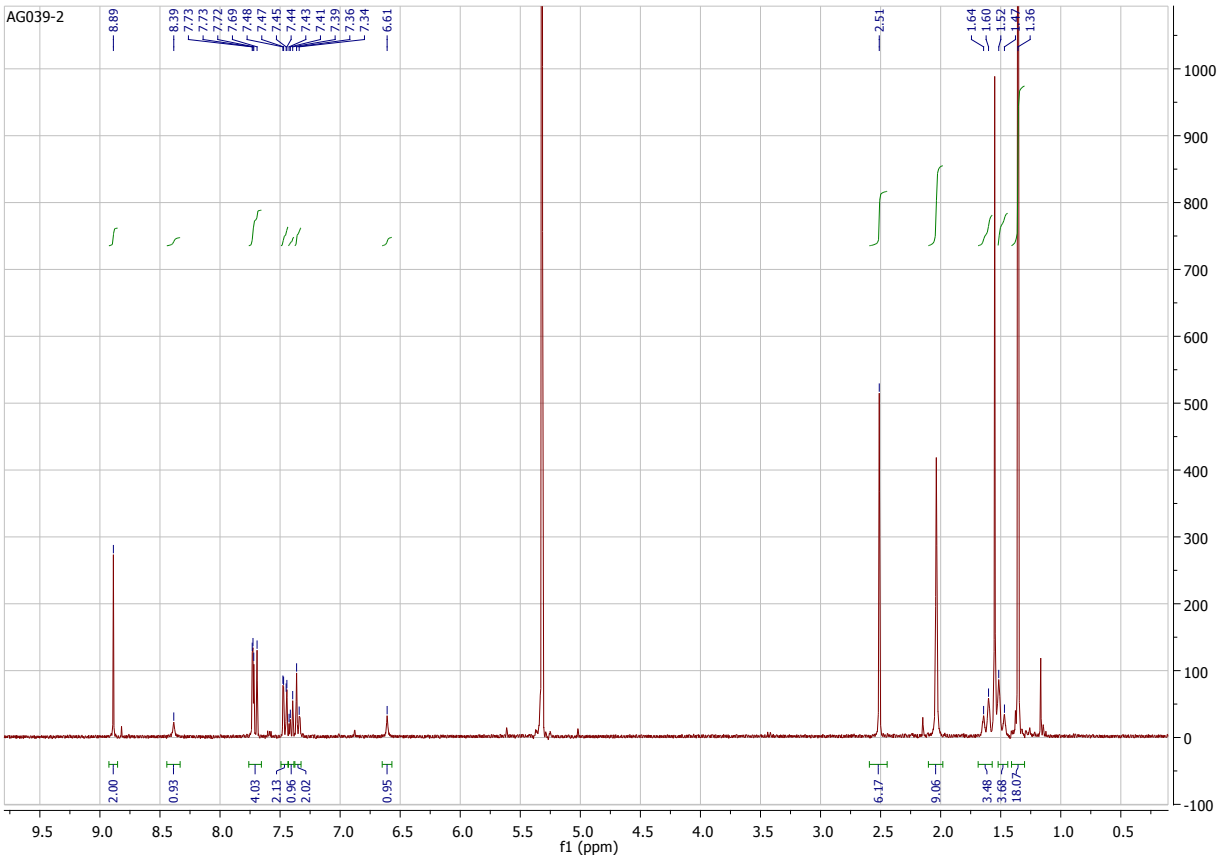

Figure S11: ^{1}H NMR spectrum of compound **5** in CD_2Cl_2

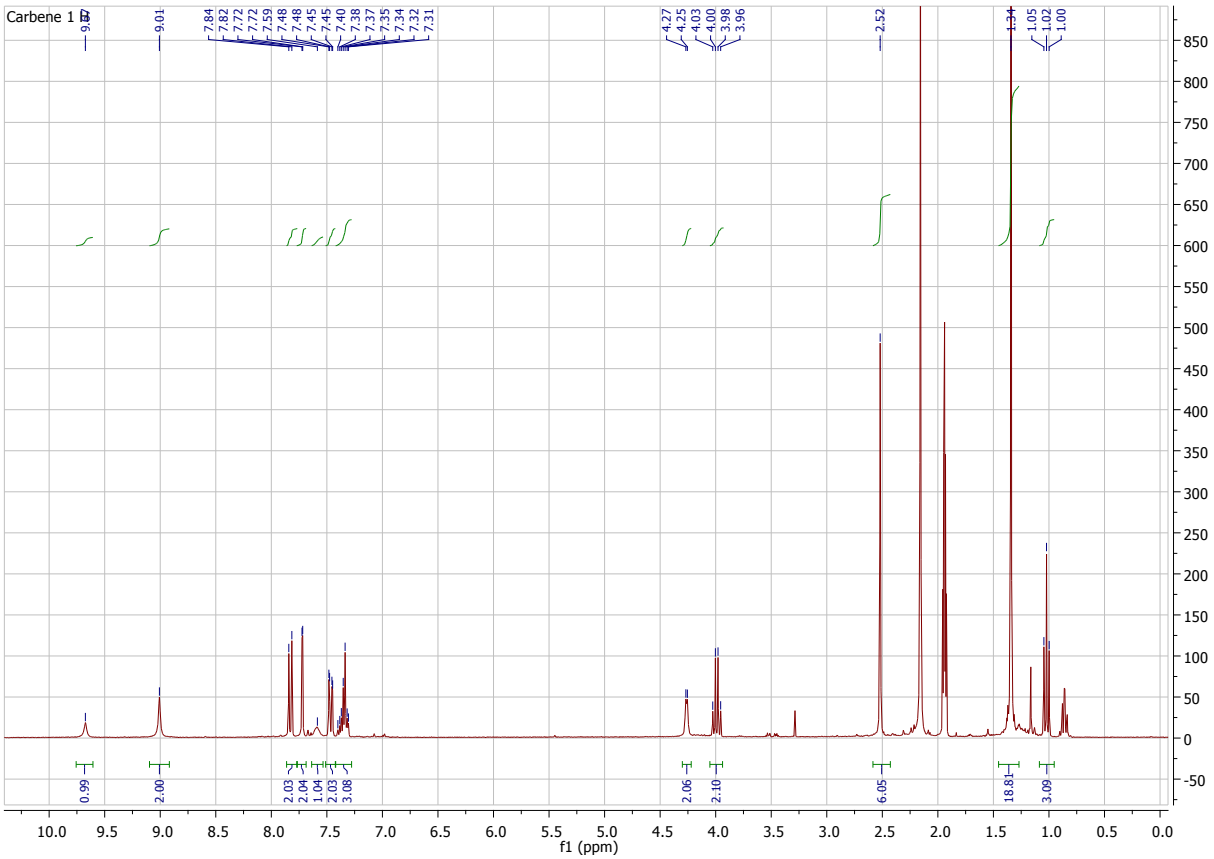

Figure S12: ^{1}H NMR spectrum of compound **6** in CD_3CN

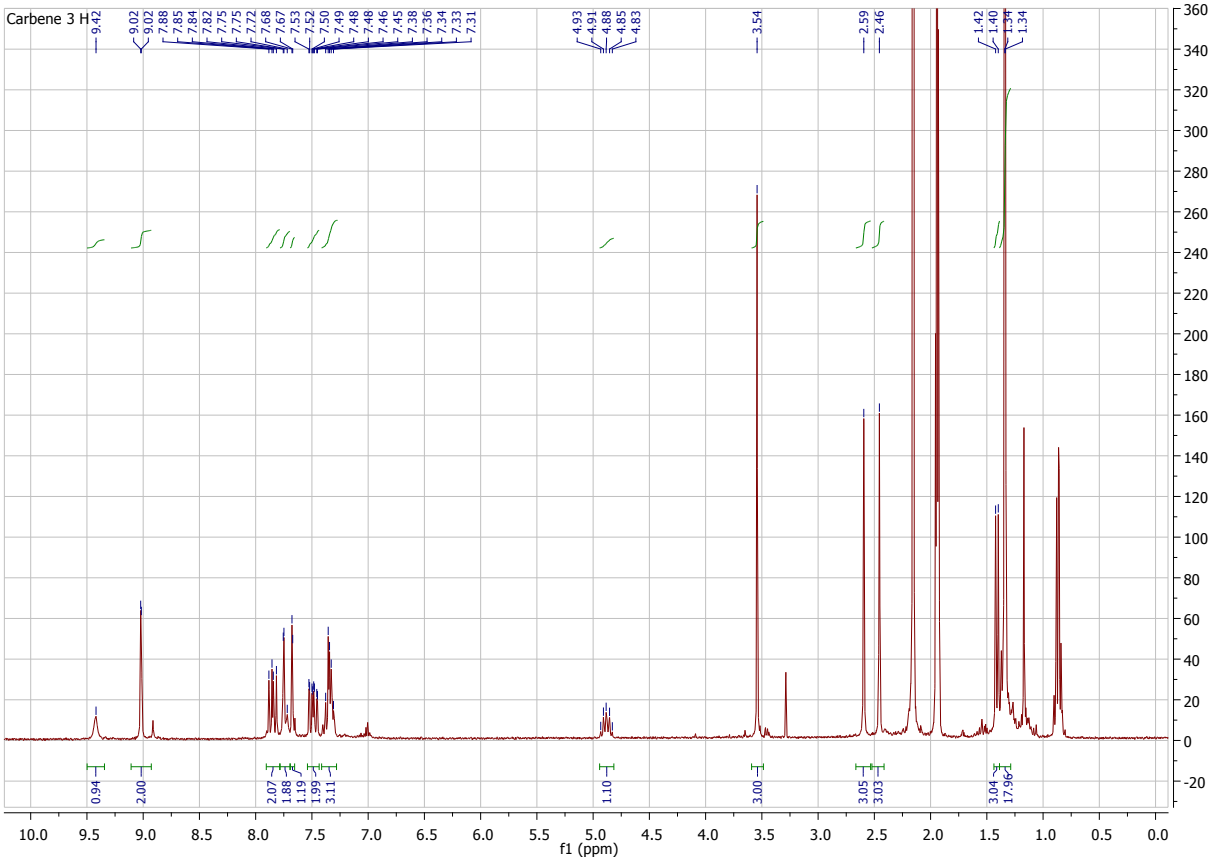

Figure S13: ^{1}H NMR spectrum of compound **7** in CD_3CN

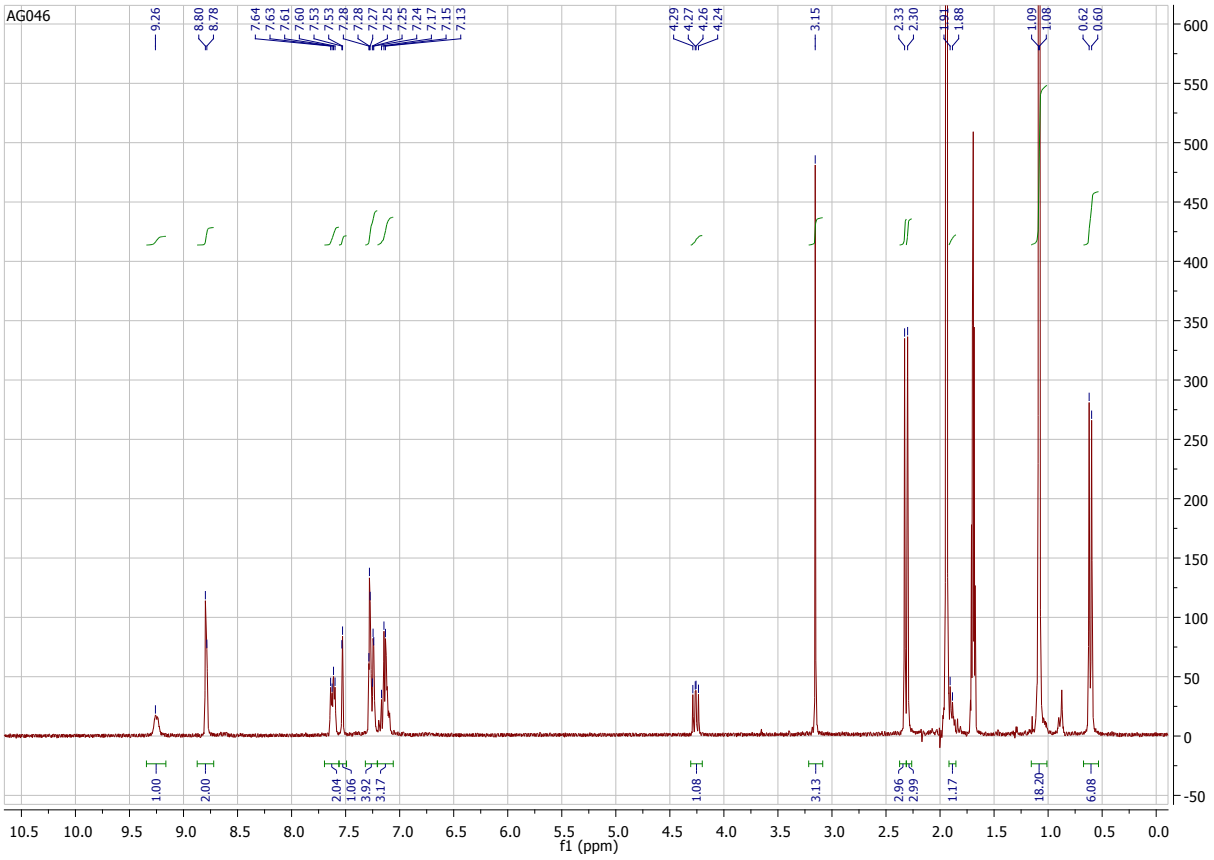

Figure S14: ^{1}H NMR spectrum of compound **8** in CD_3CN

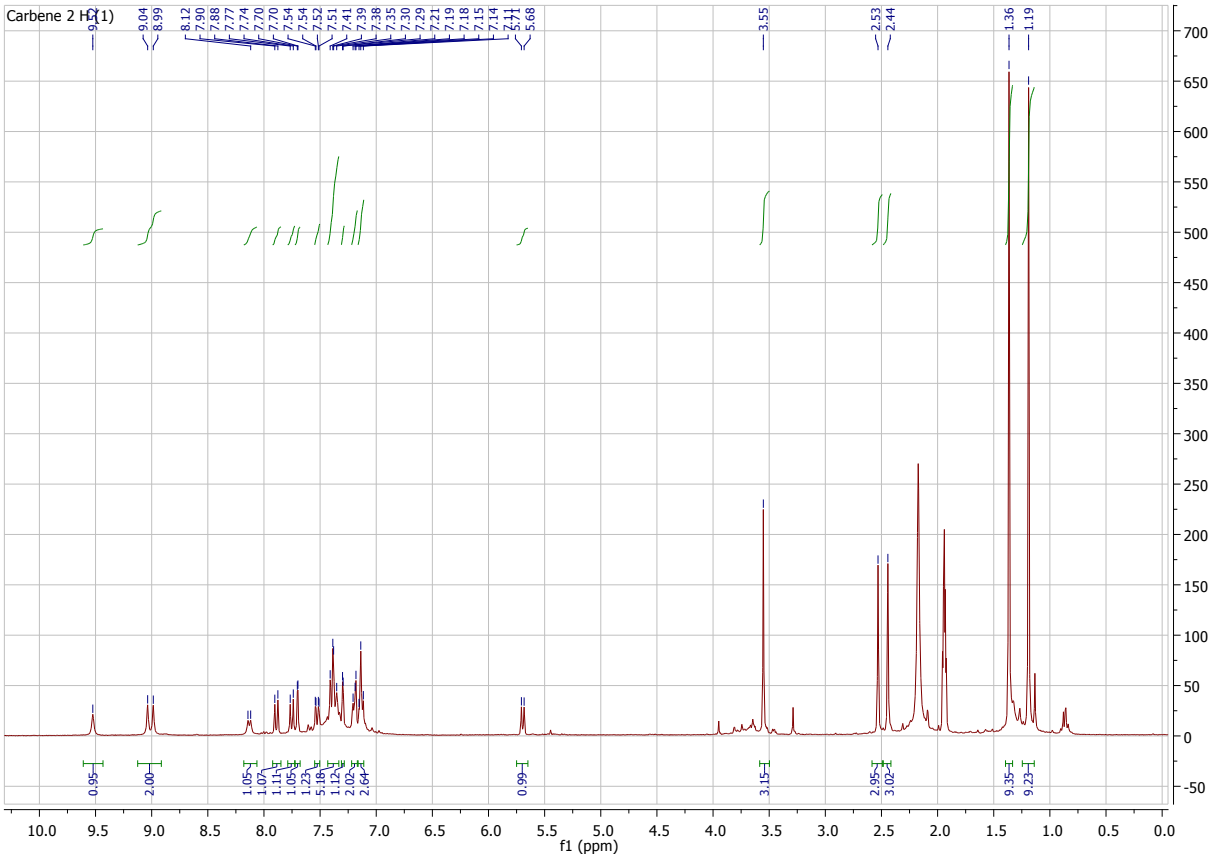

Figure S15: ^{1}H NMR spectrum of compound **9** in CD_3CN

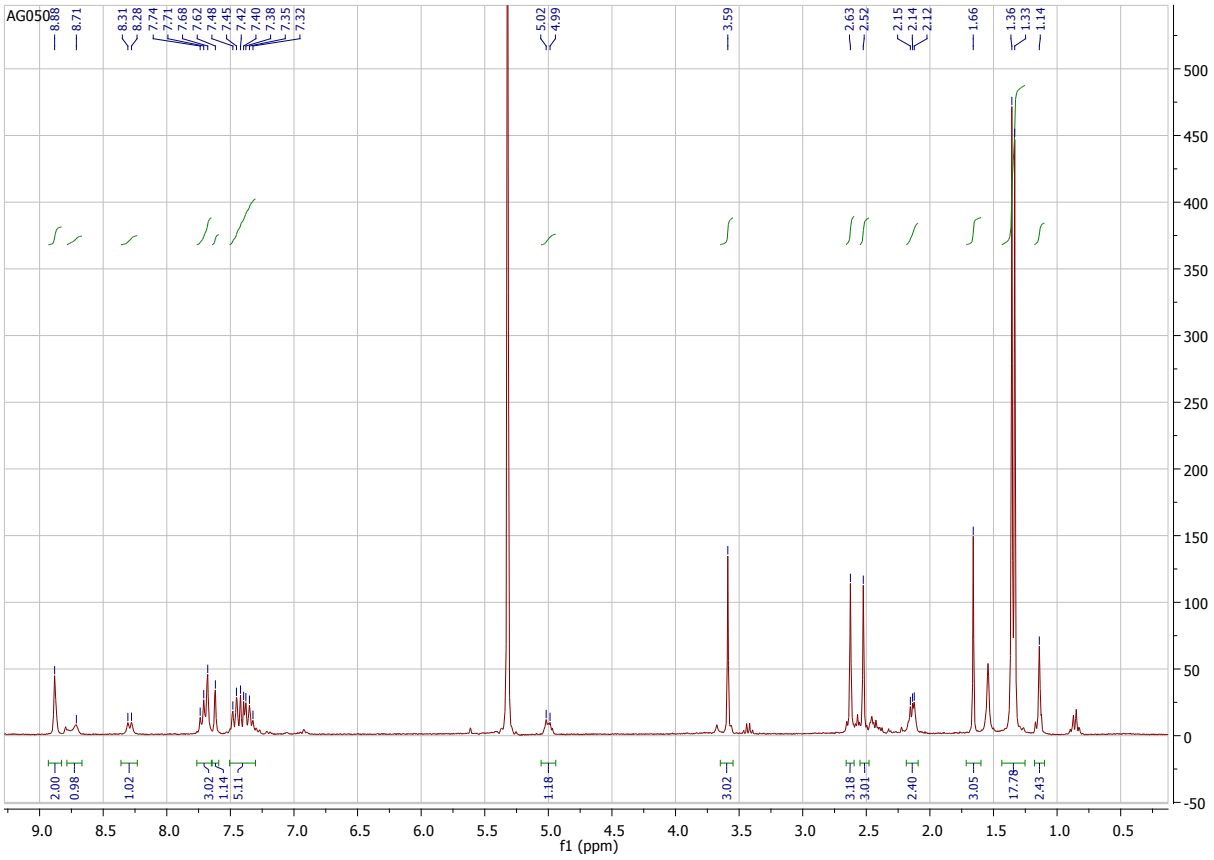

Figure S16: ^{1}H NMR spectrum of compound **10** in CD_2Cl_2

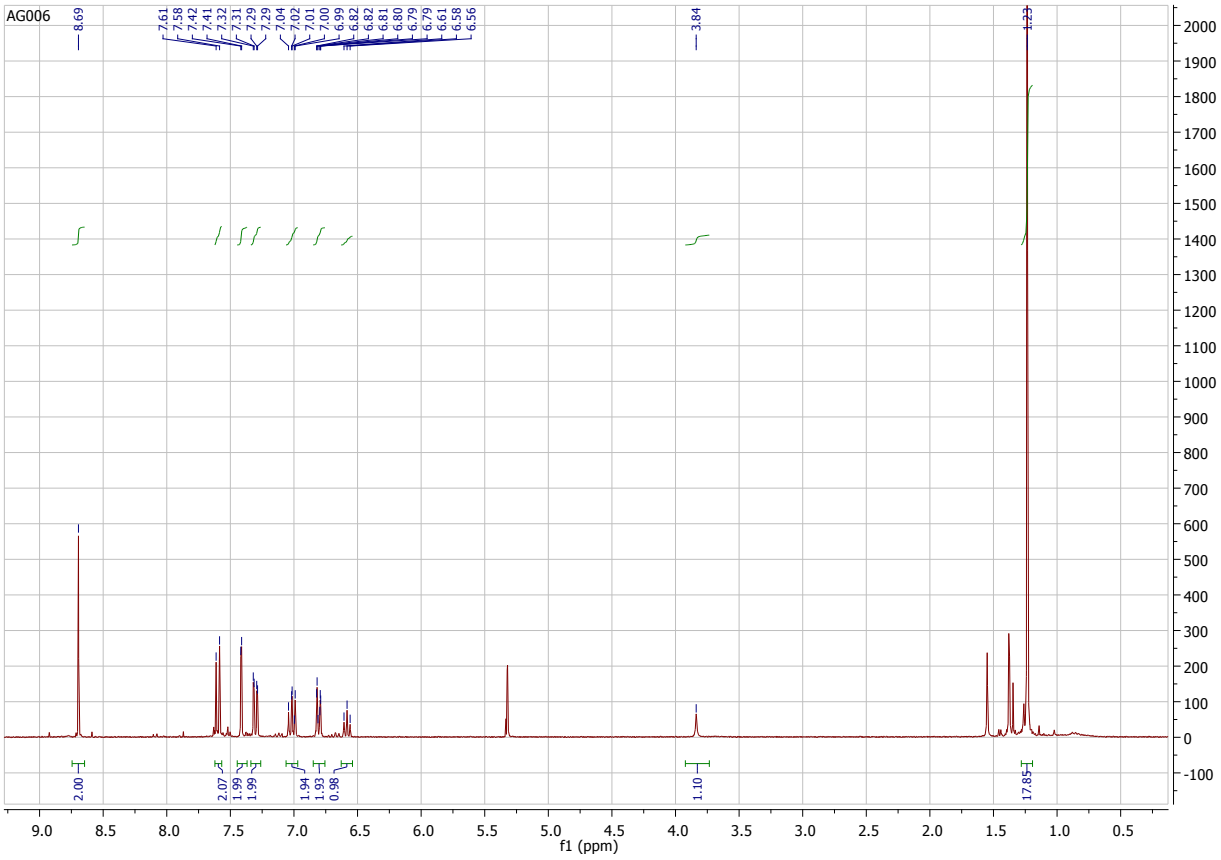

Figure S17: ^{1}H NMR spectrum of compound **11a** in CD_2Cl_2

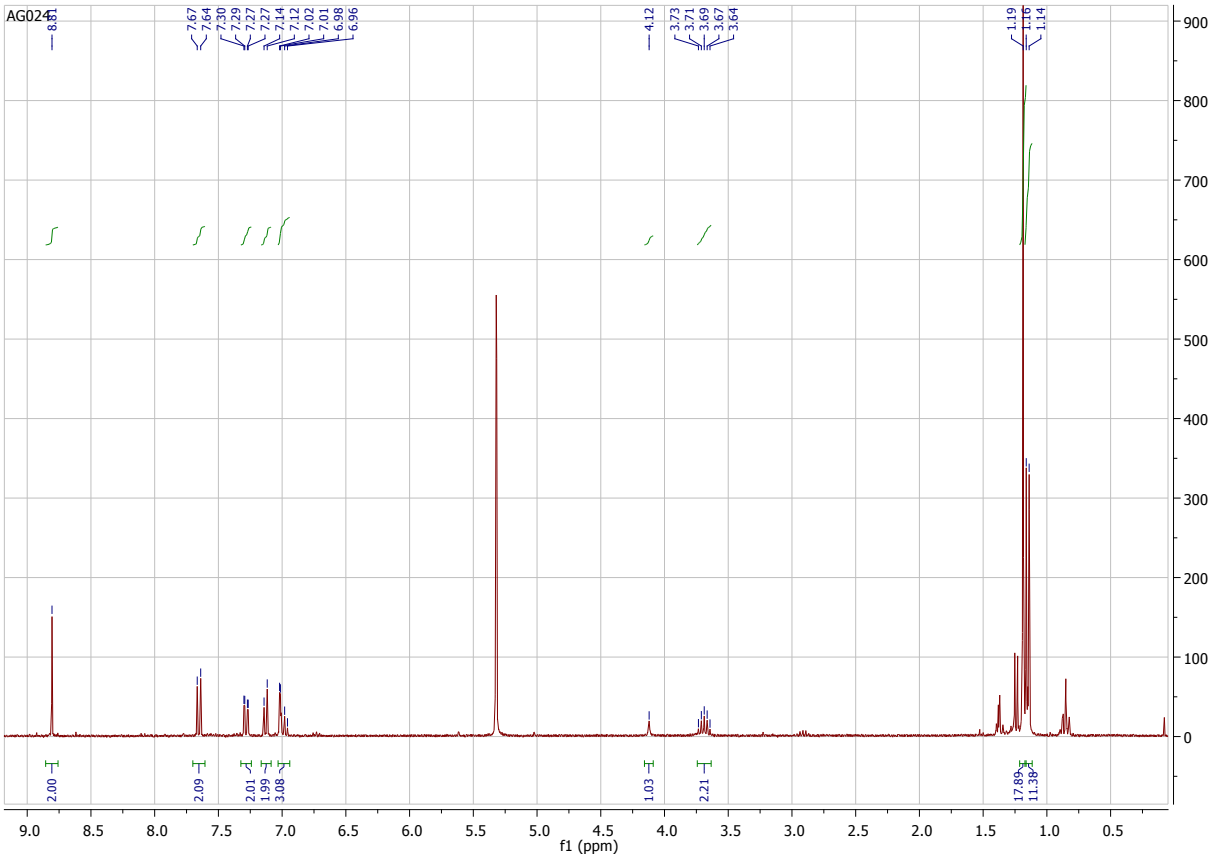

Figure S18: ^{1}H NMR spectrum of compound **11b** in CD_2Cl_2

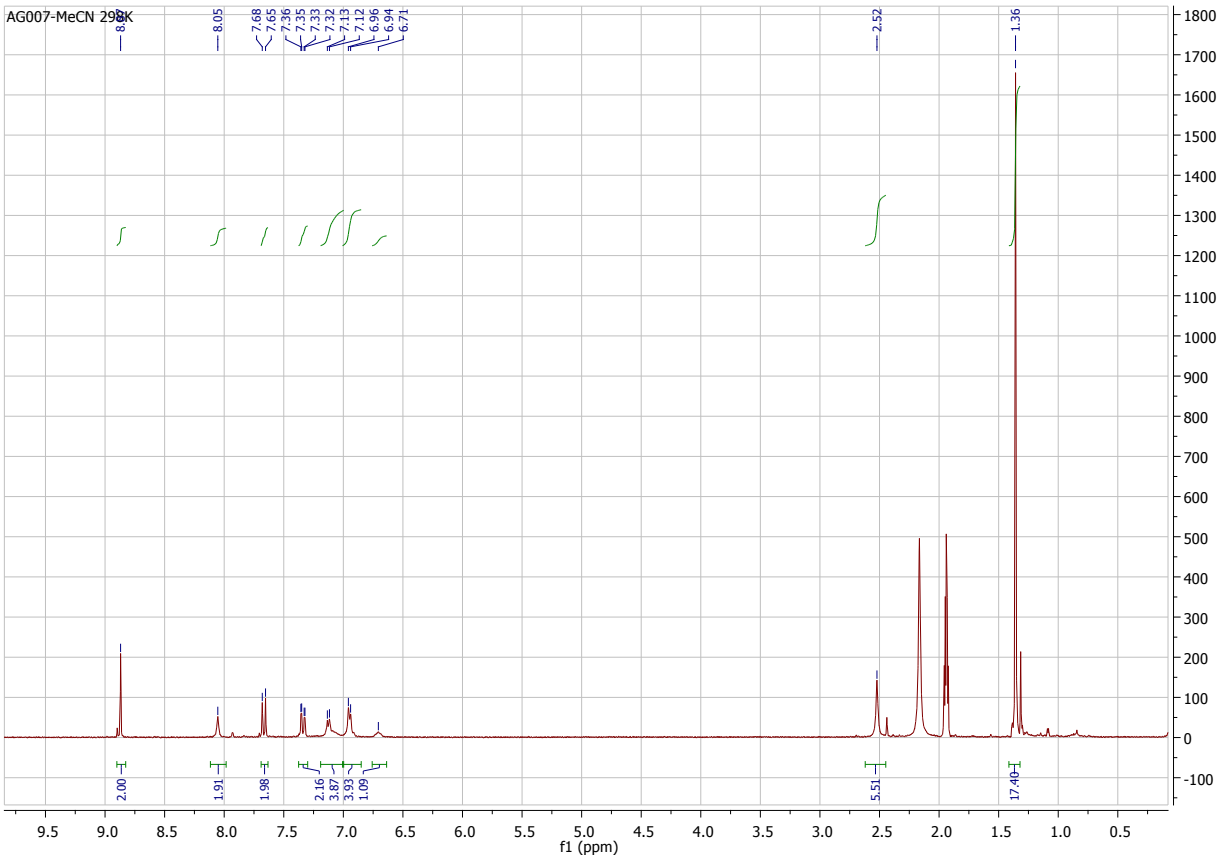

Figure S19: ^{1}H NMR spectrum of compound **12** in CD_3CN

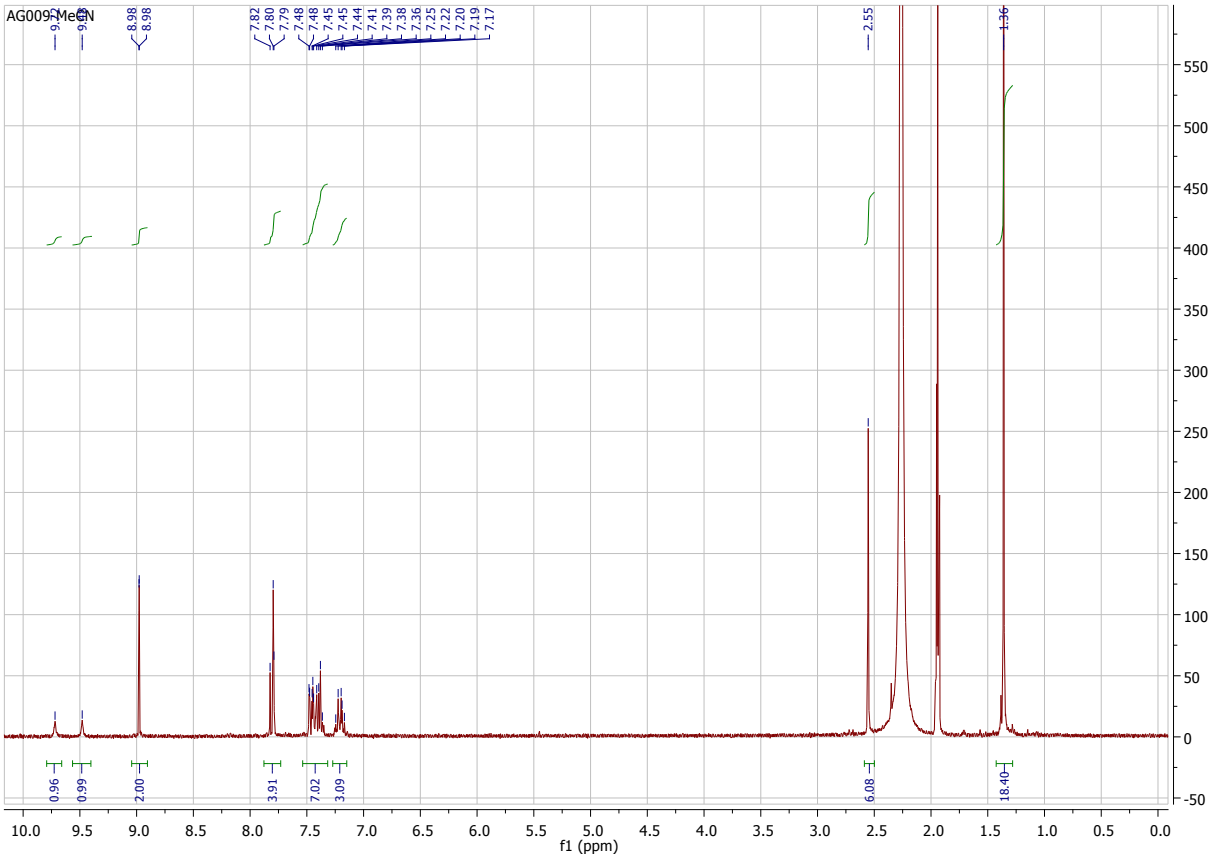

Figure S20: ^{1}H NMR spectrum of compound **4.BF$_4$** in CD_3CN