Supporting Information

for

Pyrazolate *vs* phenylethynide: direct exchange of anionic bridging ligand in cyclic trinuclear silver complex

Aleksei A. Titov,*[a] Alexander F. Smol'yakov,[a,b] Andrey Yu. Chernyadyev,[c] Ivan A. Godovikov,[a] Oleg A. Filippov,*[a] Elena S. Shubina[a]

a. A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), 119991 Moscow, Vavilov St. 28, bld. 1, Russia. E-mail: tit@ineos.ac.ru (AAT); h-bond@ineos.ac.ru (OAF);
b. Plekhanov Russian University of Economics, Stremyanny per. 36, Moscow 117997, Russia
c. A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky prosp. 31/4, 199071 Moscow, Russia.

1. Physical measurement and instrumentation

^{1}H, ^{19}F, and ^{13}C NMR measurements were carried out on Bruker Avance-III-500 spectrometer with CryoProbe Prodigy operating at 500.13 MHz. FTIR spectra were collected on a Shimadzu IRPrestige 21 FT-IR spectrometer using KBr pellets. The powder X-ray diffraction pattern for Rietveld analysis was collected at room temperature (298 K) with a Bruker D8 ADVANCE diffractometer.

Photoluminescence

The photoluminescence spectra of solid samples and frozen solutions, lifetime measurements of the phosphorescence were recorded at 77 K and 298 K, on the Fluorolog-3 spectrofluorometer system (HORIBA Jobin–Yvon) (the excitation source was a 450 W Xenon lamp with Czerny–Turner double monochromators, the registration channels were a R928 photomultiplier, while 150 W pulsed Xenon lamp was used for lifetime measurements). The samples for these measurements were packed in quartz capillaries. The phosphorescence quenching curves were analyzed using the FluoroEssence™ software for calculation of the phosphorescence lifetime values. Photoluminescence quantum yield were measured by absolute method for the solid samples at T = 298 K. Light of photoluminescence was collected by Quanta-ϕ F-3029-sphere linked with Fluorolog 3 by Fiber-Optics adaptor FL-3000 produced by Horiba

Jobin Yvon. Fluorescence quantum yields were calculated by FluoroEssence software of Horiba.

SC-XRD study

Single-crystal X-ray diffraction experiments of complexes **1Ag** and **1Ag'** were carried out with a Bruker APEX-II diffractometer. The APEX II software[1] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction. The structures were solved by dual-space algorithm and refined in anisotropic approximation for non-hydrogen atoms against $F^2(hkl)$. Hydrogen atoms of aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H bond lengths and equivalent displacement parameters (U_{eq} (H) = 1.2U_{eq} (X), X - cental atom of XH_2 group; U_{eq} (H) = 1.5U_{eq} (Y), Y - central atom of YH_3 group). All structures were solved with the ShelXT[2] program and refined with the ShelXL [3] program. Molecular graphics was drawn using OLEX2[4] program. The solvent mask was used for **1Ag'·[AgL]$_3$** and calculated for 0.5[C_6H_{14}] (*n*-hexane). The contribution of these molecules to structure factors (1Ag'·[AgL]3.) was excluded using SQUEEZE[4] routine implemented in PLATON software[6].

Table S1. Experimental details and refinement parameters for complexes **1Ag** and {**1Ag'·**$[AgPz]_3$}.

Compound	**1Ag**	{**1Ag'·**$[AgPz]_3$}**.**
CCDC number	2296782	2296783
Empirical formula	$C_{18}H_7Ag_3F_{12}N_4$	$C_{33}H_{10}Ag_6F_{30}N_{10}$
Formula weight	830.86	1763.73
Temperature/K	296.15	296.15
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	8.2213(5)	13.3037(6)
b/Å	12.3633(8)	15.8607(7)
c/Å	12.5168(8)	16.9640(8)
α/°	116.4550(10)	90.3820(10)
β/°	95.181(2)	106.1520(10)
γ/°	102.301(2)	109.6750(10)
Volume/$Å^3$	1087.63(12)	3217.5(3)
Z	1	2
$\rho_{calc}g/cm^3$	2.537	1.821
μ/mm^{-1}	2.793	1.907
F(000)	784.0	1660.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.718 to 58	3.406 to 58
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 13, -17 ≤ l ≤ 17	-18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23
Reflections collected	11538	65308
Independent reflections	5780 [R_{int} = 0.0169, R_{sigma} = 0.0264]	17054 [R_{int} = 0.0232, R_{sigma} = 0.0204]
Data/restraints/parameters	5780/36/361	17054/0/712
Goodness-of-fit on F^2	1.033	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0281, wR_2 = 0.0627	R_1 = 0.0423, wR_2 = 0.1280
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0659	R_1 = 0.0484, wR_2 = 0.1327
Largest diff. peak/hole / e $Å^{-3}$	1.82/-1.04	1.36/-1.18

2. Experimental section

Initial trinuclear silver complex $[AgL]_3$ was obtained according to a previously published procedure.[7]

Complex **1Ag.** Yield: 35.3 mg (68%). The solution of $[AgPz]_3$ (0.0625 mmol, 58.3 mg) and three equivalents of phenylacetylene (0.1875 mmol, 20.6 µl) was stirred in CH_2Cl_2 (2 mL) overnight at room temperature. The mixture was protected from light using aluminum foil. The resulting slurry precipitate was filtered and washed with CH_2Cl_2 (2 mL), hexane

(3 ml). The product was dried under reduced pressure at 40°. ^{1}H NMR (500 MHz, C_6D_6): δ = 6.55 (s, 2H, CH^{Pz}); 6.77 (br s, 3H, *m*- and *p* H in Ph); 7.29 (br s, 2H, *p*-H in Ph). ^{19}F NMR (470 MHz, C_6D_6): δ = – 60.73 (CF_3^{Pz}). ^{13}C NMR (125 MHz, C_6D_6): δ = 102.7, 119.95 (Ph*C*≡C$^-$), 120.9 (q, $J^1_{C\text{-}F}$ = 269. Hz), 128.2, 129.7, 132.5, 143.7 (q, $J^2_{C\text{-}F}$ = 36.4 Hz). IR (KBr, cm^{-1}): 3155 (νCH^{Pz}), 2054 (ν$C{\equiv}C^{PhCC}$), 1636 (δCH^{Pz}) Elemental analysis $C_{18}H_7Ag_3F_{12}N_4$ Found/Calc. (%) = **C** 26.15/26.02; **H** 1.01/0.85; **N** 6.58/6.74.

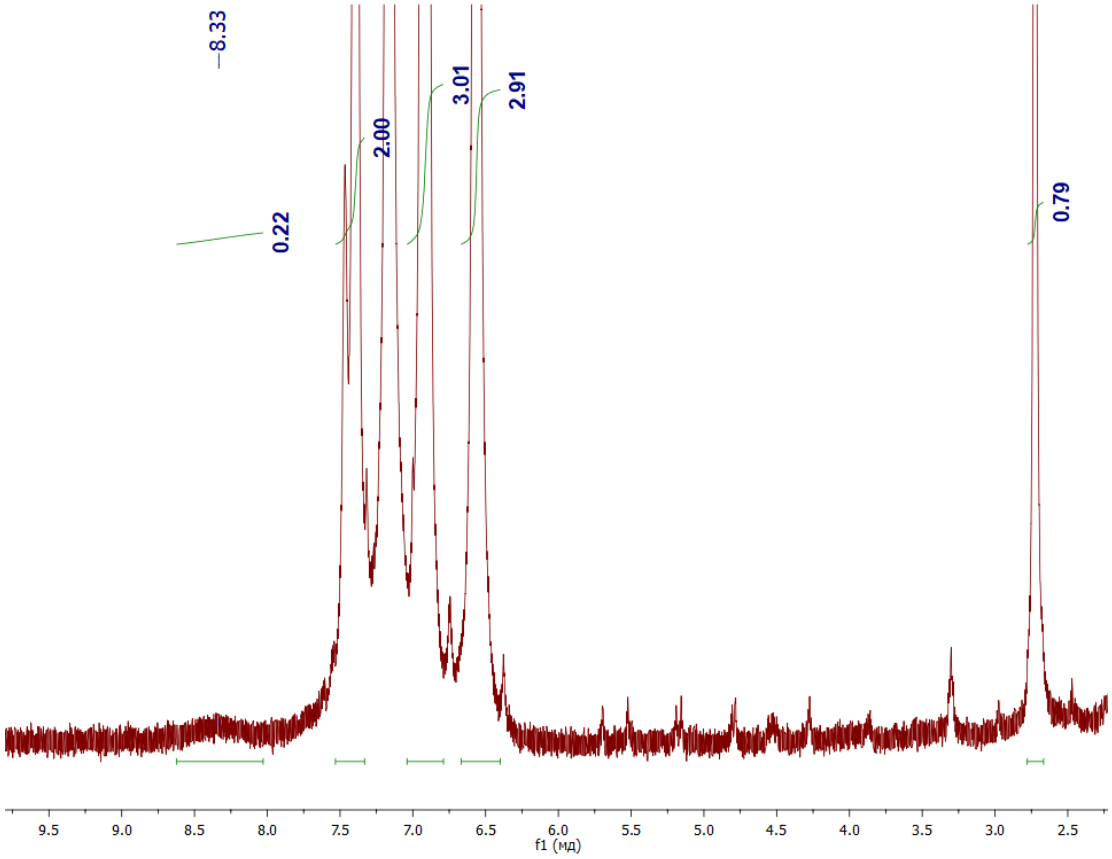


Figure S1. Zoomed ^{1}H NMR spectrum of phenylacetylene in the presence of 1 eq. of $[AgL]_3$ demonstrating the broad signal at 8.33 ppm, C_6D_6.

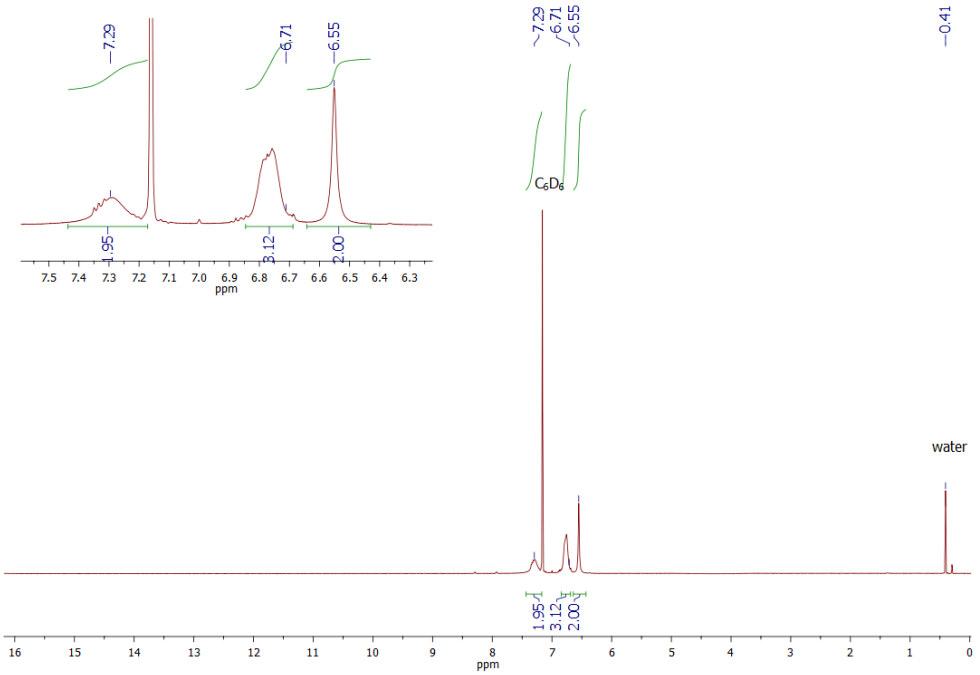


Figure S2. ^{1}H NMR (C_6D_6) spectrum for **1Ag**.

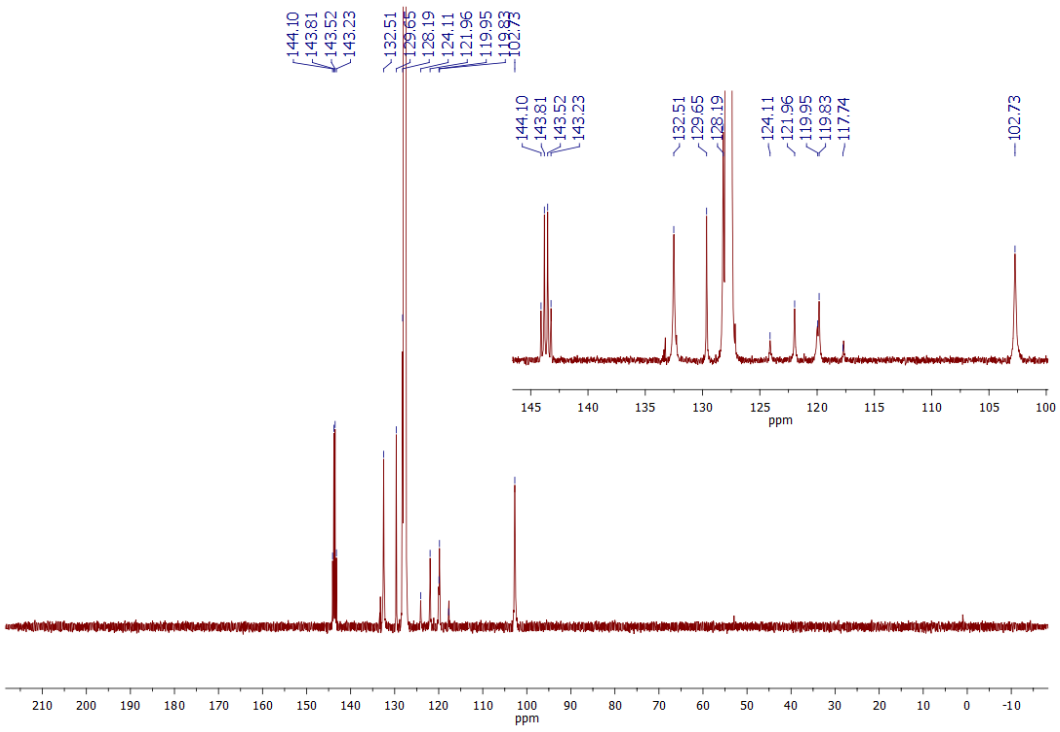


Figure S3. ^{13}C NMR (C_6D_6) spectrum for **1Ag**.

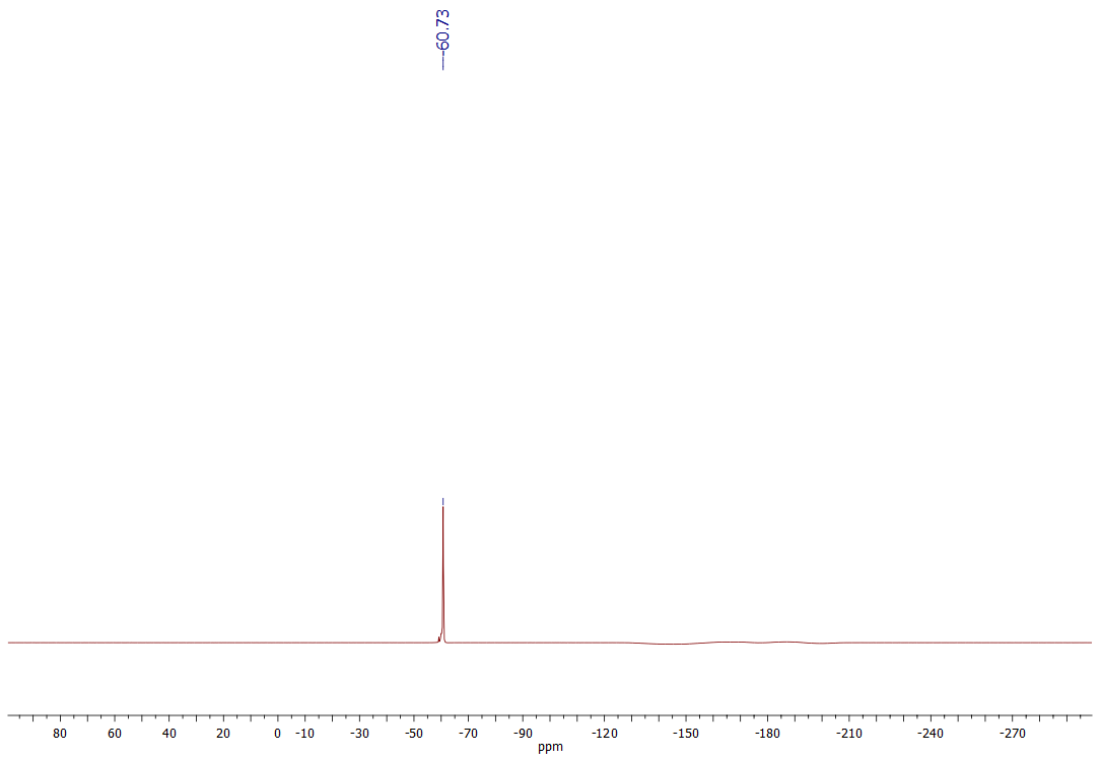


Figure S4. ^{19}F NMR (C_6D_6) spectrum for **1Ag**

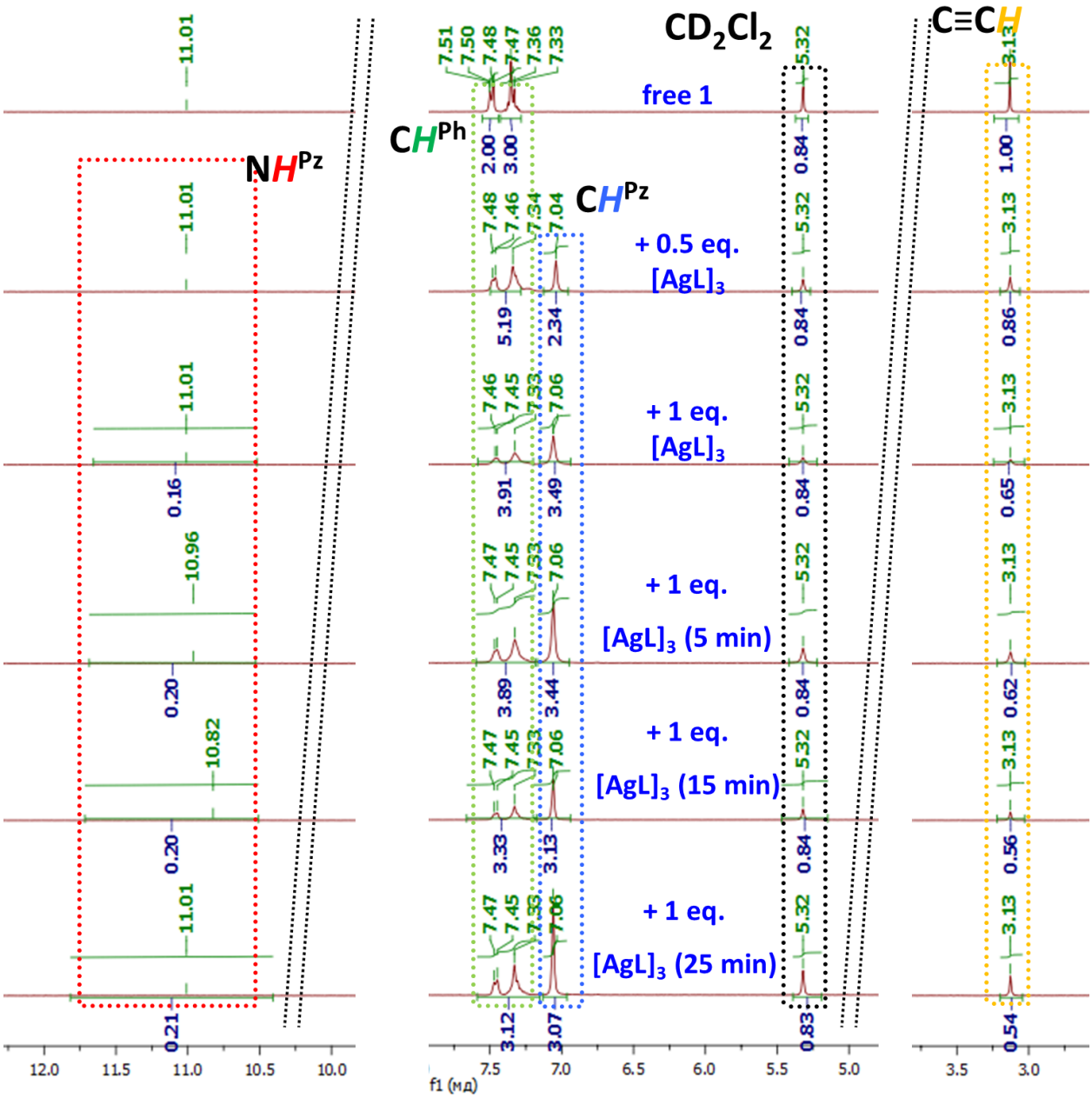


Figure S5. ^{1}H NMR spectra of phenylacetylene **1** (c = 0.05 M, *top*) and **1** in the presence of 0.5 and 1 eq. of **[AgL]$_3$.** CD_2Cl_2, T = 298 K. The integral intensity of the solvent signal referenced to 0.84 according to the spectrum of a free phenylacetylene.

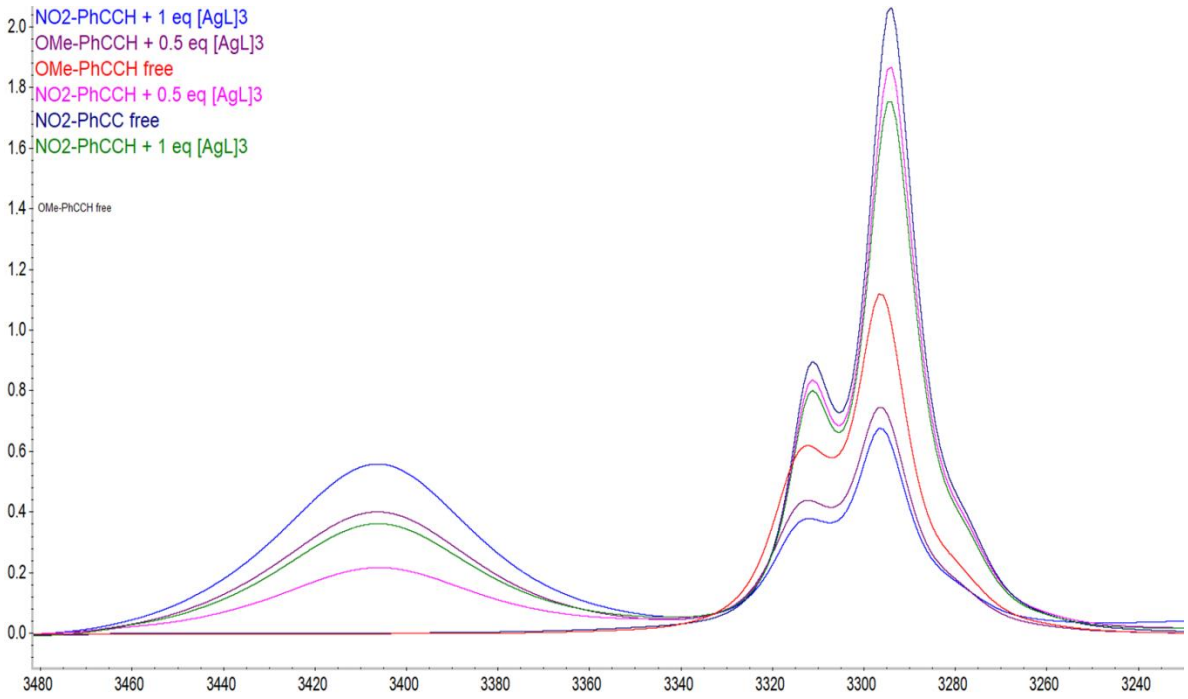


Figure S6. IR spectra of 4-Ethynylanisole and 4-Nitrophenylacetylene (c = 0.05 M) and in the presence of increasing amounts of **[AgL]$_3$** in CH_2Cl_2.

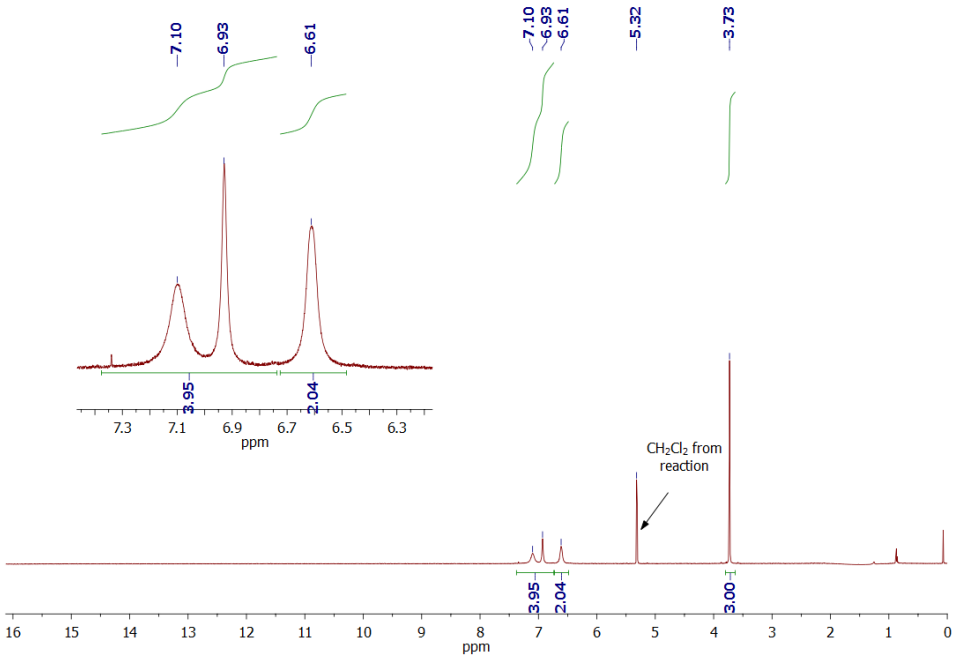


Figure S7. ^{1}H NMR (CD_2Cl_2) spectrum for complex 4-OMe-C_6H_4C≡CH with **[AgL]$_3$**.

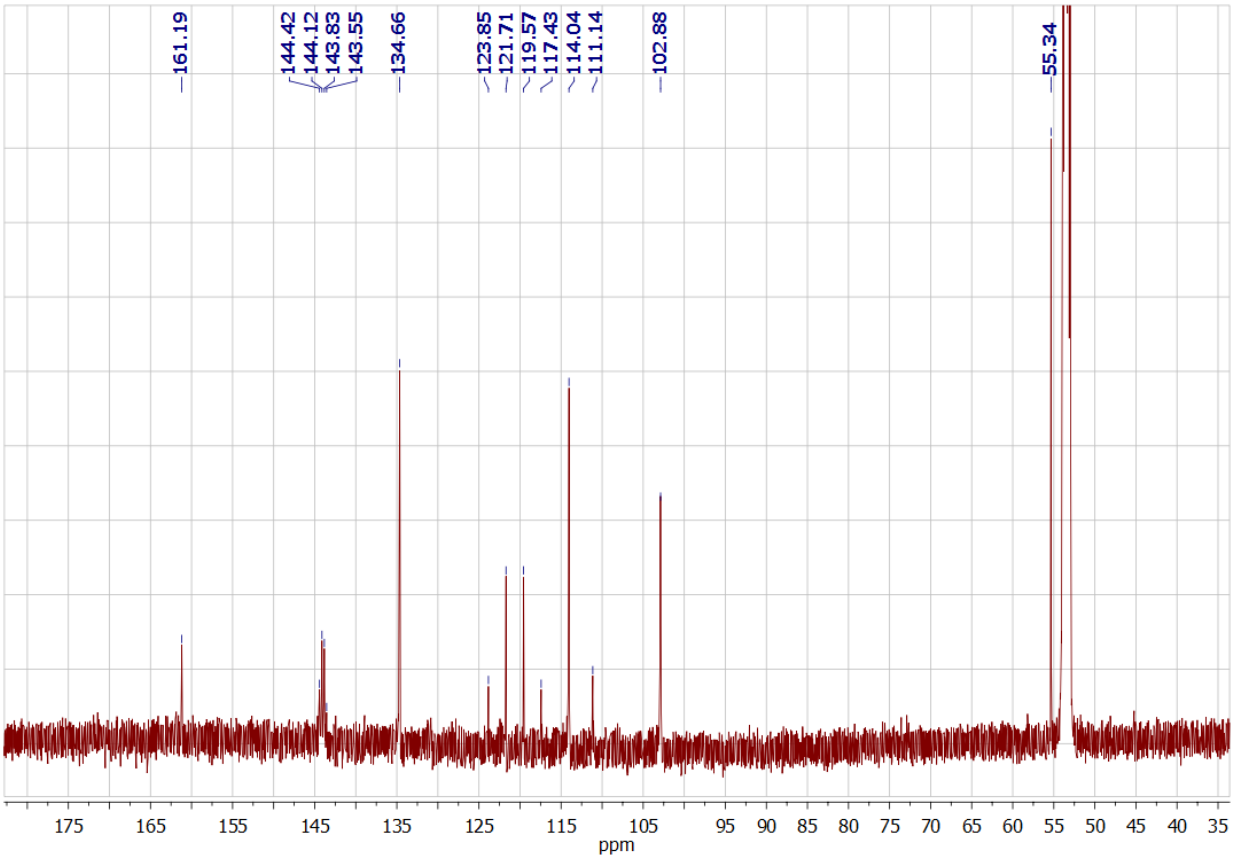


Figure S8. ^{13}C NMR (CD_2Cl_2) spectrum for complex 4-OMe-$C_6H_4C{\equiv}CH$ with **$[AgL]_3$.**

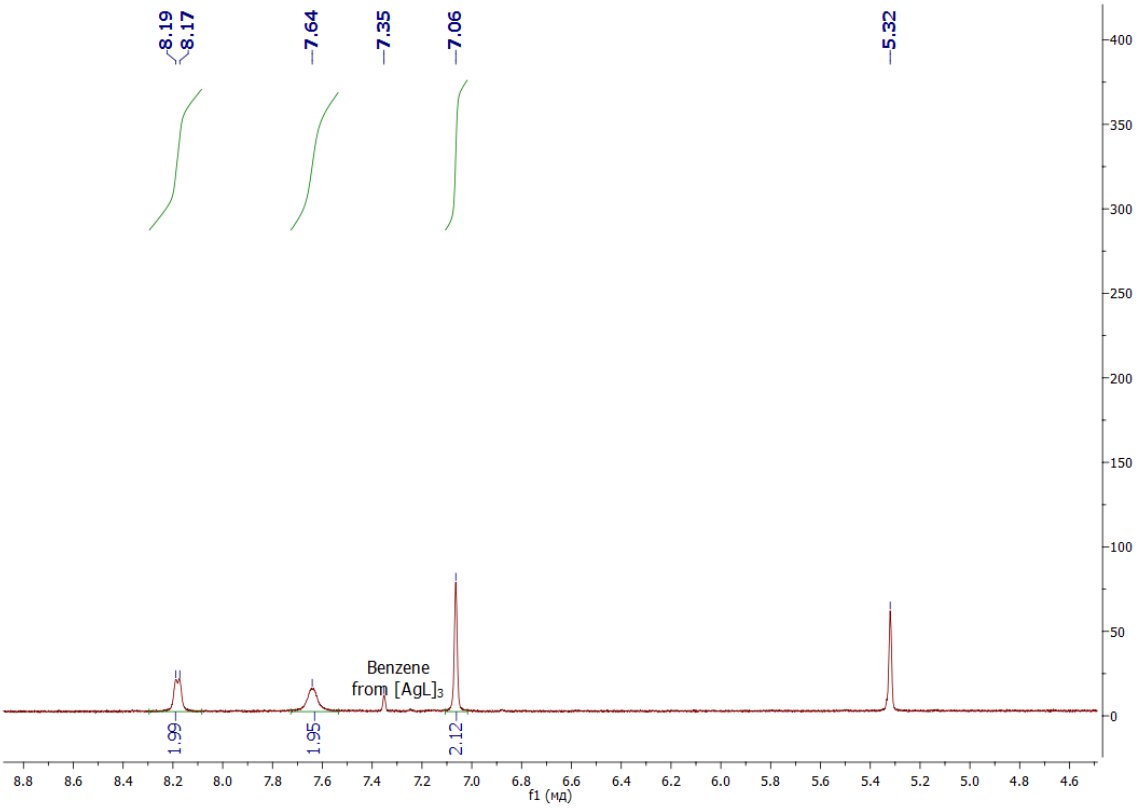


Figure S9. ^{1}H NMR (CD_2Cl_2) spectrum for complex 4-NO_2-$C_6H_4C{\equiv}CH$ with **$[AgL]_3$.**

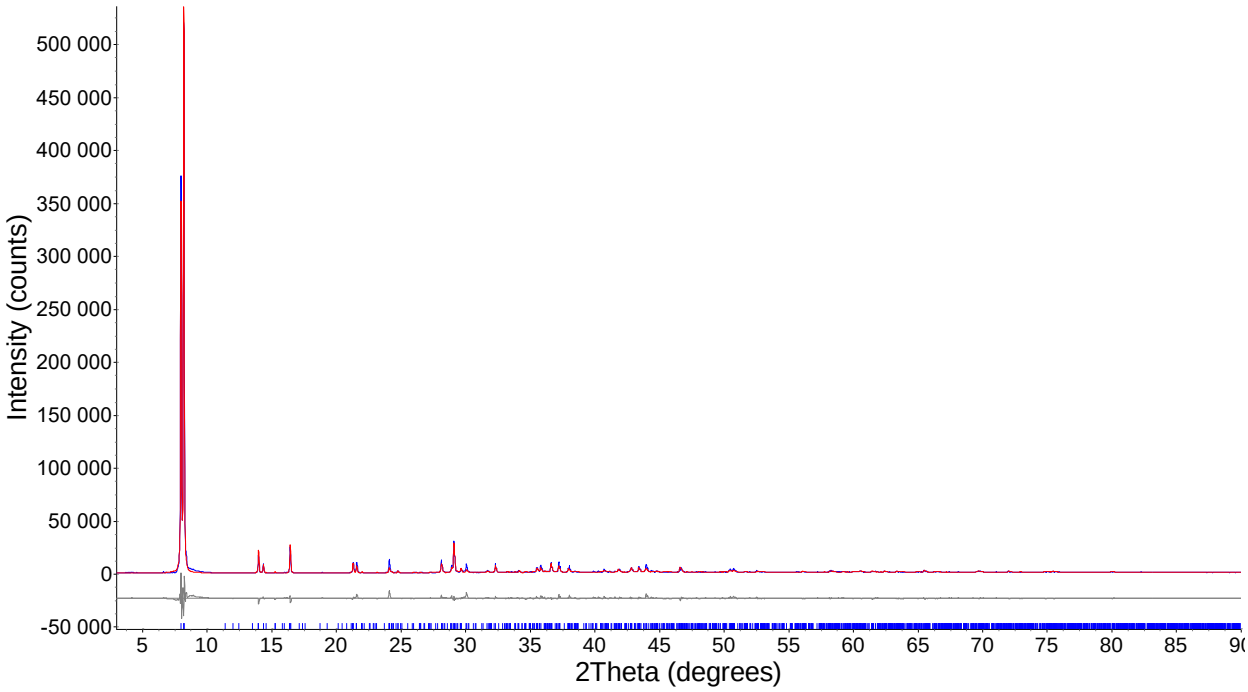


Figure S10. The powder (red) and single crystal X-ray diffraction patterns (blue) for **1Ag.**

Table S2. Crystal parameters from powder and single-crystal XRD experiments.

Rietveld	XRPD (298 K)	SC-XRD (100 K)
R-Bragg	4.310	
Spacegroup	*P*-1	*P*-1
Cell Mass	1661.721	
Cell Volume (Å^3)	1111.5(3)	1087.63
Lattice parameters		
a (Å)	8.1341(17)	8.2213(5)
b (Å)	12.6284(11)	12.3633(8)
c (Å)	12.7174(10)	12.5168(8)
α (°)	116.984(5)	116.4550(10)
β (°)	95.011(13)	95.181(2)
γ (°)	102.329(13)	102.301(2)

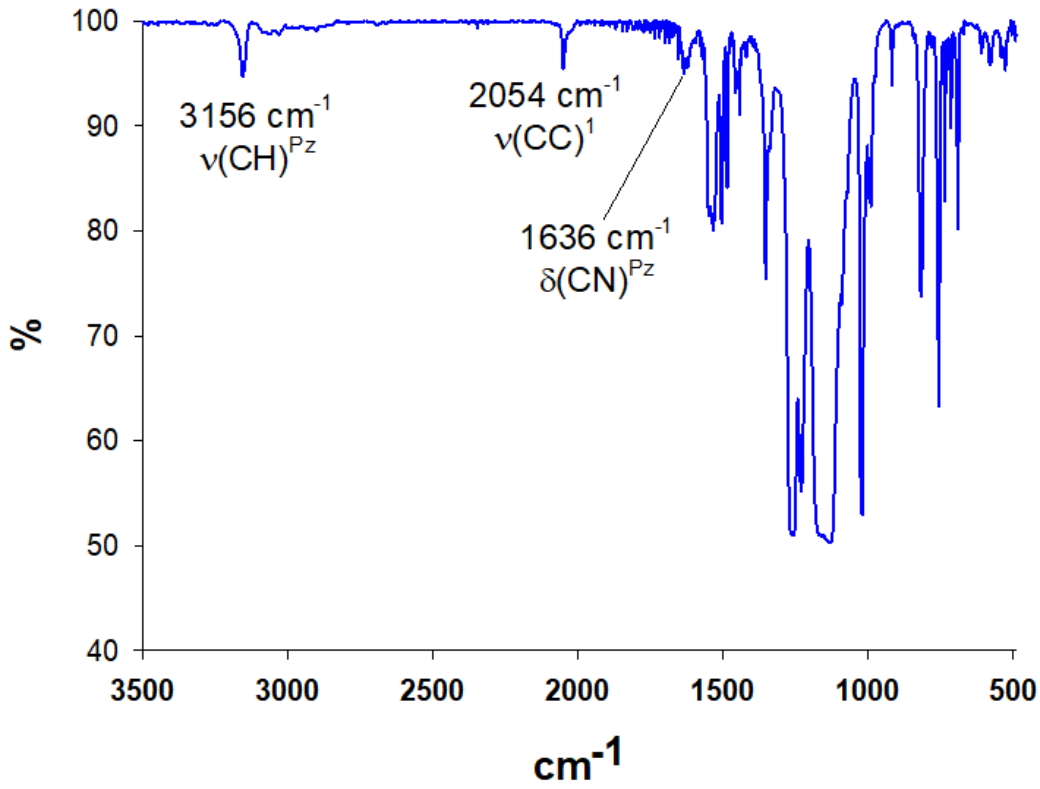


Figure S11. IR spectrum for **1Ag** in KBr pellets.

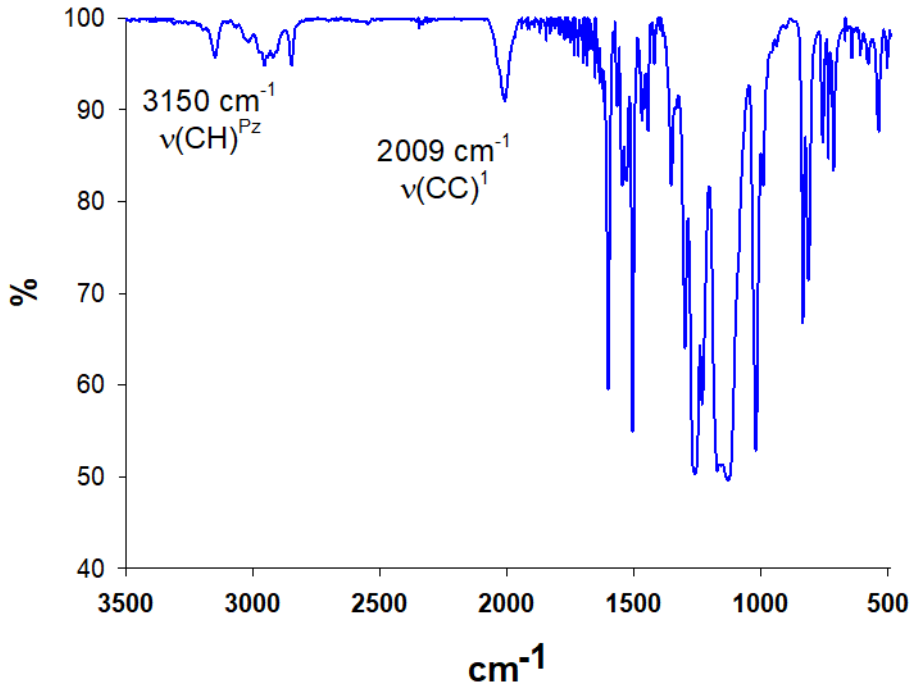


Figure S12. IR spectrum for complex 4-OMe-$C_6H_4C{\equiv}CH$ with **$[AgL]_3$** in KBr pellets.

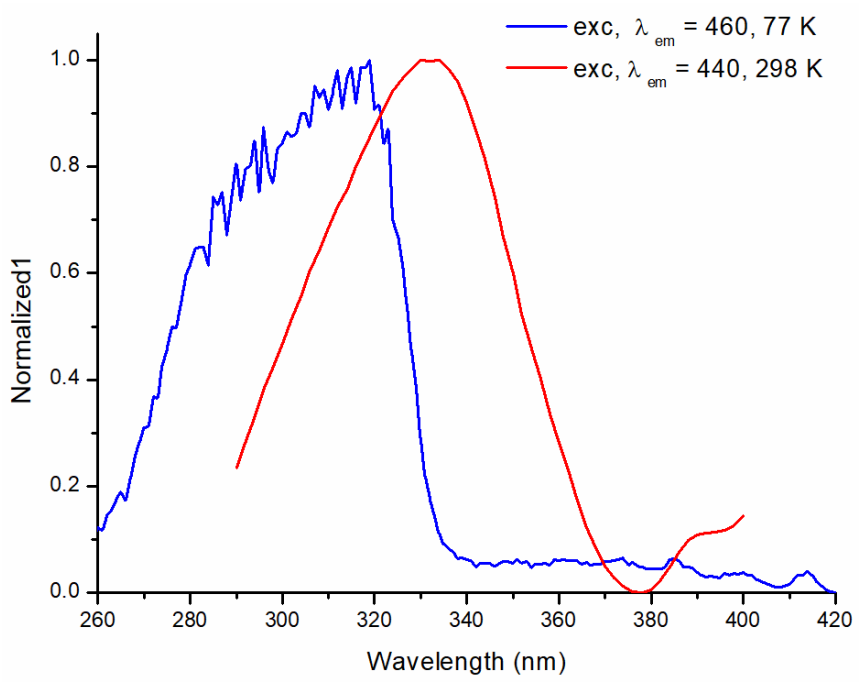


Figure S13. Excitation spectra of **1Ag** at 298 and 77K.

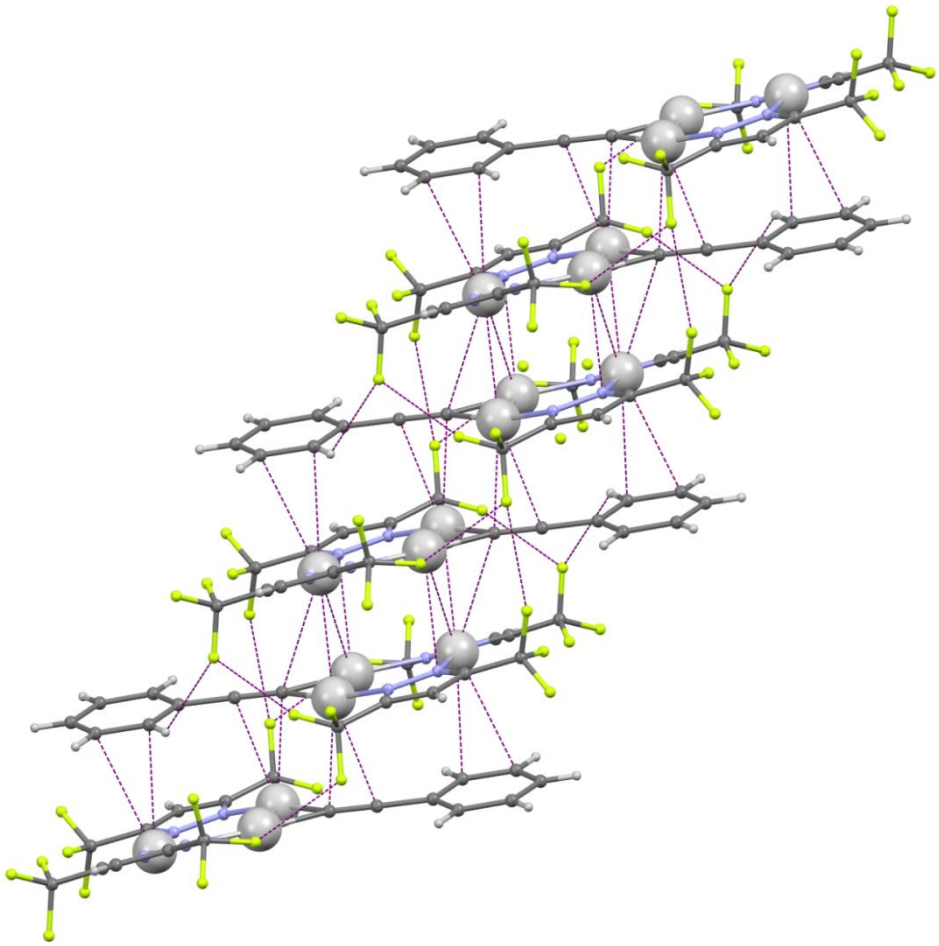


Figure S14. Portion of supramolecular packing of **1Ag**.

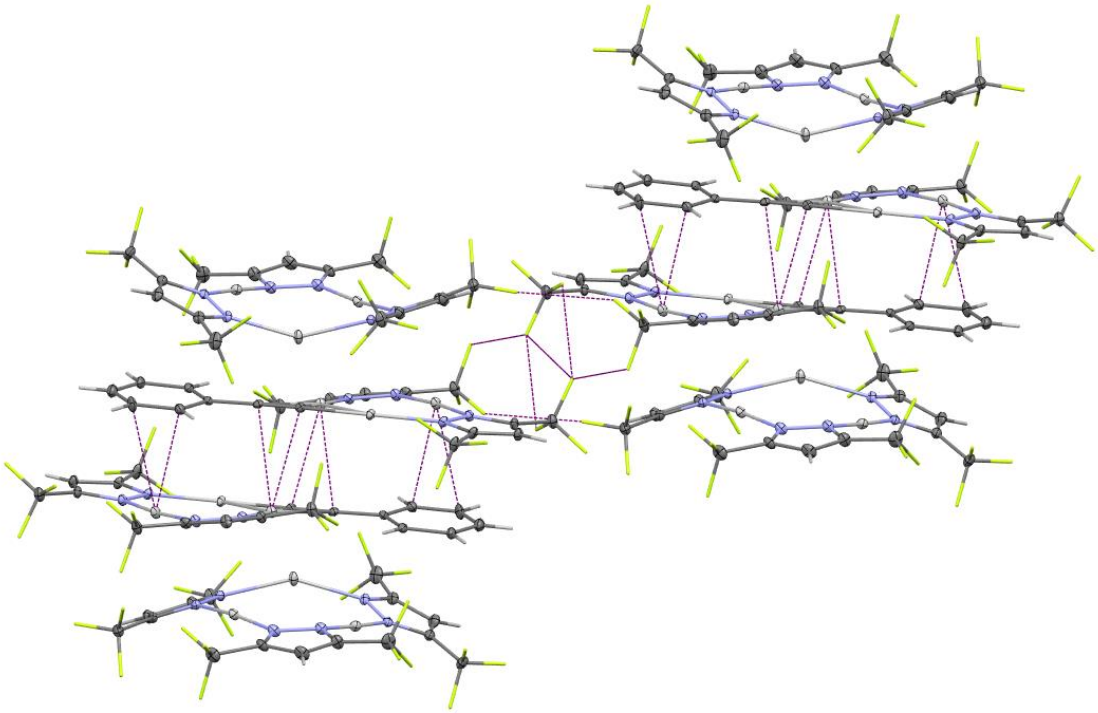


Figure S15. Portion of supramolecular packing of {**1Ag**'-[AgL]$_3$}.

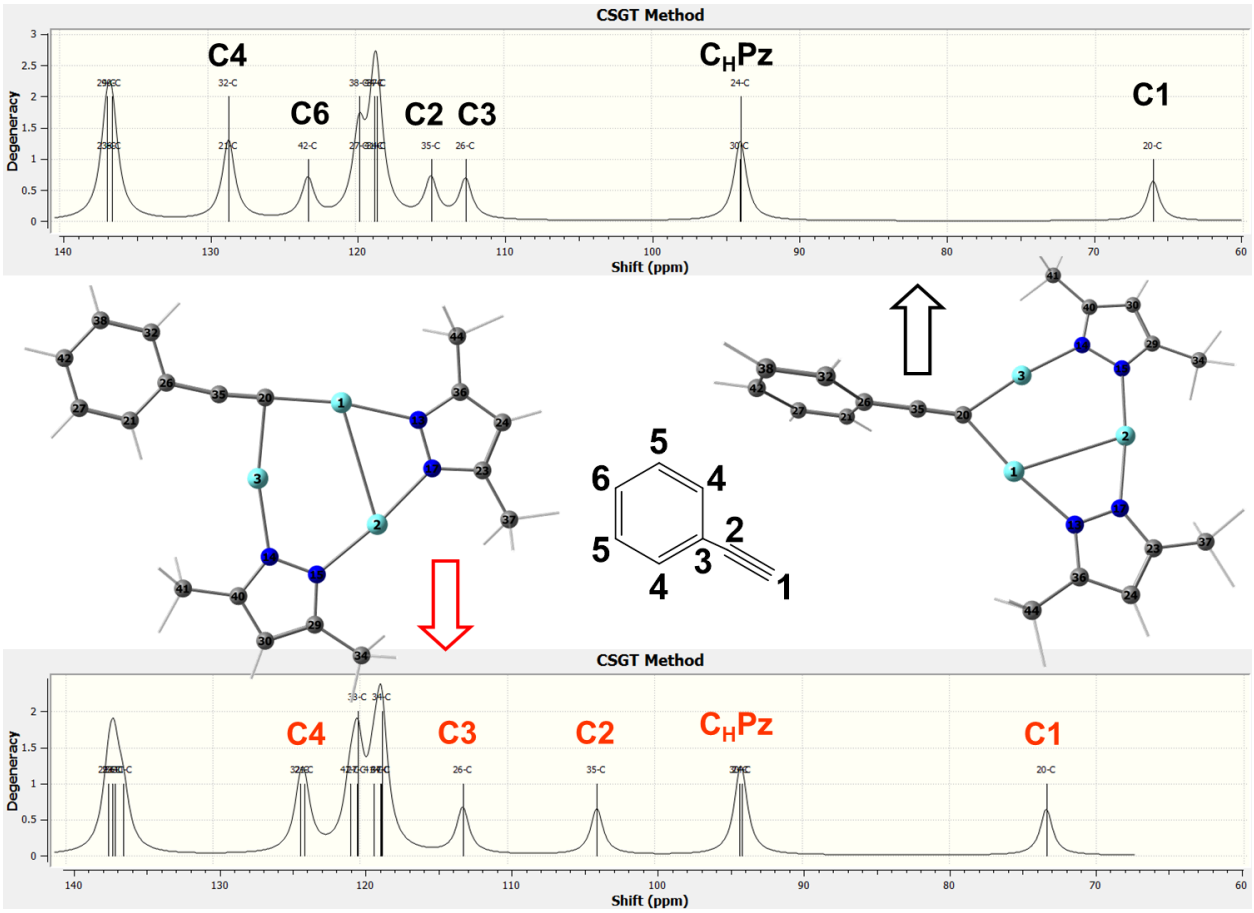


Figure S16. Calculated ^{13}C NMR shifts forconformers **1Ag** and **1Ag'**.

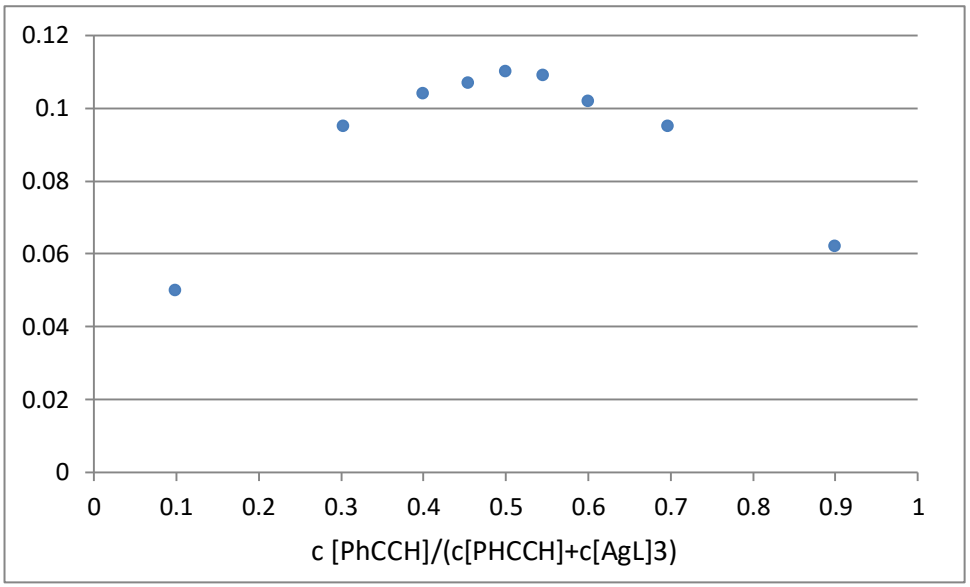


Figure S17. Dependence of the band intensity at 3354 cm^{-1} on the composition of the isomolar solution of $[AgL]_3$ and phenylacetylene, which demonstrates the Job's plot type dependency being typical for the 1:1 ratio of the interacted reagents.

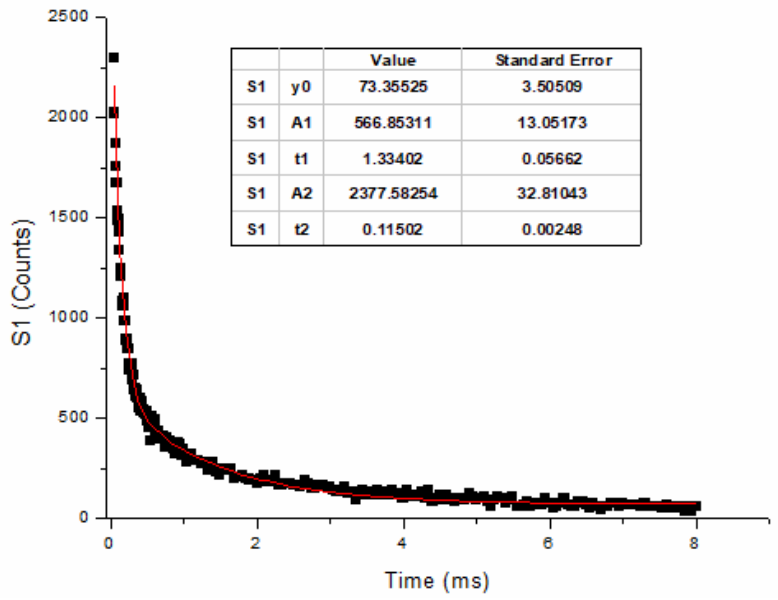
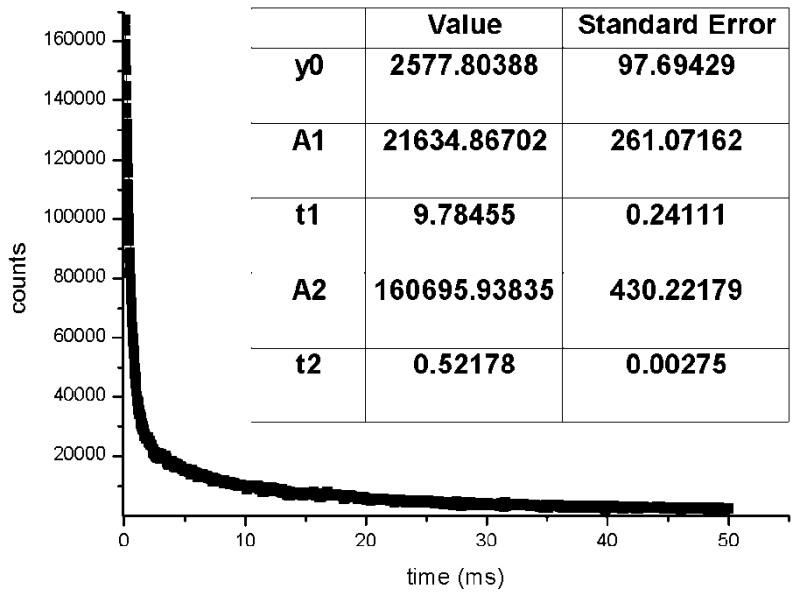


Figure S18. Phosphorescence decays of **1Ag** in the solid state at 298 K (λ_{em} = 500 nm).



	Value	Standard Error
y0	2577.80388	97.69429
A1	21634.86702	261.07162
t1	9.78455	0.24111
A2	160695.93835	430.22179
t2	0.52178	0.00275

Figure S19. Phosphorescence decays of **1Ag** in the solid state at 77 K (λ_{em} = 500 nm).

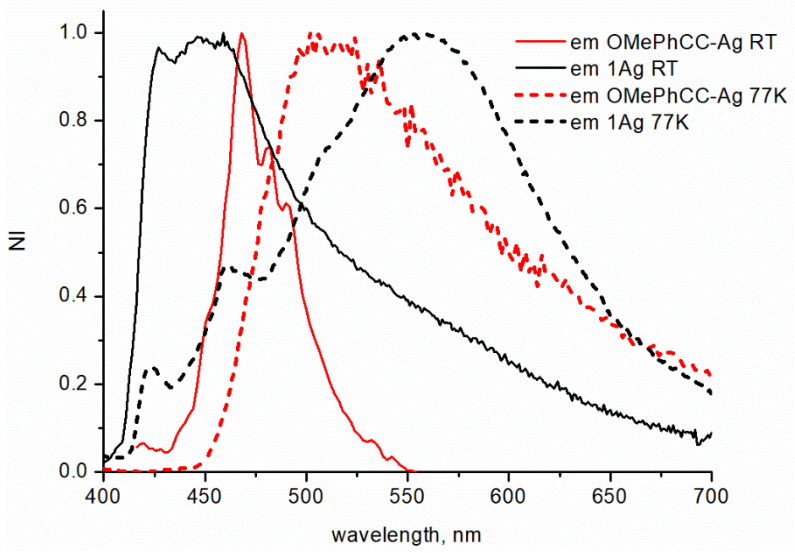


Figure S20. Normalized photoluminescence spectra at 298 (solid lines) and 77 K (dashed lines) of **1Ag** (black) and complex 4-OMe-$C_6H_4C{\equiv}CH$ with **[AgL]$_3$** (red)**.**

3. DFT and TD-DFT calculations

Calculations were performed with ORCA 5.04 software package [8, 9] applying PBE0 functional and ZORA Hamiltonian. The applied basis set was SARC-ZORA-TZVP[10] for silver atoms and ZORA-TZVP for H, C, N, and F atoms. Electronic transitions were calculated under the TD-DFT approach utilizing the same computation level as the Tamm-Dankoff approximation taking into account 20 lowest energy singlet and triplet excitations. Analysis of natural transition orbitals (NTO) and contributions from certain atomic orbitals to the electronic transitions were performed with the Multiwfn 3.7 package[11]. These data are provided in Figure S14, Figure S15 and Table S3. The triplet lifetimes were estimated from the T_1-S_0 oscillator strengths values (f_{osc}) or corresponding transition electric dipole moment components (M_x, M_y, M_z) obtained

within the calculation of the spin-orbit coupling (SOC) between singlets and triplets using equation[12]:

$$k = \frac{1}{\tau} = \frac{4}{3t_0}\alpha_0^3(\Delta E_i)^3 \sum_{\alpha\in\{x,y,z\}}\left|M_\alpha^i\right|;\ t_0 = \frac{(4\pi\varepsilon_0)^3\hbar^3}{m_e e^4}$$

where α_0 is a fine-structure constant, ε_0 - vacuum permittivity, m_e – electron mass, e – elementary charge, ΔE_i – energy difference of two levels.

which could be simplified[13] to the:

$\tau = \frac{1.499}{f_{osc}(\Delta E_i)^2}$ (Energy units are cm^{-1})

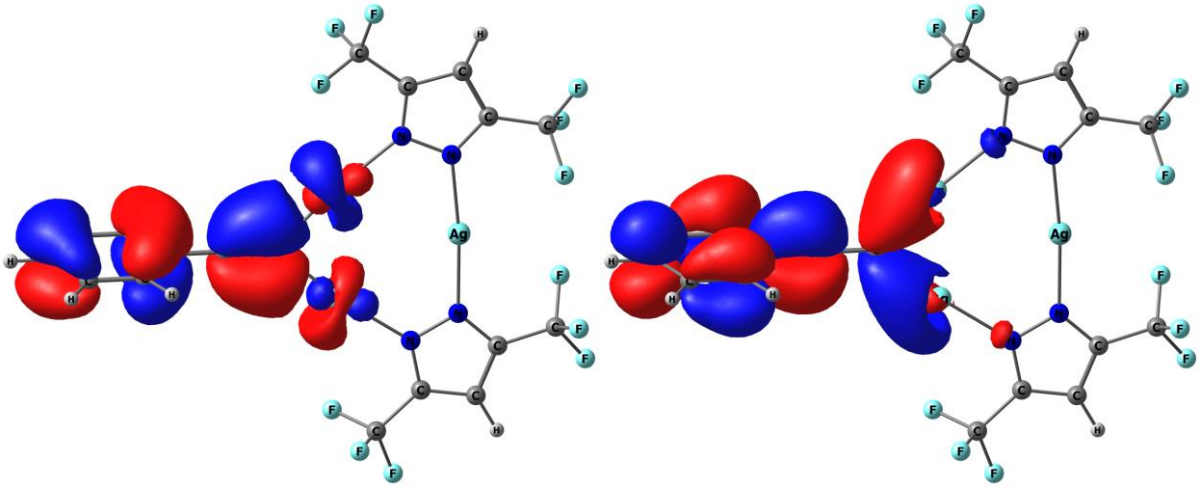


Figure S21. HONTO (left) and LUNTO (right) for T_1-S0 transition in **1Ag** (0.93 contribution, as isosurface at 0.03 a.u.); ΔE=25740.1 cm-1 (388.5 nm), τ = 2.88 ms, Ag atoms involving into the transition (Hirshfeld scheme) are 10.4 and 10.1% (electron); 9.4 and 9.7% (hole)

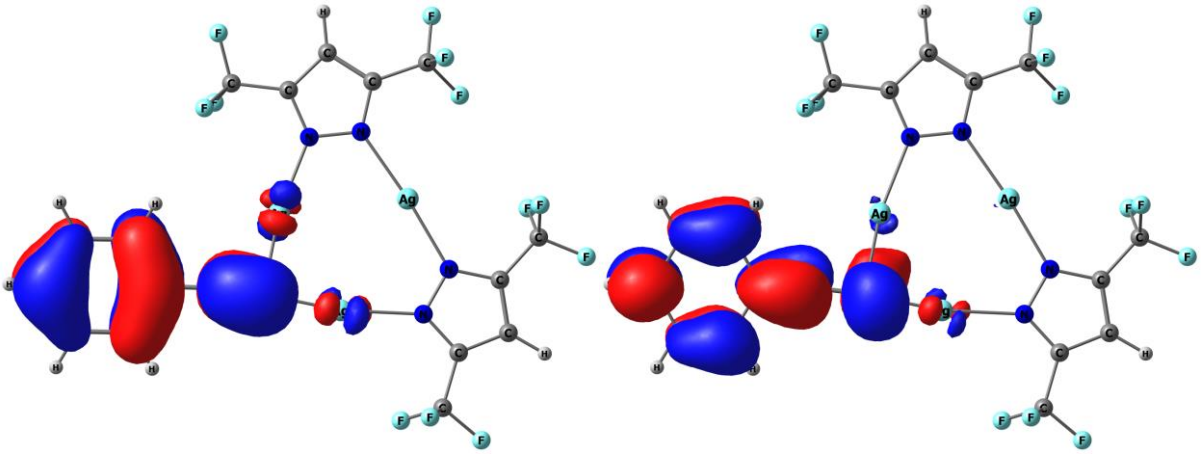


Figure S22. HONTO (left) and LUNTO (right) for T_1-S_0 transition in **1Ag'** (0.91 contribution, as isosurface at 0.03 a.u.); ΔE=27410.8 cm^{-1} (364.8 nm), τ =0.21 ms. Ag atoms involving into the transition (Hirshfeld scheme) are 4.3 and 3.9% (electron); 4.7 and 6.4% (hole)

Table S3. Calculated characteristics of the vertical electronic transitions for 10 lowest energy singlets and lowest effective triplet under SOC approach for complexes **1Ag** and **1Ag'**.

state	**1Ag**			**1Ag'**		
	E, cm^{-1}	λ, nm	f_{osc}	E, cm^{-1}	λ, nm	f_{osc}
S_1	34912.9	286.4	0.018	34233.2	292.1	0.055
S_2	35834.3	279.1	0.298	38621.8	258.9	0.303
S_3	39368.5	254.0	0.001	40413.8	247.4	0.001
S_4	39574.4	252.7	0.001	40742.2	245.4	0.084
S_5	40492.3	247.0	0.001	40931.1	244.3	0.199
S_6	41260.8	242.4	0.004	43098.9	232.0	0.096
S_7	43667.3	229.0	0.001	43539.8	229.7	0.135
S_8	43841.2	228.1	0.000	43777.2	228.4	0.011
S_9	43877.5	227.9	0.000	44006.4	227.2	0.035
S_{10}	44426.4	225.1	0.020	44548.2	224.5	0.004
T_1(SOC)	25740.1	388.5	$7.86 \cdot 10^{-7}$	27410.8	364.8	$9.38 \cdot 10^{-6}$

The Natural Orbitals for Chemical Valence (NOCV) analysis of complex formation energy [14] [15] was performed with ORCA utilizing optimized geometries of **1Ag**, **^{Et}CCAg** and parent $[AgPz]_3$ complexes. The deformation density plots were calculated and plotted with the Chemcraft 1.8 [16] program and presented in Figure S16.

The ETS-NOCV analysis reveals that the total energy of orbital interactions between $[\{3,5\text{-}(CF_3)_2Pz\}_2Ag_3]^+$ and $(CF_3)_2Pz^-$ fragments is -77.4 kcal/mol, with the highest impacts of -22.3 and -19.2 kcal/mol. These values are a few kcal/mol lower than those reported for the cyclic trinuclear silver pyrazolate analogues.[17] At that, the acetylene containing complex **1Ag** features a much higher total interaction energy of -112.2 kcal/mol. π-orbitals of acetylene significantly affect this energy, being -40.1 and -36.5 kcal/mol, respectively. The difference of the orbital interaction energies of $[\{3,5\text{-}(CF_3)_2Pz\}_2Ag_3]^+$ with $(CF_3)_2Pz^-$ and $PhC{\equiv}C^-$ is 34.8 kcal/mol, that seems to be enough to compensate for the pK_a difference between acetylene and pyrazole. It is worth noting, that the phenyl ring plays an important role in this stabilization. The model calculation for the same complex with 1-butyne reveals that the total orbital interaction energy is reduced to -104.9 kcal/mol, with the main components being -41.6 and -24.9 kcal/mol, so donation from the second π bond (conjugated with Ph ring in **1**) is reduced by ca. 10 kcal/mol for alkyl acetylene. Considering both the lower energy of the orbital interactions and lower proton donating ability (higher pK_a value) of $EtC{\equiv}CH$ compared to the $PhC{\equiv}CH$, the no interaction of $[AgPz]_3$ with alkynes becomes apparent.

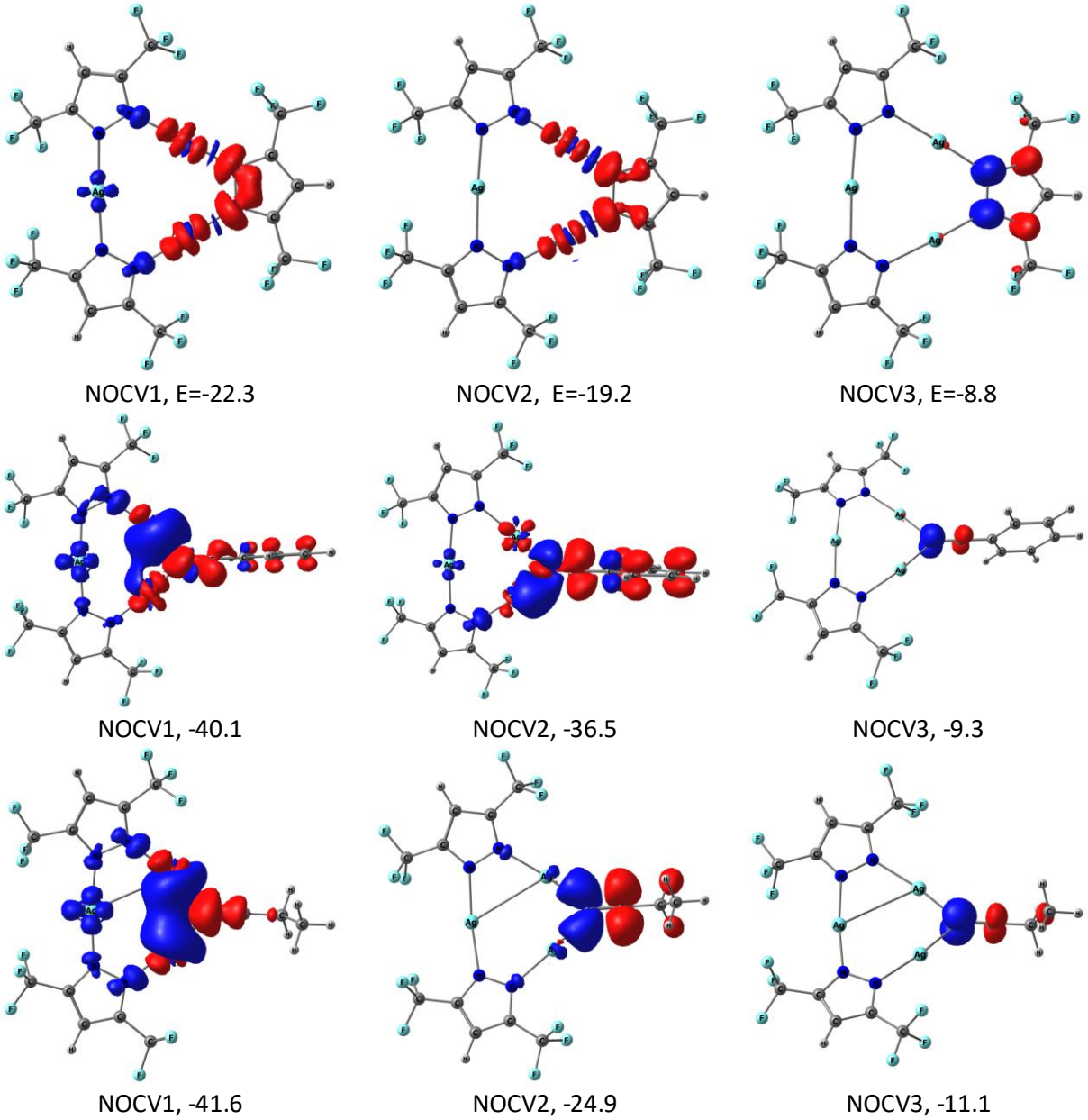


Figure S23. Contours of deformation densities (contour value 0.001), $\Delta\rho_i(r)$, describing the density inflow (blue) and outflow (red) between the interacting fragments and their corresponding energy ΔE_i^{orb} (kcal/mol). Top – $[AgPz]_3$ complex, middle - PhCC complex **1Ag**, bottom – model complex with 1-butyne ^{Et}**CCAg**.

Several DFT methods were applied for ground state optimization of **1Ag** complex in order to check preference between two possible conformers. These include PBE0 and CAM-B3LYP functionals with def2-SVP[18], and cc-pvDZ[19, 20] basis sets (supplied with corresponding ECP's for silver atoms [20, 22]). In every case, geometry was fully optimized with Gaussian16 [23] without any restrictions and verified to be a true PES minimum with the frequency analysis. Obtained energetic characteristics of conformers are summarized in the Table S4.

Table S4. Energetic characteristics of two conformers of 1Af complex computed at the different theory level.

		Energy of **1Ag**, Ha	Energy of **1Ag'**, Ha	**1Ag** favorability, kcal/mol
ORCA/ PBE0/ TZVP(SARC-TZVP)	E	-18246.706957	-18246.704879	1.30
	H	-18246.426953	-18246.425978	0.61
	G	-18246.533002	-18246.529918	1.94
G16/ PBE0/ cc-pvDZ	E	-2546.274528	-2546.273370	0.73
	H	-2545.994859	-2545.993848	0.63
	G	-2546.117400	-2546.115337	1.29
G16/ CAM-B3LYP/ cc-pvDZ	E	-2547.615305	-2547.614217	0.68
	H	-2547.334776	-2547.333799	0.61
	G	-2547.458359	-2547.456230	1.34
G16/ CAM-B3LYP/ def2-SVP	E	-2545.844214	-2545.843925	0.18
	H	-2545.560241	-2545.560020	0.14
	G	-2545.681537	-2545.679025	1.58

4. References

1. *APEX II software package; Bruker AXS Inc.: 5465, East Cheryl Parkway, Madison, WI 5317, 2005.*
2. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3-8.
3. G. Sheldrick, *Acta Crystallogr., Sect. C.*, 2015, **71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
5 A. L. Spek, J Appl Crystallogr, 2003, 36, 7–13.
6 A. L. Spek, *Acta Crystallographica*, 2015, **C71**, 9–18.
7. H. V. Rasika Dias, S. A. Polach and Z. Wang, *J. Fluor. Chem.*, 2000, **103**, 163-169.
8. F. Neese, WIREs *Comput. Mol. Sci.*, 2011, 2, 73-78.
9. F. Neese, *WIREs Comput. Mol. Sci.*, 2022, **12**.
10. J. D. Rolfes, F. Neese and D. A. Pantazis, *J.Ccomput. Chem.*, 2020, **41**, 1842-1849.
11. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
12. K. Mori, T. P. Goumans, E. van Lenthe and F. Wang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14523-14530.
13. J. Fan, L. Cai, L. Lin and C. K. Wang, *Phy.s Chem. Chem. Phys.*, 2017, **19**, 29872-29879.
14. M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem .Theor. Comput.*, 2009, **5**, 962-975.
15. A. Altun, F. Neese and G. Bistoni, *J. Chem. Theory. Comput.*, 2019, **15**, 215-228.
16. Chemcraft - graphical software for visualization of quantum chemistry computations. Version 1.8, https://www.chemcraftprog.com).
17. G. F. Caramori, R. M. Piccoli, M. Segala, A. Munoz-Castro, R. Guajardo-Maturana, D. M. Andrada and G. Frenking, *Dalton Trans.*, 2015, **44**, 377-385.
18. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
19. T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
20. K. A. Peterson and C. Puzzarini, *Theor. Chem. Acc.*, 2005, **114**, 283-296.
21. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123-141.
22. D. Figgen, G. Rauhut, M. Dolg and H. Stoll, *Chem. Phys.*, 2005, **311**, 227-244.
23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson,

D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.

5. XYZ coordinates of optimized complexes

1Ag; G16/PBE0/cc-pvDZ

47	1.184926000	-1.410440000	0.000275000
47	-1.822959000	0.002027000	-0.000036000
47	1.188552000	1.406529000	-0.000424000
9	-4.458639000	-1.982923000	1.081745000
9	-4.453212000	1.993481000	1.082127000
9	-4.458133000	-1.979514000	-1.079610000
9	-4.857678000	-3.822642000	-0.001895000
9	-4.847696000	3.834628000	-0.000761000
9	-4.453230000	1.990849000	-1.079229000
9	0.079773000	6.204094000	0.000499000
9	1.272661000	4.744157000	1.079269000
9	1.270964000	4.745438000	-1.081828000
7	-0.513769000	-2.667403000	0.000016000
7	-0.506824000	2.668015000	-0.000150000
7	-1.716365000	2.086361000	0.000055000
9	1.258775000	-4.749510000	-1.081364000
7	-1.721781000	-2.082580000	-0.000043000
9	1.260045000	-4.748201000	1.079734000
9	0.063537000	-6.205013000	0.000745000
6	2.696610000	-0.004009000	-0.000026000
6	6.069107000	-0.005243000	1.214240000
1	5.516353000	-0.004774000	2.153108000
6	-2.656292000	-3.047201000	-0.000207000
6	-2.053583000	-4.301015000	-0.000275000
1	-2.526343000	-5.274701000	-0.000405000
6	5.358663000	-0.005166000	0.000226000
6	7.459093000	-0.005910000	1.209750000
1	8.003348000	-0.005966000	2.154512000
6	-2.648345000	3.053428000	0.000134000
6	-2.042350000	4.305657000	0.000039000
1	-2.512556000	5.280579000	0.000078000
6	6.069555000	-0.005775000	-1.213524000
1	5.517149000	-0.005718000	-2.152597000
6	-4.102106000	2.718850000	0.000558000
6	3.934846000	-0.004485000	-0.000041000
6	-0.695484000	-3.997123000	-0.000109000
6	-4.109173000	-2.708819000	-0.000002000
6	7.459539000	-0.006442000	-1.208519000
1	8.004144000	-0.006912000	-2.153079000
6	-0.685052000	3.998206000	-0.000170000
6	0.483492000	4.924595000	-0.000553000
6	8.156401000	-0.006511000	0.000745000
1	9.246897000	-0.007033000	0.000947000
6	0.470621000	-4.926581000	-0.000242000

1Ag'; G16/PBE0/cc-pvDZ

47	-0.310014000	-2.149833000	-0.000163000
47	-1.383405000	1.014310000	-0.000217000
47	1.797418000	-0.061973000	-0.000061000
9	-4.621932000	1.522814000	1.076661000
9	-1.896046000	4.252184000	1.083509000
9	-4.626608000	1.518077000	-1.084719000
9	-6.226993000	0.529677000	0.001536000
9	-0.913045000	5.855935000	-0.002723000
9	-1.899903000	4.247012000	-1.077900000
9	4.289740000	4.173434000	0.001230000
9	4.147384000	2.293706000	1.080229000
9	4.147564000	2.294935000	-1.079965000
7	-2.380226000	-1.795039000	0.000118000
7	1.425927000	2.018432000	0.000209000
7	0.149279000	2.430082000	0.000121000
9	-2.641240000	-4.517312000	-1.073382000
7	-2.797625000	-0.519398000	-0.000340000
9	-2.658193000	-4.516580000	1.087740000
9	-4.528084000	-4.664871000	-0.007305000
6	1.710111000	-2.207865000	-0.000307000
6	5.302062000	-1.454119000	0.000295000
1	4.958745000	-0.419418000	0.001078000
6	-4.140732000	-0.516516000	-0.000579000
6	-4.624685000	-1.820625000	-0.000329000
1	-5.653678000	-2.156317000	-0.000491000
6	4.363670000	-2.498088000	-0.000566000
6	6.663619000	-1.738152000	0.000127000
1	7.383274000	-0.919265000	0.000793000
6	0.140628000	3.773646000	0.000287000
6	1.442525000	4.263152000	0.000562000
1	1.773422000	5.293717000	0.000713000
6	4.815469000	-3.829531000	-0.001615000
1	4.088500000	-4.640731000	-0.002306000
6	-1.143041000	4.534093000	0.000760000
6	2.955369000	-2.238307000	-0.000384000
6	-3.463499000	-2.587414000	0.000053000
6	-4.906026000	0.764135000	-0.001751000
6	6.178688000	-4.102595000	-0.001763000
1	6.519446000	-5.138373000	-0.002572000
6	2.213905000	3.104666000	0.000457000
6	3.698486000	2.970259000	0.000503000
6	7.106587000	-3.060506000	-0.000891000
1	8.174604000	-3.279543000	-0.001014000
6	-3.324402000	-4.072464000	0.001738000

1Ag; G16/CAM-B3LYP/cc-pvDZ

47	1.195664000	1.424299000	-0.000156000
47	-1.858497000	-0.002330000	0.000178000
47	1.199902000	-1.419983000	0.000290000
9	-4.467620000	2.002011000	-1.083083000
9	-4.461487000	-2.013865000	-1.083203000
9	-4.467070000	1.997508000	1.079714000
9	-4.857951000	3.844309000	0.002207000
9	-4.846631000	-3.857703000	0.001335000
9	-4.461350000	-2.010170000	1.079593000
9	0.088197000	-6.204146000	-0.000609000
9	1.277042000	-4.739297000	-1.079903000
9	1.275225000	-4.740755000	1.082609000
7	-0.517904000	2.669096000	-0.000028000
7	-0.510044000	-2.669824000	0.000110000
7	-1.724899000	-2.092086000	0.000003000
9	1.261248000	4.745302000	1.082554000
7	-1.731085000	2.087817000	0.000041000
9	1.263029000	4.743789000	-1.079993000
9	0.069847000	6.205155000	-0.000705000
6	2.716159000	0.004537000	-0.000114000
6	6.084972000	0.006112000	-1.211819000
1	5.533371000	0.005654000	-2.150202000
6	-2.658311000	3.056898000	0.000079000
6	-2.051597000	4.307034000	0.000117000
1	-2.519861000	5.281978000	0.000180000
6	5.377153000	0.005852000	-0.000254000
6	7.473970000	0.006919000	-1.208292000
1	8.017613000	0.007099000	-2.152277000
6	-2.649303000	-3.063869000	-0.000097000
6	-2.038937000	-4.312225000	0.000070000
1	-2.504363000	-5.288526000	0.000093000
6	6.085564000	0.006487000	1.210979000
1	5.534397000	0.006318000	2.149615000
6	-4.104861000	-2.737468000	-0.000583000
6	3.946671000	0.005062000	0.000061000
6	-0.696242000	3.997275000	0.000162000
6	-4.112913000	2.726247000	-0.000256000
6	7.474536000	0.007294000	1.206789000
1	8.018644000	0.007768000	2.150510000
6	-0.684487000	-3.998525000	0.000192000
6	0.486968000	-4.921343000	0.000564000
6	8.170384000	0.007506000	-0.000923000
1	9.259940000	0.008148000	-0.001171000
6	0.472477000	4.923538000	0.000500000

1Ag'; G16/CAM-B3LYP/cc-pvDZ

47	-0.313256000	-2.170988000	0.000124000
47	-1.408646000	1.035212000	-0.000069000
47	1.826020000	-0.056933000	-0.000049000
9	-4.644595000	1.510516000	1.083101000
9	-1.891785000	4.267181000	1.083202000
9	-4.640121000	1.513660000	-1.079643000
9	-6.242754000	0.515087000	-0.002969000
9	-0.901127000	5.869068000	-0.001794000
9	-1.894471000	4.263935000	-1.079609000
9	4.294786000	4.167149000	0.000718000
9	4.145294000	2.285929000	1.079280000
9	4.145010000	2.288375000	-1.082022000
7	-2.386675000	-1.797616000	0.000067000
7	1.423924000	2.021802000	-0.000149000
7	0.145747000	2.438463000	-0.000039000
9	-2.651523000	-4.520058000	-1.082732000
7	-2.809103000	-0.520367000	-0.000049000
9	-2.647825000	-4.520004000	1.079905000
9	-4.528954000	-4.671797000	0.001757000
6	1.721662000	-2.223354000	0.000114000
6	5.303076000	-1.455565000	0.000054000
1	4.954195000	-0.423855000	-0.000145000
6	-4.150410000	-0.524467000	-0.000234000
6	-4.630166000	-1.828411000	-0.000231000
1	-5.657270000	-2.167245000	-0.000357000
6	4.375365000	-2.504935000	0.000257000
6	6.665908000	-1.728277000	0.000126000
1	7.378667000	-0.904683000	-0.000029000
6	0.144756000	3.780179000	-0.000017000
6	1.446787000	4.265211000	-0.000099000
1	1.781029000	5.293822000	-0.000119000
6	4.835882000	-3.829812000	0.000540000
1	4.116327000	-4.646246000	0.000705000
6	-1.135499000	4.546332000	0.000428000
6	2.958311000	-2.254797000	0.000173000
6	-3.467274000	-2.590233000	-0.000039000
6	-4.920763000	0.753012000	0.000044000
6	6.199891000	-4.093267000	0.000608000
1	6.548408000	-5.125421000	0.000827000
6	2.212817000	3.104930000	-0.000181000
6	3.697053000	2.965490000	-0.000537000
6	7.118559000	-3.045395000	0.000400000
1	8.187309000	-3.255969000	0.000453000
6	-3.325437000	-4.075044000	-0.000263000

1Ag; G16/CAM-B3LYP/def2-SVP

47	-1.216881000	1.420664000	0.009172000
47	1.926345000	0.009226000	0.009259000
47	-1.201368000	-1.437907000	-0.001447000
9	4.489674000	2.273919000	1.191166000
9	4.456941000	-1.793366000	0.826378000
9	4.407616000	1.838920000	-0.911397000
9	4.829284000	3.851617000	-0.240136000
9	4.878672000	-3.801015000	0.139650000
9	4.473878000	-2.226866000	-1.278117000
9	-0.112028000	-6.158803000	-0.180180000
9	-1.045810000	-4.883605000	1.286541000
9	-1.411220000	-4.544964000	-0.803412000
7	0.515519000	2.665068000	0.031793000
7	0.545217000	-2.662265000	0.013675000
7	1.753404000	-2.090658000	-0.009809000
9	-1.449918000	4.506981000	-0.862528000
7	1.730265000	2.107020000	0.028543000
9	-1.119351000	4.894806000	1.224612000
9	-0.178018000	6.148539000	-0.255959000
6	-2.742041000	-0.017333000	-0.011184000
6	-6.126329000	-0.029632000	1.166616000
1	-5.583370000	-0.033374000	2.113017000
6	2.643748000	3.085021000	-0.006301000
6	2.017578000	4.326510000	-0.025436000
1	2.471407000	5.311855000	-0.057474000
6	-5.403703000	-0.022118000	-0.037519000
6	-7.515257000	-0.032245000	1.148955000
1	-8.069665000	-0.038137000	2.089526000
6	2.678013000	-3.058713000	-0.019976000
6	2.066088000	-4.307366000	-0.005456000
1	2.531184000	-5.287976000	-0.009303000
6	-6.102351000	-0.017287000	-1.255712000
1	-5.540758000	-0.011470000	-2.191164000
6	4.131999000	-2.722331000	-0.083537000
6	-3.972337000	-0.019470000	-0.023334000
6	0.666670000	3.993781000	-0.001061000
6	4.102706000	2.764867000	0.008635000
6	-7.491360000	-0.019881000	-1.265566000
1	-8.027052000	-0.016037000	-2.216931000
6	0.711533000	-3.989572000	0.014963000
6	-0.468068000	-4.903174000	0.079831000
6	-8.199473000	-0.027367000	-0.065205000
1	-9.291501000	-0.029417000	-0.076025000
6	-0.523927000	4.894936000	0.026475000

1Ag'; G16/CAM-B3LYP/def2-SVP

47	-0.229185000	-2.184505000	-0.000192000
47	-1.498991000	1.046813000	0.012273000
47	1.811689000	0.005752000	0.022054000
9	-4.885864000	1.206332000	1.184884000
9	-2.140495000	4.089140000	0.827459000
9	-4.537027000	1.456646000	-0.920385000
9	-6.242000000	0.314501000	-0.236255000
9	-1.091779000	5.847780000	0.129045000
9	-1.854404000	4.402683000	-1.279033000
9	4.184517000	4.205916000	-0.127507000
9	3.998048000	2.609515000	1.309892000
9	4.049116000	2.149507000	-0.787826000
7	-2.327547000	-1.854827000	0.019072000
7	1.330147000	2.078946000	0.037984000
7	0.054159000	2.472995000	0.005196000
9	-2.208473000	-4.544187000	-0.876913000
7	-2.805425000	-0.606131000	0.020267000
9	-2.728833000	-4.596170000	1.206997000
9	-4.269662000	-4.827015000	-0.283681000
6	1.823344000	-2.168471000	-0.014733000
6	5.370892000	-1.343628000	-0.226500000
1	4.984335000	-0.329344000	-0.344014000
6	-4.142475000	-0.666338000	-0.014645000
6	-4.563274000	-1.991287000	-0.038359000
1	-5.576776000	-2.378032000	-0.071669000
6	4.480492000	-2.413992000	-0.055715000
6	6.741908000	-1.571516000	-0.245328000
1	7.425443000	-0.730544000	-0.377801000
6	0.027434000	3.811641000	-0.011145000
6	1.322368000	4.318627000	0.008362000
1	1.641643000	5.355936000	0.002057000
6	4.991561000	-3.712533000	0.094610000
1	4.301328000	-4.546760000	0.228668000
6	-1.271269000	4.546679000	-0.084022000
6	3.057226000	-2.209489000	-0.034351000
6	-3.365201000	-2.698475000	-0.016512000
6	-4.961246000	0.582876000	0.003763000
6	6.363525000	-3.930711000	0.072237000
1	6.750315000	-4.945082000	0.189326000
6	2.105658000	3.168937000	0.038348000
6	3.591520000	3.040384000	0.110773000
6	7.242245000	-2.862843000	-0.097010000
1	8.319949000	-3.037657000	-0.112837000
6	-3.146209000	-4.175869000	0.007595000

1Ag; ORCA/PBE0/ZORA-TZVP/SARC-ZORA-TZVP

47	1.225456000	-1.372730000	-0.055357000
47	-1.804217000	0.017926000	-0.036035000
47	1.198393000	1.479483000	0.024404000
9	-4.329546000	-1.738020000	0.885564000
9	-4.554675000	2.261416000	1.149552000
9	-4.496590000	-2.281768000	-1.190927000
9	-4.788621000	-3.781802000	0.334820000
9	-4.863943000	3.751529000	-0.381793000
9	-4.354266000	1.717414000	-0.924129000
9	-0.005323000	6.255927000	0.023116000
9	0.957516000	4.956000000	1.454728000
9	1.380868000	4.732675000	-0.644689000
7	-0.471621000	-2.662020000	-0.093011000
7	-0.528118000	2.725335000	0.072573000
7	-1.721680000	2.120742000	0.003484000
9	0.940903000	-5.082153000	-1.415822000
7	-1.679240000	-2.082511000	-0.057873000
9	1.552023000	-4.492514000	0.563664000
9	0.166212000	-6.135544000	0.301187000
6	2.723831000	0.072197000	-0.021117000
6	6.078765000	-0.103517000	-1.221074000
1	5.531804000	-0.140882000	-2.155519000
6	-2.606612000	-3.047132000	-0.018983000
6	-2.002499000	-4.293167000	-0.030480000
1	-2.469324000	-5.262900000	0.001168000
6	5.368453000	-0.008183000	-0.017717000
6	7.461464000	-0.151873000	-1.210234000
1	8.004286000	-0.228818000	-2.145357000
6	-2.670110000	3.065090000	-0.004402000
6	-2.094501000	4.323338000	0.062497000
1	-2.582448000	5.283066000	0.067769000
6	6.073668000	0.041100000	1.191480000
1	5.522620000	0.115227000	2.121303000
6	-4.115779000	2.699281000	-0.040931000
6	3.950851000	0.035227000	-0.021988000
6	-0.650980000	-3.987830000	-0.075669000
6	-4.060459000	-2.712767000	0.002800000
6	7.456477000	-0.003567000	1.192120000
1	7.995487000	0.036600000	2.131735000
6	-0.737397000	4.046687000	0.107757000
6	0.401308000	5.001207000	0.233204000
6	8.152411000	-0.101268000	-0.006139000
1	9.235901000	-0.138299000	-0.001616000
6	0.504845000	-4.926488000	-0.155304000

1Ag'; ORCA/PBE0/ZORA-TZVP/SARC-ZORA-TZVP

47	0.545303000	1.752424000	0.028680000
47	-1.341639000	-0.989258000	-0.061619000
47	2.022670000	-0.833388000	-0.064238000
9	-4.837431000	-0.147086000	-1.479780000
9	-2.684687000	-4.085637000	-1.097889000
9	-4.409633000	-0.892424000	0.497491000
9	-5.849338000	0.702712000	0.226487000
9	-2.229919000	-5.731721000	0.227647000
9	-2.727199000	-3.787517000	1.034650000
9	3.225170000	-5.577956000	0.359822000
9	3.521666000	-4.176852000	-1.256425000
9	3.704396000	-3.508635000	0.782310000
7	-1.567882000	1.993445000	0.074246000
7	1.102504000	-2.746794000	-0.052677000
7	-0.236826000	-2.779639000	-0.040191000
9	-1.394866000	4.608634000	1.580951000
7	-2.306784000	0.883450000	-0.045711000
9	-0.883527000	4.706943000	-0.508689000
9	-2.851310000	5.321269000	0.154701000
6	2.601302000	1.123360000	-0.063781000
6	5.037572000	3.643411000	0.249652000
1	5.585378000	2.745550000	0.508970000
6	-3.598007000	1.238251000	-0.041355000
6	-3.717132000	2.612532000	0.081084000
1	-4.615329000	3.205232000	0.115955000
6	3.679589000	3.548995000	-0.077132000
6	5.669512000	4.874868000	0.238893000
1	6.721785000	4.937786000	0.491620000
6	-0.623839000	-4.059412000	0.027067000
6	0.480592000	-4.893636000	0.057131000
1	0.506131000	-5.968412000	0.114141000
6	2.973709000	4.710769000	-0.406632000
1	1.920906000	4.645254000	-0.656346000
6	-2.070966000	-4.419324000	0.048436000
6	3.039369000	2.275703000	-0.071863000
6	-2.400458000	3.037811000	0.150947000
6	-4.678236000	0.222253000	-0.199558000
6	3.614366000	5.937717000	-0.409023000
1	3.056226000	6.831436000	-0.663430000
6	1.545293000	-4.007956000	0.006518000
6	3.003200000	-4.318530000	-0.026391000
6	4.962229000	6.024313000	-0.088212000
1	5.460854000	6.986765000	-0.091374000
6	-1.883484000	4.421861000	0.345002000

EtCC-Ag; ORCA/PBE0/ZORA-TZVP/SARC-ZORA-TZVP

47	0.554118000	-1.590090000	1.458043000
47	-0.351621000	1.301039000	0.016920000
47	0.549120000	-1.620589000	-1.370668000
9	0.050707000	4.125257000	2.136653000
9	-0.396949000	3.940704000	-1.836493000
9	-2.021112000	3.584772000	1.915235000
9	-1.268574000	4.191182000	3.849720000
9	-1.202922000	4.125569000	-3.838178000
9	-2.448234000	3.412966000	-2.225402000
9	-0.247228000	-0.763905000	-6.139933000
9	1.253010000	-1.507934000	-4.770839000
9	-0.791656000	-2.147478000	-4.568683000
7	-0.068113000	0.027093000	2.698845000
7	-0.120337000	-0.051445000	-2.642675000
7	-0.422991000	1.126159000	-2.080562000
9	-0.461328000	-2.127578000	4.425651000
7	-0.314670000	1.209685000	2.119371000
9	1.284637000	-1.153013000	5.226759000
9	-0.650983000	-0.772603000	6.103359000
6	-0.636679000	2.086469000	3.079368000
6	-0.603221000	1.473217000	4.320381000
1	-0.816166000	1.902845000	5.284417000
6	-0.782177000	1.973441000	-3.052744000
6	-0.716486000	1.345002000	-4.285910000
1	-0.936129000	1.753727000	-5.257381000
6	-1.208789000	3.367876000	-2.738342000
6	-0.239745000	0.170308000	4.016949000
6	-0.969623000	3.502054000	2.745683000
6	-0.290851000	0.066293000	-3.964095000
6	-0.019918000	-1.089154000	-4.865750000
6	-0.016213000	-0.972453000	4.946174000
6	1.180943000	-2.998397000	0.059101000
6	1.696155000	-4.108591000	0.032238000
6	2.286988000	-5.433309000	0.004597000
1	3.031332000	-5.463925000	-0.798914000
1	2.848687000	-5.574296000	0.935103000
6	1.267634000	-6.557151000	-0.172759000
1	0.721285000	-6.441405000	-1.110049000
1	0.543411000	-6.556609000	0.643247000
1	1.771233000	-7.525707000	-0.185796000

[AgPz]$_3$; ORCA/PBE0/ZORA-TZVP/SARC-ZORA-TZVP

47	-1.203257000	-1.627472000	-0.037162000
47	-0.837541000	1.899246000	-0.069416000
47	1.984364000	-0.221654000	0.106091000
9	-5.448394000	3.300341000	0.293924000
9	-3.480162000	3.598816000	1.140916000
9	-3.734352000	3.566929000	-0.997992000
9	-0.214721000	4.832747000	-1.450294000
9	-0.086670000	5.369743000	0.631562000
9	1.341023000	6.176095000	-0.774756000
9	5.575388000	2.925147000	0.212555000
9	4.849188000	0.968770000	-0.364185000
9	4.715262000	1.604230000	1.688332000
9	4.374737000	-2.094561000	0.961768000
9	4.562374000	-2.559183000	-1.133323000
9	4.767526000	-4.129228000	0.334309000
9	-0.176052000	-6.327948000	-0.512337000
9	-1.287722000	-4.716833000	-1.434010000
9	-1.360296000	-4.986230000	0.700805000
7	-2.855541000	-0.340160000	0.065909000
7	-2.728275000	0.993392000	0.050945000
7	1.114744000	2.674453000	-0.115660000
7	2.163680000	1.871361000	0.112920000
7	1.726157000	-2.303821000	0.009389000
7	0.504430000	-2.841105000	-0.104667000
6	-4.158627000	-0.631585000	0.164154000
6	-4.910239000	0.529197000	0.216409000
1	-5.979165000	0.631037000	0.293420000
6	-3.953424000	1.526701000	0.141788000
6	1.569429000	3.930373000	-0.217872000
6	2.944372000	3.959300000	-0.056180000
1	3.602949000	4.810170000	-0.090402000
6	3.267524000	2.629205000	0.148510000
6	2.622531000	-3.297826000	-0.031307000
6	1.981673000	-4.517366000	-0.176236000
1	2.418281000	-5.499603000	-0.237720000
6	0.642591000	-4.168508000	-0.217960000
6	-4.626090000	-2.046236000	0.226883000
6	-4.155870000	3.004681000	0.144623000
6	0.647661000	5.081372000	-0.453769000
6	4.607976000	2.030698000	0.421170000
6	4.088182000	-3.020456000	0.033983000
6	-0.549501000	-5.055308000	-0.365733000
9	-5.955002000	-2.109692000	0.135672000
9	-4.267246000	-2.639904000	1.375876000
9	-4.105538000	-2.780262000	-0.769050000