Supporting Information

Synthesis of stable polymetalated aromatic complexes through metal-macrocycle capsule-triggered cyclization

Xin He,[a] Yang Xue,[a] Cui-Cui Li,[a] Yuechao Wang,[b] Hong Jiang,[b] and Liang Zhao*,[a]

[a] The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China
[b] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

E-mail: zhaolchem@mail.tsinghua.edu.cn

Table of Contents

Crystal structure refinement details.

Crystal data for $[Ag_5(C_8NH_5)(Py[8])](CF_3SO_3)_3$ (2a) (CCDC-1558954): $C_{58}H_{48}Ag_5F_6N_{17}O_6S_2$, M = 1796.60, orthorhombic, space group *Cmcm* (No. 63), a = 12.842(6) Å, b = 21.083(5) Å, c = 25.145(5) Å, α = β = γ = 90°, V = 6808(4) Å^3, Z = 4, T = 173 K, D_c = 1.753 g cm^{-3}. The structure, refined on F^2, converged for 3913 unique reflections (R_{int} = 0.1303) and 4196 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.1818 and wR_2 = 0.3422 and a goodness-of-fit = 1.098. Several highly disordered additional solvents and one triflate group could not be located in the difference map. The SQUEEZE procedure of PLATON was used in the processing of **2a**. Silver atom Ag1 was disordered at three positions with site occupancy ratio of 0.80:0.10:0.10. Silver atom Ag2 was disordered at two positions owing to the symmetry with site occupancy ratio of 0.50:0.50. Indole skeleton was disordered at two set of positions (C1-C1S-C2-C3-C4-C5-C4S-C6-N1/C1S-C1-C2S-C3S-C4S-C5-C4-C6S-N1S) with occupancy ratio of 0.50:0.50 (S denoted atoms generated by symmetry operation). The total anion numbers are confirmed by ESI-MS and elemental analysis.

Crystal data for $[(Ag_5C_8NH_5)(Py[8])](CF_3SO_3)_3$ (2a) (CCDC-1558955): $C_{58}H_{53}Ag_5F_6N_{17}O_6S_2$, M = 1801.64, 1801.64, space group *P*-1 (No. 2), a = 12.278(3) Å, b = 25.145(5) Å, c = 12.408(3) Å, α = 90.00(3)°, β = 117.31(3)°, γ = 90.00(3)°, V = 3403.6(12) Å^3, Z = 2, T = 173 K, D_c = 1.758 g cm^{-3}. The structure, refined on F^2, converged for 15934 unique reflections (R_{int} = 0.1303) and 17911 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0889 and wR_2 = 0.2260 and a goodness-of-fit = 1.027. Several highly disordered additional solvents and one triflate group could not be located in the difference map. The SQUEEZE procedure of PLATON was used in the processing of **2a**. Lower symmetry compared to *Cmcm* caused the Alert A of low diffrn_measured_fraction_theta_full value. The total anion numbers are confirmed by ESI-MS and elemental analysis.

Crystal data for $[Ag_5(C_9NH_7)(Py[8])](CF_3SO_3)_3$ (2b) (CCDC-1558956): $C_{59}H_{55}Ag_5F_6N_{17}O_6S_2$, M = 1815.67, monoclinic, space group *P*-1 (No. 2), a = 14.3867(3) Å, b = 15.4794(3) Å, c = 18.9913(6) Å, α = 101.197(2)°, β = 93.200(2)°, γ = 94.368(2)°, V = 4125.97(18) Å^3, Z = 2, T = 173 K, D_c = 1.462 g cm^{-3}. The structure, refined on F^2, converged for 12054 unique reflections (R_{int} = 0.0792) and 15629 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0884 and wR_2 = 0.2632 and a goodness-of-fit = 1.066. Several highly disordered additional solvents and one triflate group could not be located in the difference map. The SQUEEZE procedure of PLATON was used in the processing of **2b**. N-methyl indole skeleton was disordered at two set of positions (C1-C2-C3-C4-C5-C6-C7-C8-N1-C9/C1-C2-C3'-C4'-C5'-C6'-C7'-C8'-N1'-C9') with refined occupancy ratio of 0.46:0.54. The total anion numbers are confirmed by ESI-MS and elemental analysis.

Crystal data for $[Ag_5(C_9NH_5)H(Py[8])](CF_3SO_3)_4 \cdot 1.5CHCl_3 \cdot 0.75H_2O \cdot 0.5CH_3OH$ (2c) (CCDC-1558958): $C_{63}H_{55}Ag_5Cl_{4.5}F_{12}N_{17}O_{13.25}S_4$, M = 2317.36, triclinic, space group P-1 (No. 2), a = 13.189(3) Å, b = 13.561(3) Å, c = 28.427(6) Å, α = 103.51(3)°, β = 90.23(3)°, γ = 118.57(3)°, V = 4301.6(16) Å^3, Z = 2, T = 173 K, D_c = 1.447 g cm^{-3}. The structure, refined on F^2, converged for 13790 unique reflections (R_{int} = 0.0701) and 15156 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0795 and wR_2 = 0.2003 and a goodness-of-fit = 1.140. The total number of triflate group was calculated to be 4 based on the observation of protonation of quinolone in ESI-MS and elemental analysis. Based on the data refinement, the site occupancy ratios of triflate groups S1, S2, S3, S4 and S5 were determined to be 1, 0.75, 1, 0.5, and 0.75, respectively. Solvent molecule $CHCl_3$ (C64 and C65) was disordered at two positions with site occupancy of 0.80:0.20. Solvent molecule CH_3OH (C67) had a site occupancy ratio of 0.50. Water molecule O16, O18, and O19 each had a site occupancy ratio of 0.25.

Crystal data for $[Ag_5(C_{16}N_2H_{10})(Py[8])](CF_3SO_3)_3 \cdot 2.5CH_3OH \cdot Et_2O$ (2d) (CCDC-1558960): $C_{73.5}H_{68}Ag_5F_9N_{18}O_{12.5}S_3$, M = 2209.99, triclinic, space group P-1 (No. 2), a = 14.8347(3) Å, b = 15.7643(3) Å, c = 18.6915(4) Å, α = 96.459(2)°, β = 93.928(2)°, γ = 95.369(2)°, V = 4310.55(15) Å^3, Z = 2, T = 173 K, D_c = 1.703 g cm^{-3}. The structure, refined on F^2, converged for 14704 unique reflections (R_{int} = 0.0557) and 16326 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0534 and wR_2 = 0.1578 and a goodness-of-fit = 1.021.

Crystal data for $[Ag_5(C_{16}NH_9)(Py[8])](CF_3SO_3)_3$ (2e) (CCDC-1558959): $C_{67}H_{57}Ag_5F_9N_{17}O_9S_3$, M = 2050.82, monoclinic, space group $P2_1/c$ (No. 14), a = 14.3943(4) Å, b = 31.0527(14) Å, c = 22.6971(8) Å, α = γ = 90°, β = 125.685(2)°, V = 8240.3(6) Å^3, Z = 4, T = 173 K, D_c = 1.653 g cm^{-3}. The structure, refined on F^2, converged for 9503 unique reflections (R_{int} = 0.2739) and 15612 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.2130 and wR_2 = 0.5615 and a goodness-of-fit = 1.092. Triflate groups S3 was disordered at two positions with refined site occupancy ratio of 0.67:0.33. Several highly disordered additional solvents could not be located in the difference map. The SQUEEZE procedure of PLATON was used in the processing of **2e**. The crystals of **2e** suffered from instant solvent losing out of mother liquor. We tried several times to mount the crystal as soon as possible, but still observed severe efflorescence. This observation accounted for the high R_1 value, wR_2 value and R_{int} in Alert A.

Crystal data for $[Ag_4(C_8NH_6)(Py[8])](CF_3SO_3)_2(CF_3CO_2) \cdot 2CH_3OH$ (2f) (CCDC-1558963): $C_{64}H_{58}Ag_4F_9N_{17}O_{10}S_2$, M = 1891.87, monoclinic, space group $C2/c$ (No. 15), a = 32.1129(19) Å, b = 12.1233(3) Å, c = 24.0913(16) Å, α = γ = 90°, β = 130.309(10)°, V = 7152.2(7) Å^3, Z = 4, T = 173 K, D_c = 1.757 g cm^{-3}. The structure, refined on F^2, converged for 6142 unique

reflections (R_{int} = 0.0409) and 6779 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0965 and wR_2 = 0.2531 and a goodness-of-fit = 1.136. 2-Amino phenyl ethynide group and $CF_3CO_2^-$ group had orientation disorder with occupancy ratio of 0.50:0.50. Triflate group S1 was disordered at two positions with refined site occupancy of 0.50:0.50.

Geometrical coordinates of model complexes **2a'**, **2c'**, **2d'**, **2e'**.

Complex 2a'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.266115	5.448758	-1.644794
2	1	0	0.019757	3.037804	-3.177487
3	6	0	0.010082	1.796794	-1.437611
4	47	0	1.674550	0.423892	-1.590280
5	47	0	-1.088737	0.010853	-1.879692
6	6	0	-0.220617	3.599379	0.013382
7	47	0	1.081602	0.940126	1.265278
8	47	0	-1.672645	0.972133	0.871137
9	6	0	-0.354397	4.526417	1.071895
10	6	0	-0.400402	6.334546	-0.576902
11	1	0	-0.231492	5.803026	-2.673226
12	6	0	-0.176538	4.081871	-1.328991
13	1	0	-0.377832	4.177243	2.104138
14	6	0	-0.442596	5.881566	0.767805
15	1	0	-0.471428	7.401475	-0.778211
16	1	0	-0.540790	6.611927	1.568213
17	7	0	3.332732	-0.980894	-1.385754
18	6	0	4.611606	-0.639399	-1.718057
19	6	0	3.112338	-2.055309	-0.568401
20	6	0	5.721087	-1.321699	-1.181129
21	6	0	4.175943	-2.785919	-0.013792
22	6	0	5.482873	-2.397019	-0.322417
23	1	0	6.730358	-1.028037	-1.458281
24	1	0	3.975685	-3.636238	0.632138
25	1	0	6.323315	-2.954357	0.087154
26	7	0	-2.100750	-1.898923	-2.162621
27	6	0	-1.347126	-3.004268	-2.416019
28	6	0	-3.403501	-2.056146	-1.788126
29	6	0	-1.841616	-4.301971	-2.261259
30	6	0	-3.971431	-3.336732	-1.622319
31	6	0	-3.175570	-4.453281	-1.856049
32	1	0	-1.215238	-5.162722	-2.481251
33	1	0	-5.014154	-3.432251	-1.333339
34	1	0	-3.597783	-5.450608	-1.750634
35	7	0	-3.282002	-0.277306	1.642175
36	6	0	-4.533223	0.241460	1.802012
37	6	0	-3.117748	-1.631161	1.577832
38	6	0	-5.675625	-0.580116	1.841740
39	6	0	-4.215476	-2.506644	1.631583
40	6	0	-5.497103	-1.961259	1.752097
41	1	0	-6.662007	-0.140910	1.967476
42	1	0	-4.058491	-3.581267	1.593754
43	1	0	-6.361902	-2.620132	1.807141
44	7	0	2.221952	-0.361808	2.593382
45	6	0	1.543854	-1.164380	3.462489
46	6	0	3.570850	-0.521033	2.459762
47	6	0	2.167714	-2.181795	4.187028
48	6	0	4.267976	-1.522214	3.173730
49	6	0	3.552509	-2.349835	4.029194
50	1	0	1.598208	-2.798581	4.877597

51	1	0	5.343568	-1.619549	3.054534
52	1	0	4.070364	-3.121097	4.595678
53	7	0	-0.003582	-2.760445	-2.764682
54	1	0	0.452189	-3.575954	-3.177744
55	1	0	0.107049	-1.955108	-3.386269
56	7	0	-4.113715	-0.911735	-1.511807
57	1	0	-5.110193	-1.010645	-1.342008
58	1	0	-3.858522	-0.058172	-2.002994
59	7	0	-4.625862	1.619415	1.839349
60	1	0	-5.521518	2.005335	2.127813
61	1	0	-3.832742	2.121248	2.234496
62	7	0	-1.819123	-2.082494	1.379589
63	1	0	-1.729196	-3.095104	1.440733
64	1	0	-1.089241	-1.607222	1.932122
65	7	0	0.151313	-0.949853	3.536394
66	1	0	-0.095211	0.043824	3.540359
67	1	0	-0.268401	-1.402613	4.350400
68	7	0	4.232093	0.350076	1.636177
69	1	0	3.689898	0.918038	0.988965
70	1	0	5.157104	0.092511	1.306898
71	7	0	1.784261	-2.319066	-0.264647
72	1	0	1.130393	-2.305591	-1.063207
73	1	0	1.651667	-3.148682	0.310672
74	7	0	4.758635	0.467254	-2.530198
75	1	0	4.017670	0.639057	-3.207074
76	1	0	5.687962	0.631736	-2.909558
77	6	0	-0.108003	2.153908	-0.034554
78	7	0	-0.034764	2.983672	-2.164867

Complex 2c’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.340369	5.400872	1.280563
2	47	0	0.548559	0.315928	1.664503
3	47	0	2.057728	0.767933	-0.831945
4	47	0	-0.476271	0.235963	-1.760362
5	47	0	-2.015632	0.436174	0.801658
6	7	0	-0.953968	3.031735	1.179914
7	6	0	-0.449587	1.961656	0.561100
8	6	0	0.282042	2.035042	-0.709597
9	6	0	0.405919	3.303023	-1.295143
10	1	0	0.912372	3.422496	-2.254564
11	6	0	-0.125997	4.456582	-0.656778
12	6	0	-0.021771	5.766657	-1.203368
13	1	0	0.484993	5.905680	-2.157840
14	6	0	-0.558420	6.847680	-0.524027
15	1	0	-0.476434	7.848578	-0.942845
16	6	0	-1.217785	6.663354	0.722488
17	1	0	-1.629247	7.527604	1.240232
18	1	0	-1.839781	5.241506	2.233840
19	6	0	-0.801846	4.272648	0.606354
20	7	0	3.727121	-0.672635	-1.085618
21	6	0	3.427197	-2.000855	-1.114627
22	6	0	5.030621	-0.289011	-1.170919
23	6	0	4.412306	-2.984216	-1.281673
24	6	0	6.071625	-1.221079	-1.328543
25	6	0	5.743786	-2.575067	-1.395518
26	1	0	4.139213	-4.036141	-1.306081
27	1	0	7.101616	-0.882616	-1.407909
28	1	0	6.529426	-3.315924	-1.528208
29	7	0	2.273968	-0.954431	2.197260
30	6	0	2.197962	-2.279630	2.506776
31	6	0	3.500852	-0.377044	2.028018
32	6	0	3.361772	-3.066108	2.651676
33	6	0	4.688242	-1.100019	2.148682
34	6	0	4.601326	-2.464381	2.463562
35	1	0	3.275806	-4.122348	2.894523
36	1	0	5.647152	-0.607922	2.014636
37	1	0	5.509995	-3.052511	2.572298
38	7	0	-2.049564	-1.251278	-2.205154
39	6	0	-3.327774	-0.828649	-1.962850
40	6	0	-1.836249	-2.552660	-2.551815
41	6	0	-4.426823	-1.681669	-2.048177
42	6	0	-2.908443	-3.467168	-2.663932
43	6	0	-4.198268	-3.020230	-2.403830
44	1	0	-5.428060	-1.308453	-1.853907
45	1	0	-2.710444	-4.501277	-2.935085
46	1	0	-5.036520	-3.708806	-2.484900
47	7	0	-3.577154	-1.102864	1.178940
48	6	0	-3.228059	-2.418337	1.195366
49	6	0	-4.891782	-0.766525	1.293095
50	6	0	-4.178323	-3.438821	1.360708
51	6	0	-5.898023	-1.734665	1.444823
52	6	0	-5.521285	-3.078404	1.487586

53	1	0	-3.867094	-4.480221	1.378207
54	1	0	-6.938035	-1.434133	1.543689
55	1	0	-6.278879	-3.848358	1.617970
56	7	0	2.069910	-2.326833	-1.018890
57	1	0	1.560855	-1.747438	-0.346388
58	1	0	1.899903	-3.313340	-0.826954
59	7	0	5.292399	1.069071	-1.014647
60	1	0	4.556269	1.693140	-1.346896
61	1	0	6.209096	1.367847	-1.344070
62	7	0	3.473592	0.971506	1.618898
63	1	0	2.977566	1.597814	2.257793
64	1	0	4.400883	1.341360	1.399924
65	7	0	0.943101	-2.847003	2.554772
66	1	0	0.135241	-2.234402	2.668529
67	1	0	0.858878	-3.720791	3.067920
68	7	0	-1.866281	-2.697655	1.086325
69	1	0	-1.351329	-2.036568	0.500350
70	1	0	-1.655554	-3.659707	0.827448
71	7	0	-5.196709	0.588405	1.161833
72	1	0	-6.131764	0.841192	1.479097
73	1	0	-4.497464	1.225124	1.548329
74	7	0	-3.442512	0.506304	-1.518325
75	1	0	-4.392620	0.758957	-1.234591
76	1	0	-3.063163	1.202332	-2.165273
77	7	0	-0.533795	-2.971032	-2.684434
78	1	0	0.209805	-2.274437	-2.730256
79	1	0	-0.366548	-3.800974	-3.246266

Complex 2d’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	47	0	-2.252781	-0.334613	0.172735
2	47	0	-0.021333	-0.392494	1.826899
3	47	0	2.179714	-0.248768	-0.217823
4	47	0	-0.046340	-0.362164	-1.875660
5	7	0	-0.770254	-4.240809	1.147937
6	1	0	-0.218985	-5.089521	1.059343
7	7	0	0.842617	-4.205785	-1.204332
8	1	0	0.328348	-5.077966	-1.121092
9	7	0	-3.447563	1.570214	0.041801
10	7	0	-1.449738	2.786207	0.170930
11	7	0	-0.530420	2.383187	3.418170
12	7	0	1.282797	0.999031	2.900965
13	7	0	2.983834	-0.466735	2.250268
14	7	0	5.305074	0.103395	0.293546
15	7	0	3.524192	1.577954	-0.071458
16	7	0	1.648712	2.935582	-0.403331
17	7	0	-3.101761	-0.385755	-2.336354
18	7	0	-1.350900	1.043714	-2.923289
19	7	0	0.528001	2.337423	-3.420644
20	7	0	-5.350084	0.242070	-0.278342
21	6	0	-1.256749	-2.007133	1.096147
22	6	0	-0.476011	-3.038562	0.513178
23	6	0	-1.696611	-4.039450	2.166204
24	6	0	-2.255324	-4.951418	3.072937
25	1	0	-1.990774	-6.007247	3.061871
26	6	0	-3.171940	-4.444010	3.996263
27	1	0	-3.629501	-5.117953	4.717288
28	6	0	-3.519342	-3.070650	4.012345
29	1	0	-4.236536	-2.714664	4.749461
30	6	0	-2.956502	-2.174515	3.103699
31	1	0	-3.219461	-1.115009	3.121449
32	6	0	-2.022374	-2.653658	2.158915
33	6	0	1.215328	-1.949277	-1.159434
34	6	0	0.484689	-3.015994	-0.576888
35	6	0	1.762114	-3.961242	-2.218892
36	6	0	2.369434	-4.846325	-3.121017
37	1	0	2.156409	-5.913727	-3.109314
38	6	0	3.264664	-4.296774	-4.041270
39	1	0	3.757461	-4.949047	-4.758987
40	6	0	3.545698	-2.908204	-4.058282
41	1	0	4.249058	-2.519413	-4.792211
42	6	0	2.935050	-2.038840	-3.154455
43	1	0	3.147290	-0.967793	-3.171340
44	6	0	2.018967	-2.560727	-2.214043
45	6	0	-4.795226	1.520270	-0.151795
46	6	0	-5.574756	2.676163	-0.302493
47	1	0	-6.650293	2.601074	-0.442077
48	6	0	-4.930711	3.916904	-0.244036
49	1	0	-5.511541	4.831694	-0.343702
50	6	0	-3.551940	3.987061	-0.055959
51	1	0	-3.030356	4.940361	-0.025373
52	6	0	-2.830263	2.783756	0.077365

53	6	0	0.835890	2.164824	3.442439
54	6	0	1.732293	3.142422	3.921651
55	1	0	1.352002	4.075044	4.331132
56	6	0	3.097527	2.880637	3.860925
57	1	0	3.807022	3.616439	4.233211
58	6	0	3.562883	1.660068	3.350241
59	1	0	4.621918	1.422503	3.321876
60	6	0	2.621169	0.746838	2.876857
61	6	0	4.838010	1.421315	0.247529
62	6	0	5.659733	2.501188	0.607114
63	1	0	6.707050	2.339307	0.850003
64	6	0	5.093373	3.778828	0.630562
65	1	0	5.706184	4.637325	0.898134
66	6	0	3.753892	3.960641	0.287152
67	1	0	3.301667	4.949472	0.277719
68	6	0	2.995521	2.832539	-0.078261
69	6	0	-2.696477	0.851763	-2.875769
70	6	0	-3.603095	1.852522	-3.236932
71	1	0	-4.672248	1.669722	-3.186405
72	6	0	-3.089654	3.084839	-3.659116
73	1	0	-3.770167	3.885380	-3.940638
74	6	0	-1.711832	3.278582	-3.758458
75	1	0	-1.297075	4.217172	-4.117669
76	6	0	-0.861647	2.219368	-3.398346
77	1	0	-1.111468	1.544929	3.400160
78	1	0	-0.876987	3.085544	4.067964
79	1	0	2.572164	-1.296850	2.684673
80	1	0	3.996497	-0.576845	2.136301
81	1	0	6.321015	0.019160	0.280820
82	1	0	4.879489	-0.516903	-0.398897
83	1	0	1.318505	2.282193	-1.119233
84	1	0	1.352576	3.881243	-0.637342
85	1	0	-2.702423	-1.199103	-2.810553
86	1	0	-4.116911	-0.472920	-2.235468
87	1	0	1.015999	1.472283	-3.659908
88	1	0	0.874931	3.118530	-3.976055
89	1	0	-1.038488	3.589654	0.639137
90	1	0	-1.022460	1.915547	0.492764
91	1	0	-6.363916	0.215857	-0.173364
92	1	0	-4.907468	-0.467977	0.309720

Complex 2e'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	47	0	0.494476	0.417301	1.606008
2	47	0	2.209851	0.857950	-0.690903
3	47	0	0.012287	-0.317129	-1.919988
4	47	0	-1.849804	-0.294270	0.359815
5	6	0	-0.634351	1.544929	0.145203
6	6	0	0.220698	1.662551	-1.002122
7	6	0	0.138378	2.839298	-1.855218
8	6	0	-0.792390	3.905587	-1.569761
9	6	0	-0.851651	5.032893	-2.430449
10	6	0	-1.619926	3.740877	-0.416513
11	7	0	4.164631	-0.080535	-0.358114
12	6	0	4.222704	-1.443225	-0.383085
13	6	0	5.318349	0.628230	-0.199941
14	6	0	5.438273	-2.137226	-0.323581
15	6	0	6.573427	-0.006717	-0.126644
16	6	0	6.619184	-1.396625	-0.206814
17	1	0	5.451925	-3.223618	-0.356777
18	1	0	7.477717	0.585862	-0.013842
19	1	0	7.577742	-1.909390	-0.161187
20	7	0	2.172919	-0.577053	2.601445
21	6	0	2.200461	-1.923064	2.815391
22	6	0	3.327145	0.144894	2.716373
23	6	0	3.395575	-2.593023	3.137116
24	6	0	4.552650	-0.463046	3.018376
25	6	0	4.571002	-1.846376	3.224590
26	1	0	3.391163	-3.666788	3.306989
27	1	0	5.455080	0.135820	3.101168
28	1	0	5.507340	-2.341466	3.472900
29	7	0	-1.034074	-2.189196	-2.437128
30	6	0	-2.399683	-2.112034	-2.395623
31	6	0	-0.441682	-3.406280	-2.598778
32	6	0	-3.215262	-3.240431	-2.489215
33	6	0	-1.211068	-4.587394	-2.714949
34	6	0	-2.596971	-4.489254	-2.651987
35	1	0	-4.296435	-3.142884	-2.447412
36	1	0	-0.714988	-5.546297	-2.843812
37	1	0	-3.207184	-5.385635	-2.740873
38	7	0	-3.292558	-1.919109	0.787697
39	6	0	-2.913741	-3.224502	0.850661
40	6	0	-4.620446	-1.605411	0.831725
41	6	0	-3.851821	-4.266670	0.953226
42	6	0	-5.611065	-2.598901	0.913251
43	6	0	-5.207217	-3.934757	0.977051
44	1	0	-3.518294	-5.299861	1.005638
45	1	0	-6.661900	-2.322489	0.947222
46	1	0	-5.955241	-4.721249	1.053939
47	7	0	3.002152	-2.107108	-0.537400
48	1	0	2.234739	-1.694742	-0.002007
49	1	0	3.055206	-3.108066	-0.354811
50	7	0	5.205454	1.999074	-0.046834
51	1	0	4.334795	2.421165	-0.367248
52	1	0	6.027289	2.545252	-0.295246

53	7	0	3.217923	1.499884	2.413610
54	1	0	2.436338	1.989289	2.850275
55	1	0	4.087043	2.026176	2.486227
56	7	0	1.022771	-2.610254	2.572785
57	1	0	0.154787	-2.086259	2.684599
58	1	0	0.959014	-3.543714	2.972458
59	7	0	-1.547394	-3.475542	0.853144
60	1	0	-0.974857	-2.756946	0.407862
61	1	0	-1.285661	-4.409686	0.545944
62	7	0	-4.939765	-0.259313	0.698768
63	1	0	-5.914410	-0.033916	0.890370
64	1	0	-4.314238	0.403460	1.165154
65	7	0	-2.916986	-0.828673	-2.147280
66	1	0	-3.934280	-0.794157	-2.074522
67	1	0	-2.576325	-0.099554	-2.778269
68	7	0	0.929699	-3.454815	-2.543551
69	1	0	1.455874	-2.582894	-2.593831
70	1	0	1.388628	-4.251647	-2.975346
71	6	0	-1.537176	2.609108	0.436616
72	6	0	-0.027895	5.119932	-3.543587
73	6	0	0.881148	4.075741	-3.840763
74	6	0	0.956272	2.964765	-3.013425
75	1	0	-1.547137	5.844044	-2.217657
76	1	0	-0.083711	5.991306	-4.192714
77	1	0	1.515992	4.145276	-4.721911
78	1	0	1.644513	2.149469	-3.247530
79	6	0	-2.533832	2.788703	1.477358
80	6	0	-3.194336	4.020509	1.200212
81	6	0	-4.242097	4.504527	1.995599
82	6	0	-4.628611	3.726484	3.091514
83	1	0	-5.436996	4.075313	3.730680
84	6	0	-3.980280	2.507230	3.396035
85	1	0	-4.290572	1.942009	4.272866
86	6	0	-2.930740	2.034504	2.601270
87	1	0	-2.409026	1.112537	2.864827
88	7	0	-2.611994	4.572800	0.058281
89	1	0	-2.885082	5.458791	-0.352931
90	1	0	-4.736516	5.448385	1.774396

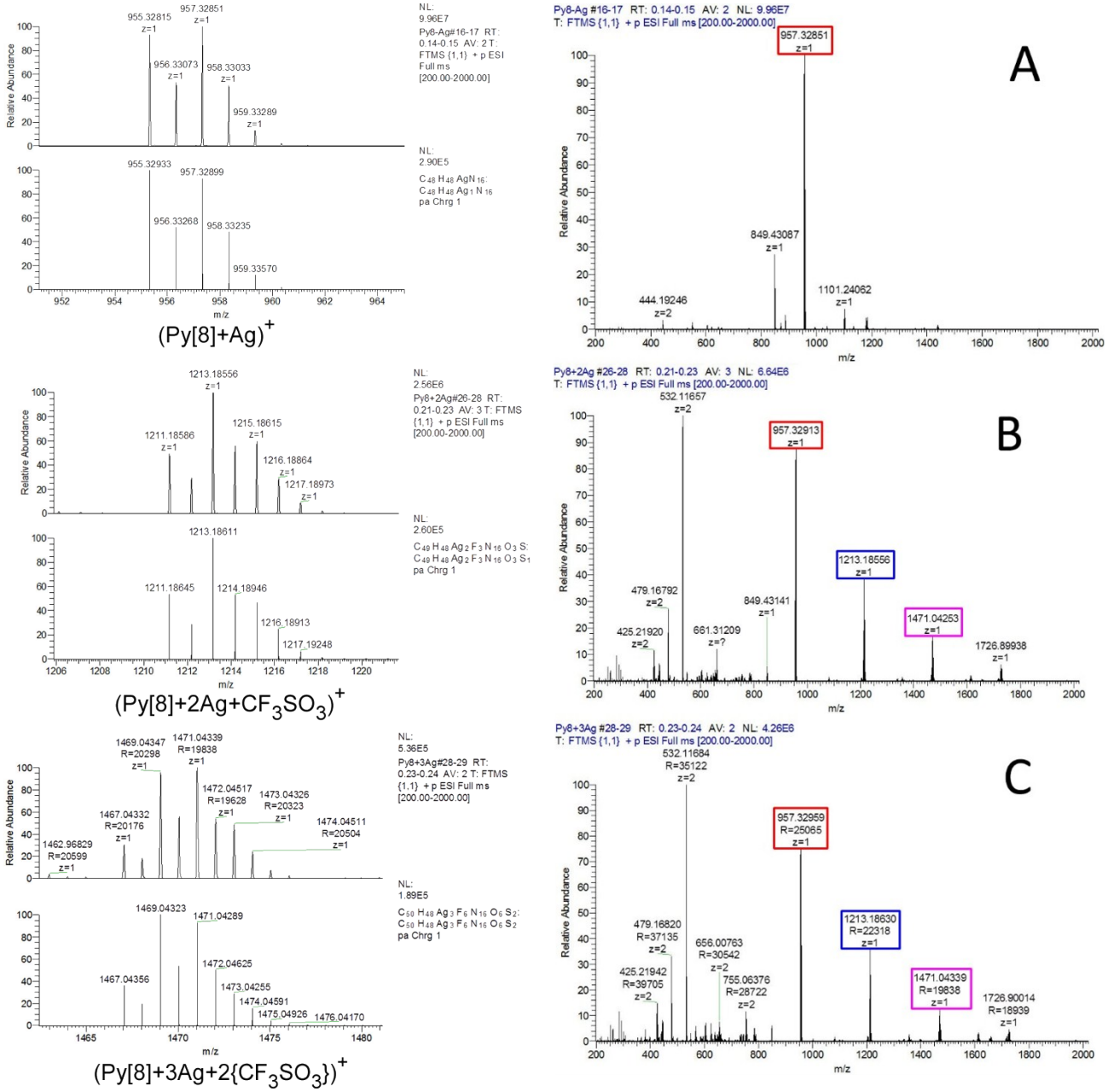


Fig. S1 (left) Experimental (top) and theoretical (bottom) isotopic distribution of the species (**Py[8]**+Ag)$^+$, (**Py[8]**+2Ag+CF_3SO_3)$^+$ and (**Py[8]**+3Ag+2{CF_3SO_3})$^+$ in ESI-MS spectra. (right) ESI-MS spectra of the methanol solution containing **Py[8]** and (A) 1 equiv., (B) 2 equiv., and (C) 3 equiv. $AgCF_3SO_3$.

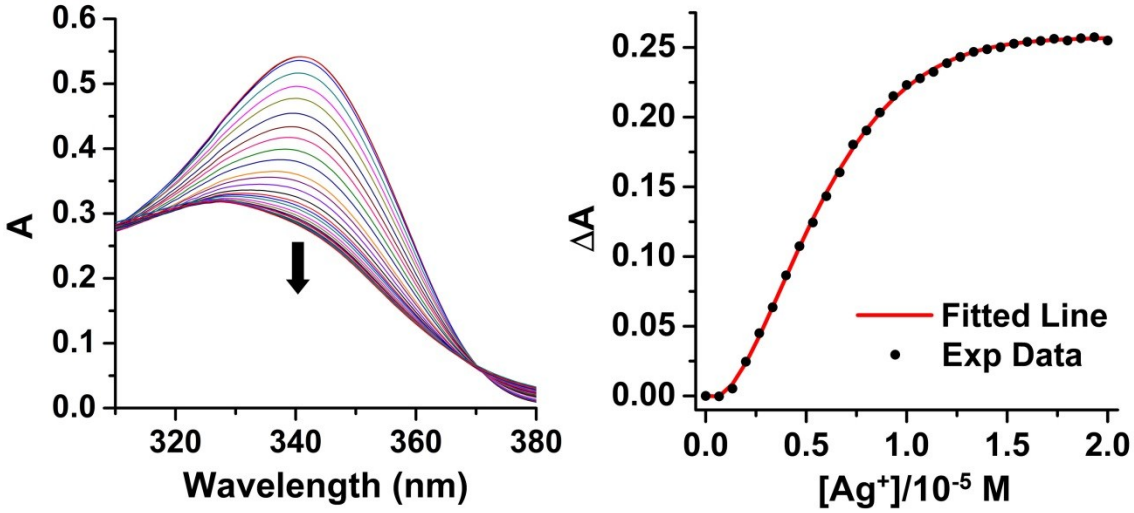


Fig. S2 (left) UV-vis titration curves of **Py[8]** (6.7 μM) in response to $AgCF_3SO_3$ from 0 to 4 equivalents with a variation step of 0.67 μM (CH_2Cl_2/CH_3OH = 1:1, 298 K). (right) The fitting line (at 340 nm) with a **Py[8]**:$AgCF_3SO_3$ = 3:1 model. The binding constants for the complexation of **Py[8]** with three silver ions are acquired by using the Hyperquad 2003 program to fit the binding isotherm curve.

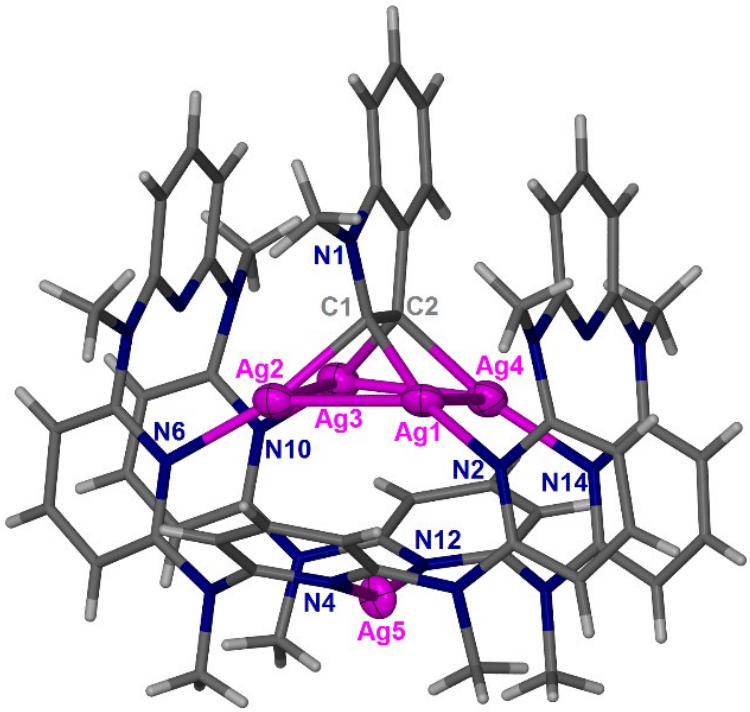


Fig. S3 Crystal structure of complex **2b**. Peripheral $CF_3SO_3^-$ anions and solvent molecules are omitted for clarity. Color coding: Ag, purple (ellipsoids set at 50% probability); C, gray; H, white; N, blue.

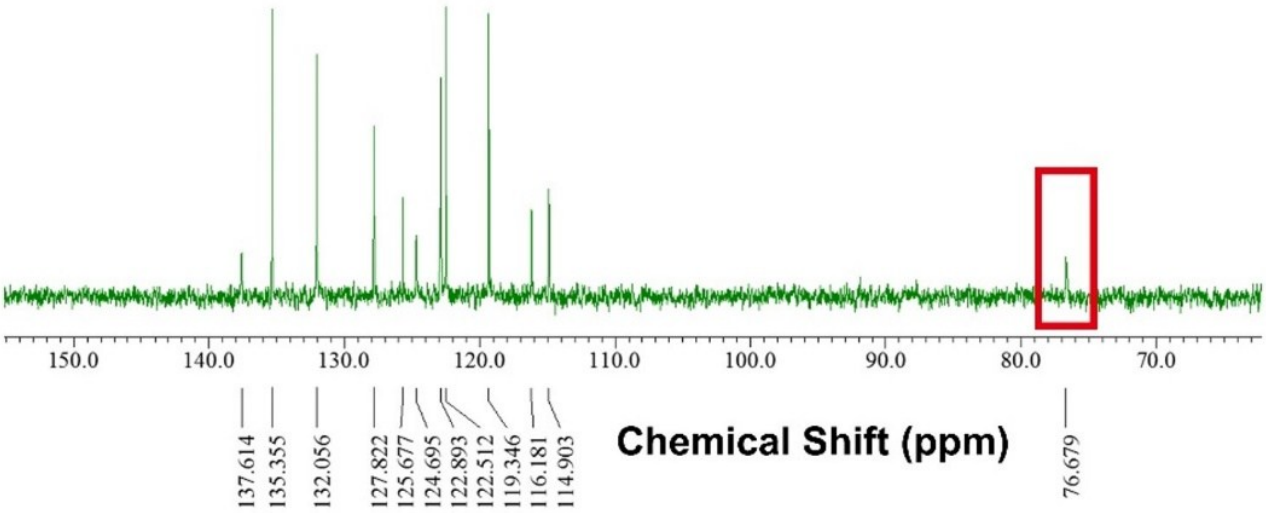


Fig. S4 ^{13}C-NMR spectrum of the CD_3OD mixture of 1 equiv. **1a** and 4 equiv. $AgCF_3SO_3$ stirred for ten hours.

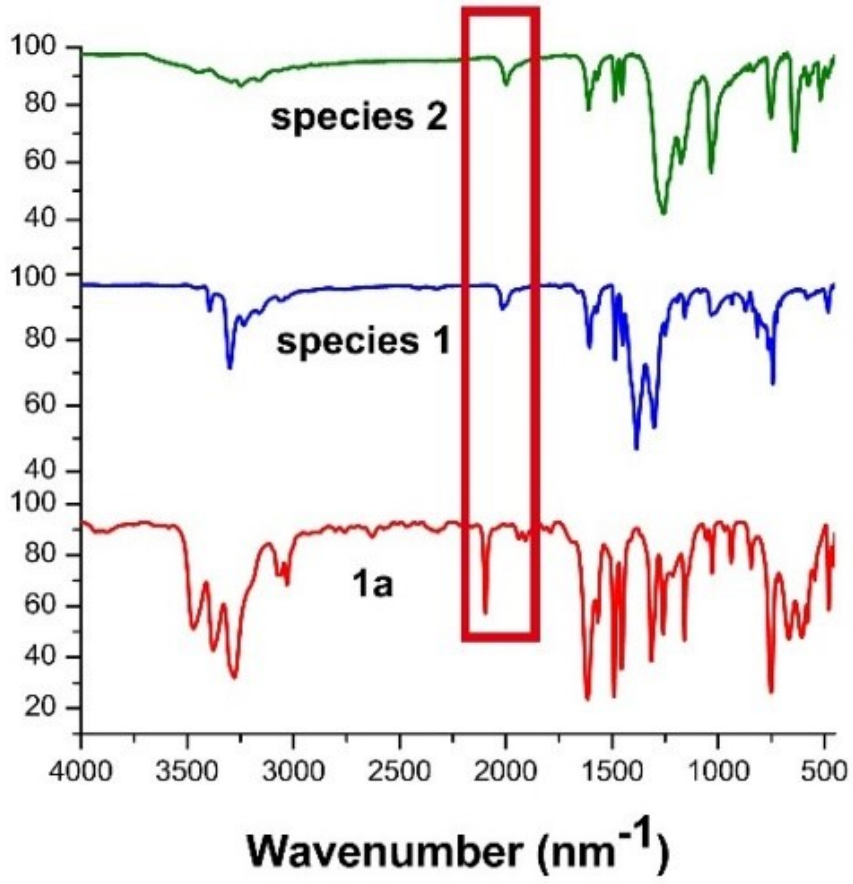


Fig. S5 IR spectra of **1a**, species **1** and **2**. Species **1** ($[RC{\equiv}CAg]_n$) was purposefully synthesized by mixing **1a** with 1 equiv. silver nitrate in the presence of triethylamine. Species **2** ($[RC{\equiv}CAg_n](CF_3SO_3)_{n-1}$) was prepared by diluting the methanol mixture of 1 equiv. **1a** and 4 equiv. $AgCF_3SO_3$ and collecting the precipitate.

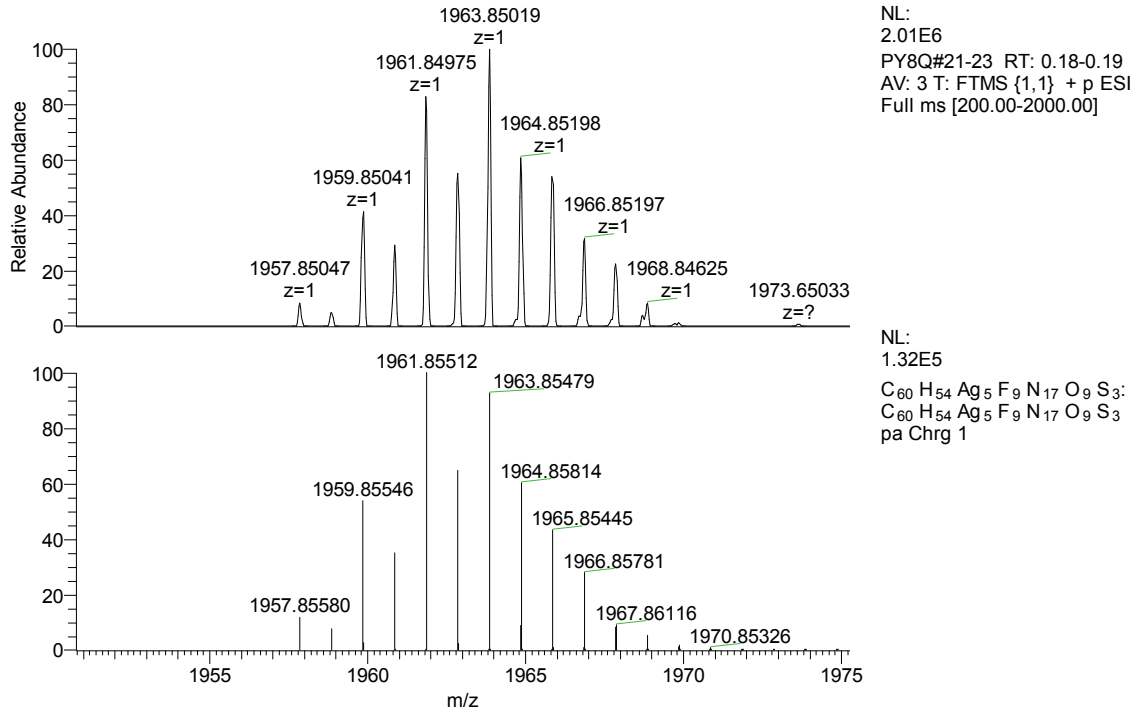


Fig. S6 Experimental (above) and theoretical (bottom) isotopic distribution of the ion fragment [**2c**–CF_3SO_3]$^+$, confirming the existence of a quinolinium cationic species.

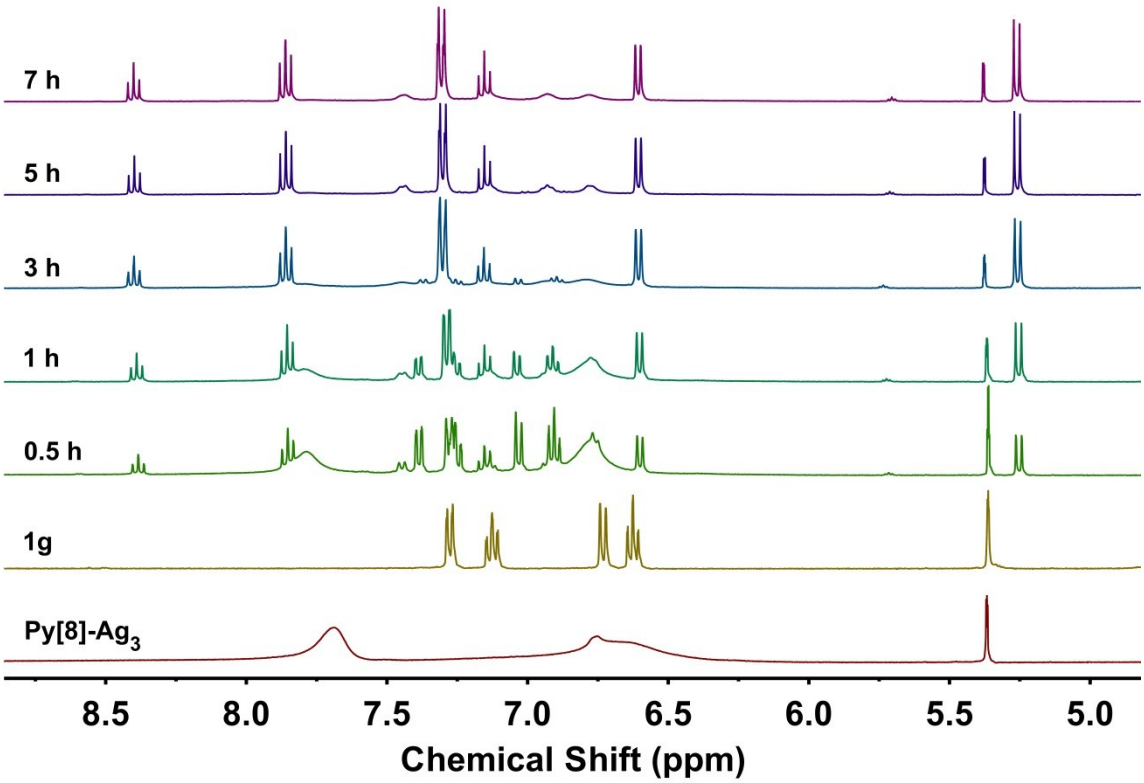


Fig. S7 ^{1}H-NMR (400 MHz, CD_3OD-CD_2Cl_2, 298 K) monitoring for the transformation of **1d** to **2d** in different time intervals.

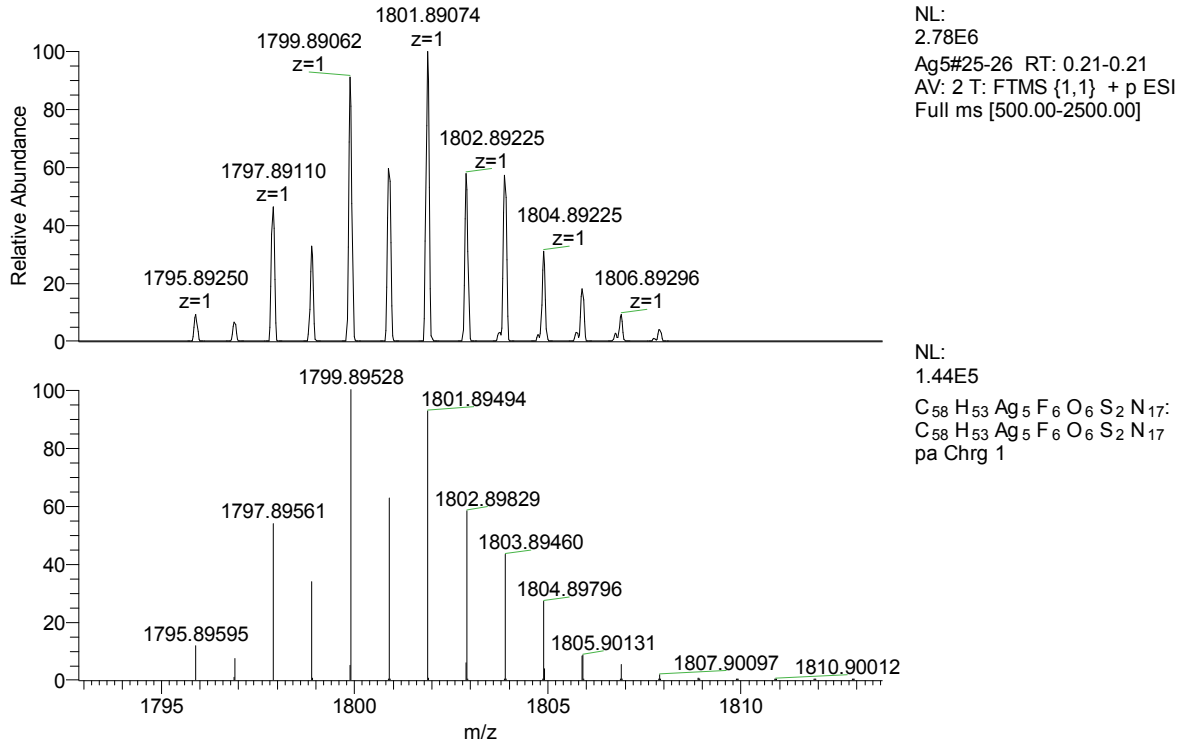


Fig. S8 Experimental (above) and theoretical (bottom) isotopic distribution of the ion fragment [**2a**–CF_3SO_3]$^+$.

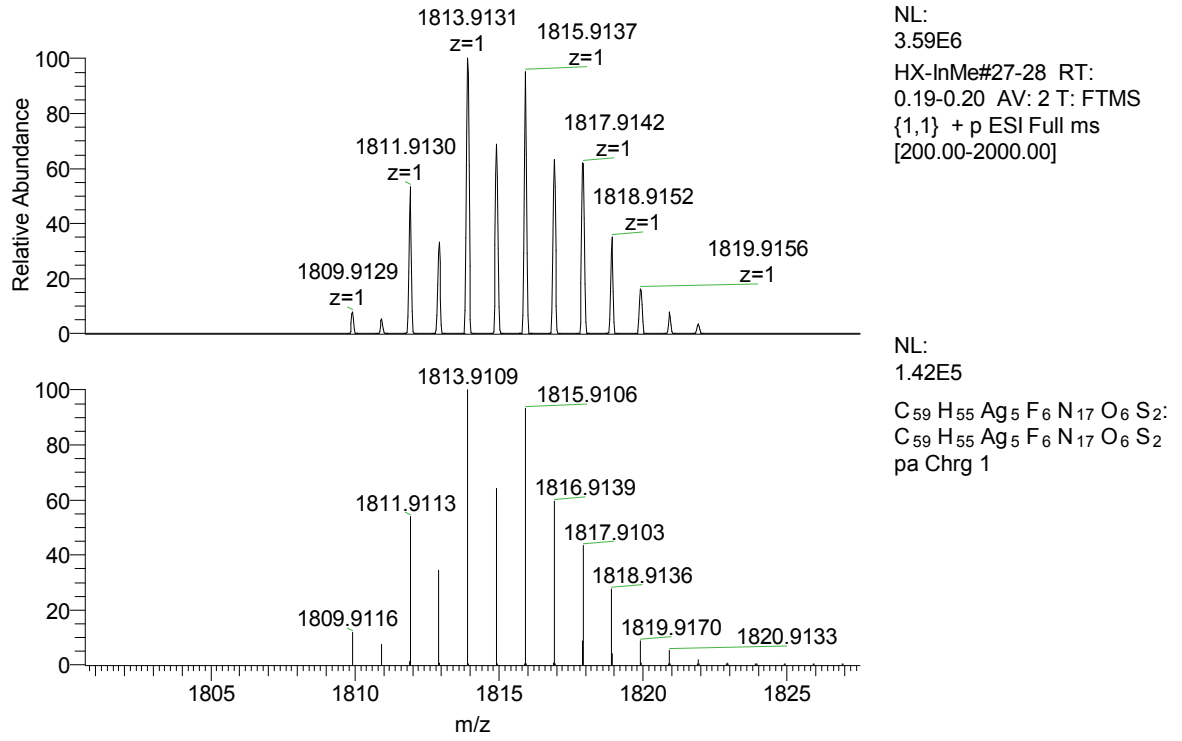


Fig. S9 Experimental (above) and theoretical (bottom) isotopic distribution of the ion fragment [**2b**–CF_3SO_3]$^+$.

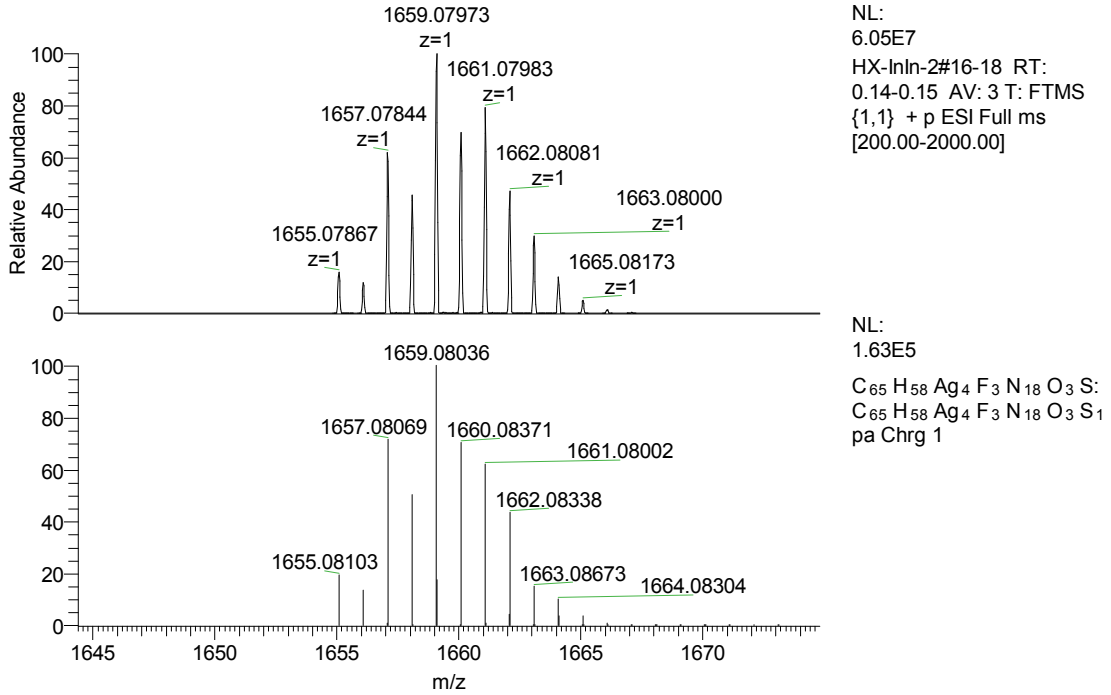


Fig. S10 Experimental (above) and theoretical (bottom) isotopic distribution of the ion fragment [**2d**–Ag^+–$2CF_3SO_3^-$]$^+$.

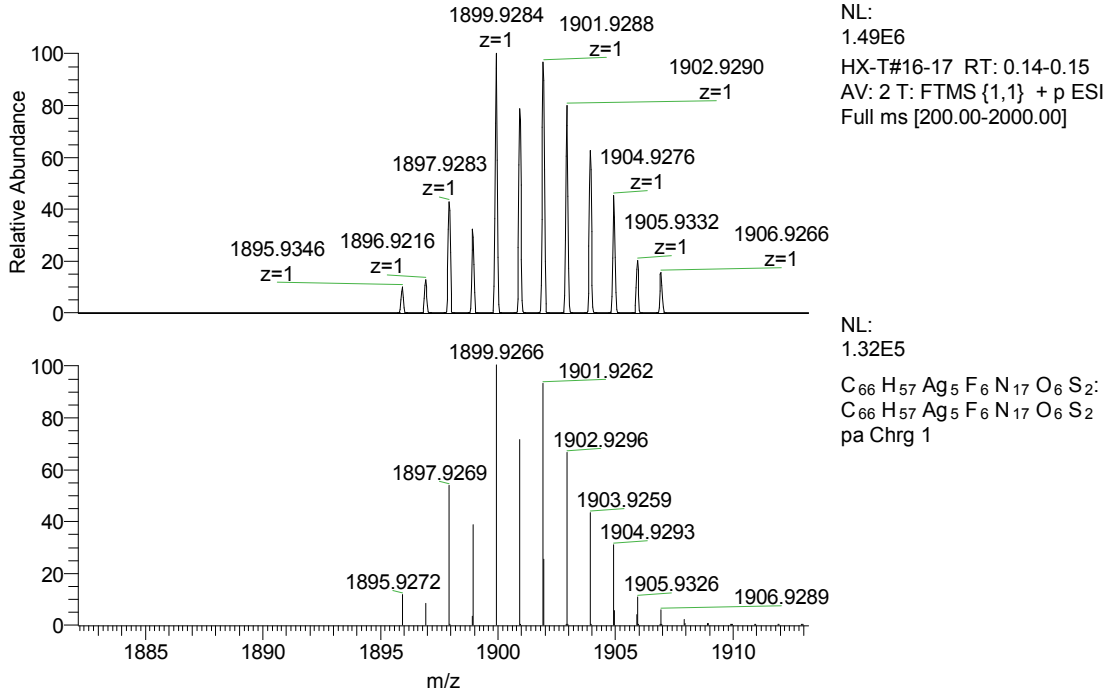


Fig. S11 Experimental (above) and theoretical (bottom) isotopic distribution of the ion fragment [**2e**–CF_3SO_3]$^+$.

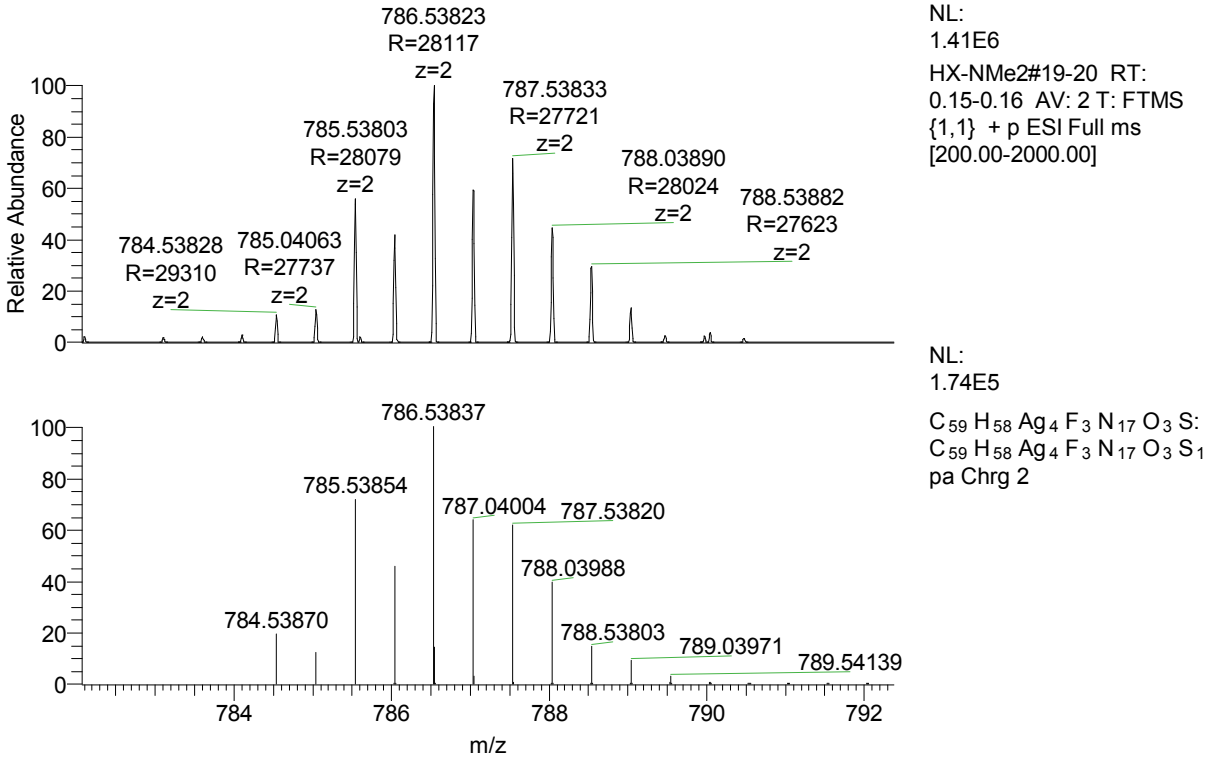


Fig. S12 Experimental (above) and theoretical (bottom) isotopic distribution of the ion fragment [**2f**–CF_3SO_3]$^+$.

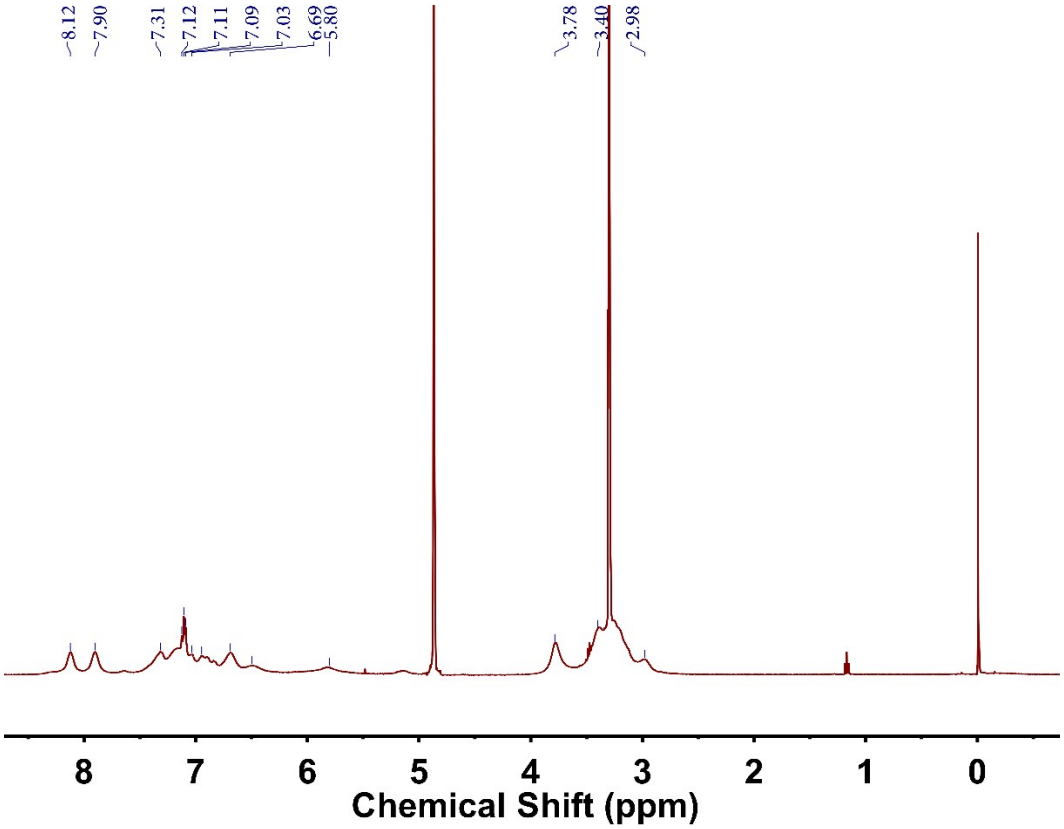


Fig. S13 ^{1}H-NMR spectrum of **2a** (400 MHz, CD_3OD, 298 K).

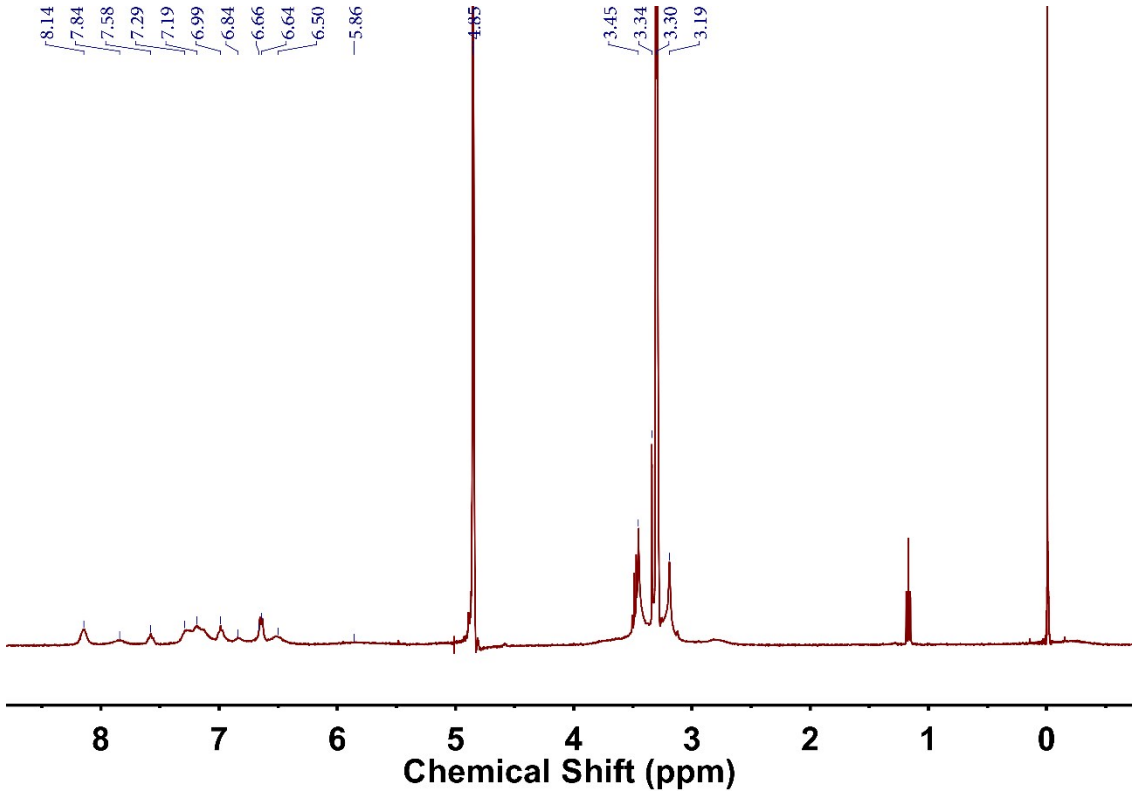


Fig. S14 ^{1}H-NMR spectrum of **2b** (400 MHz, CD_3OD, 298 K).

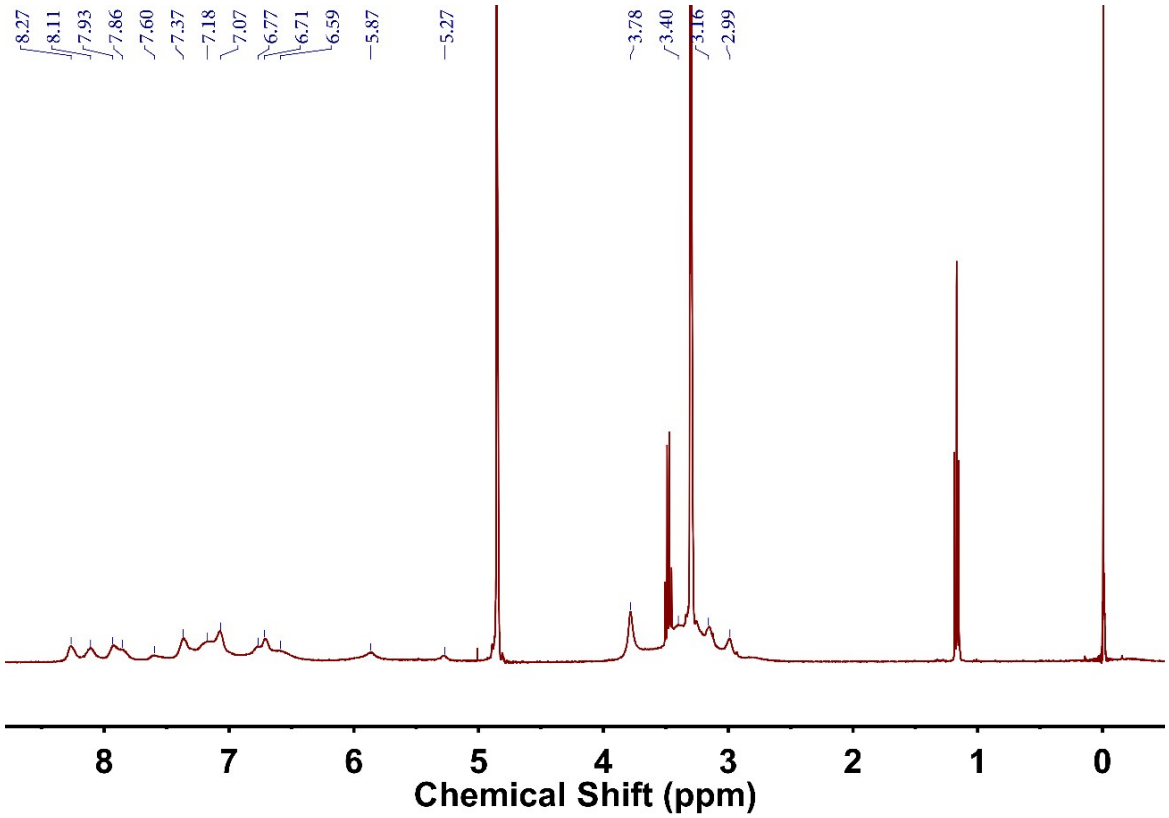


Fig. S15 ^{1}H-NMR spectrum of **2c** (400 MHz, CD_3OD, 298 K).

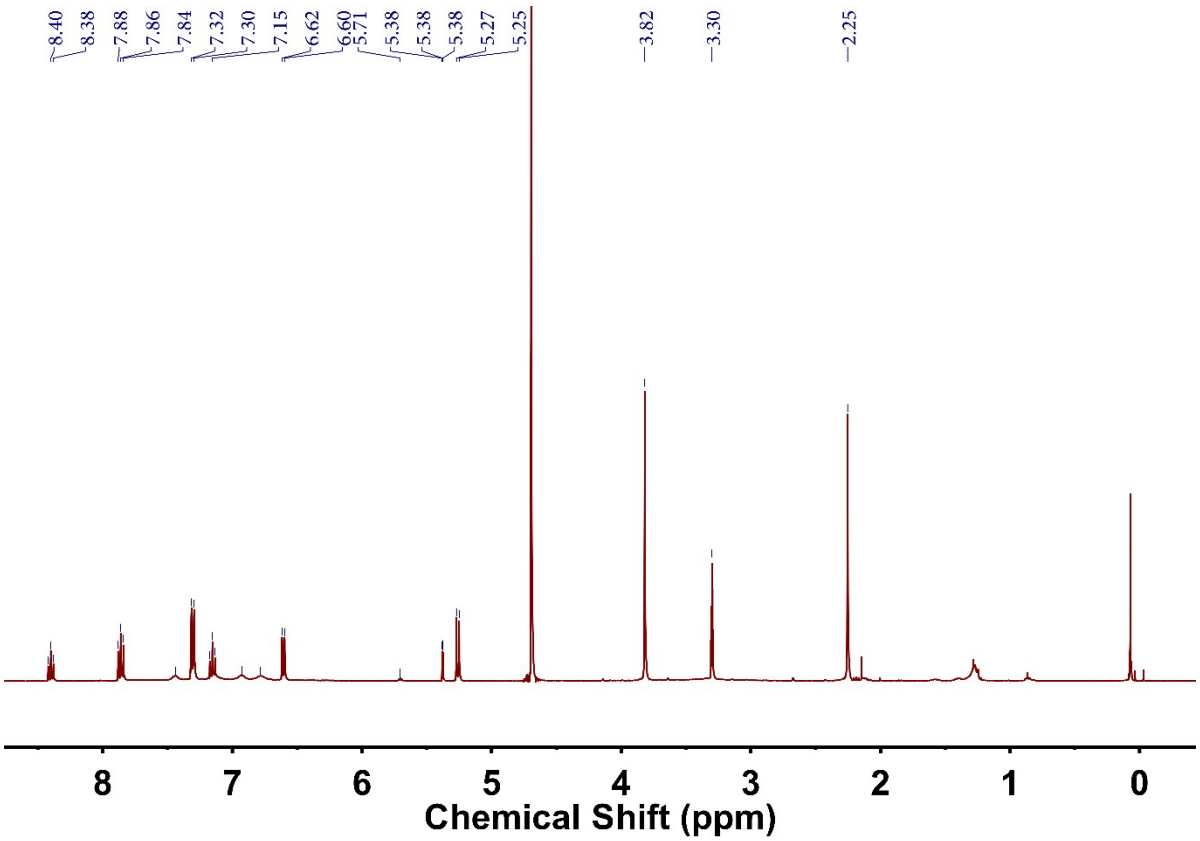


Fig. S16 ^{1}H NMR spectrum of **2d** (400 MHz, CD_3OD:CD_2Cl_2 = 1:1, 298 K).

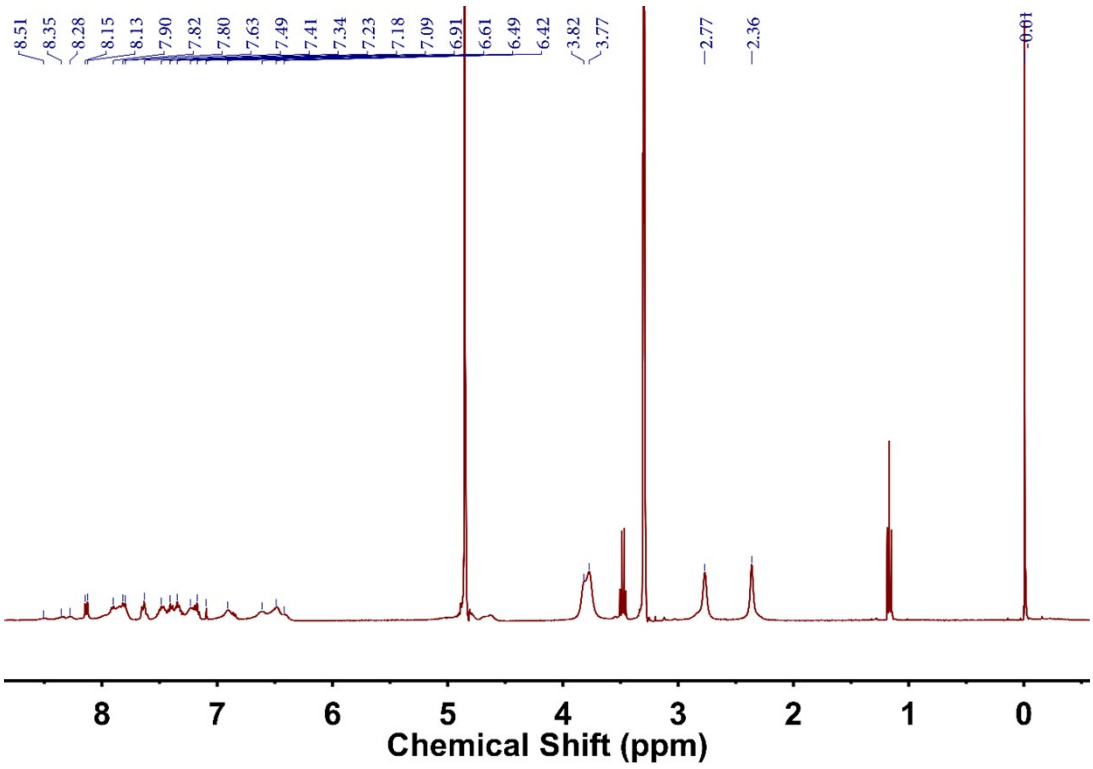


Fig. S17 ^{1}H NMR spectrum of **2e** (400 MHz, CD_3OD, 298 K).

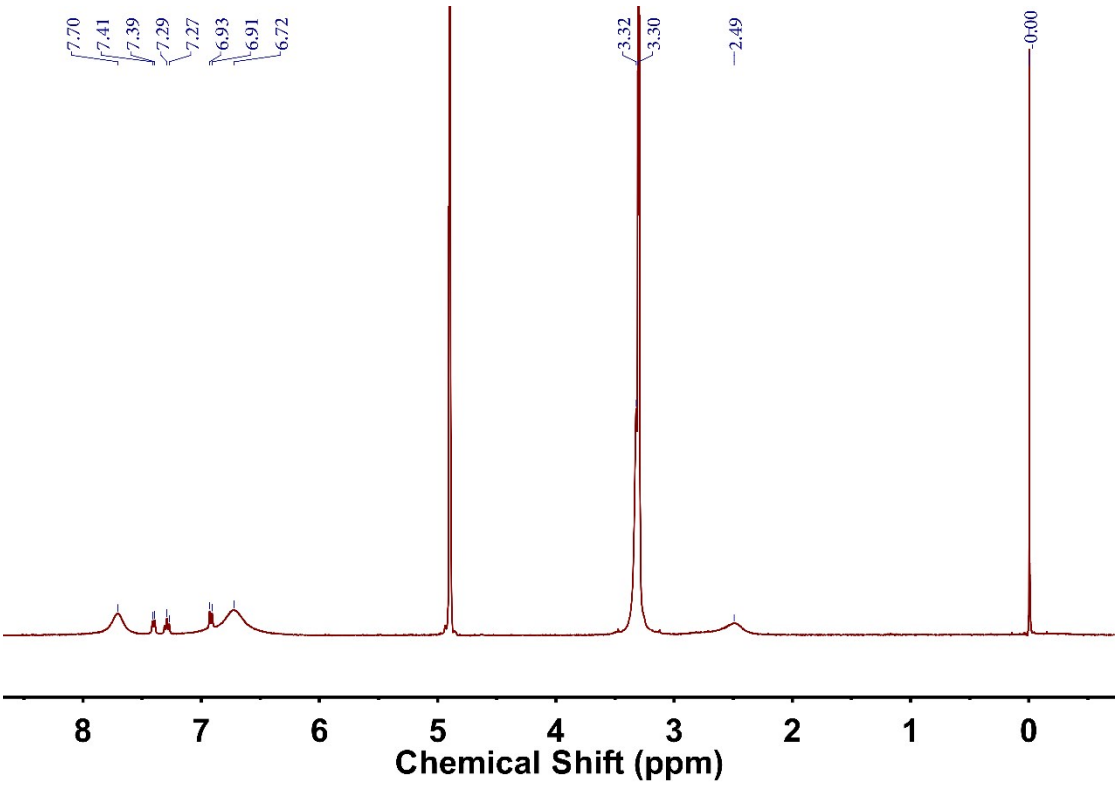


Fig. S18 ^{1}H NMR spectrum of **2f** (400 MHz, CD_3OD, 298 K).

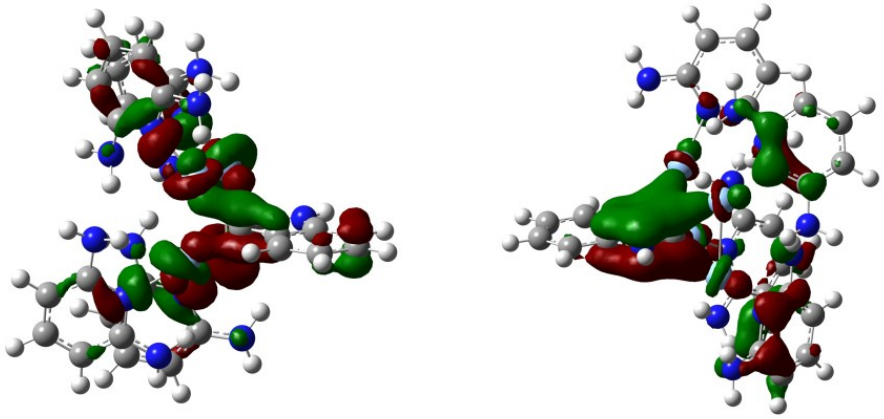


Fig. S19 Molecular orbitals of **2a'** manifesting the participation of p_{π} orbitals of indole ring in the bonding with silver atoms. The energy is given in atomic unit, similarly hereinafter.

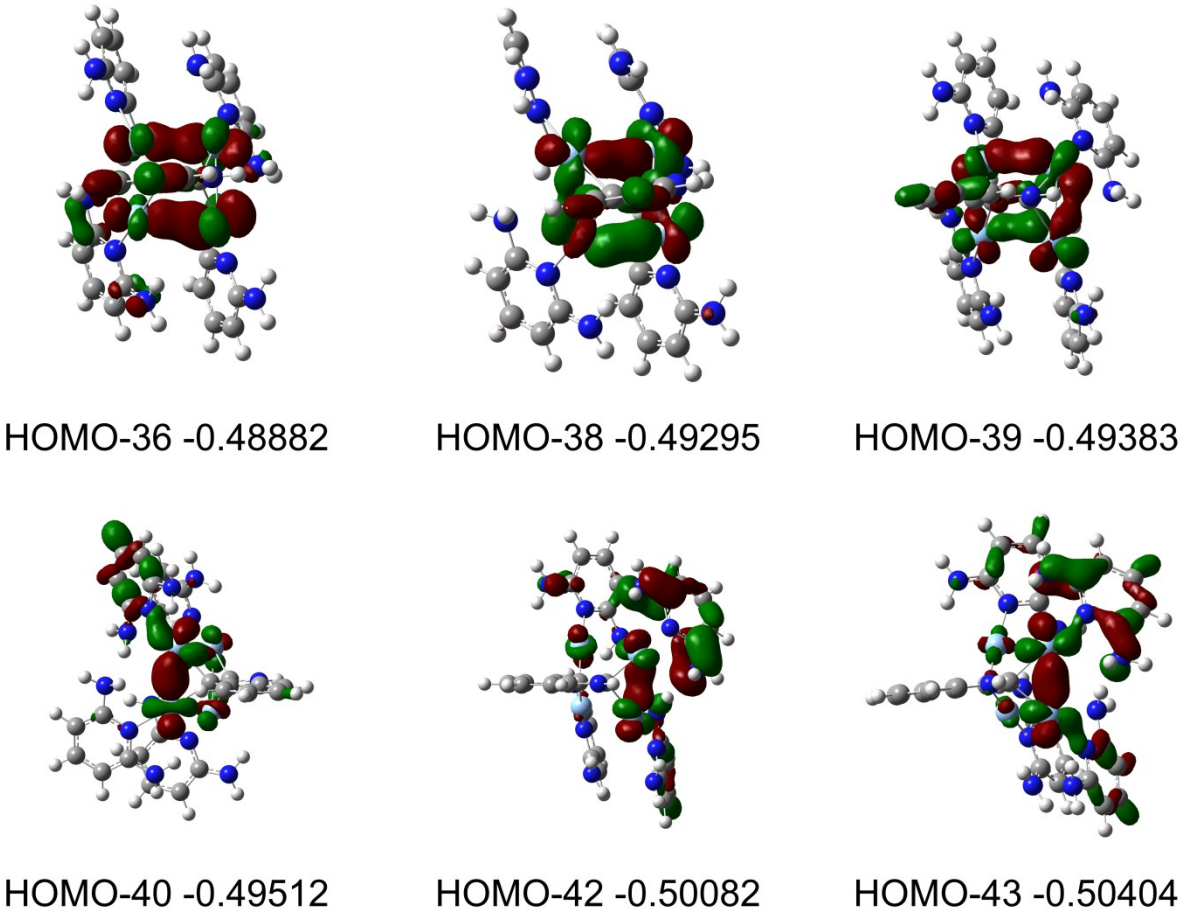


Fig. S20 Molecular orbitals related to argentophilic interactions in **2a'**.

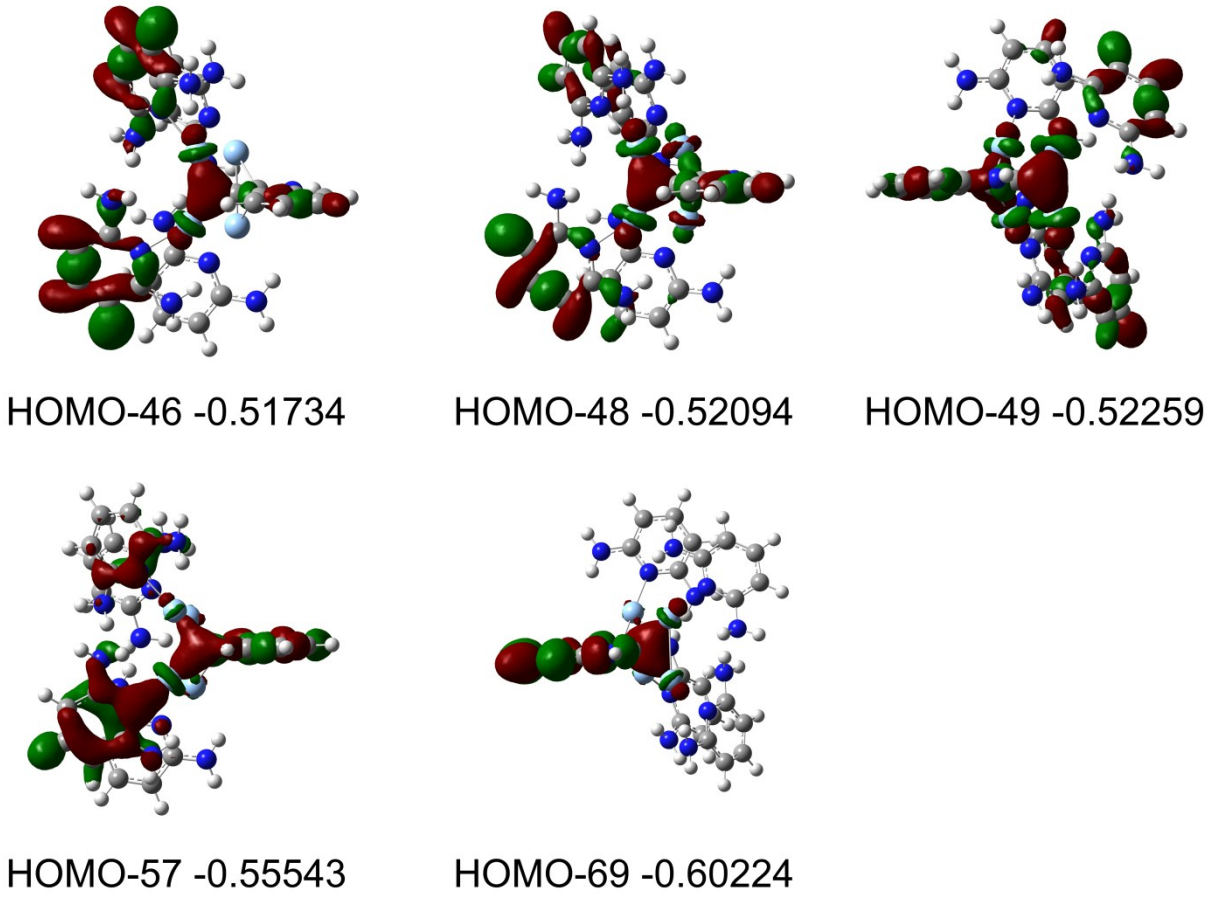


Fig. S21 Molecular orbitals related to three-centered Ag-C bonds in **2a'**.

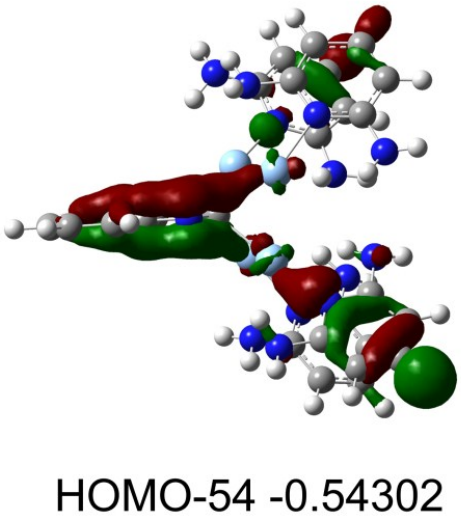
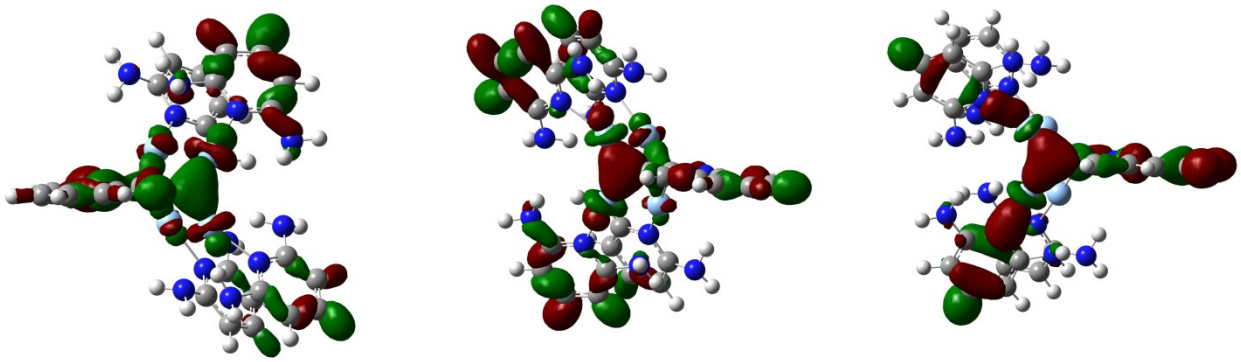
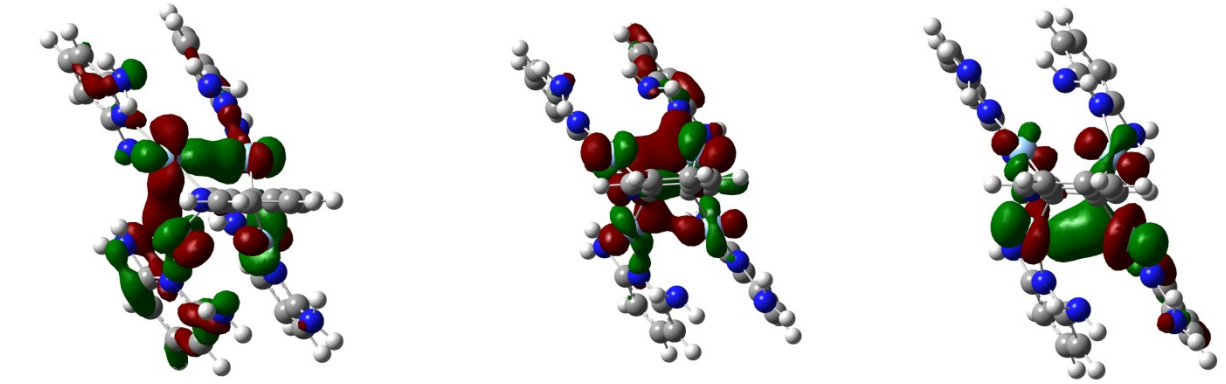


Fig. S22 Molecular orbitals manifesting the participation of p_{π} orbitals in bonding with silver atoms of **2c'.**

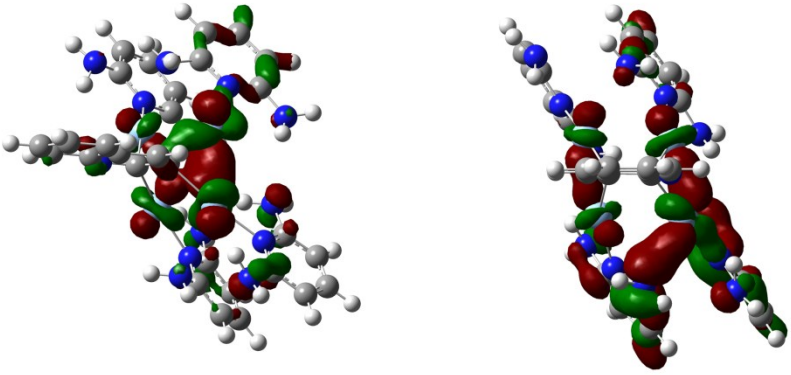


HOMO-49 -0.52110 HOMO-50 -0.52352 HOMO-62 -0.56459

Fig. S23 Molecular orbitals related to three-centered Ag-C bonds in **2c'**.

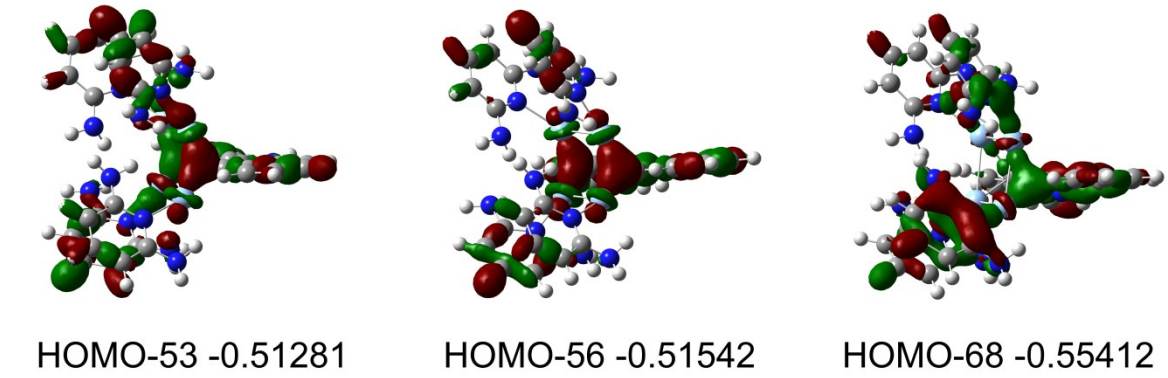


HOMO-36 -0.48844 HOMO-37 -0.48929 HOMO-40 -0.49311



HOMO-41 -0.49889 HOMO-45 -0.50698

Fig. S24 Molecular orbitals related to argentophilic interactions in **2c'**.



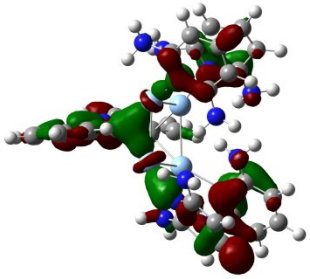
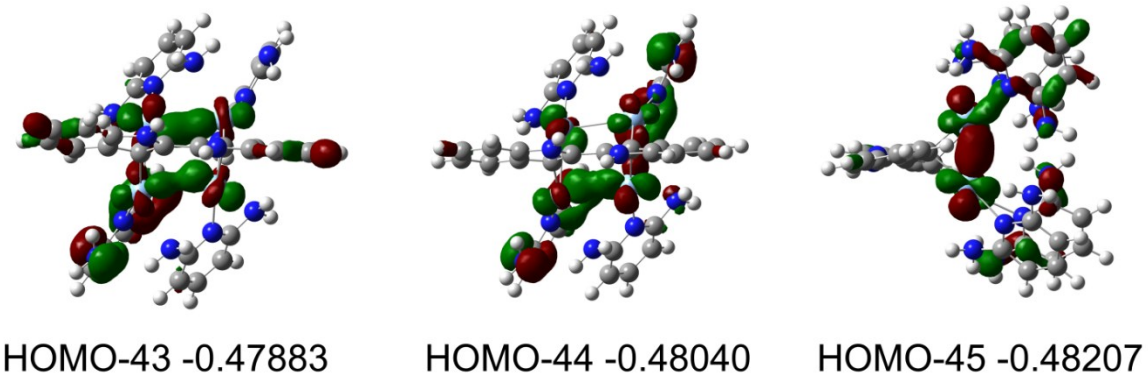


Fig. S25 Molecular orbitals related to three-centered Ag-C bonds in **2d'**.



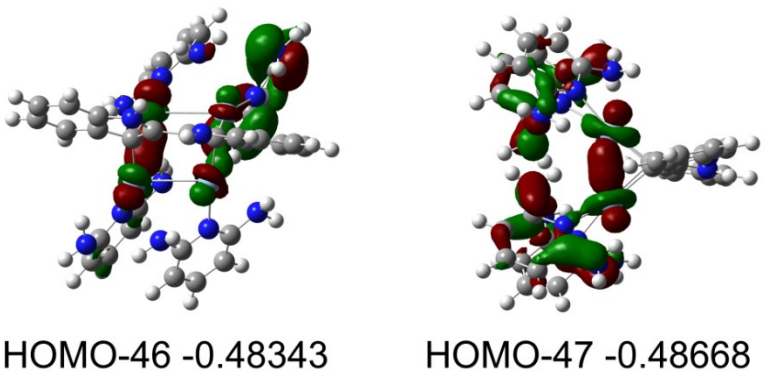
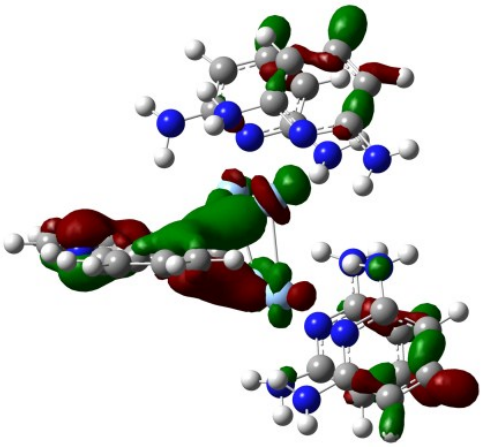
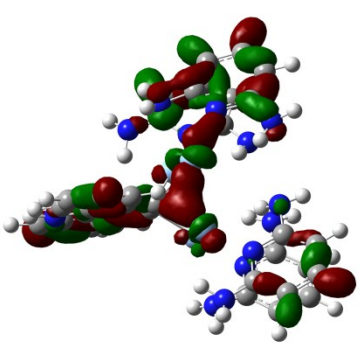


Fig. S26 Molecular orbitals related to argentophilic interactions in **2d'**.

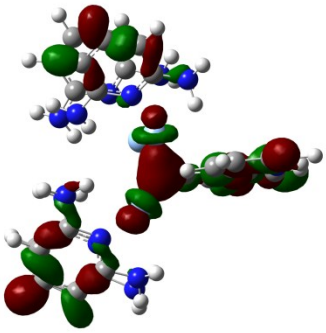


HOMO-55 -0.51889

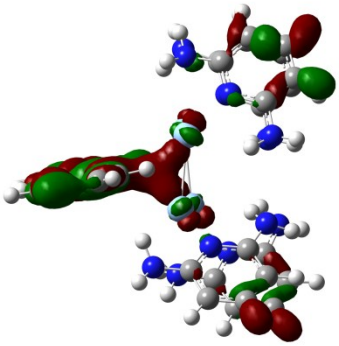
Fig. S27 Molecular orbitals manifesting the participation of p_π orbitals in bonding with silver atoms of **2e'.**



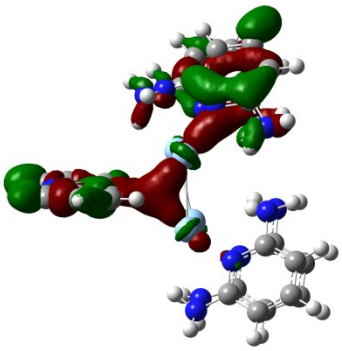
HOMO-52 -0.51151



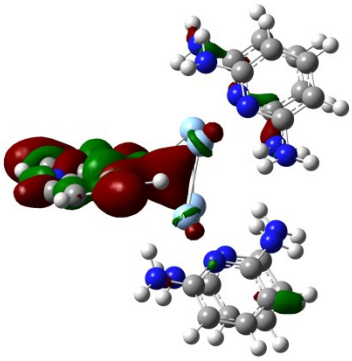
HOMO-53 -0.51215



HOMO-57 -0.52237



HOMO-72 -0.56883



HOMO-79 -0.59720

Fig. S28 Molecular orbitals related to three-centered Ag-C bonds in **2e'**.

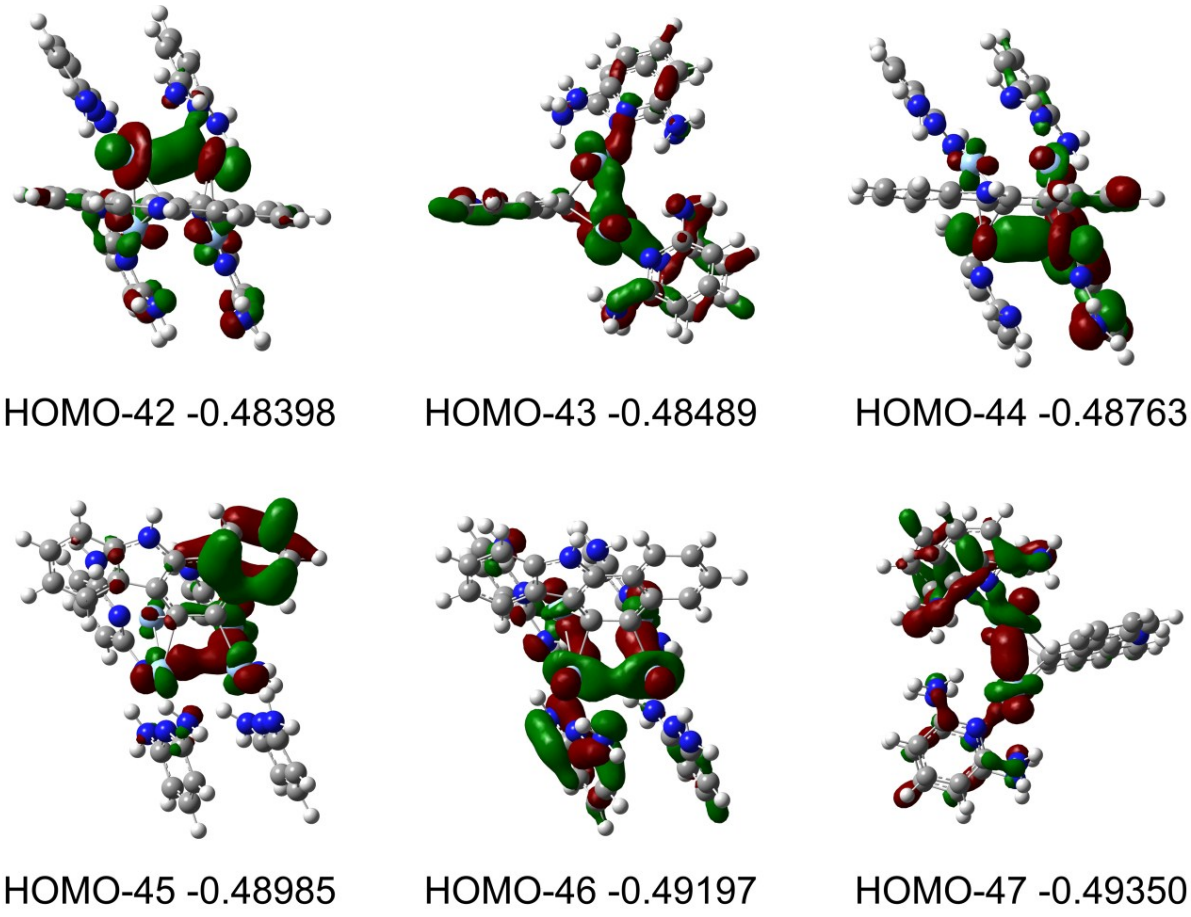


Fig. S29 Molecular orbitals related to argentophilic interactions in **2e'**.