Supplementary Information

Triaza-adamantyl *N*-heterocyclic carbenes (NHC-TA) water-soluble ligands and silver complexes.

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General procedures and characterization techniques

All operations were performed in a fume hood under either air or argon atmosphere using standard Schlenk techniques, when required, dry solvents were dried using an MBraun-Solvent Purification System and deoxygenated prior to use. Alternatively, solvents and other chemicals were dried and purified as described elsewhere [1]. Unless otherwise stated, chemicals were used as received from commercial sources. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV water purification system. Argon N-50 (O_2 and H_2O < 3 ppm) and other gases were purchased from Abelló-Linde. NMR spectra were recorded at room temperature (25 ºC) using Varian Mercury Plus-300, Bruker 400 Ultrashield

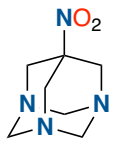
or Varian NMR System 500 spectrometers. When required, mono-dimensional ^{1}H selective excitation, NOE 1D, and two-dimensional ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC, or ^{1}H,^{1}H-COSY experiments were performed for unequivocal assignment of resonances for the new ligands, precursors or complexes. The ^{15}N and ^{109}Ag resonance frequencies were determined by indirect detection via ^{1}H,^{15}N- and ^{1}H,^{109}Ag-HMBC experiments, respectively. In the latter case, the experiments were carried out at 233 K and with a pulse optimized for a coupling constant of 1.2 Hz. Chemical shifts (δ, parts per million) are quoted relative to $SiMe_4$, and were measured by internal referencing to residual signals of the deuterated solvents (DMSO-d_6, ^{1}H: δ 2.50 and ^{13}C: δ 39.52; D_2O, ^{1}H: δ 4.79; CD_3OD, ^{1}H: δ 3.31 and ^{13}C: δ 49.00; CD_2Cl_2, ^{1}H: δ 5.32 and ^{13}C: δ 53.84), and in the case of ^{15}N and ^{109}Ag were referenced using $NH_{3(liq)}$ and $AgNO_{3(aq)}$ as external standard, respectively. Coupling constants (J) are given in Hertz. The abbreviations Mes, TA py and Imz used here refer to mesityl and triazaadamantyl groups, and pyridinic and imidazolic heterocycles, respectively. Elemental analysis (C, H, N,) and high-resolution ESI/TOF mass spectra were conducted at the Chemical Research Support Center of the University of Alcalá in a LECO CHNSO 932 elemental analyzer and in a Triple TOF 5600 plus Sciex mass spectrometer, respectively. 7-Nitro-1,3,5-triazaadamantane [2] and 1,3,5-triazaadamantan-7-amine [3] were prepared by adapting reported procedures as described in the following section. Water solubility was assessed by placing an accurately weighed 1 g of the compound (balance readability: 0.1 mg) in a vial followed by the slow addition of water *via* a 2±0.05 mL syringe with stirring.

The numbering in the figure for some compound below is for NMR assignment purposes only. They are not intended to be locants.

Synthesis of ligands and precursors

7-Nitro-1,3,5-triazaadamantane [2]

Hexamethylenetetramine (70 g, 0.50 mol) is suspended in 250 mL of 80% ethanol in a 500 mL round bottom flask and stirred at 80 ºC for 5 min. Formic acid (22 mL, 0.59 mol) and nitromethane (27 mL, 0.50 mol) are added, and the mixture is stirred for 4 h. The solution turns from colorless to yellowish that intensifies to orange as the reaction progresses. The flask is then brought to room temperature and cooled overnight at 5 ºC. The resulting orange suspension is centrifugated and the solid washed several times with H_2O and cold EtOH, and dried under vacuum. A second crop of nitro compound is obtained by cooling the mother liquor again for a few days.

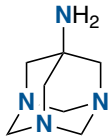


Yellow solid; Yield: 33 g (0.18 mol, 36%). **^{1}H NMR** (300 MHz, DMSO-d_6): δ 4.37 (d, $^{2}J_{H\text{-}H}$ = 13, 3H, CH_{ax}), 4.01 (d, $^{2}J_{H\text{-}H}$ = 13, 3H, CH_{ecu}), 3.74 (s, 6H, CCH_2). **^{1}H NMR** (300 MHz, D_2O): δ 4.51 (d, $^{2}J_{H\text{-}H}$ = 12, 3H, CH_{ax}), 4.18 (d, $^{2}J_{H\text{-}H}$ = 12, 3H, CH_{ecu}), 3.90 (s, 6H, CCH_2). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.47 (d, $^{2}J_{H\text{-}H}$ = 13, 3H, CH_{ax}), 4.11 (d, $^{2}J_{H\text{-}H}$ = 13, 3H, CH_{ecu}), 3.82 (s, 6H, CCH_2).

1,3,5-Triazaadamantan-7-amine **TA-NH$_2$** [3]

7-Nitro-1,3,5-triazaadamantane (9.04 g, 49.08 mmol), Ni-Raney (0.8 g; ≥89%Ni) and water (150 mL) are introduced into a 200 mL glass-vessel of a Büchi Miniclave. The atmosphere of the reactor is then replaced with H_2 gas at 7-8 bar, and the reaction is left to evolve, stirring at 60 ºC and repressurizing the vessel

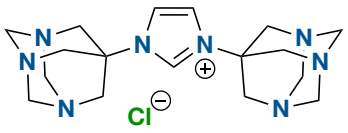
during the first 6 h, until no hydrogen consumption is detected (*ca.* 72 h). The catalyst in suspension is separated from the resulting orange solution by doble filtration, first using a paper filter to recover most of Ni-Raney and then through a sintered glass filter G4 with a plug of Celite to remove the traces of catalyst. The solution is evaporated in a rotary evaporator to remove as much H_2O as possible. The remaining water is removed by the addition of 200 mL of toluene and subsequent refluxing at 90-110 °C of the azeotropic mixture using a Dean-Stark. The toluene solution is allowed to slowly cool, the resulting precipitate after 48 h is collected and dried under vacuum.



Clear yellowish crystals; Yield: 3.7 g (24 mmol, 49%), **^{1}H NMR** (300 MHz, DMSO-d_6): δ 4.25 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{axi}), 3.83 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{ecu}), 2.98 (s, 6H, CCH_2), 1.24 (s, 2H, NH_2). **^{1}H NMR** (300 MHz, D_2O): δ 4.40 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{axi}), 4.04 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{ecu}), 3.21 (s, 6H, CCH_2), NH_2 not observed.

1,3-Bis(1,3,5-triazazaadamantan-7-yl)imidazolium chloride **ITA**·HCl

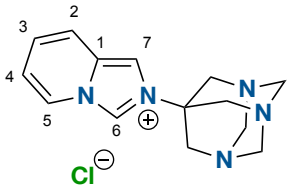
A solution of 1,3,5-triazaadamantan-7-amine (1.00 g, 6.48 mmol) and acetic acid (3 mL) is stirred and warmed at 60 °C under air in a 25 mL schlenk for 5 min until formation of a homogeneous solution (ca. 10 min). In a second 25 mL flask, glyoxal (390 µL, 40% in H_2O, 3.28 mmol), formaldehyde (246 µL, 37% in H_2O, 3.28 mmol) and acetic acid (3 mL) are also heated and stirred in the same oil bath for 5 min. The content of this flask is then poured dropwise over the content of the first one, washing down with another 0.50 mL of acetic acid, and the mixture is stirred into the bath for 15 min. The acetic acid is then removed under vacuum. The crude is dissolved in H_2O (6.5 mL), HCl is added (300 µL, 37% in H_2O, 3.6 mmol), the mixture is stirred 5 min and the volatiles removed again. The remaining traces of acetic acid are eliminated by washing the solid dissolved in H_2O (6.5 mL) with ethyl acetate (3 × 10 mL) in a separatory funnel. The aqueous solution is separated and evaporated to dryness in a rotary evaporator to furnish a brown oily solid. The oil is treated with ethanol (20 mL), sonicated for 5 min and evaporated in a rotary evaporator to form a solid.



Off-white solid. Yield: 1.23 g (quantitative). The reaction was scaled starting with 5.0 g of 1,3,5-triazaadamantan-7-amine (Yield: 6.1 g (>99%)). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.17 (t, $^4J_{H\text{-}H}$ = 2, 1H, Imz-H^2), 8.12 (d, $^4J_{H\text{-}H}$ = 2, 2H, Imz-$H^{4,5}$), 4.45 (d, $^2J_{H\text{-}H}$ = 13, 6H, CH_{axi}), 4.05 (d, $^4J_{H\text{-}H}$ = 13, 6H, CH_{ecu}), 3.73 (s, 12H, CCH_2). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6): δ 132.7 (Imz-C^2), 119.6 (Imz-$C^{4,5}$), 72.1 (NCH_2N), 59.3 (CCH_2N), 48.4 (CCH_2N). **^{15}N NMR** (51 MHz; DMSO-d_6): δ 196.9 (Imz-$N^{1,3}$); 47.4 (TA-$N^{1,3,5}$). **^{1}H NMR** (300 MHz, D_2O) δ 9.29 (t, $^4J_{H\text{-}H}$ = 2, 1H, Imz-H^2), 7.95 (d, $^4J_{H\text{-}H}$ = 2, 2H, Imz-$H^{4,5}$), 4.94 (d, $^2J_{H\text{-}H}$ = 13, 6H, CH_{axi}), 4.66 (d, $^4J_{H\text{-}H}$ = 13, 6H, CH_{ecu}), 4.15 (s, 12H, CCH_2). **^{13}C{^{1}H} NMR** (75 MHz, D_2O): δ 133.4 (Imz-C^2), 120.6 (Imz-$C^{4,5}$), 71.0 (NCH_2N), 56.4 (CCH_2N), 48.8 (CCH_2N). **^{15}N NMR** (51 MHz, D_2O): δ 188.7 (Imz-$N^{1,3}$), 42.5 (TA-$N^{1,3,5}$). **Anal. calc.** for $C_{17}H_{27}N_8Cl\cdot 1/2H_2O$ (387.91): C: 52.64, H: 7.28 and N: 28.89 %; found: C: 52.80, H: 7.33 and N: 28.33. %. **HR-MS** (ESI/TOF, positive mode, MeCN/MeOH): *m/z* 343.2351 [**M** – Cl]$^+$ (343.2353 calcd for $C_{17}H_{27}N_8$). **Solubility in water**: 150 ± 7 g/100mL (4.0 M).

2-(1,3,5-triazaadamantan-7-yl)imidazo[1,5-a]pyridinium chloride **IpyTA**·HCl

1,3,5-Triazaadamantan-7-amine (200 mg, 1.3 mmol) and H_2O (2.6 mL) are stirred in a 50 mL round-bottom flask at room temperature until formation of a homogeneous solution (ca. 10 min.). Then, formaldehyde (146 µL, 37% in H_2O, 1.95 mmol), HCl (217 µL, 37% M in H_2O, 2.6 mmol), and pyridine-2-carbaldehyde (125 µL, 1.3 mmol) are added in this order, and the reaction is stirred overnight at room temperature. The volatiles are removed in a rotary evaporator, the oily crude is dissolved in CH_2Cl_2/MeOH (20:1), the solution neutralized by adding a spatula tip of $NaHCO_3$, treated with activated carbon (20 min.), filtrated through a cannula-filter with celite and dried under vacuum to give an oily solid. The oil is treated with pentane (20 mL), sonicated for 5 min and evaporated in a rotary evaporator to form a solid.

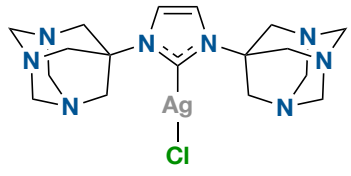


Yellowish-white solid. Yield: 373 mg (1.27 mmol, 98%). The reaction was scaled starting with 4.0 g of 1,3,5-triazaadamantan-7-amine (Yield: 7.57 g (>99%)). **^{1}H NMR** (300 MHz, DMSO-d_6): δ 9.96 (d, $^4J_{H\text{-}H}$ = 2, 1H, Imz-H^6), 8.52 (d, $^3J_{H\text{-}H}$ = 7, 1H, py-H^5), 8.47 (d, $^4J_{H\text{-}H}$ = 2, 1H, Imz-H^7), 7.85 (d, $^3J_{H\text{-}H}$ = 9, 1H, py-H^2), 7.29 (dd, $^3J_{H\text{-}H}$ = 9 and 7, 1H, py-H^3), 7.20 (dd, $^3J_{H\text{-}H}$ = 7, 1H, py-H^4), 4.48 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{axi}), 4.10 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{ecu}), 3.83 (s, 6H, CCH_2). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6): δ 129.3 (C^1), 125.1 (Imz-C^6), 124.8 (py-C^3), 124.0 (py-C^5), 118.1 (py-C^2), 117.7 (py-C^4), 110.2 (Imz-C^7), 72.1 (NCH_2N), 59.5 (CCH_2N), 49.0 (CCH_2N). **^{15}N NMR** (51 MHz, DMSO-d_6): δ 204.5 (Imz-N), 192.8 (py-N-Imz), 47.7 (TA-N^{1,3,5}). **^{1}H NMR** (500 MHz, D_2O): δ 8.37 (d, $^3J_{H\text{-}H}$ = 7, 1H, py-H^5), 8.13 (s, 1H, Imz-H^7), 7.77 (d, $^3J_{H\text{-}H}$ = 10, 1H, py-H^2), 7.32-7-26 (m, 1H, py-H^3), 7.17 (t, $^3J_{H\text{-}H}$ = 7, 1H, py-H^4), 4.64 (d, $^2J_{H\text{-}H}$ = 13, 3H, CH_{axi}), 4.32 (d, $^2J_{H\text{-}H}$ = 13, 3H, CH_{ecu}), 3.99 (s, 6H, CCH_2), H^6 not observed. **^{13}C{^{1}H} NMR** (126 MHz, D_2O): δ 130.5 (C^1), 125.2 (py-C^3), 123.4 (py-C^5), 118.2 (py-C^4), 117.9 (py-C^2), 109.5 (Imz-C^7), 70.7 (NCH_2N), 58.4 (CCH_2N), 48.8 (CCH_2N), Imz-C^6 not observed. **^{15}N NMR** (51 MHz, D_2O): δ 198.6 (Imz-N), 193.6 (py-N-Imz), 46.5 (TA-N^{1,3,5}). **Anal. calc.** for $C_{14}H_{18}N_5Cl·H_2O$ (309.80): C: 54.28, H: 6.51 and N: 22.61 %; found: C: 53.84, H: 6.44 and N: 22.50. %. **HR-MS** (positive mode, MeCN/H_2O, 0.1% formic acid): *m/z* 256.1555 [**M** – Cl]$^+$ (256.1562 calcd for $C_{14}H_{18}N_5$). **Solubility in water**: 144 ± 7 g/100mL (4.9 M).

Synthesis of silver complexes

(*L*-2)-Chloride[1,3-bis(1,3,5-triazazaadamantan-7-yl)imidazole-2-ylidene]silver(I) [AgCl(**ITA**)] [10]

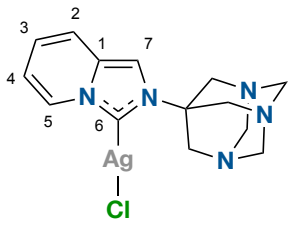
A mixture of **ITA**·HCl (100 mg, 0.26 mmol) and Ag_2O (60 mg, 0.26 mmol) in dry CH_2Cl_2 (4 mL) and MeOH (2 mL) with molecular sieve (4 Å) is stirred under an inert atmosphere in an ampoule equipped with a PTFE plug valve for 24 h, at room temperature and protected from light. The solvent is evaporated to dryness under vacuum, and the product is extracted with dry CH_2Cl_2 (4 × 5 mL). The silver complex is obtained as a powder after evaporation of the solvent.



Ocre solid; Yield: 85 mg (67%). **^{1}H NMR** (300 MHz, DMSO-d_6): δ 7.67 (s, 2H, Imz-H^{4,5}), 4.42 (d, $^2J_{H\text{-}H}$ = 12, 6H, CH_{axi}), 4.05 (d, $^4J_{H\text{-}H}$ = 12, 6H, CH_{ecu}), 3.87 (s, 12H, CCH_2). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6): δ 174.6 (Imz-C^2), 118.3 (Imz-C^{4,5}), 72.2 (NCH_2N), 61.3 (CCH_2N), 46.7 (CCH_2N). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 (s, 2H, Imz-H^{4,5}), 4.53 (d, $^2J_{H\text{-}H}$ = 12, 6H, CH_{axi}), 4.21 (d, $^4J_{H\text{-}H}$ = 12, 6H, CH_{ecu}), 3.97 (s, 12H,

CCH_2). **^{109}Ag NMR** (23.3 MHz, $CDCl_3$): δ 679. **Anal. calc.** for $C_{17}H_{26}AgClN_8 \cdot 1/2H_2O \cdot 1/2CH_2Cl_2$ (537.24): C: 39.12, H: 5.25 and N: 20.86 %; found: C: 39.36 H: 5.27 and N: 20.69 %.

(*L*-2)-Chloride[2-(1,3,5-triazaadamantan-7-yl)imidazo[1,5-a]pyridine-3-ylidene]silver(I) [AgCl(**IpyTA**)]
A mixture of **IpyTA**·HCl (300 mg, 1.0 mmol) and Ag_2O (166.8 mg, 0.72 mmol) in dry CH_2Cl_2/MeOH 20:1 (10 mL) is stirred under an inert atmosphere in an ampoule equipped with a PTFE plug valve for 24 h, at room temperature and protected from light. Filtration through a cannula-filter with celite and evaporation of the solvent to dryness, gives the silver compound as a solid



Light brown solid; Yield: 205.3 mg (65%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.58 (d, $^3J_{H\text{-}H}$ = 7, 1H, py-H^5), 8.04 (s, 1H, Imz-H^7), 7.58 (d, $^3J_{H\text{-}H}$ = 9, 1H, py-H^2), 7.01 (dd, $^3J_{H\text{-}H}$ = 9 and 7, 1H, py-H^3), 6.83 (t, $^3J_{H\text{-}H}$ = 7, 1H, py-H^4), 4.46 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{axi}), 4.11 (d, $^2J_{H\text{-}H}$ = 12, 3H, CH_{ecu}), 3.98 (s, 6H, CCH_2). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 168.1 (Imz-C^6), 129.5 (Imz-C^1), 129.3 (Imz-C^5), 123.0 (Imz-C^3), 117.7 (Imz-C^2), 114.5 (Imz-C^4), 110.1 (Imz-C^7), 72.2 (NCH_2N), 61.3 (CCH_2N), 47.6 (CCH_2N). **^{15}N NMR** (51 MHz, DMSO-d$_6$): δ 216.8 (Imz-N), 208.9 (py-N-Imz), 48.2 (TA-N^{1,3,5}). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44 (d, $^3J_{H\text{-}H}$ = 7, 1H, py-H^5), 7.43-7.29 (m, 2H, Imz-H^7 and py-H^2), 6.93 (dd, $^3J_{H\text{-}H}$ = 9 and 6, 1H, py-H^3), 6.72 (t, $^3J_{H\text{-}H}$ = 7, 1H, py-H^4), 4.56 (d, $^2J_{H\text{-}H}$ = 13, 3H, CH_{axi}), 4.25 (d, $^2J_{H\text{-}H}$ = 13, 3H, CH_{ecu}), 4.05 (s, 6H, CCH_2). **HR-MS** (ESI/TOF, positive mode, MeCN/H_2O, 0.1% formic acid): *m/z* 256.1563 [**M** – AgCl + H]$^+$ (256.1557 calcd for $C_{14}H_{18}N_5$).

X-Ray molecular structure determinations

Crystals of **ITA**-HCl suitable for X-ray diffraction studies were obtained by vapor diffusion of ethanol to a solution of the imidazolium salt in water at room temperature. Single crystals were coated with mineral oil, mounted on Mitegen MicroMounts with the aid of a microscope, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets for all complexes were collected at 200 K on a Bruker D8 Venture diffractometer equipped with multilayer optics for monochromatization and collimator, Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryostream 800 unit. Crystallographic data for the imidaziolium salt is presented in Table S1 in this Supporting Information.

Table S1. Experimental data for the X-ray diffraction studies on compound **ITA**·HCl.

Formula	$C_{17}H_{35}ClN_8O_4$	μ [mm^{-1}]	0.220
M	450.98	*F(000)*	968
T [K]	200	Crystal size [mm^3]	0.35 x 0.27 x 0.26
λ[Å]	0.71073	θ range [deg]	3.44 to 27.51 º
Crystal system	monoclinic	Index ranges	29 to -29, 14 to -14, 11 to -12
Space group	*C*2/*c*	Reflections collected	28584
a [Å]; α [º]	22.879(2)	Unique data	2450 [R_{int}= 0.047]
b [Å]; β [º]	10.888(1); 112.30(1)	Reflections [*I*>2σ(*I*)]	2160
c [Å]; γ [º]	9.328(1)	Goodness-of-fit on F^2	1.116
V [Å^3]	2149.9(3)	Final R indices [*I*>2σ(*I*)] [a]	R1 = 0.043 / wR2 = 0.096
Z	4	R indices (all data)	R1 = 0.050 / wR2 = 0.100
ρ_{calcd} [g cm^{-3}]	1.393	Largest diff. peak/hole [e·Å^{-3}]	0.361/-0.176

[a] $R1=\Sigma(||F_o|-|F_c||)/[\Sigma|F_o|]$ $\quad wR2=\{[\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$

The structure was solved by applying intrinsic phasing (SHELXT) [4] using the Olex2 package [5]. All were refined by least-squares against F^2 (SHELXL) [6]. All non-hydrogen atoms were anisotropically refined, while hydrogen atoms were placed at idealized positions and refined using a riding model.

CCDC 2505167 (for **ITA**-HCl), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectra for ligands and precursors

1,3-Bis(1,3,5-triazazaadamantan-7-yl)imidazolium chloride **ITA**·HCl

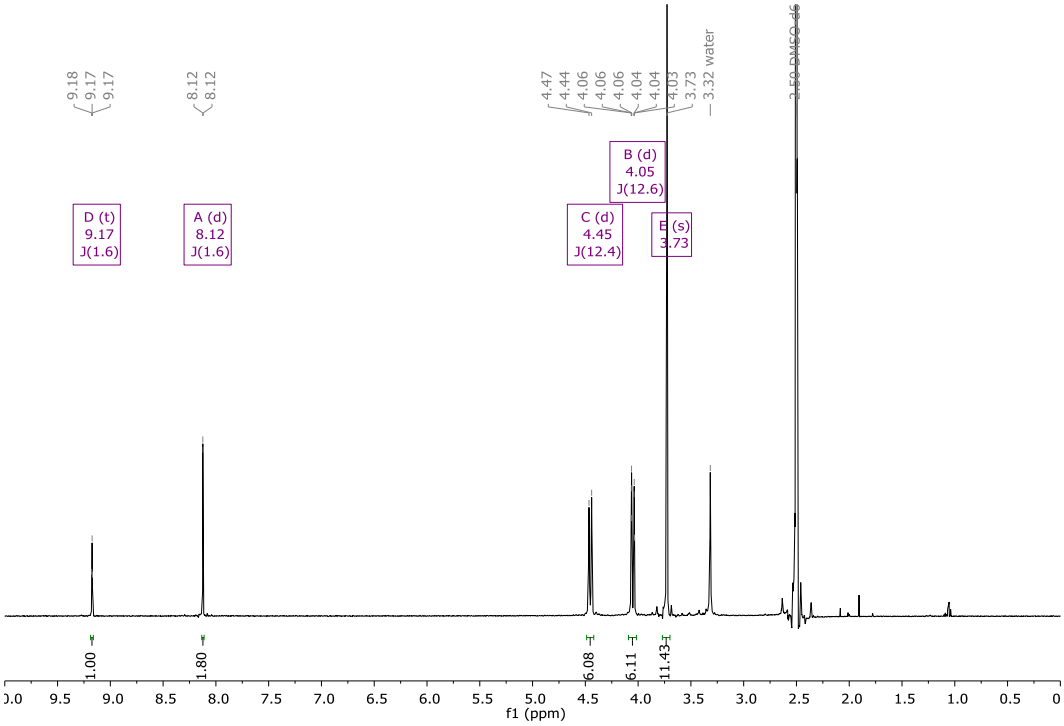


Figure S1. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **ITA**·HCl.

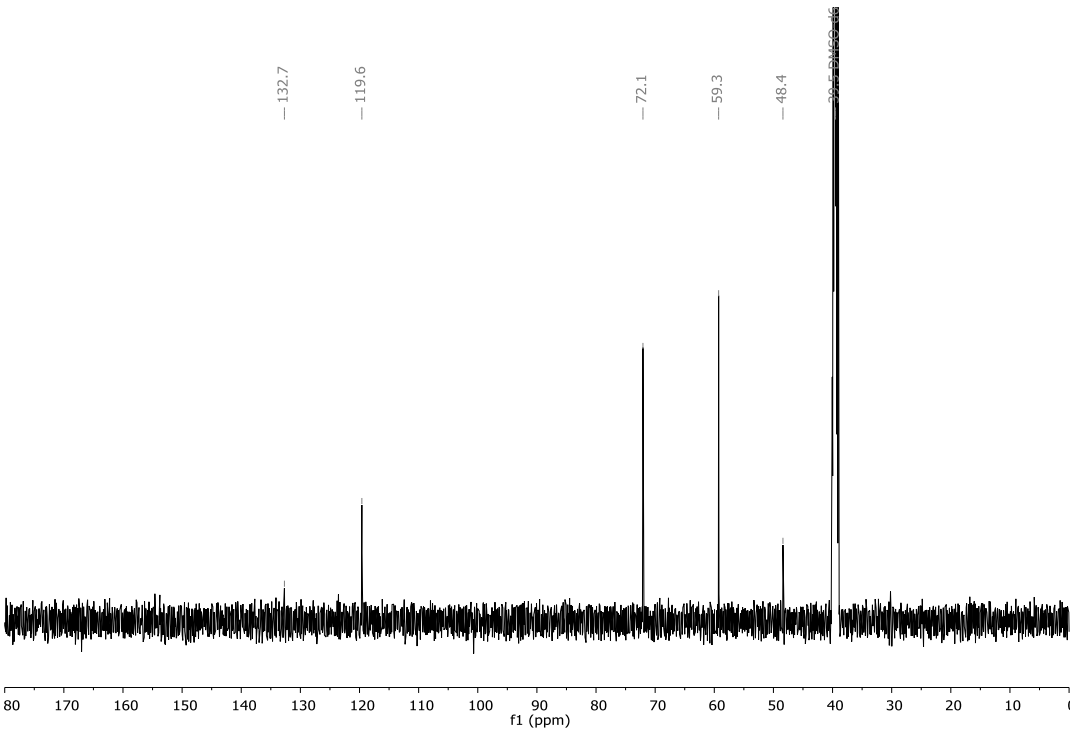


Figure S2. ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) spectrum of **ITA**·HCl.

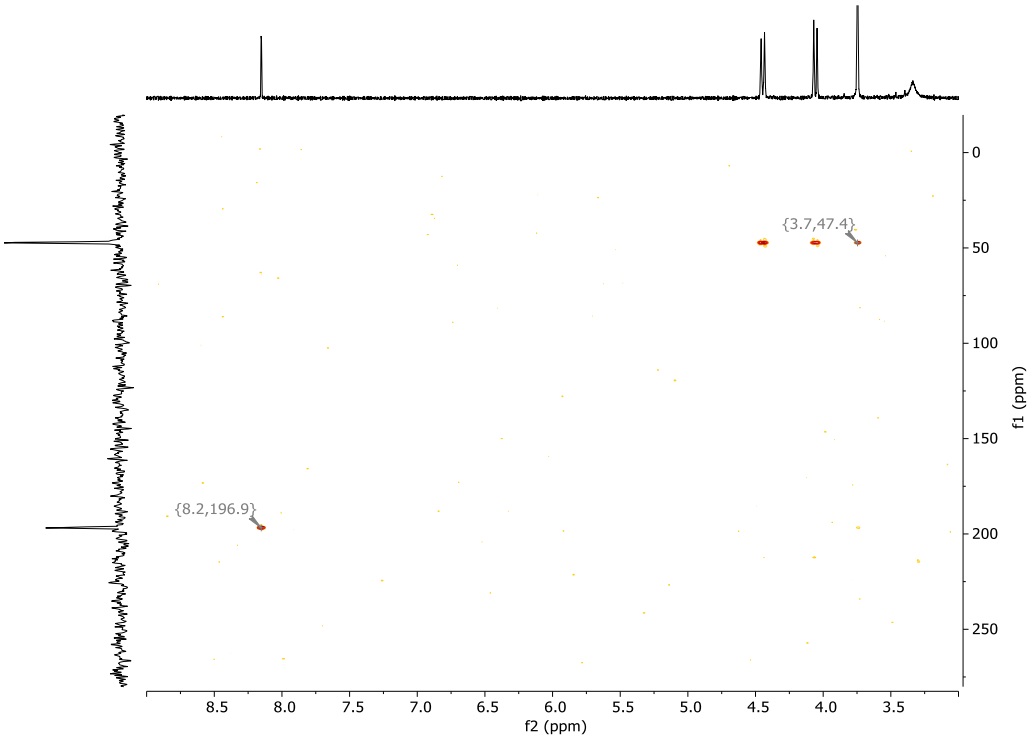


Figure S3. $^{1}H,^{15}N$-HMBC NMR (500, 51 MHz, DMSO-d_6) spectrum of **ITA**·HCl.

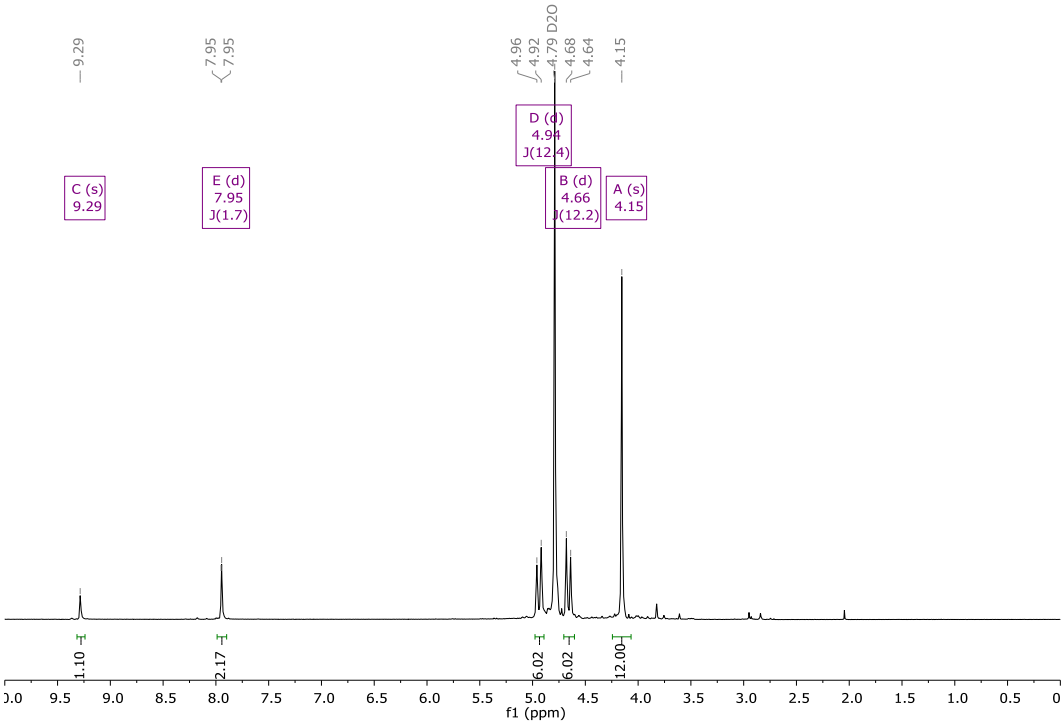


Figure S4. ^{1}H NMR (500 MHz, D_2O) spectrum of **ITA**·HCl.

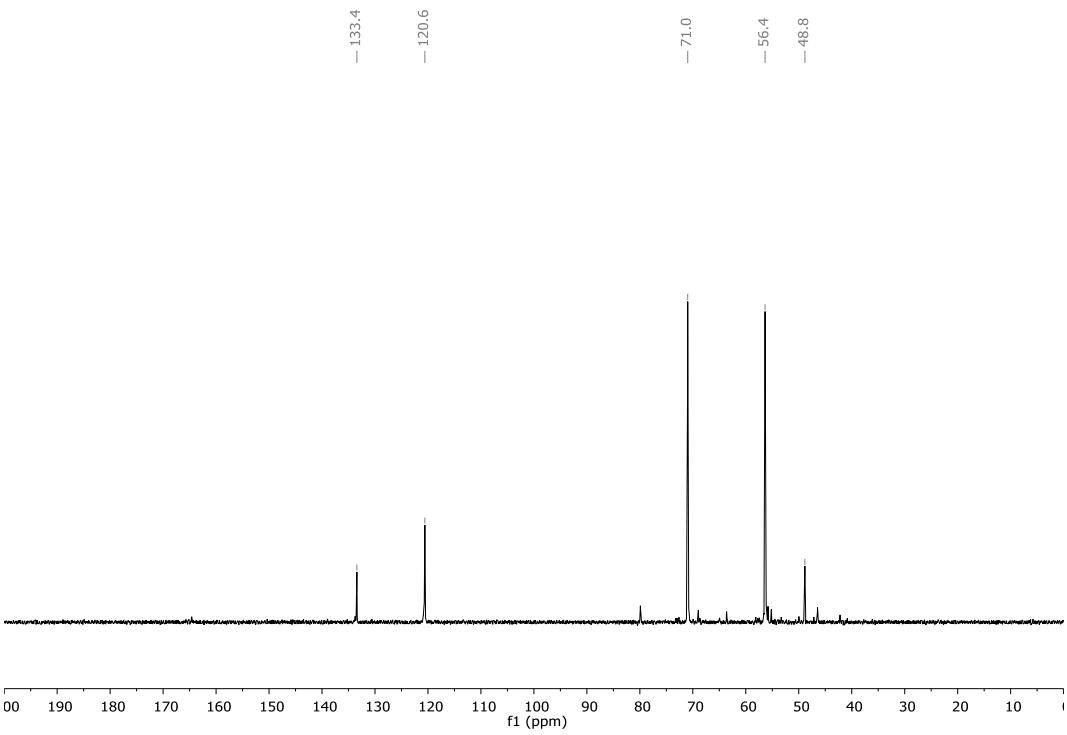


Figure S5. $^{13}C\{^{1}H\}$ NMR (126 MHz, D_2O) spectrum of **ITA**·HCl.

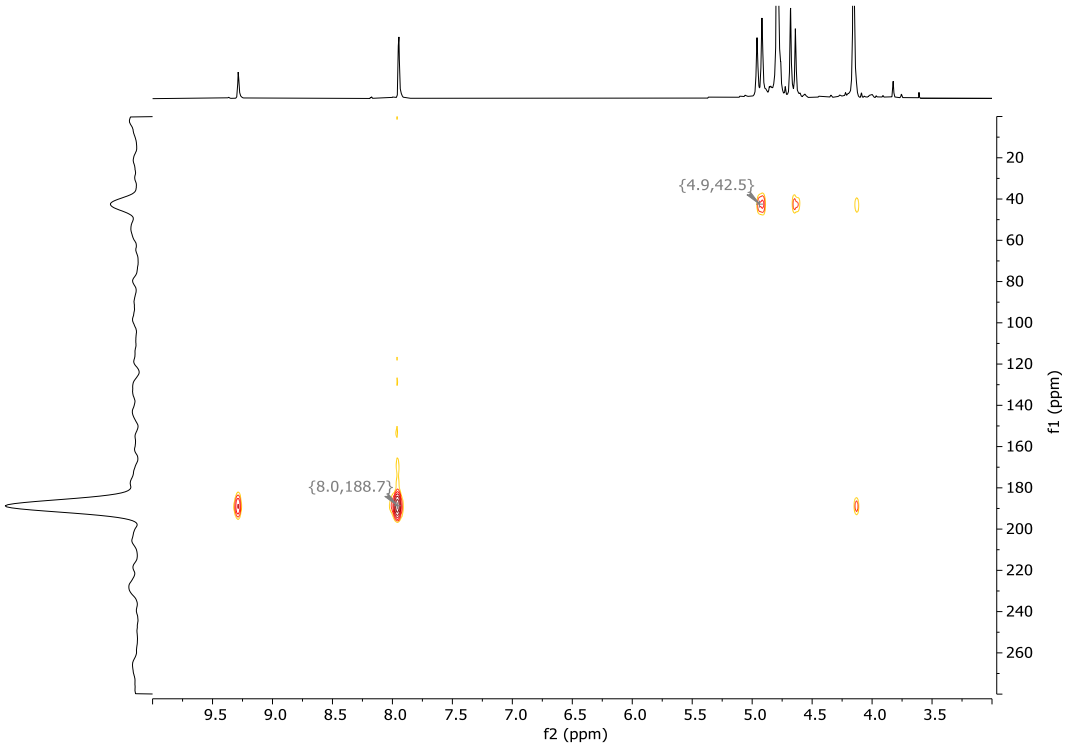


Figure S6. $^{1}H,^{15}N$-HMBC NMR (500, 51 MHz, D_2O) spectrum of **ITA**·HCl.

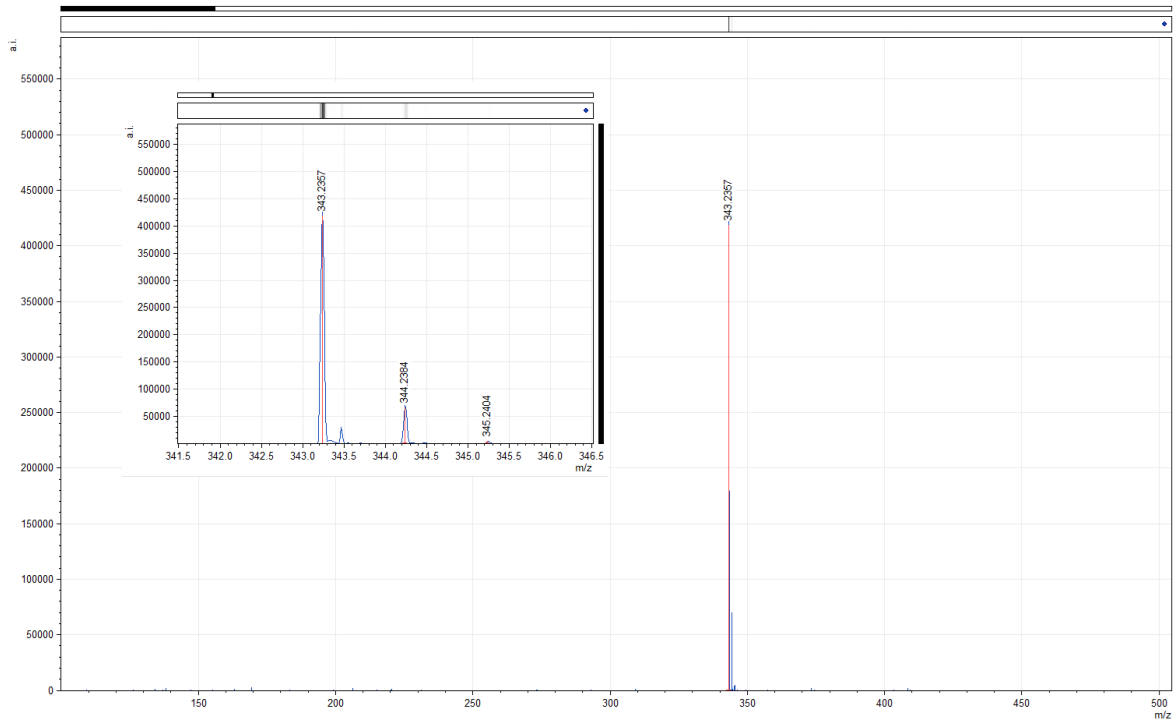


Figure S7. HR-MS (ESI/TOF, positive mode, MeOH) of **ITA**·HCl.

2-(1,3,5-triazaadamantan-7-yl)imidazo[1,5-a]pyridinium chloride **IpyTA**·HCl

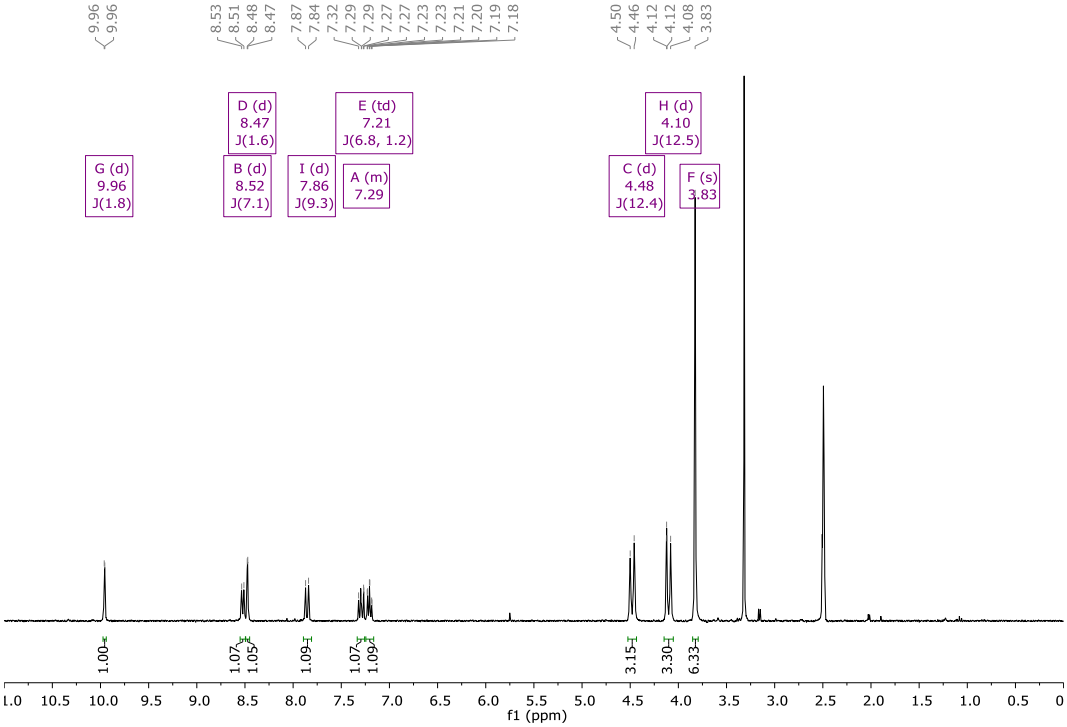


Figure S8. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **IpyTA**·HCl.

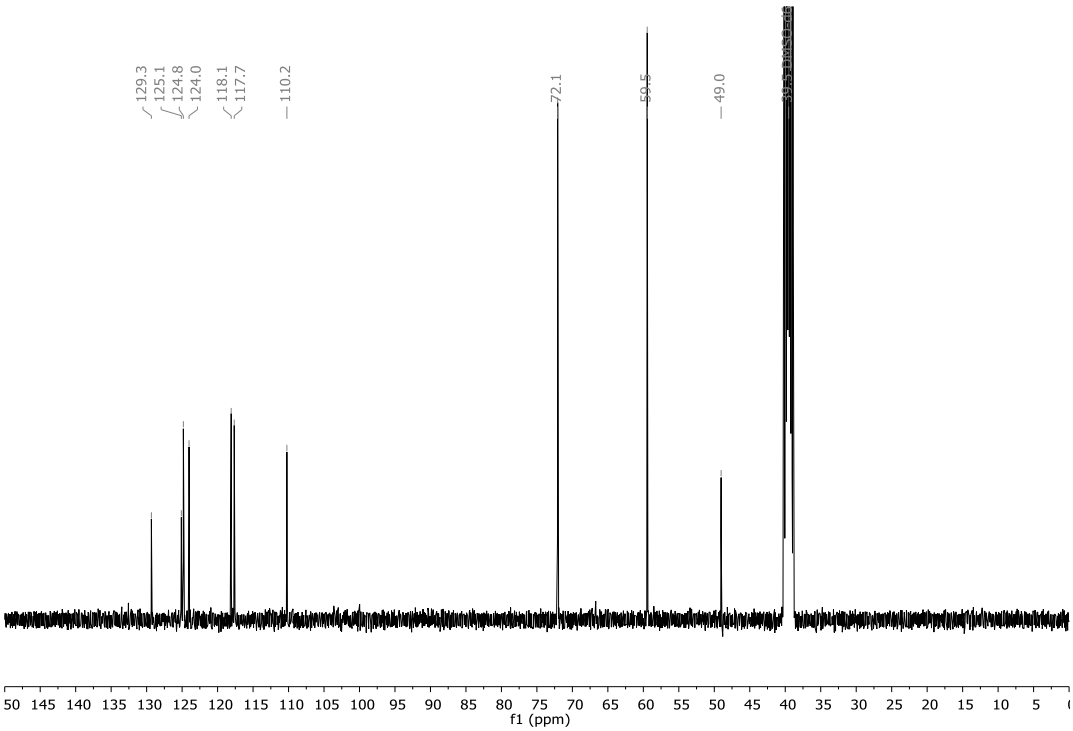


Figure S9. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) spectrum of **IpyTA**·HCl.

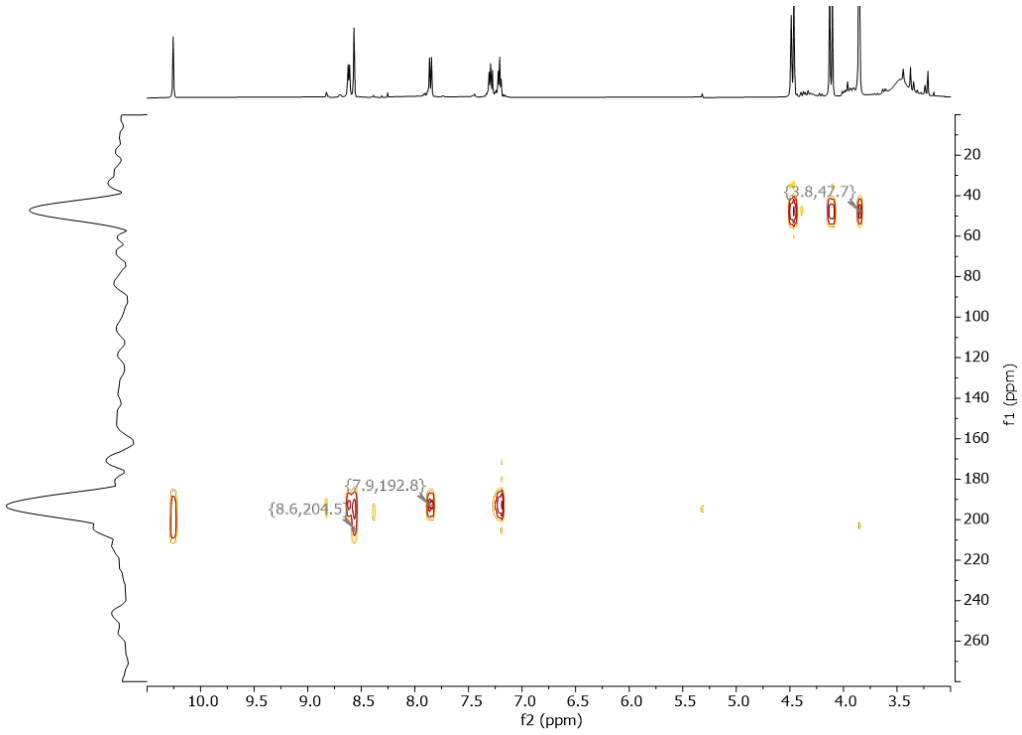


Figure S10. $^{1}H,^{15}N$-HMBC NMR (500, 51 MHz, DMSO-d_6) spectrum of **IpyTA**·HCl.

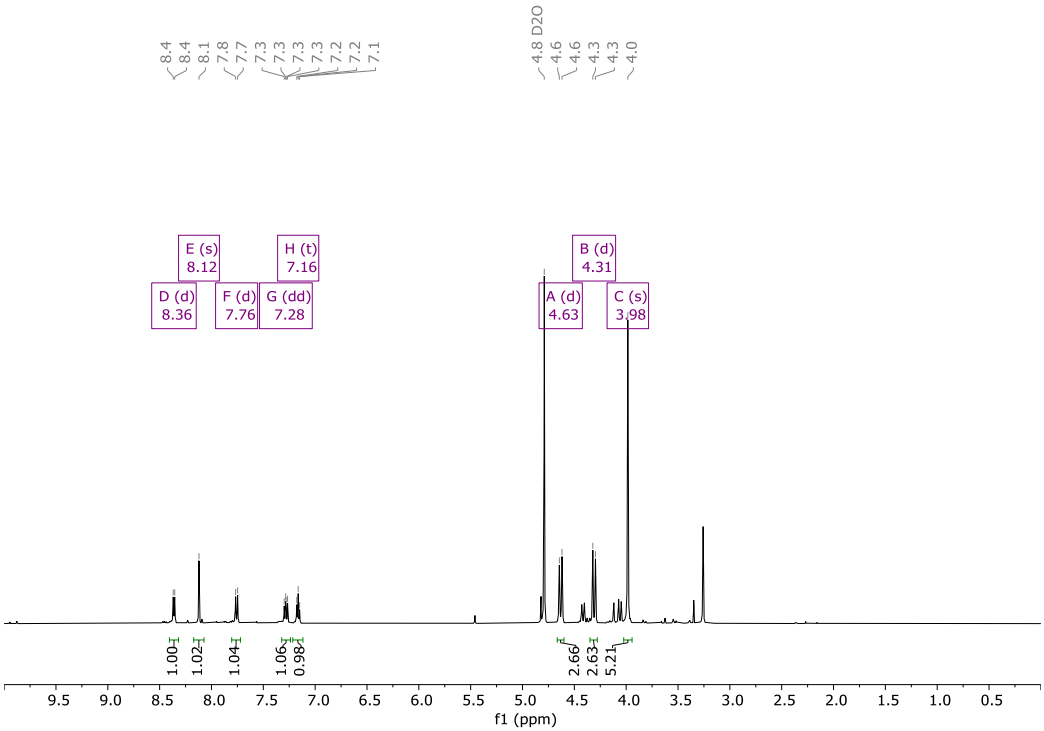


Figure S11. ^{1}H NMR (500 MHz, D_2O) spectrum of **IpyTA**·HCl.

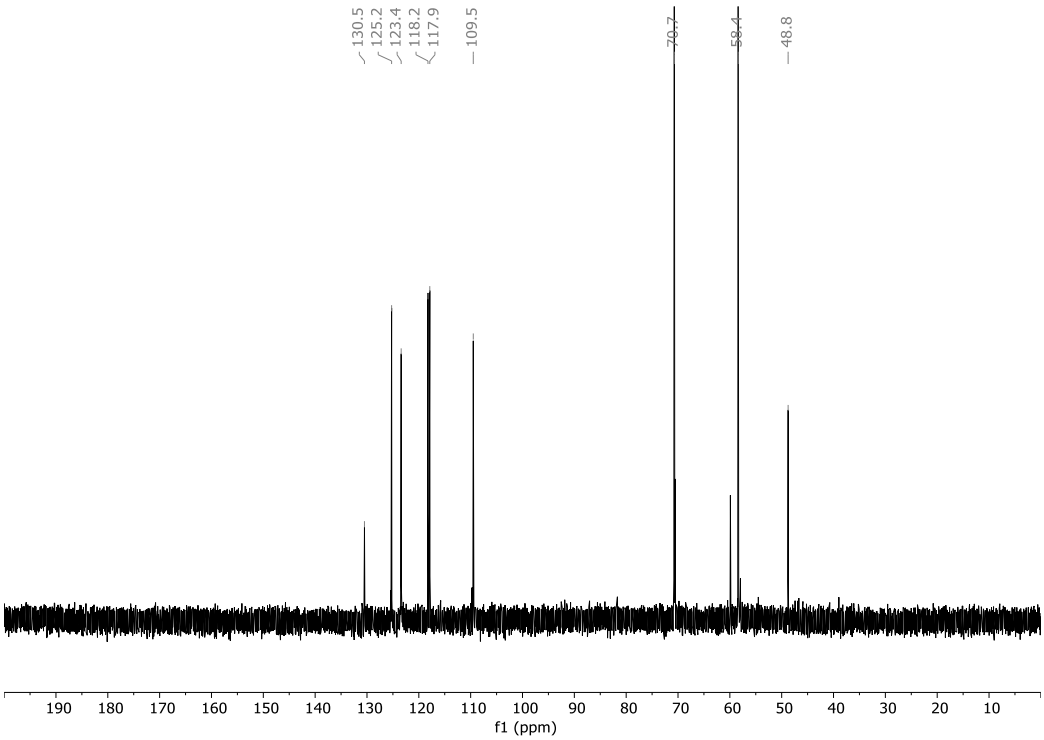


Figure S12. ^{13}C{^{1}H} NMR (126 MHz, D_2O) spectrum of **IpyTA**·HCl.

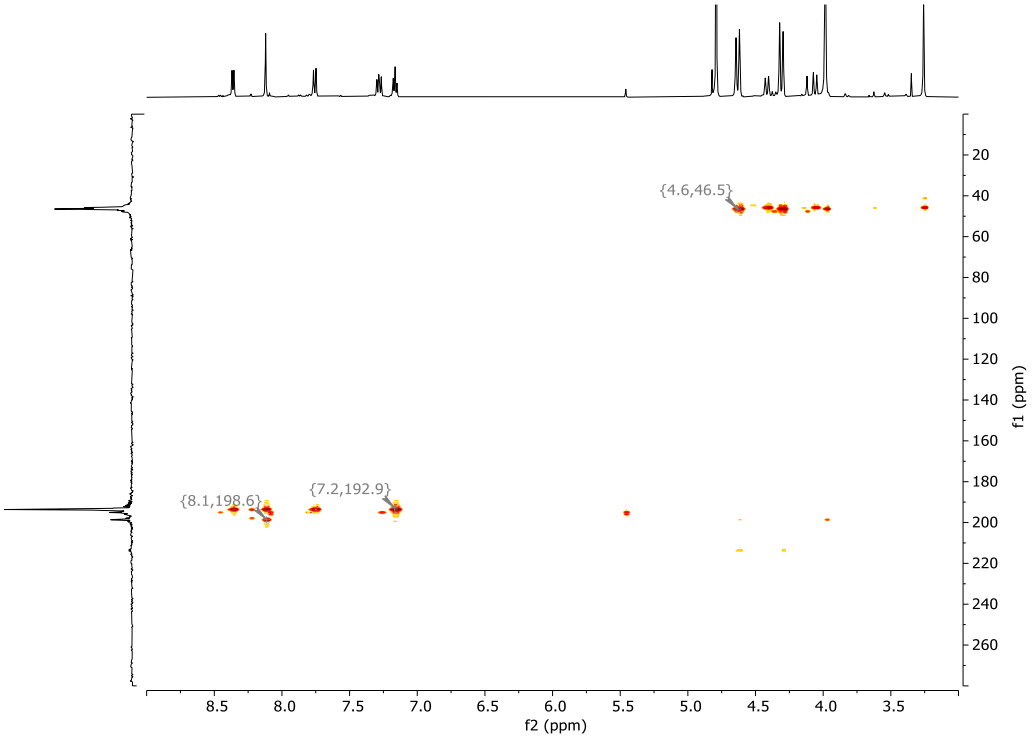


Figure S13. $^{1}H,^{15}N$-HMBC NMR (500, 51 MHz, D_2O) spectrum of **IpyTA**·HCl.

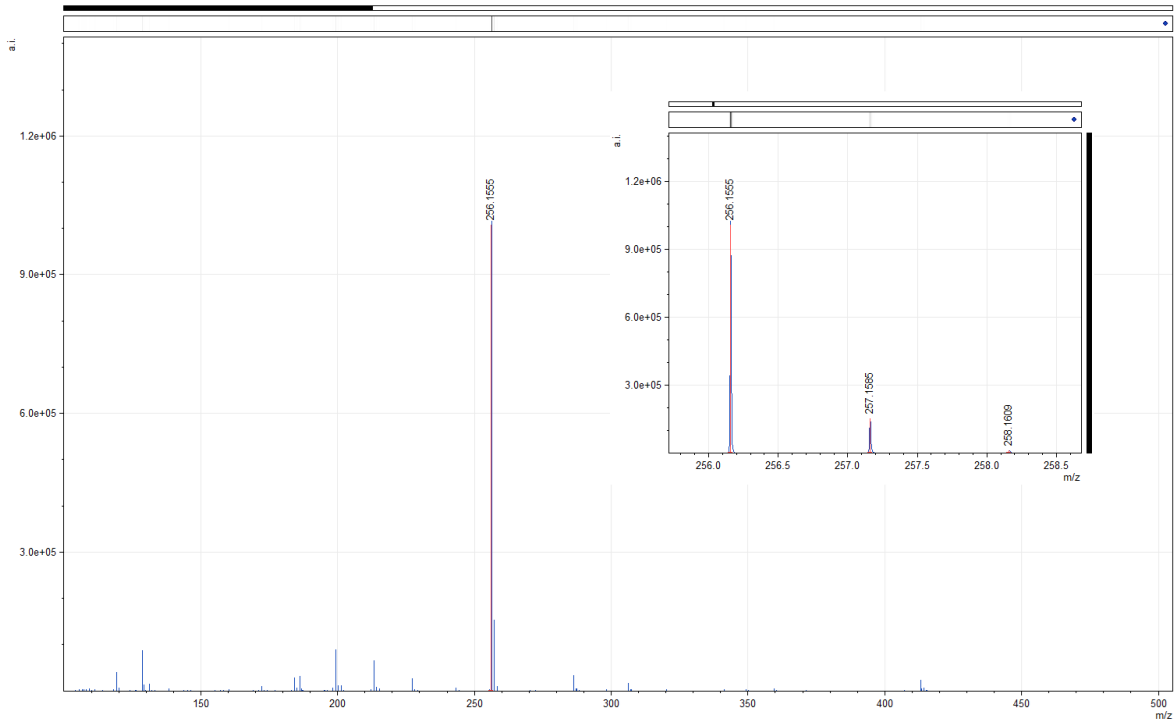


Figure S14. HR-MS (ESI/TOF, positive mode, MeOH) of **IpyTA**·HCl.

Spectra for silver complexes.

(*L*-2)-Chloride[1,3-bis(1,3,5-triazazaadamantan-7-yl)imidazole-2-ylidene]silver(I) [AgCl(**ITA**)]

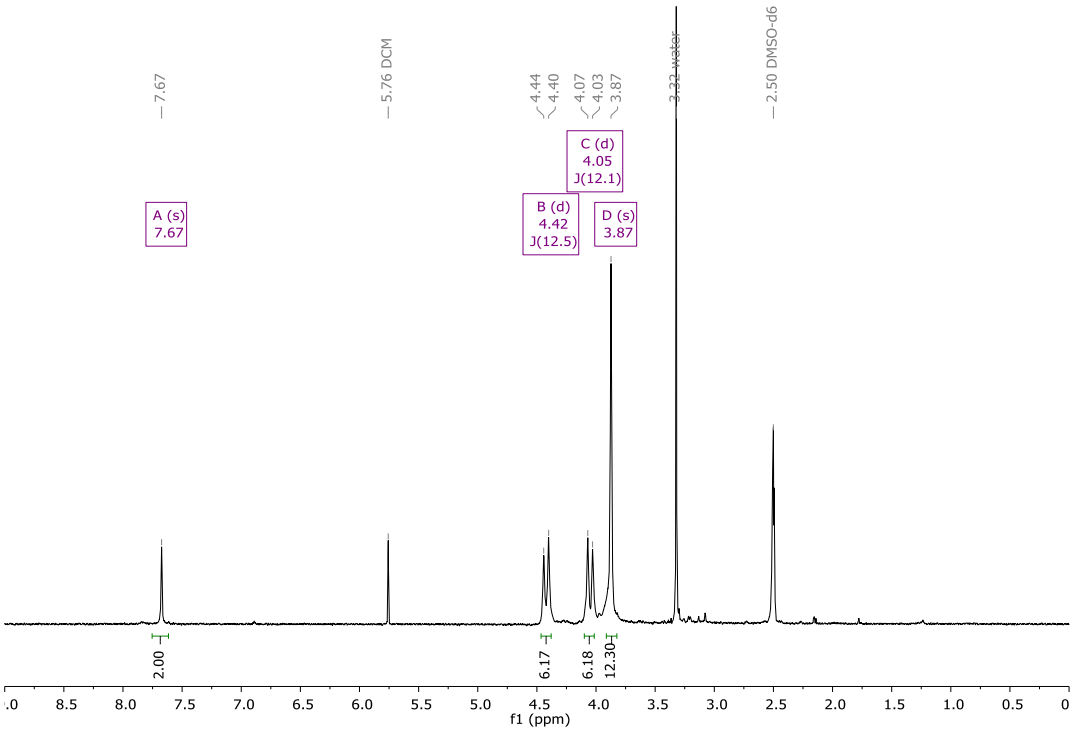


Figure S15. ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of [AgCl(**ITA**)].

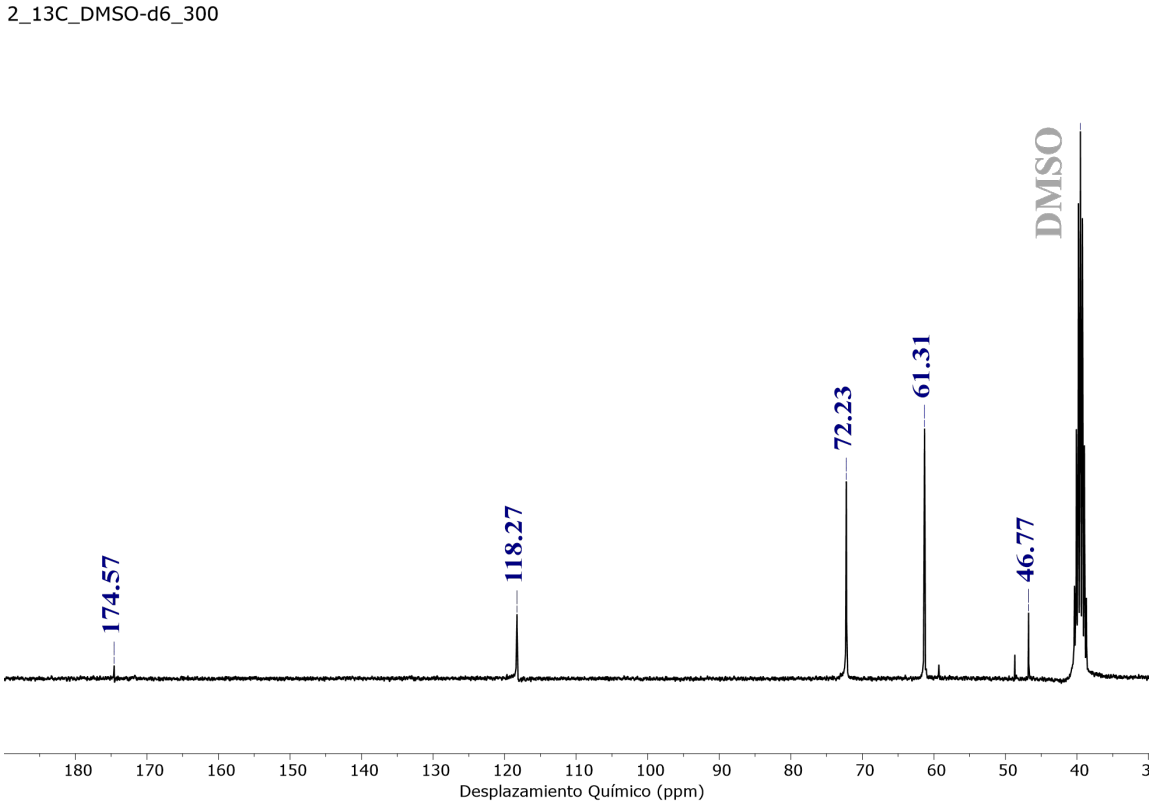


Figure S16. ^{13}C{^{1}H} NMR (76 MHz, DMSO-d_6) spectrum of [AgCl(**ITA**)].

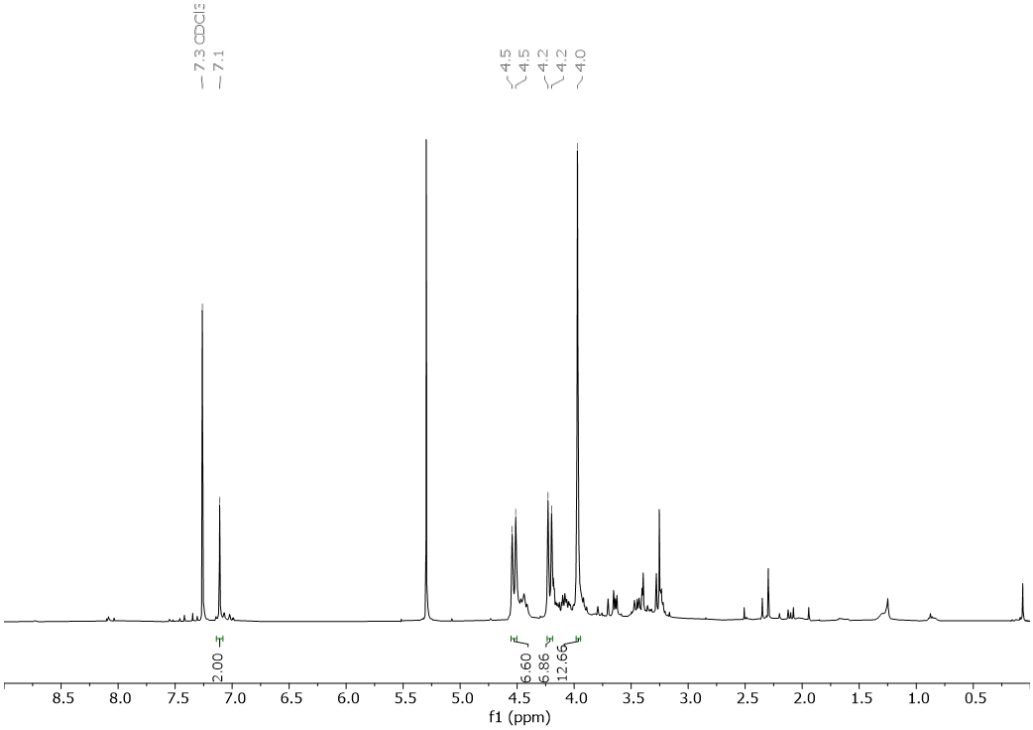


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [AgCl(**ITA**)].

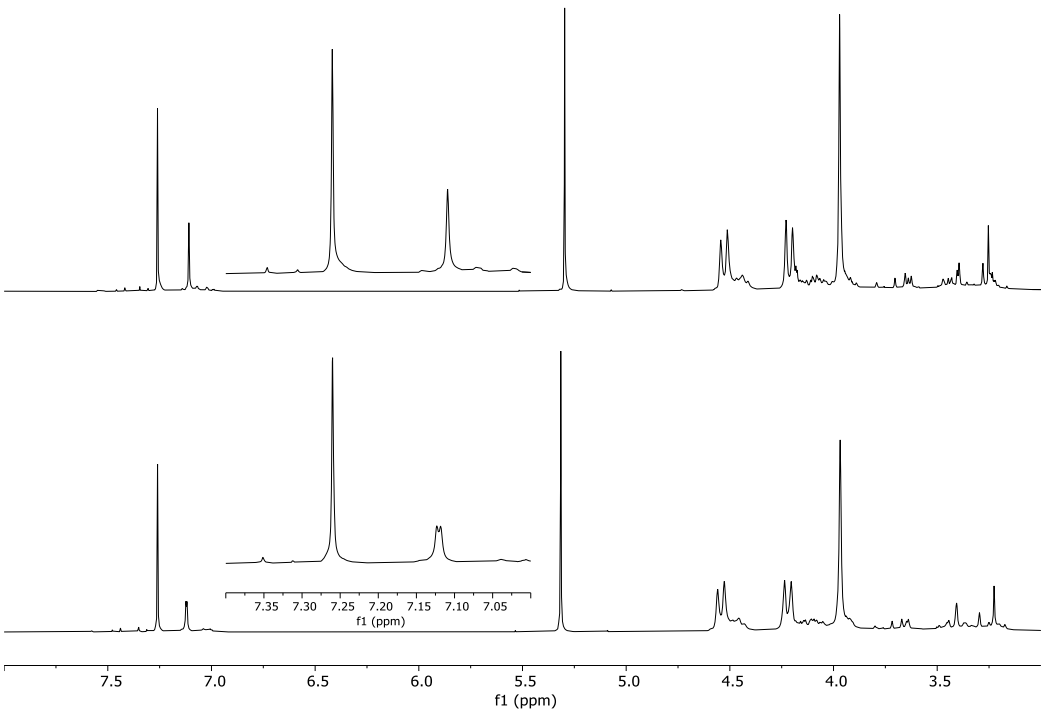


Figure S18. Comparison of ^{1}H NMR (400 MHz, $CDCl_3$) spectra of [AgCl(**ITA**)] at 298 K (top) and 233 K (bottom).

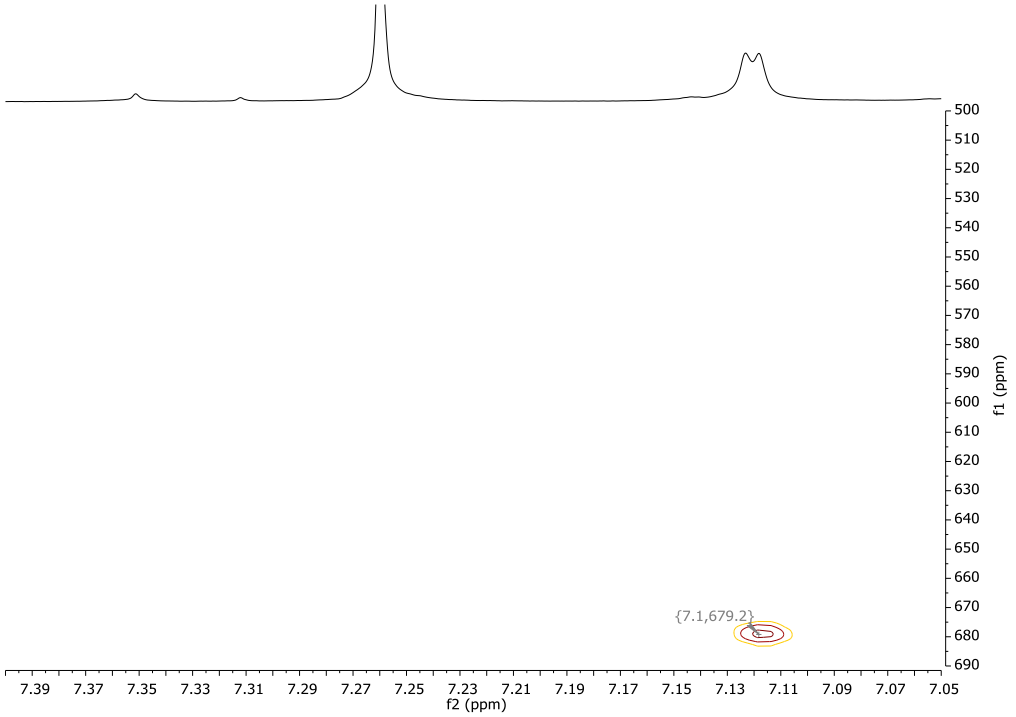


Figure S19. Expansion of the $^{1}H,^{109}Ag$-HMBC NMR (400, 19 MHz, $CDCl_3$) spectrum of [AgCl(**ITA**)].

(*L*-2)-Chloride[2-(1,3,5-triazaadamantan-7-yl)imidazo[1,5-a]pyridin-3-ylidene]silver(I) [AgCl(**IpyTA**)]

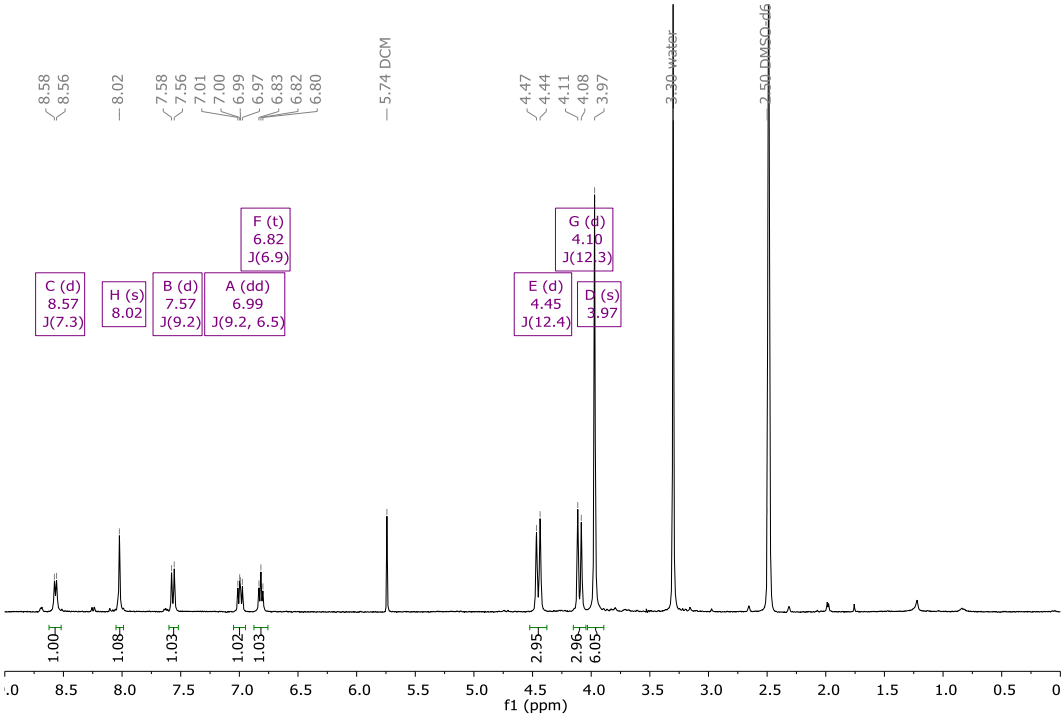


Figure S20. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [AgCl(**IpyTA**)].

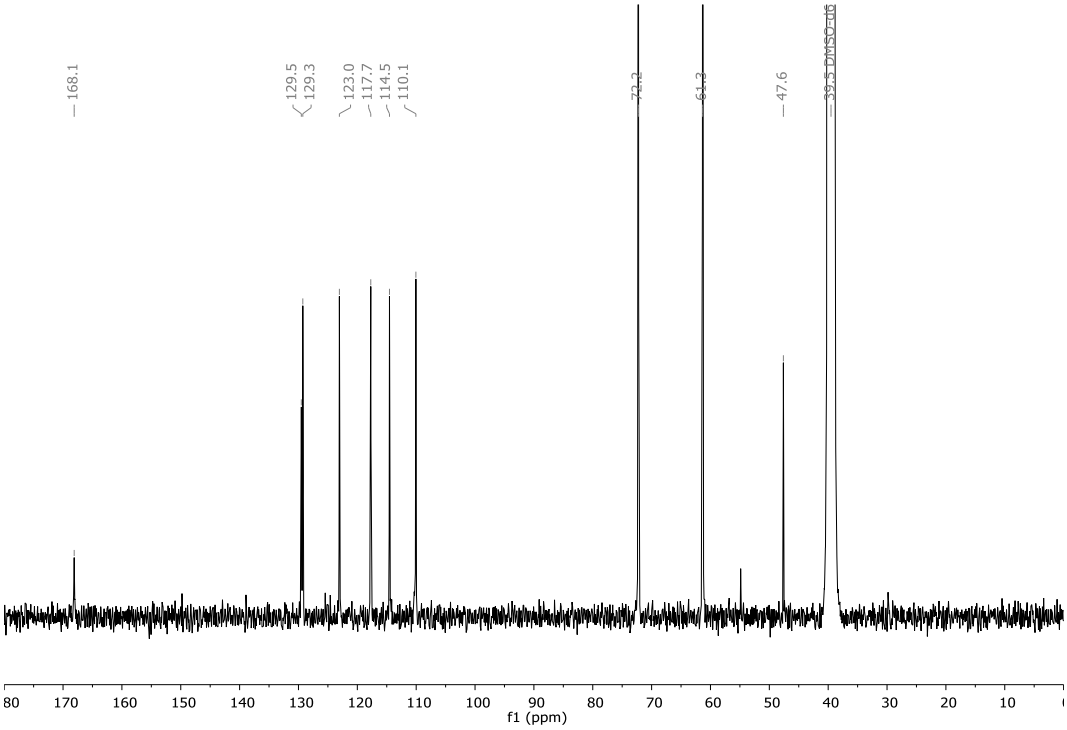


Figure S21. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) spectrum of [AgCl(**IpyTA**)].

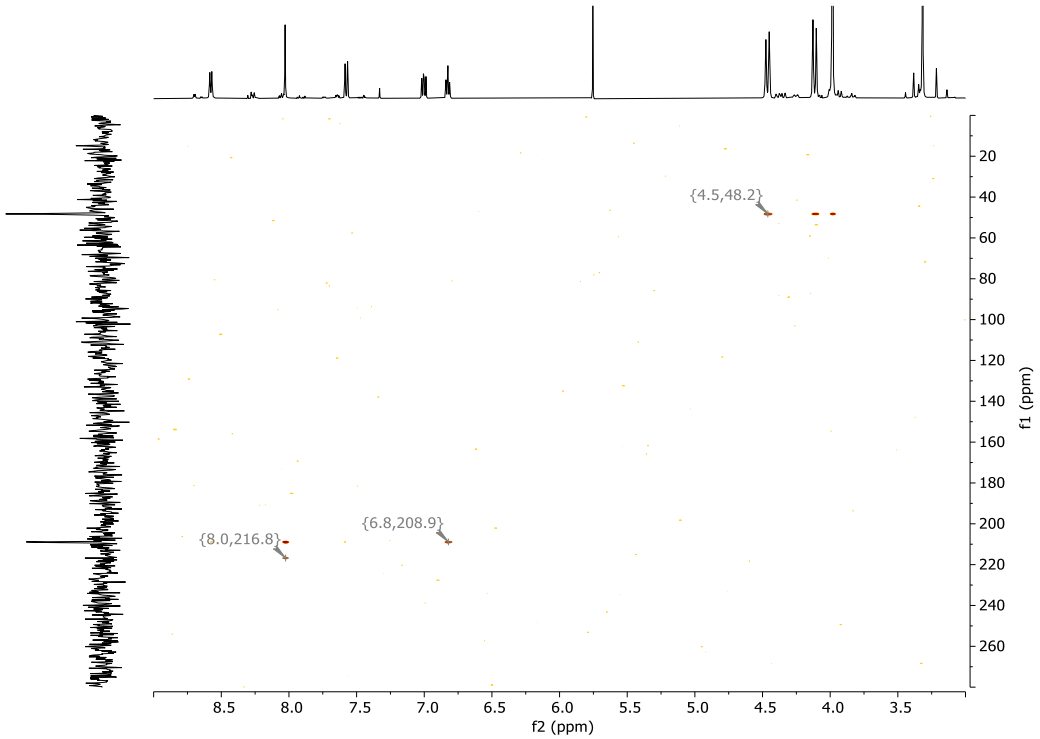


Figure S22. $^{1}H,^{15}N$-HMBC NMR (500, 51 MHz, DMSO-d_6) spectrum of [AgCl(**IpyTA**)].

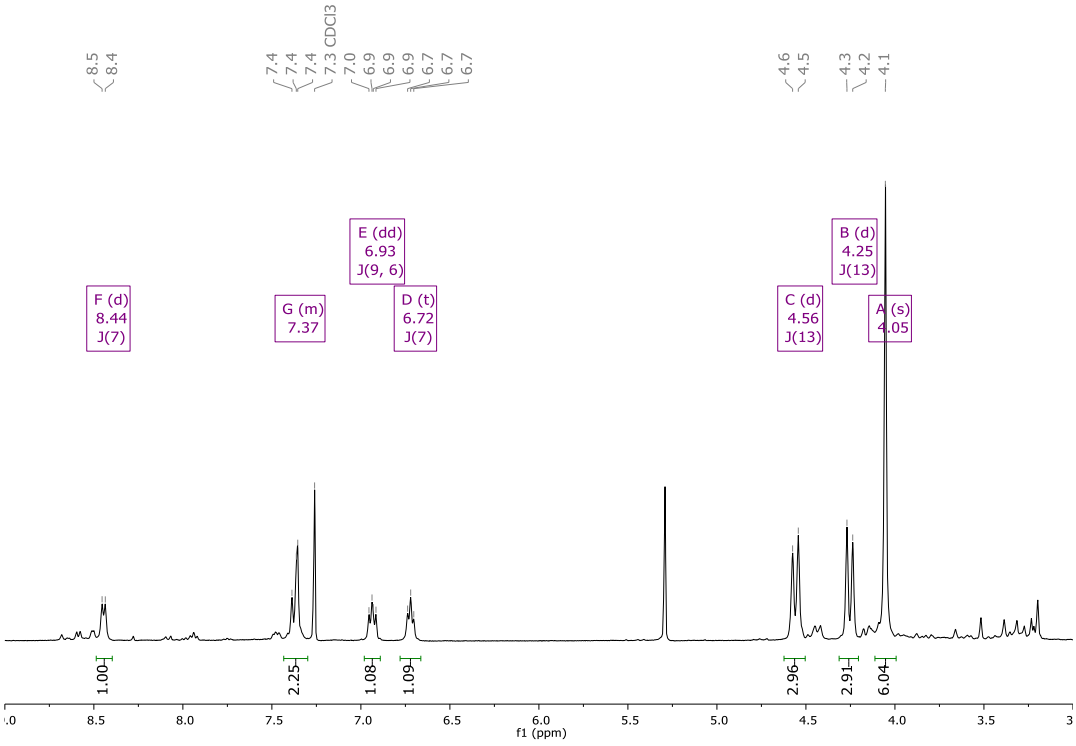


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [AgCl(**IpyTA**)].

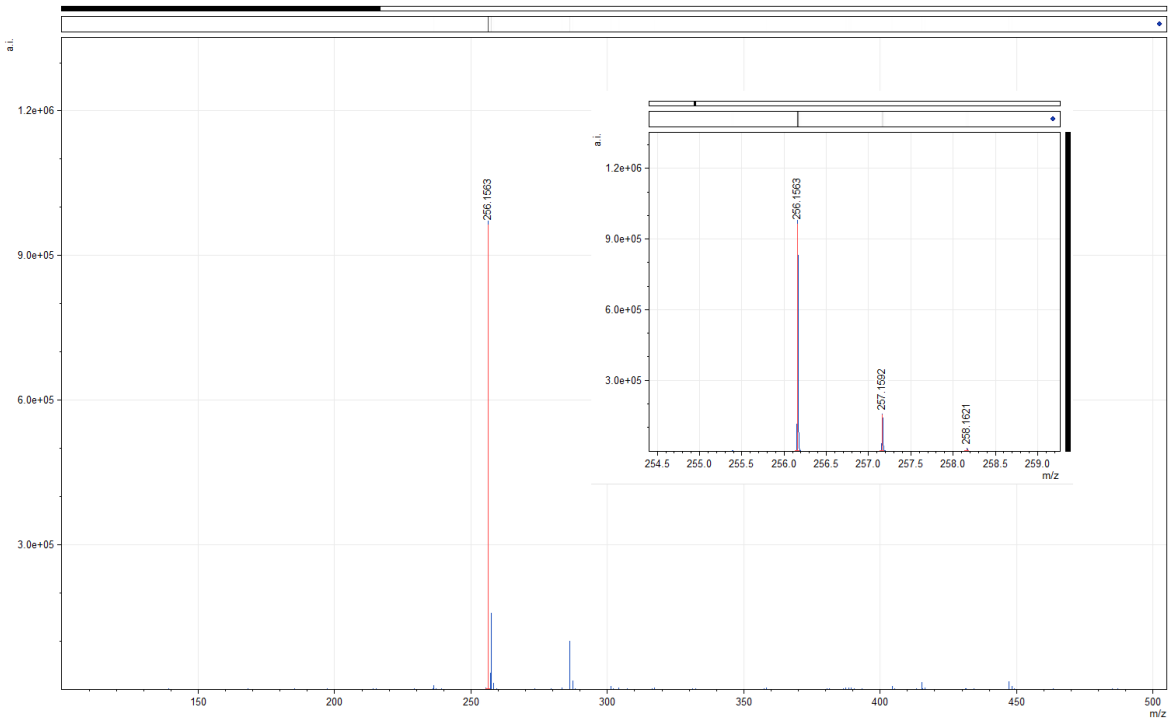


Figure S24. HR-MS (ESI/TOF, positive mode, MeOH, 0.1% formic acid) of [AgCl(**IpyTA**)].

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