

Electronic Supplementary Information

Concurrent tandem catalysis enabled by nanomechanical motion in heteroleptic four-component dual-catalyst machinery

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[‡] Equal contribution.

1. Synthesis

1.1 General information

All reagents and the substrates **4** and **5** were purchased from commercial suppliers and used without further purification.

Bruker Avance (400 MHz), Jeol ECZ (500 MHz) and Varian (600 MHz) spectrometer were used to record ^1H -, ^{13}C -, DOSY NMR spectra at 298 K applying the deuterated solvent as the lock. The chemical shifts refer to the residual protiated fraction of the solvent (CHCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.0$ ppm; CH_2Cl_2 : $\delta_{\text{H}} = 5.32$ ppm, $\delta_{\text{C}} = 53.8$ ppm; CD_2HOH : $\delta_{\text{C}} = 49.3$ ppm). Coupling patterns of ^1H NMR signals were described as follows (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, brs: broad singlet, td: triplet of doublets, m: multiplet). Values of coupling constant(s) are reported in Hertz (Hz) and the number of protons is implied. The numbering of carbon atoms is simply made for the assignment and usually not in accordance with IUPAC nomenclature guidelines. Melting points were measured on a Büchi SMP-11 instrument. UV-vis spectra were measured on a Cary Win 50. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer. Column chromatography was performed on silica gel 60 (60–230 mesh). Thin layer chromatography (TLC) was performed using Merck silica gel (60 F254). The *tris*-phenanthroline deck **1**¹ and compound **6**², **7**³, **8**⁵ and **9**⁴ were synthesized according to known procedures. The spectral data of these compounds are in good agreement with those in the literature reports.

1.2 Ligands

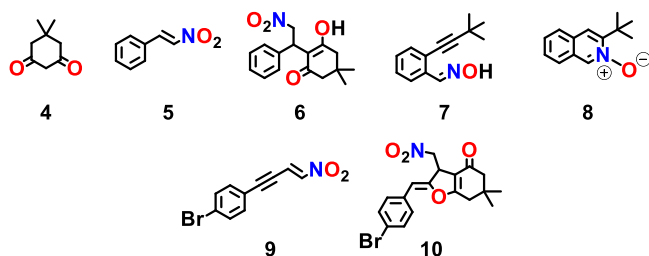
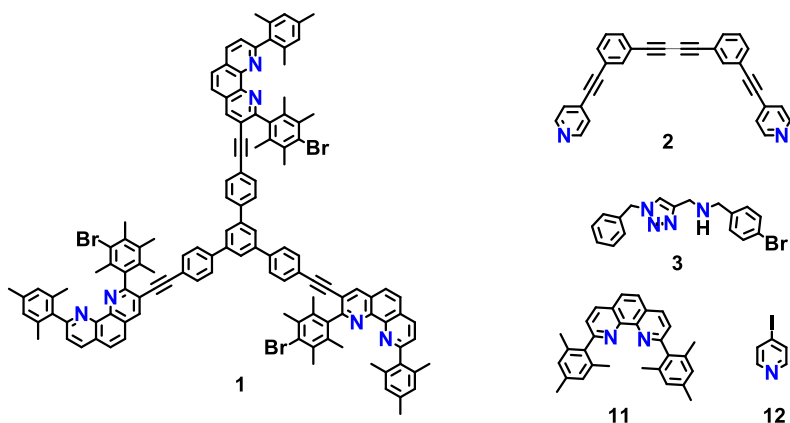
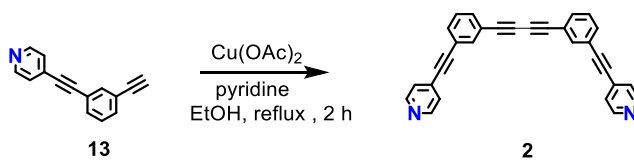
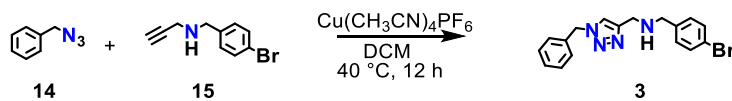


Figure S1. Chemical structures of all ligands used in the present study.

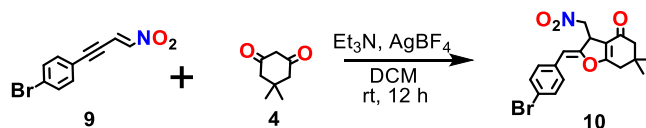
1.3 Synthesis of ligands 2, 3 and product 10



Scheme S1. Final step of the synthesis of ligand 2.



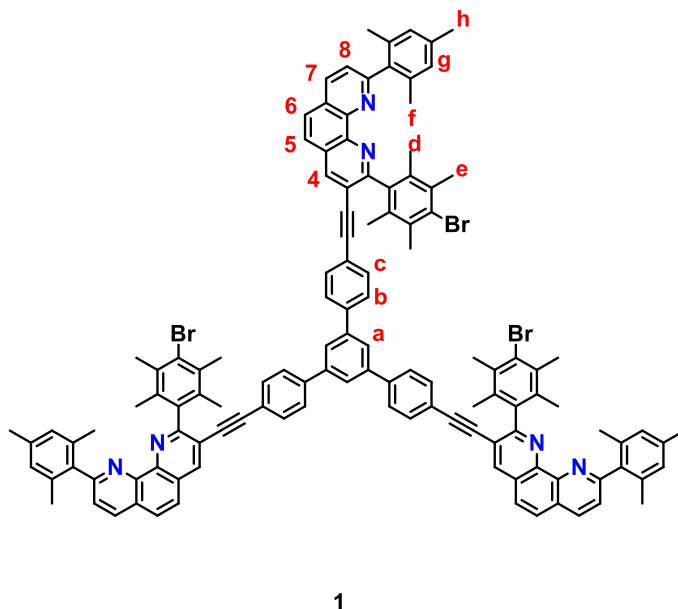
Scheme S2. Final step of the synthesis of base 3.



Scheme S3. Final step of the synthesis of product 10.

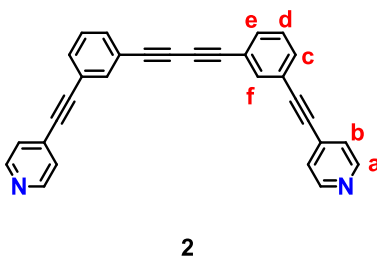
1.4 Synthesis and characterization data of ligands and product 6, 8, 10

Literature known deck 11



MP > 250 °C, ^1H NMR (CDCl_3 , 500 MHz): δ = 2.04 (s, 18H, e-H), 2.11 (s, 18H, f-H), 2.31 (s, 9H, h-H), 2.47 (s, 18H, d-H), 6.93 (s, 6H, g-H), 7.21 (d, 3J = 8.0 Hz, 6H, b-H), 7.58-7.62 (m, 9H, c-, 8-H), 7.73 (s, 3H, a-H), 7.86 (d, 3J = 8.0 Hz, 3H, 6-H), 7.90 (d, 3J = 8.0 Hz, 3H, 5-H), 8.30 (d, 3J = 8.0 Hz, 3H, 7-H), 8.51 (s, 3H, 4-H) ppm.

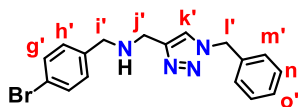
Ligand 2



To a solution of (2.00 g, 10.0 mmol) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in pyridine : methanol 1:1 (20 mL), compound **13** (99.0 mg, 487 μmol) was added. The solution was heated under reflux for 2 h. After cooling to rt, DCM was added and washed with water. The organic phase was dried over anhydrous Na_2SO_4 , then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (R_f = 0.4, EtOAc: hexane = 1:5) on silica gel using 20% EtOAc in hexane,

then it was precipitated from DCM by adding pentane to furnish compound **2** as a yellow solid (45.0 mg, 111 μ mol, 46%). **Mp**: 163-164 °C. **¹H NMR** (CDCl₃, 500 MHz): δ = 7.37 (td, ³*J* = 7.9 Hz, ⁵*J* = 0.7 Hz, 2H, d-H), 7.38 (d, ³*J* = 6.0 Hz, 4H, b-H), 7.54 (dt, ³*J* = 7.9 Hz, ⁴*J* = 1.7 Hz, 2H, c/e-H), 7.55 (dt, ³*J* = 7.9 Hz, ⁴*J* = 1.7 Hz, 2H, e/c-H), 7.72 (td, ⁴*J* = 1.7 Hz, ⁵*J* = 0.7 Hz, 2H, f-H), 8.62 (d, ³*J* = 6.0 Hz, 4H, a-H) ppm. **¹³C NMR** (CDCl₃, 125 MHz): δ = 74.5, 80.7, 87.5, 92.5, 122.3, 122.8, 125.5, 128.8, 131.0, 132.5, 133.0, 135.6, 149.9 ppm. **Elemental analysis**: Calcd. for C₃₀H₁₆N₂•CH₂Cl₂: C, 85.35; H, 3.91; N, 6.58. Found C, 85.55; H, 3.67; N, 6.27. **ESI-MS**: *m/z* (%) = 405.3 (100) [**2**+H]⁺.

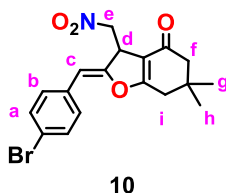
Ligand 3



3

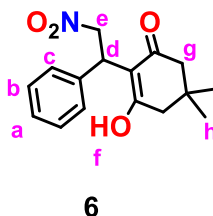
Benzyl azide (**14**, 250 mg, 1.87 mmol) and alkyne **15** (460 mg, 1.88 mmol) were dissolved in DCM. Then, [Cu(CH₃CN)₄]PF₆ (210 mg, 563 μ mol) was added to the reaction mixture, which was heated at 40 °C for 12 h. The reaction mixture was cooled and washed with cyclam (501 mg, 2.50 mmol) dissolved in water. Afterwards, the solvent from the collected organic phase was evaporated under reduced pressure. The crude mixture was purified by column chromatography (\varnothing = 2.5 cm, *l* = 15 cm) eluting with 5% EtOAc in *n*-hexane on silica gel (*R_f* = 0.46, SiO₂, 5% EtOAc in *n*-hexane) to furnish **3** as a colorless solid (550 mg, 1.54 mmol, 82%). **Mp**: 81-83 °C. **¹H NMR** (CD₂Cl₂, 500 MHz): δ = 3.75 (s, 2H, i'-H), 3.83 (s, 2H, j'-H), 5.49 (s, 2H, l'-H), 7.21 (d, ³*J* = 8.4 Hz, 2H, h'-H), 7.27 (dd, ³*J* = 7.4 Hz, ⁴*J* = 2.2 Hz, 2H, m'-H), 7.35-7.38 (m, 3H, n',o'-H), 7.39 (s, 1H, k'-H), 7.43 (d, ³*J* = 8.4 Hz, 2H, g'-H) ppm. **¹³C NMR** (CD₂Cl₂, 125 MHz): δ = 44.4, 52.8 (2C), 120.9, 122.0, 128.3, 128.9, 129.4, 130.3, 131.7, 135.6, 139.8, 147.4 ppm. **Elemental analysis**: Calcd for C₁₇H₁₇BrN₄: C, 57.15; H, 4.80; N, 15.68. Found, C, 57.35; H, 4.82; N, 14.95. **ESI-MS**: *m/z* (%) = 358.8 (100) [**3**+H]⁺.

Product 10



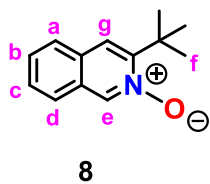
A mixture of dimedone **4** (99.0 mg, 0.713 mmol), β -nitroalkenyne **9** (196 mg, 0.785 mmol), triethylamine (2 mol%), and AgBF_4 (5 mol%) in CH_2Cl_2 (15 mL) was stirred at r.t. until both the starting substrate and the intermediate Michael adduct were completely converted as indicated by TLC. The crude product was directly subjected to column chromatography ($\varnothing = 2.5$ cm, $l = 20$ cm) eluting with 50% DCM in *n*-hexane on silica gel ($R_f = 0.4$, SiO_2 , 50% DCM in *n*-hexane) to furnish **10** as a colorless solid (195 mg, 0.497 mmol, 70%). **Mp**: 128-130 °C. **$^1\text{H NMR}$** (CD_2Cl_2 , 500 MHz): $\delta = 1.15$ (s, 3H, g/h-H), 1.16 (s, 3H, h/g-H), 2.29 (d, $^5J = 2.8$ Hz, i-H), 2.54 (d, $^5J = 2.8$ Hz, f-H), 4.50-4.55 (m, 1H, d-H), 4.76 (dd, $^2J = 13.2$ Hz, $^3J = 6.7$ Hz, 1H, e-H), 4.86 (dd, $^2J = 13.2$ Hz, $^3J = 6.7$ Hz, 1H, e-H), 5.70 (d, $^5J = 2.3$ Hz, 1H, c-H), 7.44-7.48 (m, 4H, a,b-H) ppm. **$^{13}\text{C NMR}$** (CD_2Cl_2 , 125 MHz): $\delta = 28.3, 28.9, 34.6, 37.4, 42.4, 51.4, 76.2, 105.5, 111.8, 121.2, 130.5, 131.9, 133.0, 154.6, 175.0, 193.6$ ppm. **Elemental analysis**: Calcd for $\text{C}_{18}\text{H}_{18}\text{BrNO}_4$: C, 55.12; H, 4.63; N, 3.57. Found, C, 55.02; H, 4.42; N, 3.69. **ESI-MS**: m/z (%) = 393.8 (100) [**10**+H] $^+$.

Product 6²



Using the same procedure as mentioned in the literature. **Mp**: 137-138 °C. **$^1\text{H NMR}$** (CD_2Cl_2 , 500 MHz): $\delta = 1.02$ (s, 6H, h-H), 2.30 (s, 4H, g-H), 5.01-5.09 (m, 2H, e-H), 5.17-5.25 (m, 1H, d-H), 7.19-7.23 (m, 1H, a-H), 7.26-7.33 (m, 5H, b,c,f-H) ppm. **$^{13}\text{C NMR}$** (CD_3OD , 125 MHz): 28.6, 33.2, 39.8, 40.0, 48.2, 52.2, 78.4, 114.0, 127.9, 129.2, 129.6, 142.0, 188.0, 195.0 ppm. **Elemental analysis**: Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4$: C, 66.42; H, 6.62; N, 4.84. Found, C, 66.20; H, 6.43; N, 4.92. **ESI-MS**: m/z (%) = 289.9 (100) [**6**+H] $^+$.

Product 8⁵

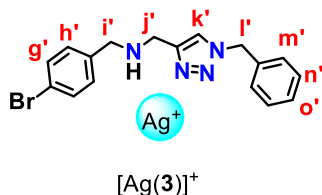


¹H NMR (CD₂Cl₂, 400 MHz): δ = 1.60 (s, 9H, f-H), 7.50-7.58 (m, 2H, c-, b-H), 7.65-7.69 (m, 1H, a-H), 7.73 (s, 1H, g-H), 7.75-7.8 (m, 1H, d-H) 8.85 (s, 1H, e-H) ppm.

2. Synthesis and characterization of model complexes

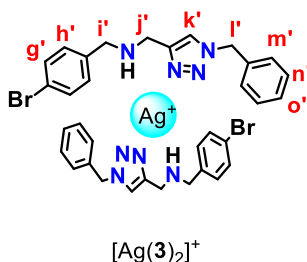
All solid components of the complexes were placed in an NMR tube and dissolved in CD₂Cl₂.

Complex [Ag(**3**)]⁺



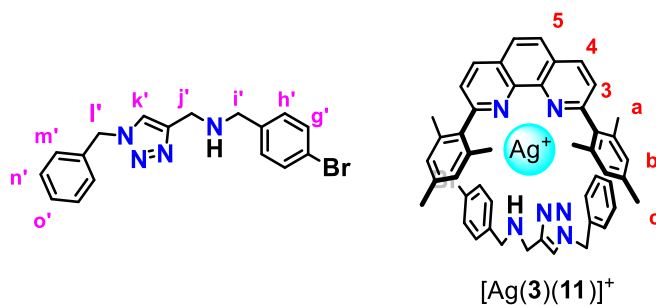
In an NMR tube, AgBF₄ (200 μg, 1.03 μmol) and ligand **3** (367 μg, 1.03 μmol) were dissolved in 500 μL of CD₂Cl₂. The NMR spectrum indicated clean formation of the complex **C1** = [Ag(**3**)]⁺. **¹H NMR** (CD₂Cl₂, 400 MHz): δ = 3.95 (s, 2H, i'-H), 4.24 (s, 2H, j'-H), 5.56 (s, 2H, l'-H), 7.35 (dd, ³J = 7.4 Hz, ⁴J = 2.2 Hz, 2H, m'-H), 7.39 (d, ³J = 8.4 Hz, 2H, h'-H), 7.42-7.45 (m, 3H, n', o'-H), 7.52 (d, ³J = 8.4 Hz, 2H, g'-H), 7.97 (s, 1H, k'-H) ppm.

Complex [Ag(**3**)₂]⁺



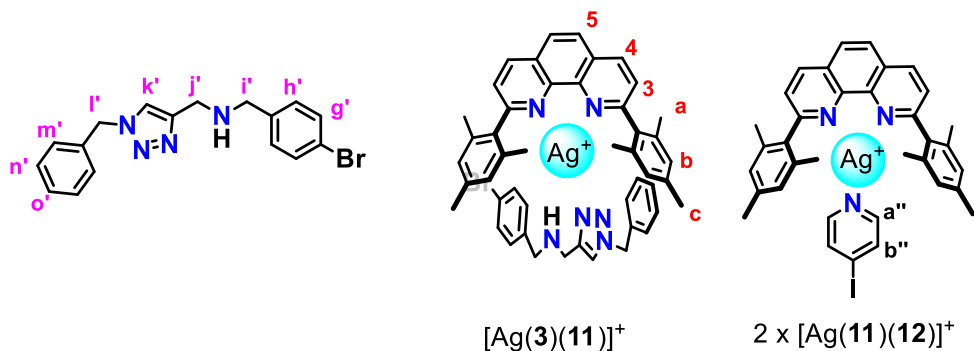
In an NMR tube, AgBF₄ (200 μg, 1.03 μmol) and ligand **3** (734 μg, 2.05 μmol) were mixed in CD₂Cl₂ (500 μL). The NMR spectrum indicated quantitative formation of complex [Ag(**3**)₂]⁺. **¹H NMR** (CD₂Cl₂, 400 MHz): δ = 3.67 (s, 2H, i'-H), 3.83 (s, 2H, j'-H), 5.53 (s, 2H, l'-H), 7.15 (d, ³J = 8.4 Hz, 2H, h'-H), 7.32 (d, ³J = 8.4 Hz, 2H, g'-H), 7.34 (dd, ³J = 7.4 Hz, ⁴J = 2.2 Hz, 2H, m'-H), 7.40 (m, 3H, n', o'-H), 7.59 (s, 1H, k'-H) ppm.

Complex $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+$



In an NMR tube, AgBF_4 (200 μg , 1.03 μmol) as well as ligands **11** (427 μg , 1.03 μmol) and **3** (367 μg , 1.03 μmol) were dissolved in CD_2Cl_2 (500 μL). The NMR spectrum indicated quantitative formation of complex **C3** = $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+$. $^1\text{H NMR}$ (CD_2Cl_2 , 400 MHz): δ = 1.83 (s, 12H, a-H), 2.16 (s, 6H, c-H), 3.21 (brs, 4H, i',j'-H), 5.50 (s, 2H, l'-H), 6.64 (s, 4H, b-H), 6.97 (d, $^3J = 7.4$ Hz, 2H, h'-H), 7.28 (d, $^3J = 7.4$ Hz, 2H, g'-H), 7.37-7.44 (m, 5H, m',n',o'-H), 7.57 (s, 1H, k'-H), 7.84 (d, $^3J = 8.0$ Hz, 2H, 3-H), 8.14 (s, 2H, 5-H), 8.62 (d, $^3J = 8.0$ Hz, 2H, 4-H) ppm.

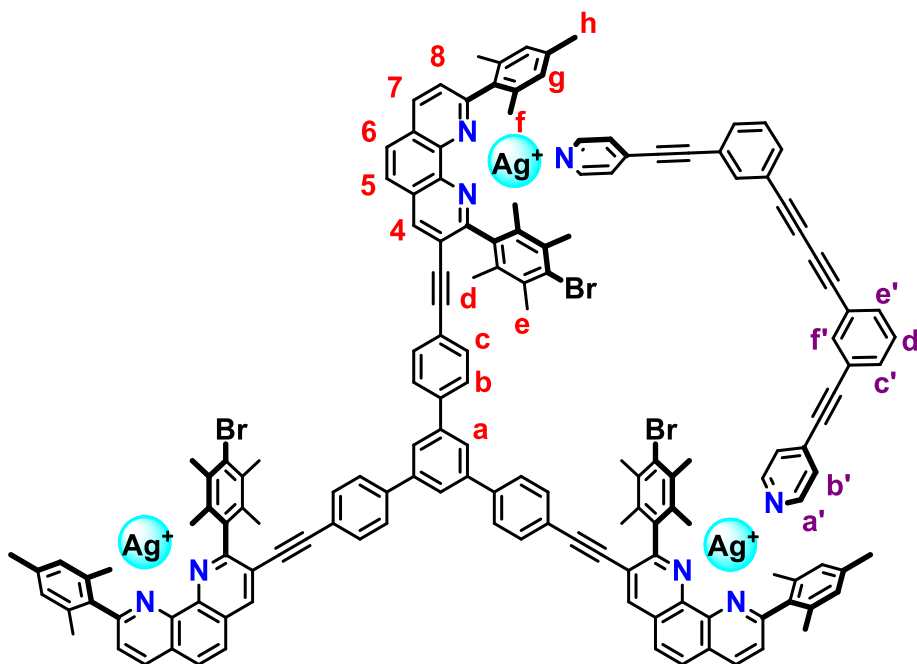
Mixture of $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+ + 2 \times [\text{Ag}(\mathbf{11})(\mathbf{12})]^+$



In an NMR tube AgBF_4 (200 μg , 1.03 μmol) as well as ligands **11** (427 μg , 1.03 μmol), **3** (122 μg , 0.342 μmol) and **12** (140 μg , 0.685 μmol) were dissolved in CD_2Cl_2 (500 μL). $^1\text{H NMR}$ (CD_2Cl_2 , 400 MHz): δ = 2.02 (s, 36H, a-H), 2.33 (s, 18H, c-H), 3.17 (brs, 4H, i',j'-H), 5.51 (s, 2H, l'-H), 6.47 (d, $^3J = 6.3$ Hz, 4H, a''-H), 6.97 (brs, 14H, b,h'-H), 7.28 (d, $^3J = 7.4$ Hz, 2H, g'-H), 7.37-7.47 (m, 5H, m',n',o'-H), 7.57 (s, 1H, k'-H), 7.88 (d, $^3J = 8.0$ Hz, 6H, 3-H), 7.89 (d, $^3J = 6.3$ Hz, 4H, b''-H), 8.15 (s, 6H, 5-H), 8.68 (d, $^3J = 8.0$ Hz, 6H, 4-H) ppm.

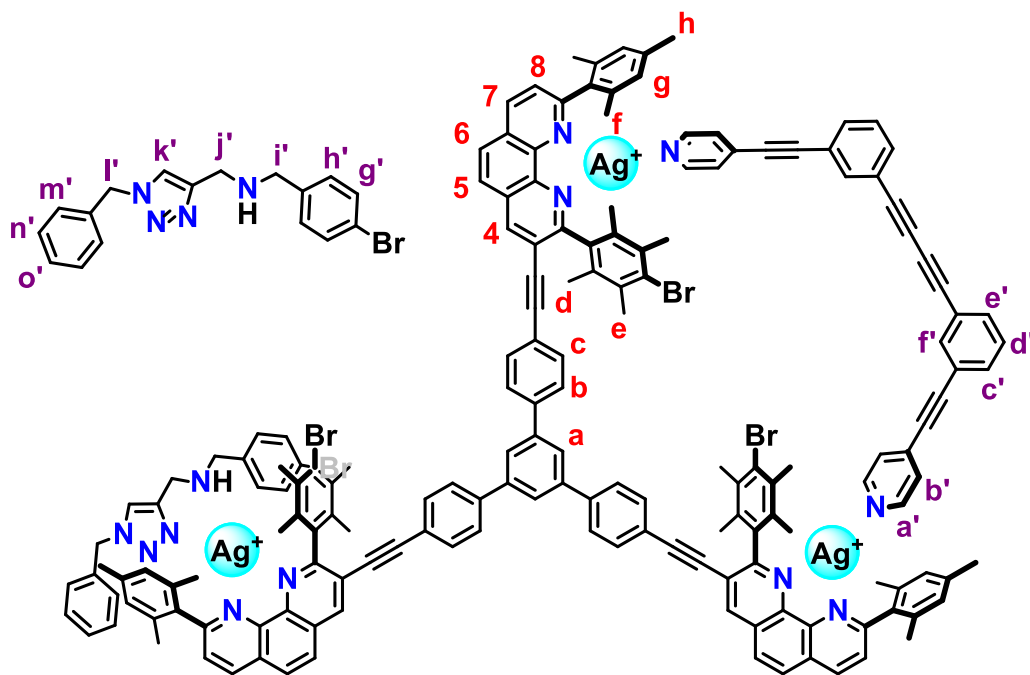
3. Synthesis and characterization of slider-on-deck complexes

Slider-on-deck $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]^{3+}$



In an NMR tube, AgBF_4 (200 μg , 1.03 μmol), deck **1** (562 μg , 343 nmol) and ligand **2** (139 μg , 343 nmol) were dissolved in 500 μL of CD_2Cl_2 . The NMR spectrum indicated quantitative formation of slider-on-deck $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]^{3+}$. **^1H NMR** (600 MHz, CD_2Cl_2): δ = 2.04 (s, 18H, e-H), 2.05 (s, 18H, f-H), 2.40 (s, 9H, h-H), 2.52 (s, 18H, d-H), 6.84 (d, 3J = 6.0 Hz, 4H, a'-H), 7.06 (s, 6H, g-H), 7.29 (d, 3J = 7.6 Hz, 6H, b-H), 7.32 (d, 3J = 6.0 Hz, 2H, b'-H), 7.46 (t, 3J = 7.7 Hz, 2H, d'-H), 7.62 (dt, 3J = 7.7 Hz, 4J = 1.2 Hz, 2H, c'/e'-H), 7.64 (dt, 3J = 7.7 Hz, 4J = 1.2 Hz, 2H, e'/c'-H), 7.70 (d, 3J = 7.6 Hz, 6H, c-H), 7.82 (s, 3H, a-H), 7.83 (d, 4J = 1.2 Hz, 2H, f'-H), 7.90 (d, 3J = 8.0 Hz, 3H, 8-H), 8.16 (d, 3J = 8.9 Hz, 3H, 5/6-H), 8.19 (d, 3J = 8.9 Hz, 3H, 6/5-H), 8.69 (d, 3J = 8.0 Hz, 3H, 7-H), 8.83 (s, 3H, 4-H) ppm. **Elemental analysis:** Calcd for $\text{C}_{153}\text{H}_{115}\text{Ag}_3\text{B}_3\text{Br}_3\text{F}_{12}\text{N}_8 \cdot \text{CH}_2\text{Cl}_2$: C, 62.19; H, 3.97; N, 3.77. Found: C, 61.98; H, 3.76; N, 3.87. **ESI-MS:** m/z (%) = 876.1 (100) $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]^{3+}$, 1358.0 (80) $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]\text{BF}_4^{2+}$.

Slider-on-deck $[Ag_3(1)(2)(3)]^{3+}$



In an NMR tube, $AgBF_4$ (200 μ g, 1.03 μ mol), deck **1** (562 μ g, 0.343 μ mol), ligand **2** (139 μ g, 0.343 μ mol) and ligand **3** (122 μ g, 0.343 μ mol) were dissolved in 500 μ L of CD_2Cl_2 . The NMR spectrum indicated quantitative formation of **SII** = $[Ag_3(1)(2)(3)]^{3+}$. **1H NMR** (600 MHz, CD_2Cl_2): δ = 2.01 (s, 18H, e-H), 2.05 (s, 18H, f-H), 2.36 (s, 9H, h-H), 2.47 (s, 18H, d-H), 3.33 (brs, 4H, i',j'-H), 5.53 (s, 2H, l'-H), 6.79 (d, 3J = 6.0 Hz, 4H, a'-H), 6.98 (brs, 6H, g-H), 7.03 (d, 3J = 6.0 Hz, 2H, h'-H), 7.29 (d, 3J = 7.6 Hz, 6H, b-H), 7.32 (d, 3J = 6.0 Hz, 6H, b',g'-H), 7.36 (d, 3J = 7.4 Hz, 2H, m'-H), 7.39-7.42 (m, 3-H, n',o'-H), 7.46 (t, 3J = 7.7 Hz, 2H, d'-H), 7.60 (brs, 1H, k'-H), 7.64 (td, 3J = 7.7 Hz, 4J = 1.2 Hz, 2H, c',e'-H), 7.70 (d, 3J = 7.6 Hz, 6H, c-H), 7.82 (s, 3H, a-H), 7.84 (d, 4J = 1.2 Hz, 2H, f'-H), 7.91 (d, 3J = 8.0 Hz, 3H, 8-H), 8.17 (d, 3J = 8.9 Hz, 3H, 5/6-H), 8.20 (d, 3J = 8.9 Hz, 3H, 6/5-H), 8.69 (d, 3J = 8.0 Hz, 3H, 7-H), 8.85 (s, 3H, 4-H) ppm. **Elemental analysis:** Calcd for $C_{173}H_{140}Br_3Cu_3F_{18}N_9OP_3 \cdot CH_2Cl_2$: C, 61.65; H, 4.05; N, 5.05. Found: C,61.61; H,3.87; N,5.19. **ESI-MS:** m/z (%) = 995.5 (100) $[Ag_3(1)(2)(3)]^{3+}$.

4. NMR spectra: ^1H , ^{13}C , ^1H - ^1H COSY

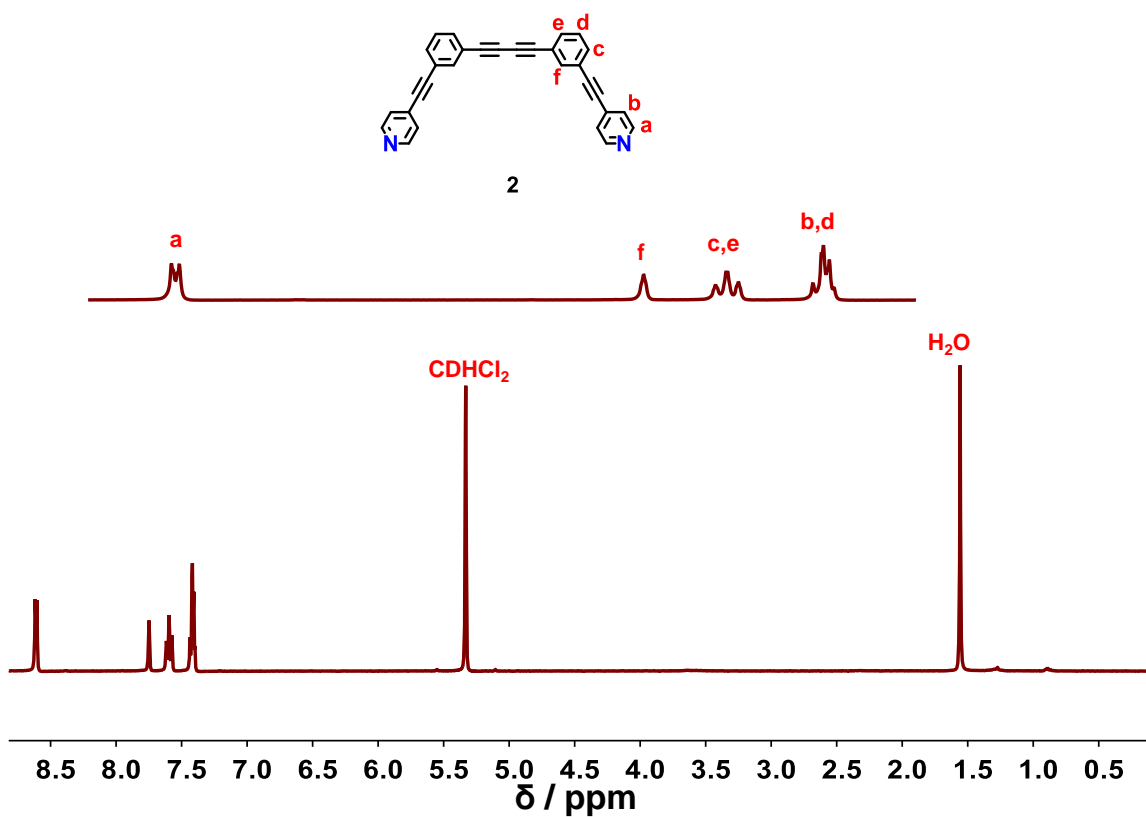


Figure S2. ^1H NMR spectrum (CD_2Cl_2 , 500 MHz) of compound 2.

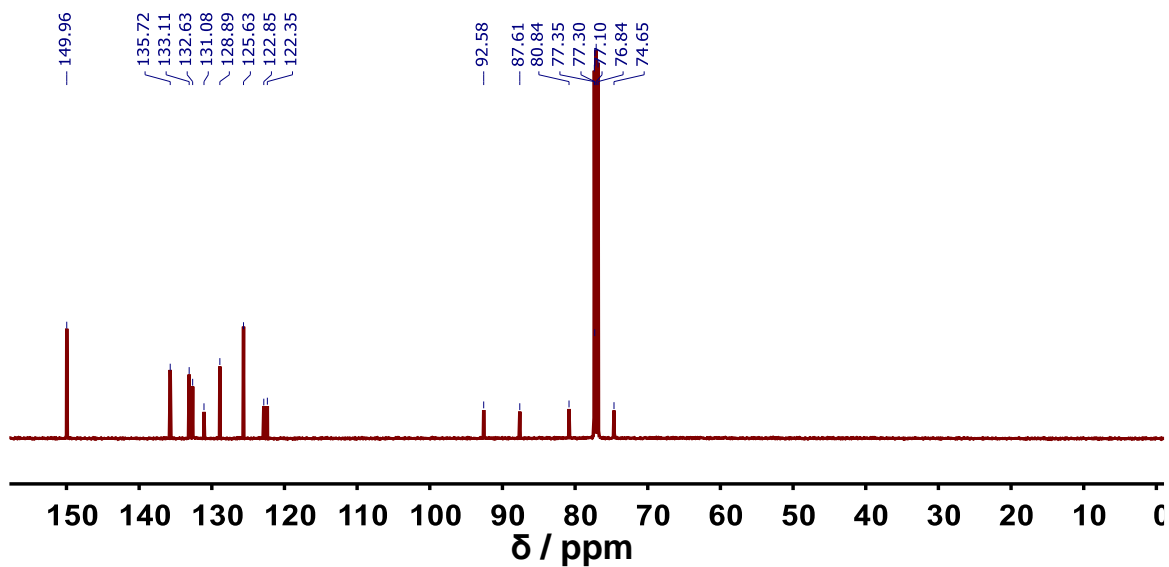


Figure S3. ^{13}C NMR spectrum (CDCl_3 , 125 MHz) of compound 2.

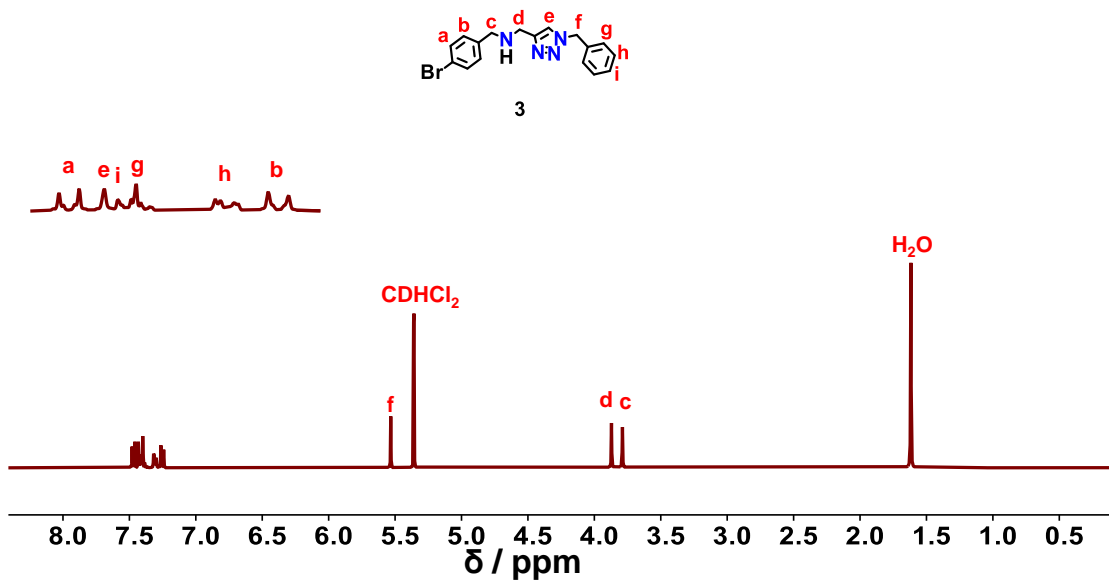


Figure S4. ¹H NMR spectrum (CD₂Cl₂, 500 MHz) of compound 3.

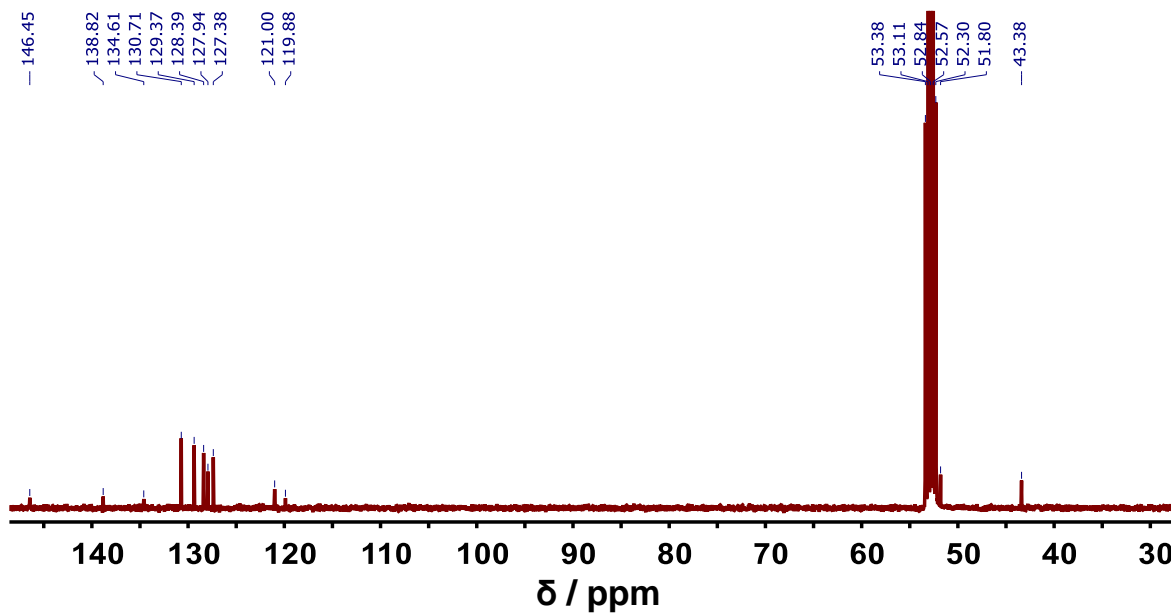


Figure S5. ¹³C NMR spectrum (CD₂Cl₂, 125 MHz) of compound 3.

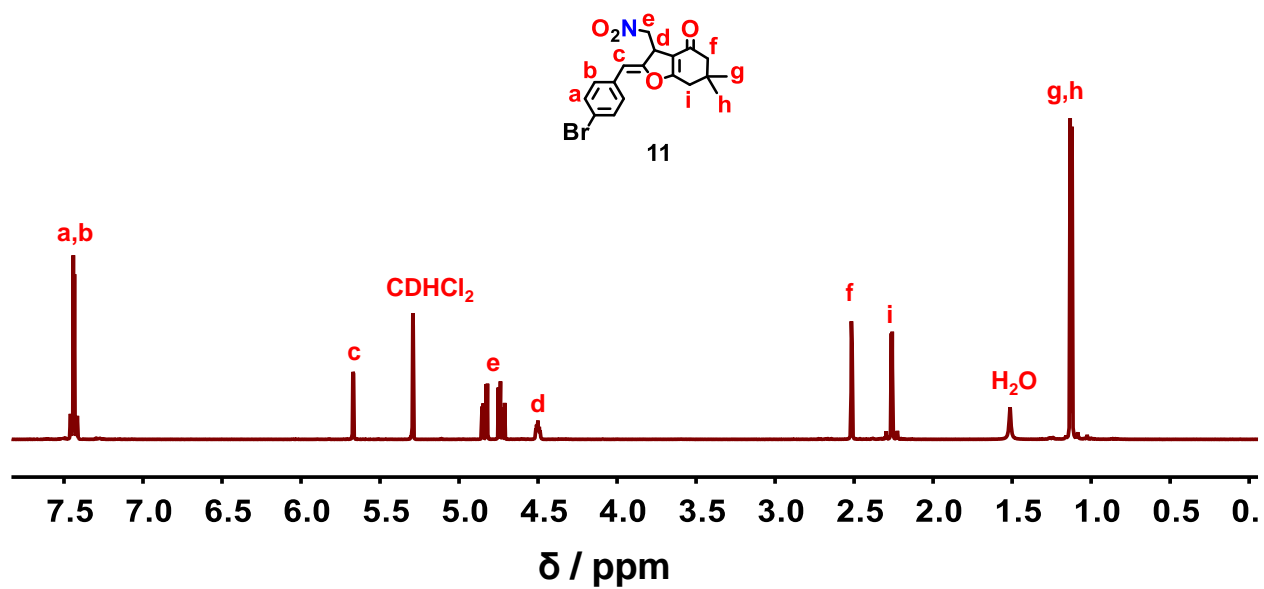


Figure S6. ¹H NMR spectrum (CD₂Cl₂, 500 MHz) of compound 10.

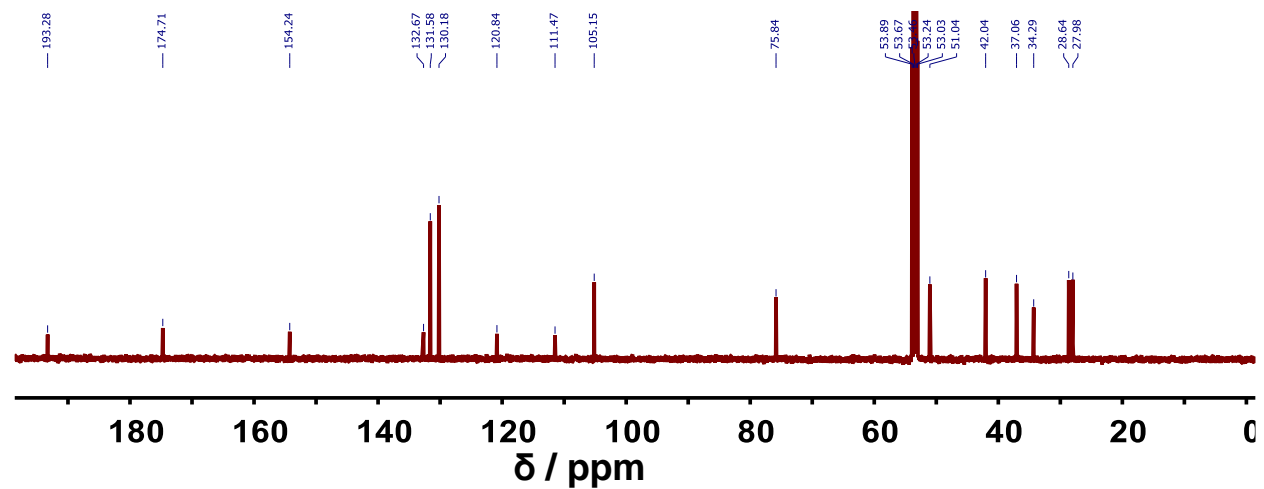


Figure S7. ¹³C NMR spectrum (CD₂Cl₂, 125 MHz) of compound 10.

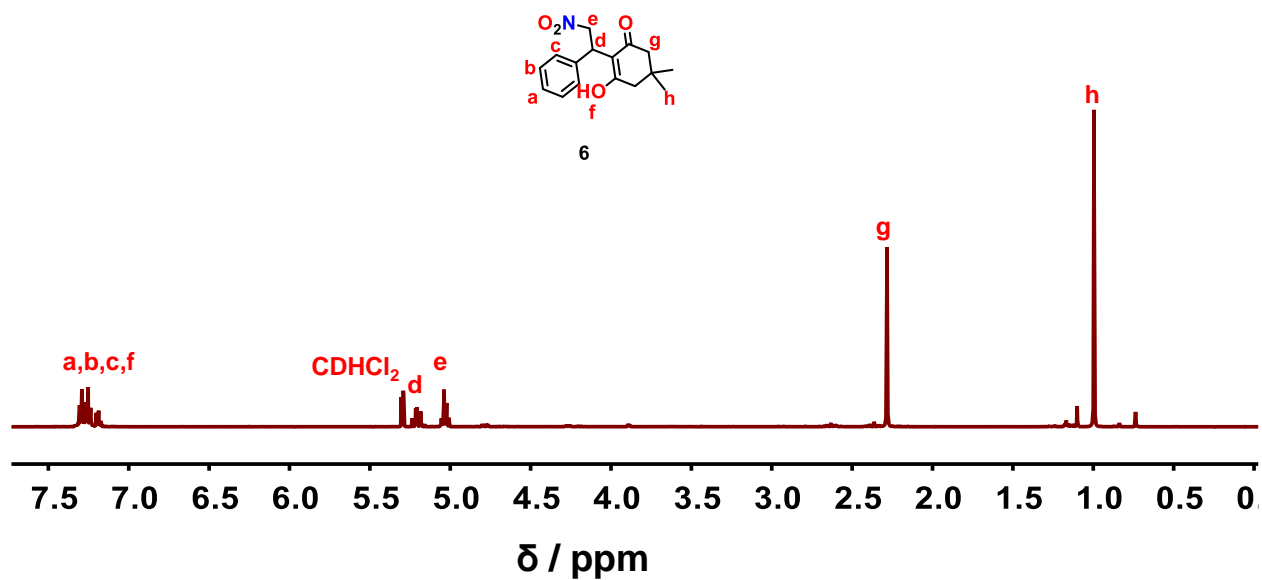


Figure S8. ¹H NMR spectrum (CD₂Cl₂, 500 MHz) of compound 6.

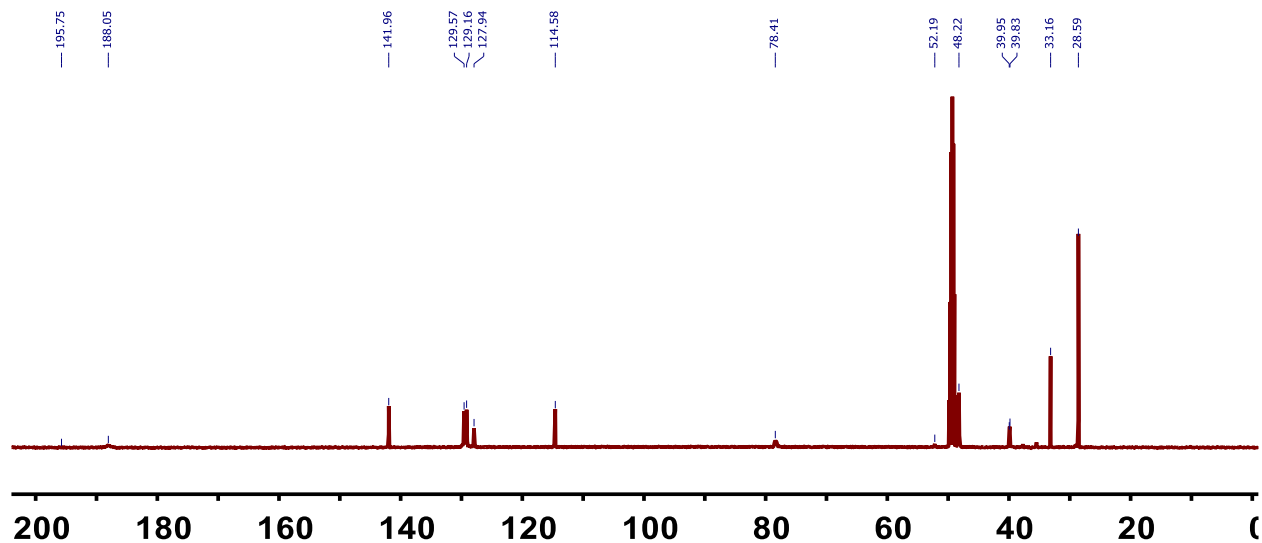


Figure S9. ¹³C NMR spectrum (CD₃OD, 125 MHz) of compound 6.

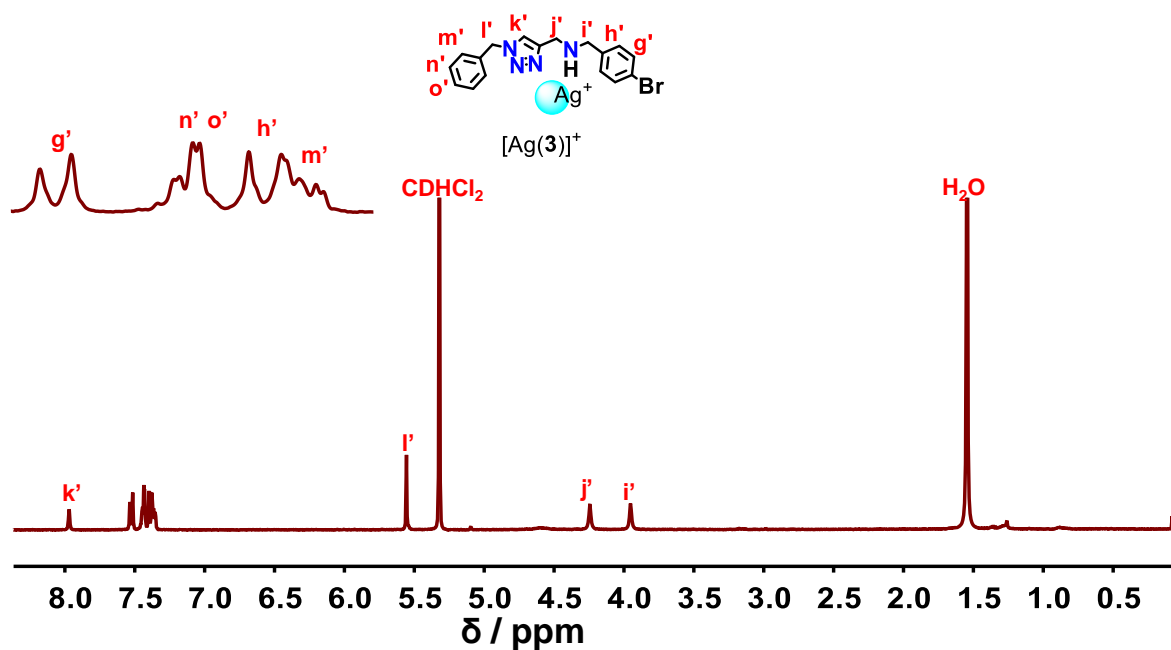


Figure S10. ^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of complex $[\text{Ag}(\mathbf{3})]^+$.

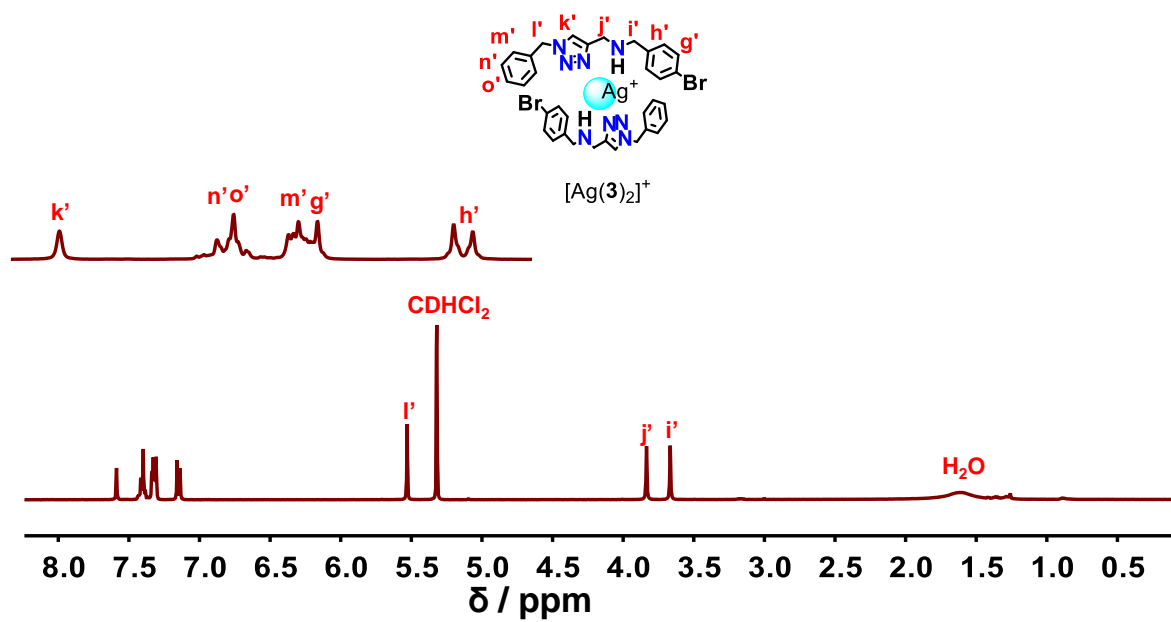


Figure S11. ^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of complex $[\text{Ag}(\mathbf{3})_2]^+$.

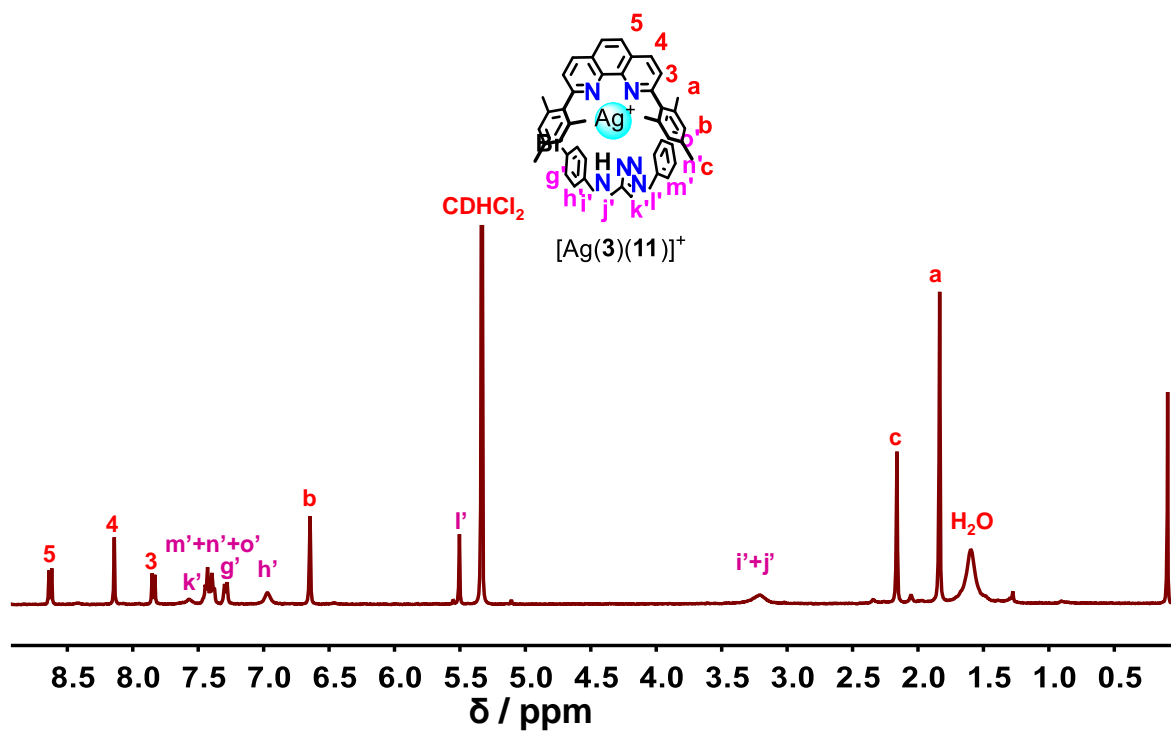


Figure S12. ^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of complex $[\text{Ag}(3)(11)]^+$.

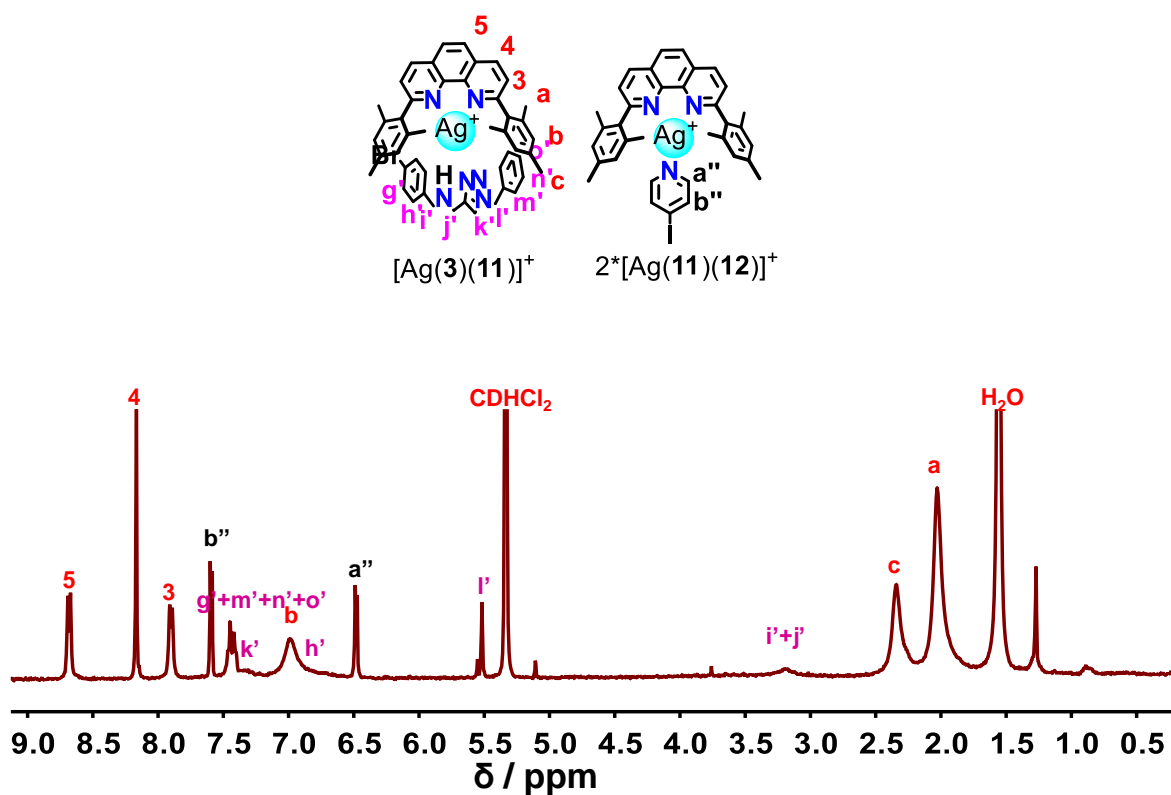


Figure S13. ^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of complexes $[\text{Ag}(3)(11)]^+ + 2^*[\text{Ag}(11)(12)]^+$.

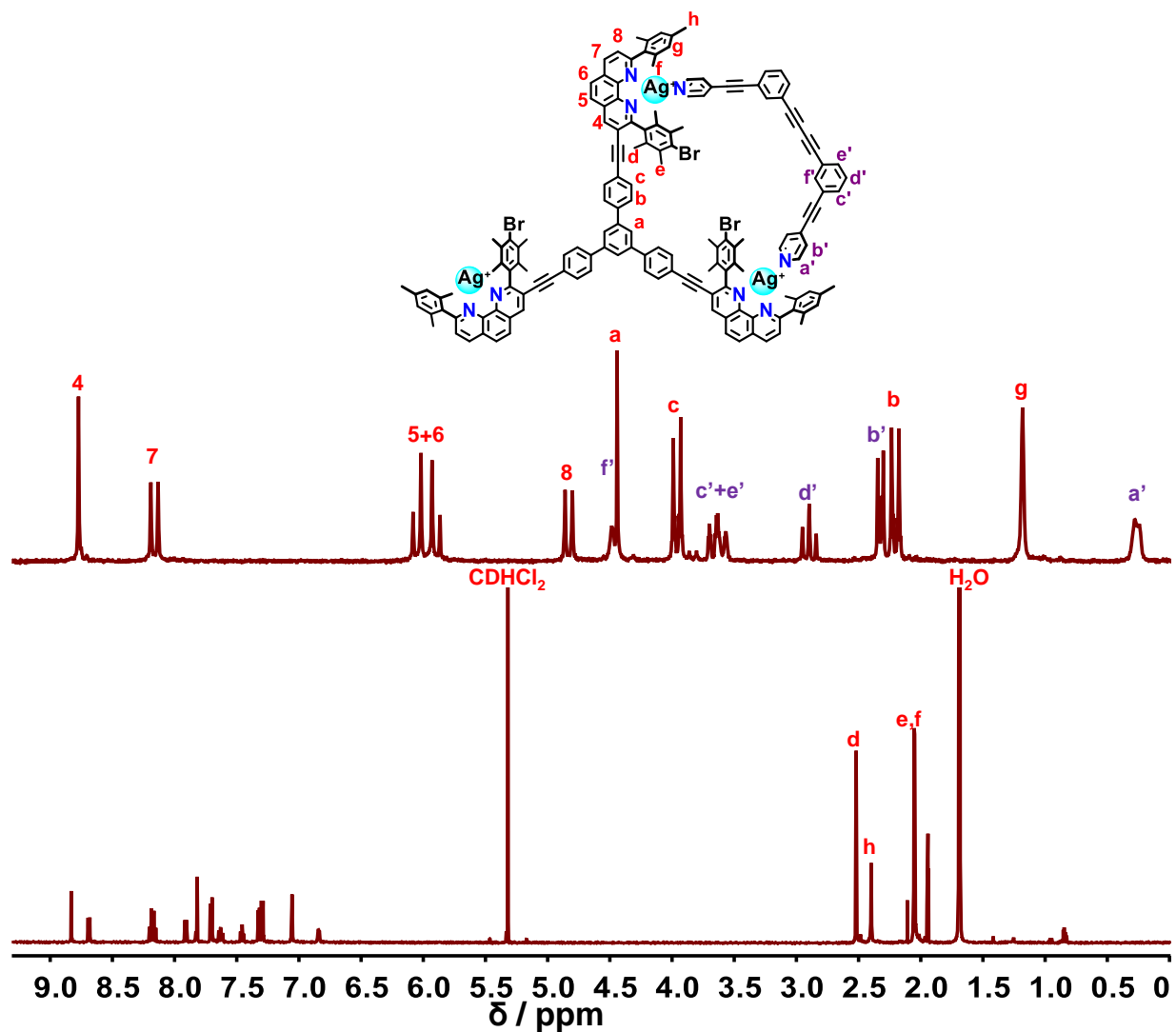


Figure S14. ¹H NMR spectrum (CD₂Cl₂, 600 MHz) of slider-on-deck [Ag₃(1)(2)]³⁺

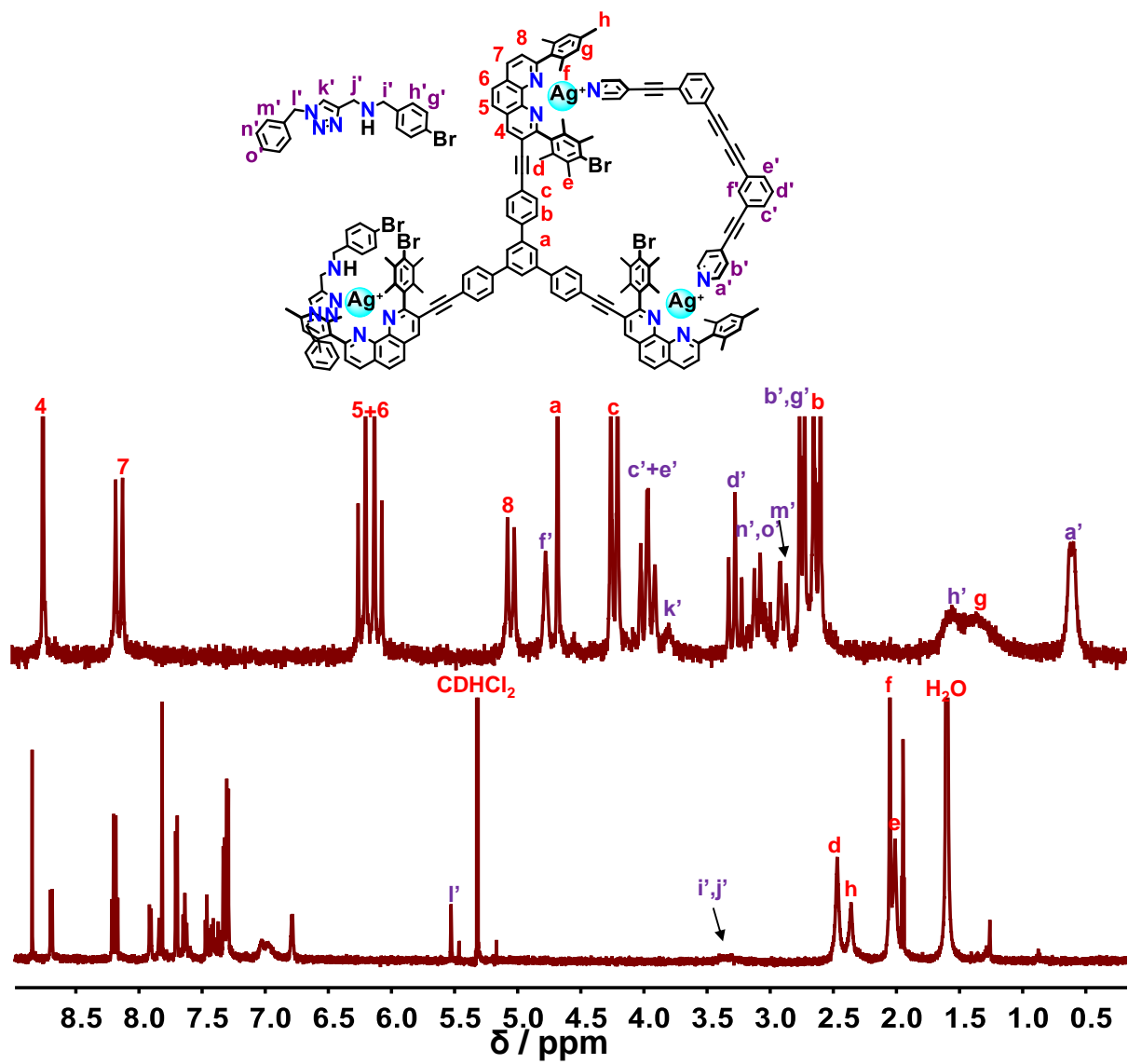


Figure S15. ^1H NMR spectrum (CD_2Cl_2 , 600 MHz) of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$.

5. Comparison of model complexes by NMR

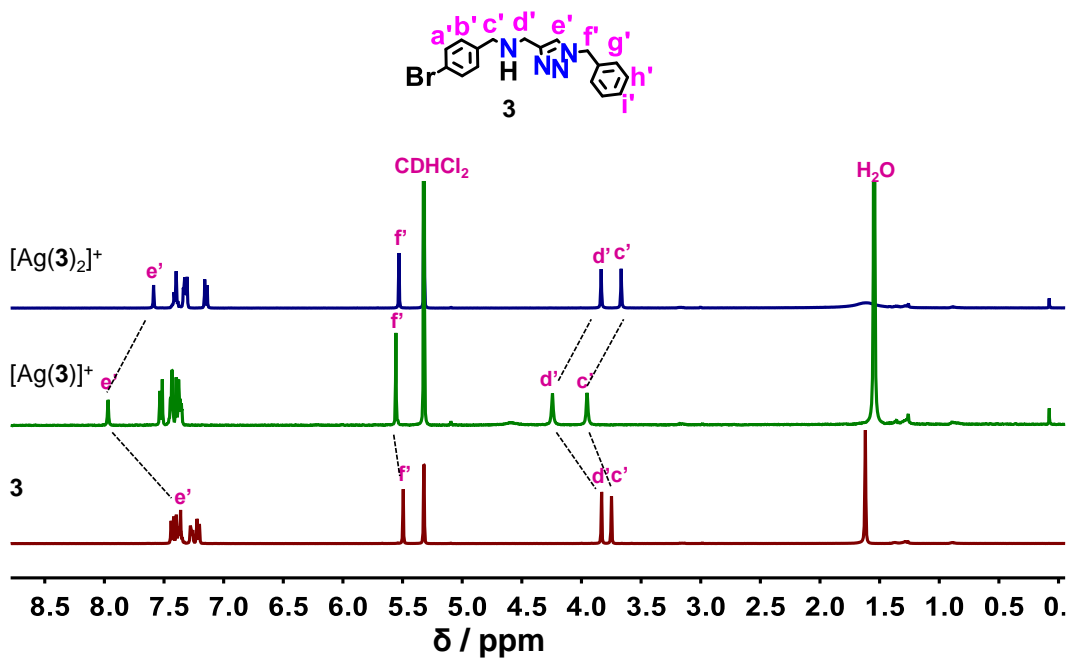


Figure S16. Comparison of ^1H NMR spectra (CD $_2$ Cl $_2$, 400 MHz) of ligand **3** and its 1:1 and 2:1 complexes with silver(I).

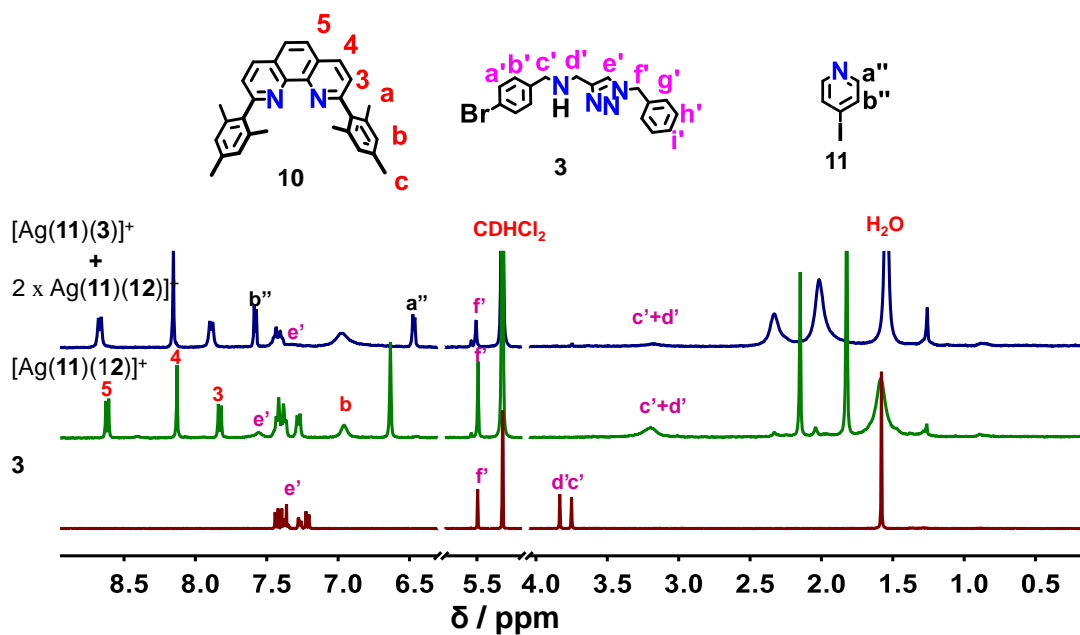


Figure S17. Comparison of ^1H NMR spectra (CD $_2$ Cl $_2$, 400 MHz) of **3**, $[\text{Ag}(\mathbf{11})(\mathbf{12})]^+$ and $[\text{Ag}(\mathbf{11})(\mathbf{3})]^+ + 2 \times [\text{Ag}(\mathbf{11})(\mathbf{12})]^+$.

6. Comparison of slider-on-desk complexes by NMR

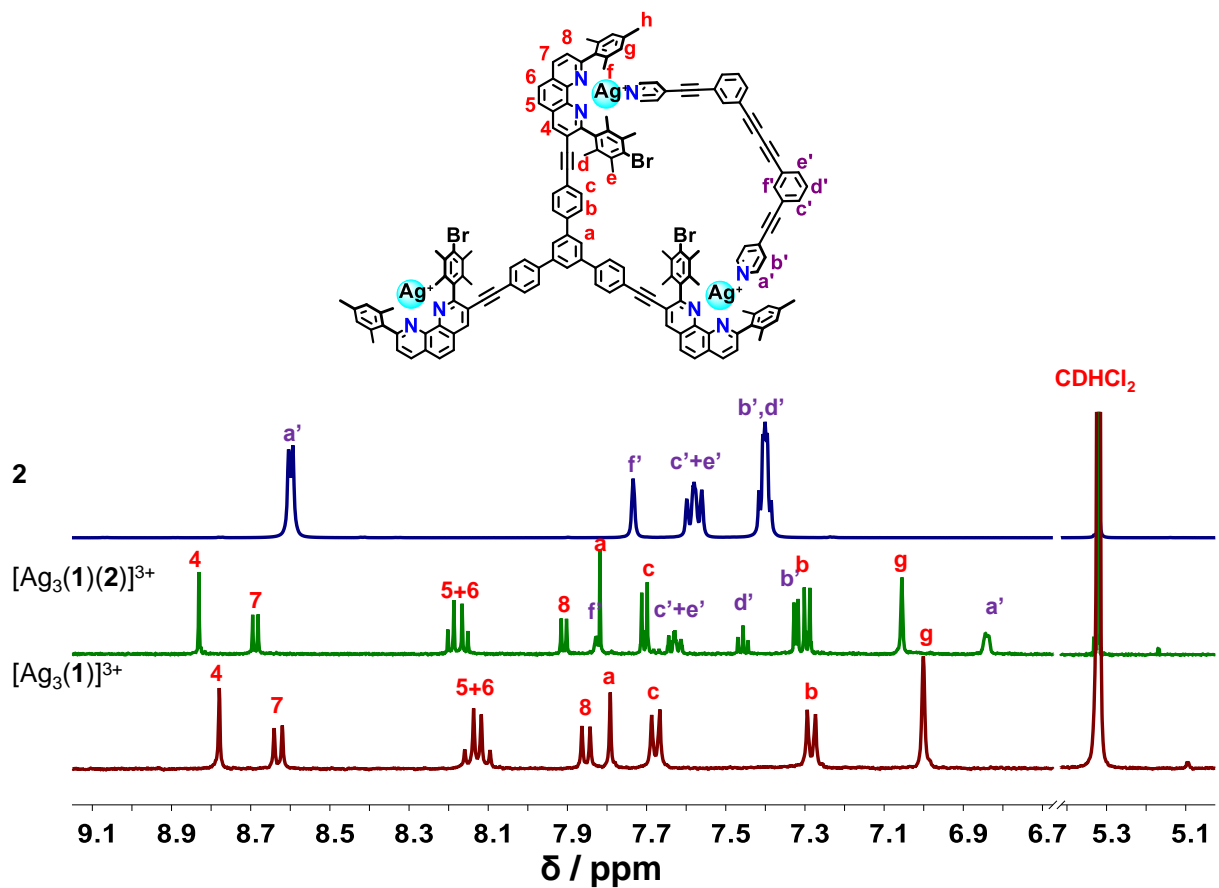


Figure S18. Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of **2**, [Ag₃(**1**)]³⁺ and [Ag₃(**1**)(**2**)]³⁺.

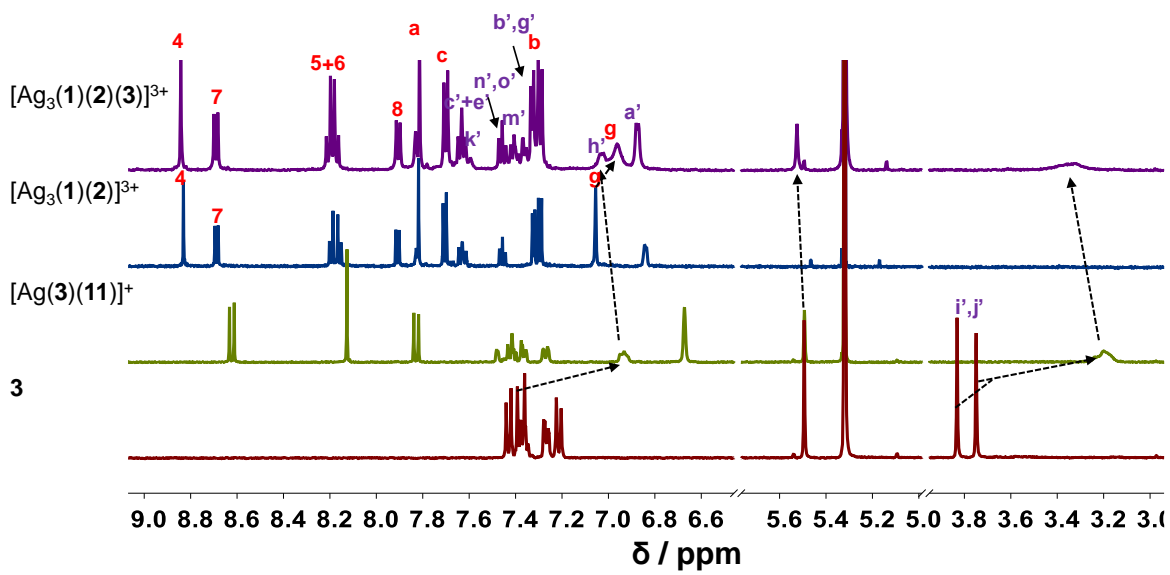


Figure S19. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of **3**, $[\text{Ag}(3)(11)]^+$, $[\text{Ag}_3(1)(2)]^{3+}$ and $[\text{Ag}_3(1)(2)(3)]^{3+}$ (from bottom to top).

7. DOSY NMR spectra

Calculation of hydrodynamic radius. The diffusion coefficients D for the 3- and 4-component sliders were obtained from their corresponding DOSY spectrum. The hydrodynamic radius r was calculated by using the Stokes Einstein equation

$$r = k_B T / 6\pi\eta D$$

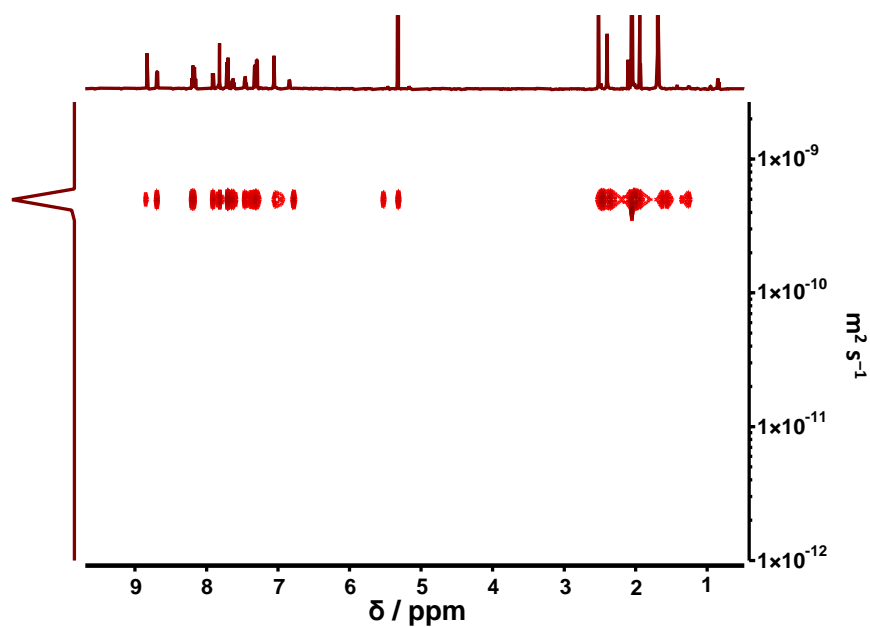


Figure S20. DOSY NMR of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]^{3+}$ in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient $D = 4.99 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, hydrodynamic radius $r = 10.6 \text{ \AA}$.

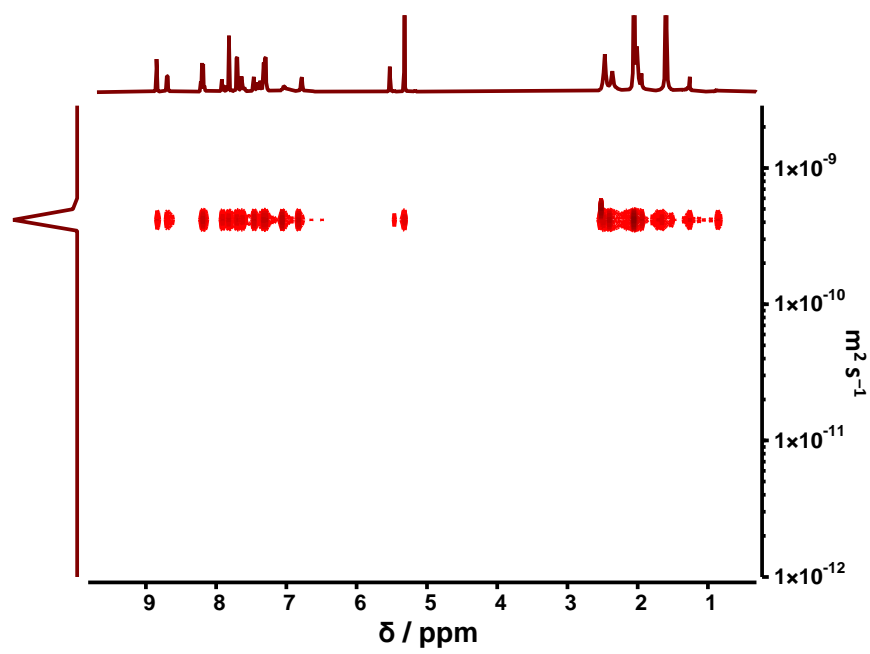


Figure S21. DOSY NMR of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient $D = 4.17 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, hydrodynamic radius $r = 12.6 \text{ \AA}$.

8. ESI-MS spectra

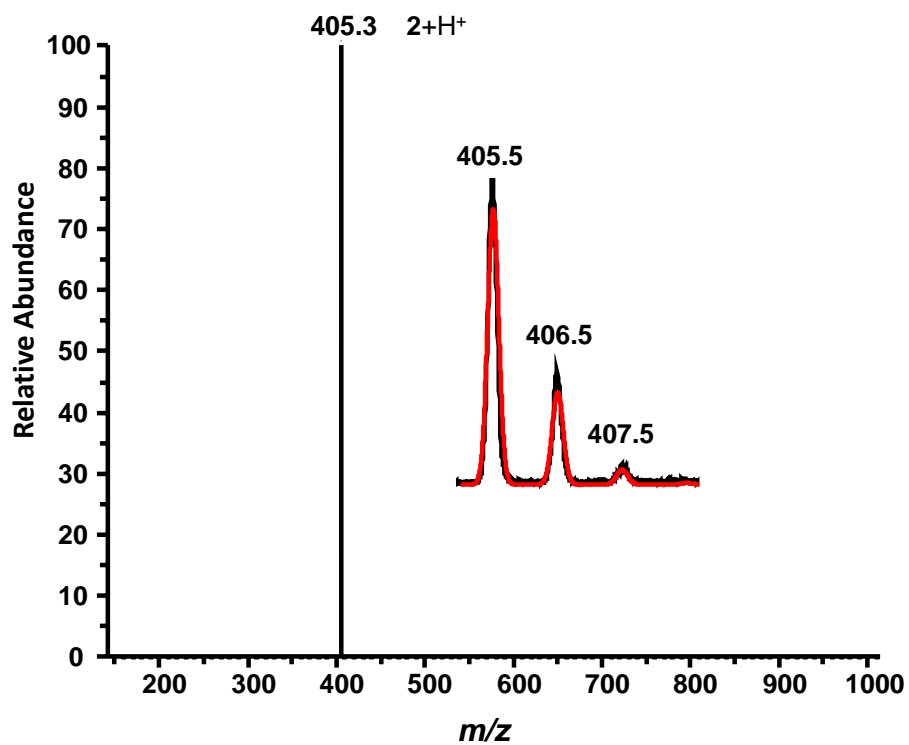


Figure S22. ESI-MS of 2 in CH₂Cl₂.

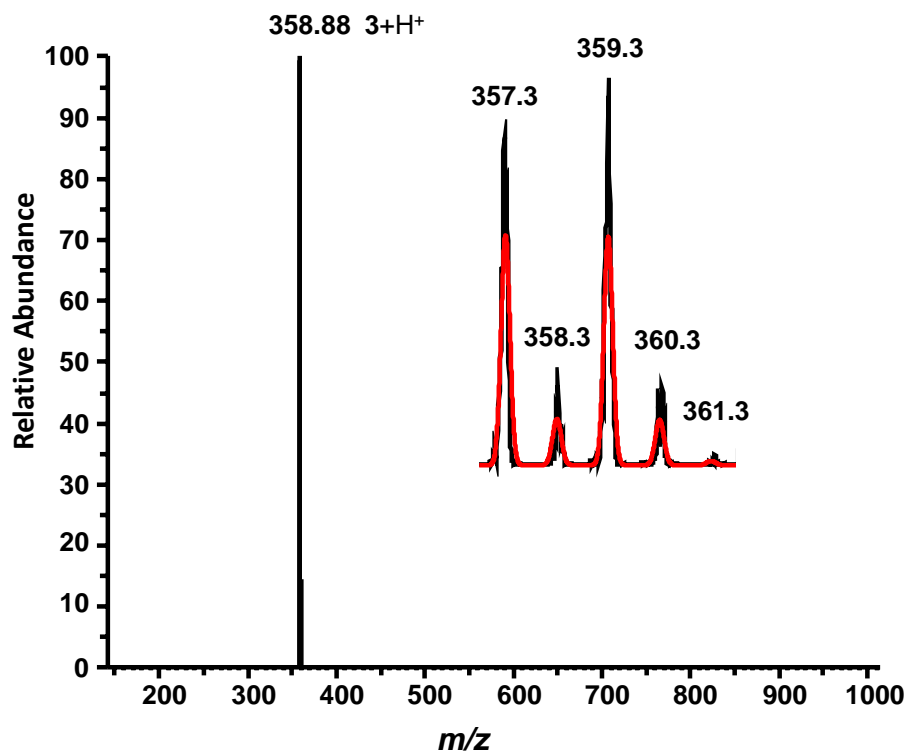


Figure S23. ESI-MS of 3 in CH₂Cl₂.

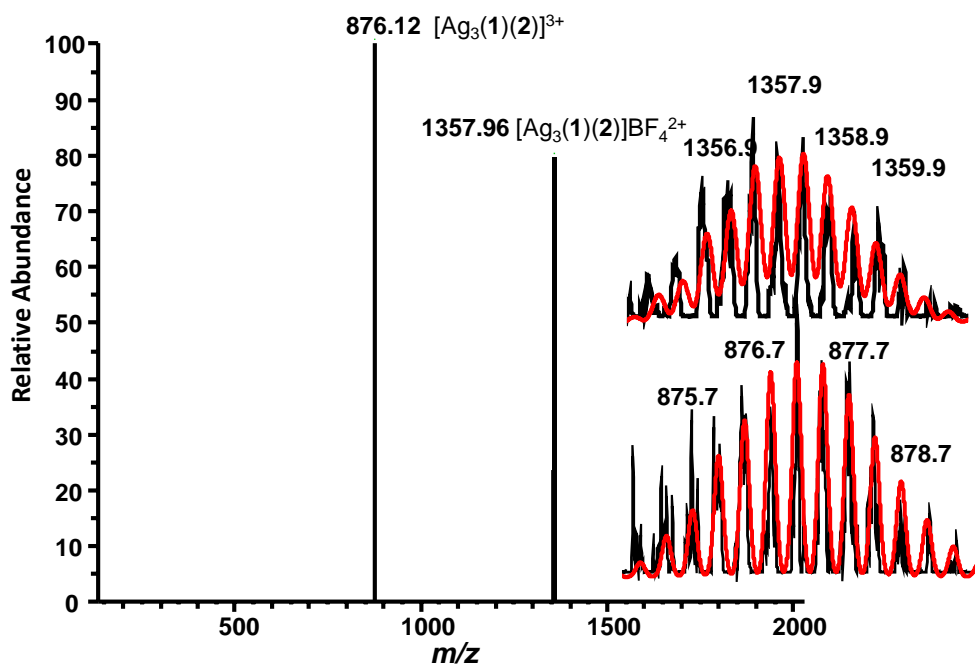


Figure S24. ESI-MS of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]^{3+}$ in CH_2Cl_2 .

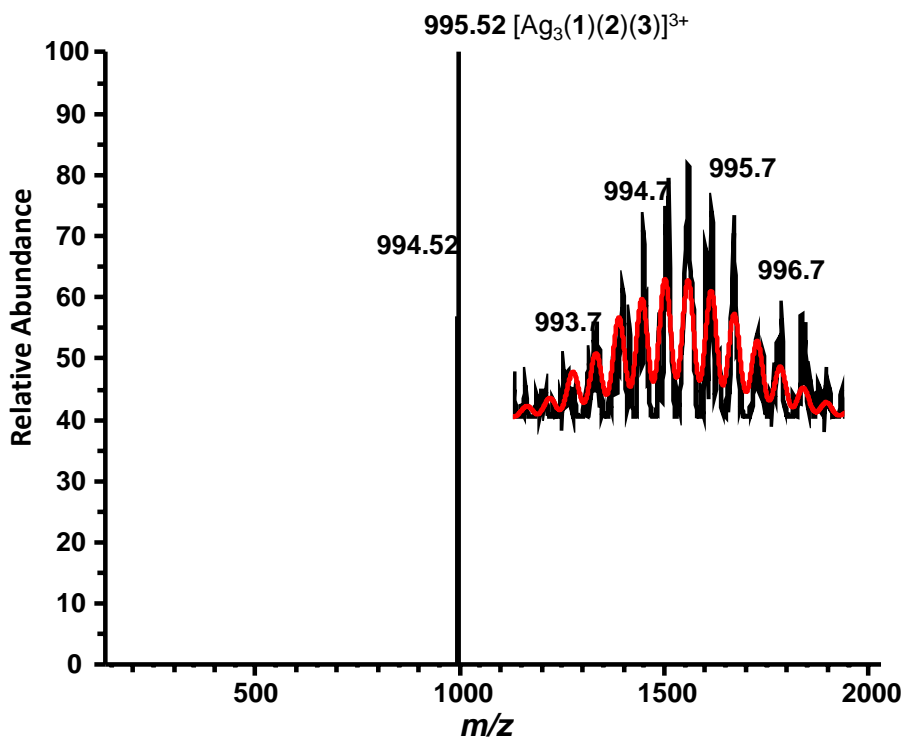


Figure S25. ESI-MS of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ in CH_2Cl_2 .

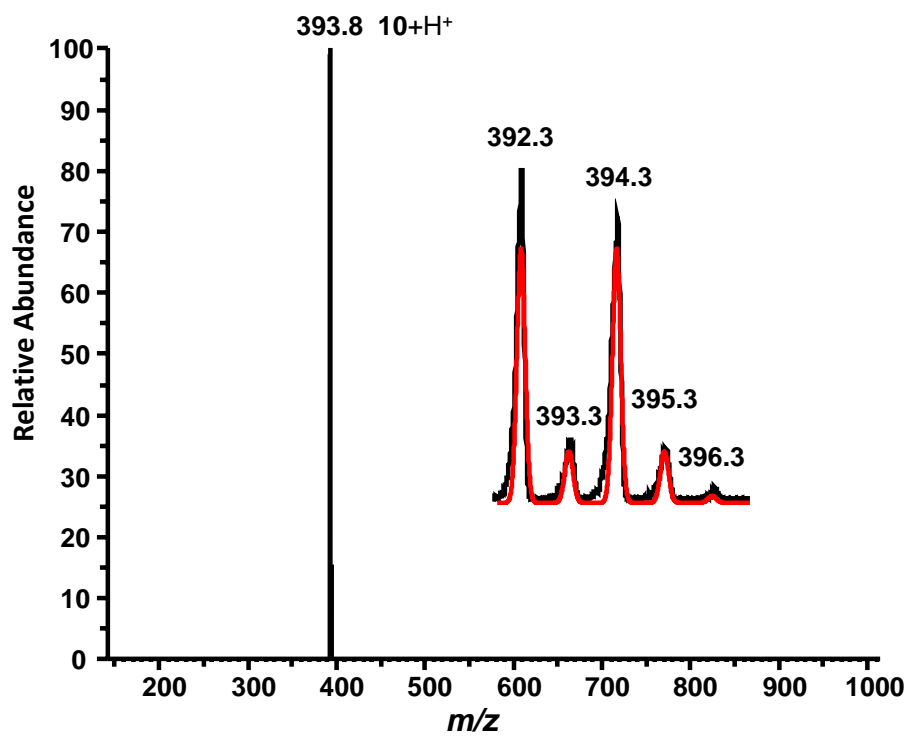


Figure S26. ESI-MS of 10 in CH₂Cl₂.

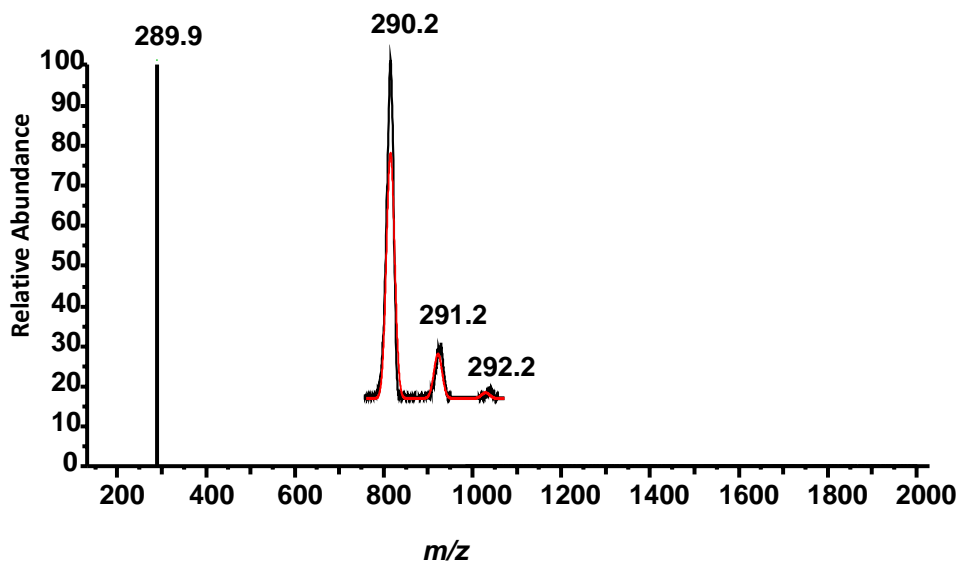


Figure S27. ESI-MS of 6 in CH₂Cl₂

9. Variable temperature NMR studies and determination of kinetic data

The kinetics of sliding exchange at various temperatures was analyzed using the program WinDNMR through simulation of the experimental ^1H NMR spectra.⁶ The spectra simulation, which was performed using the model of a 2-spin system undergoing mutual exchange, provided the rate constants. Activation parameters were determined from an Eyring plot

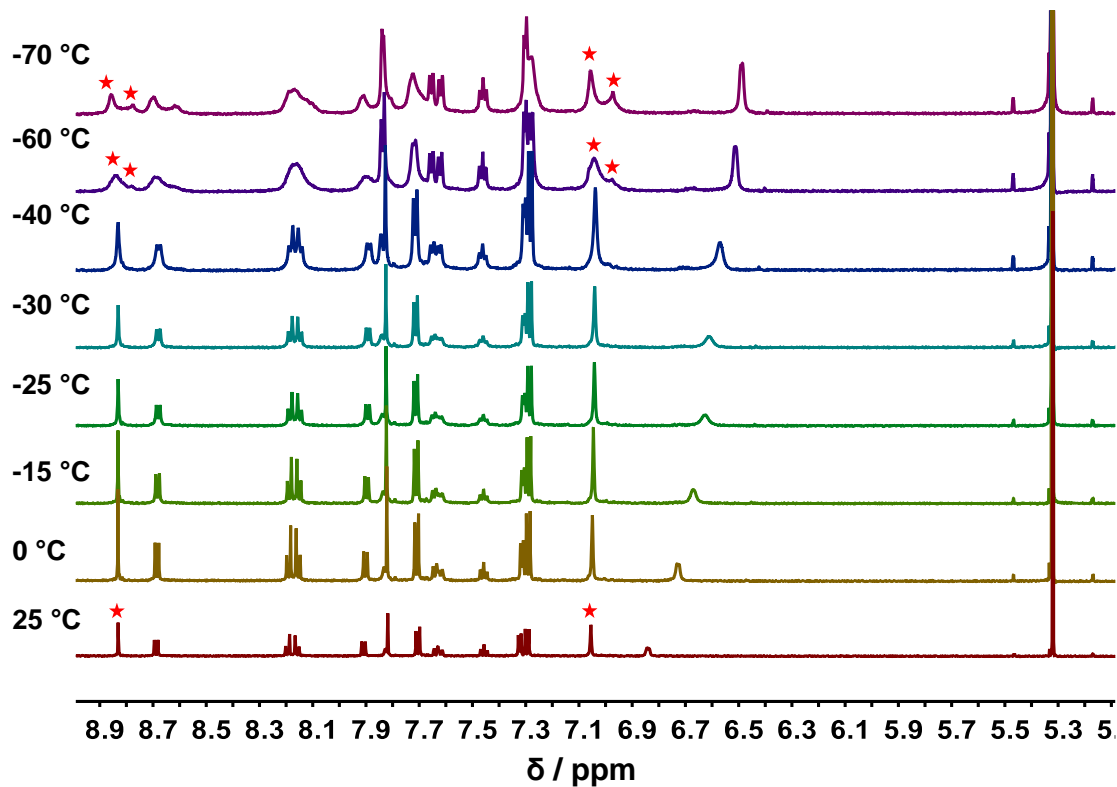


Figure S28. Partial ^1H VT-NMR (CD_2Cl_2 , 600 MHz) of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})]^{3+}$ showing the splitting of proton signal 4-H (red asterisk marked).

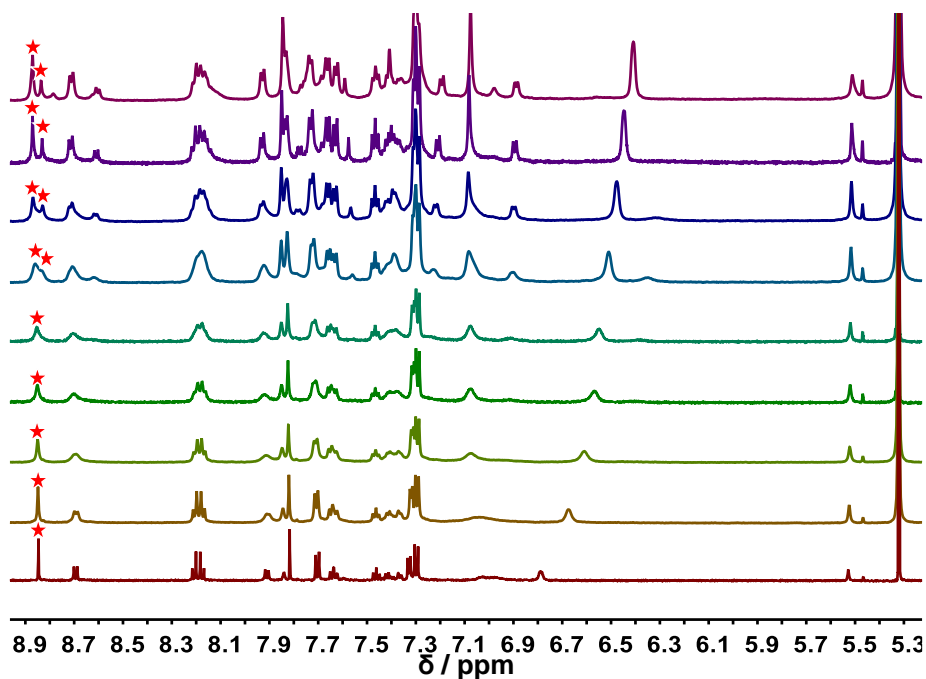
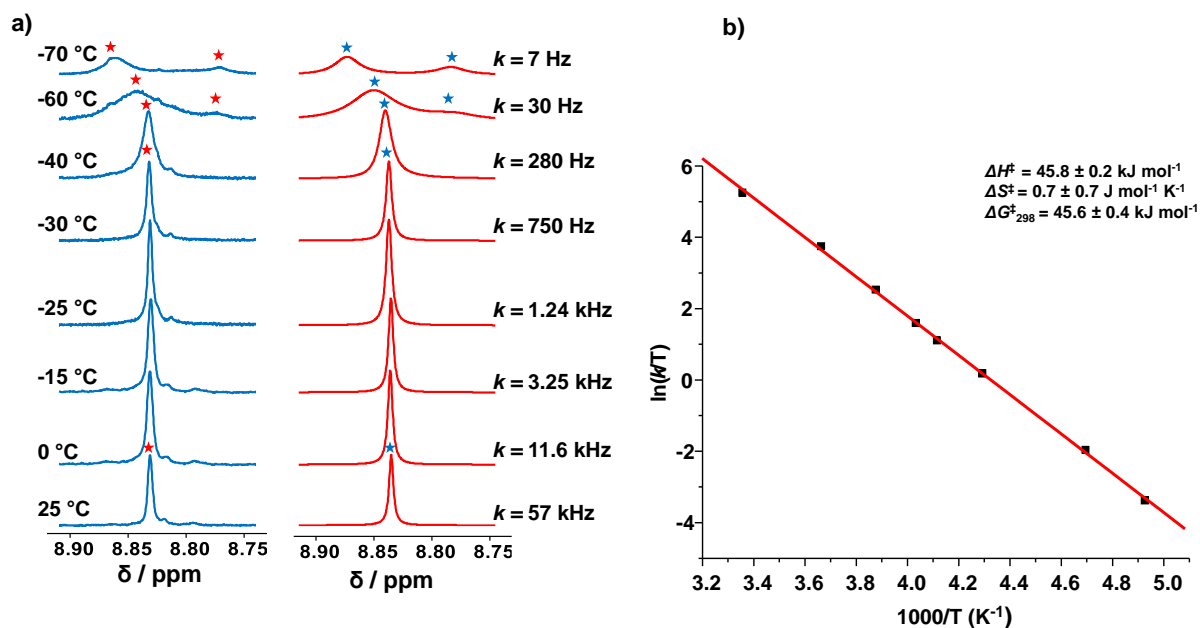


Figure S30. Partial ^1H VT-NMR (CD_2Cl_2 , 600 MHz) of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ showing the splitting of proton signal 4-H (red asterisk marked).

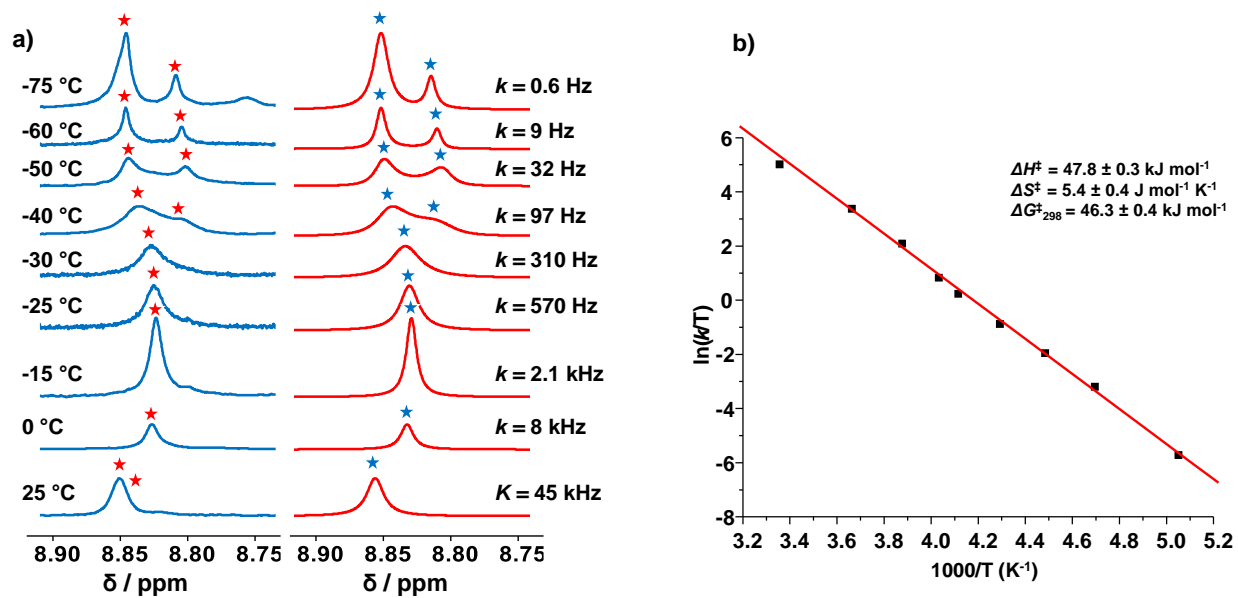
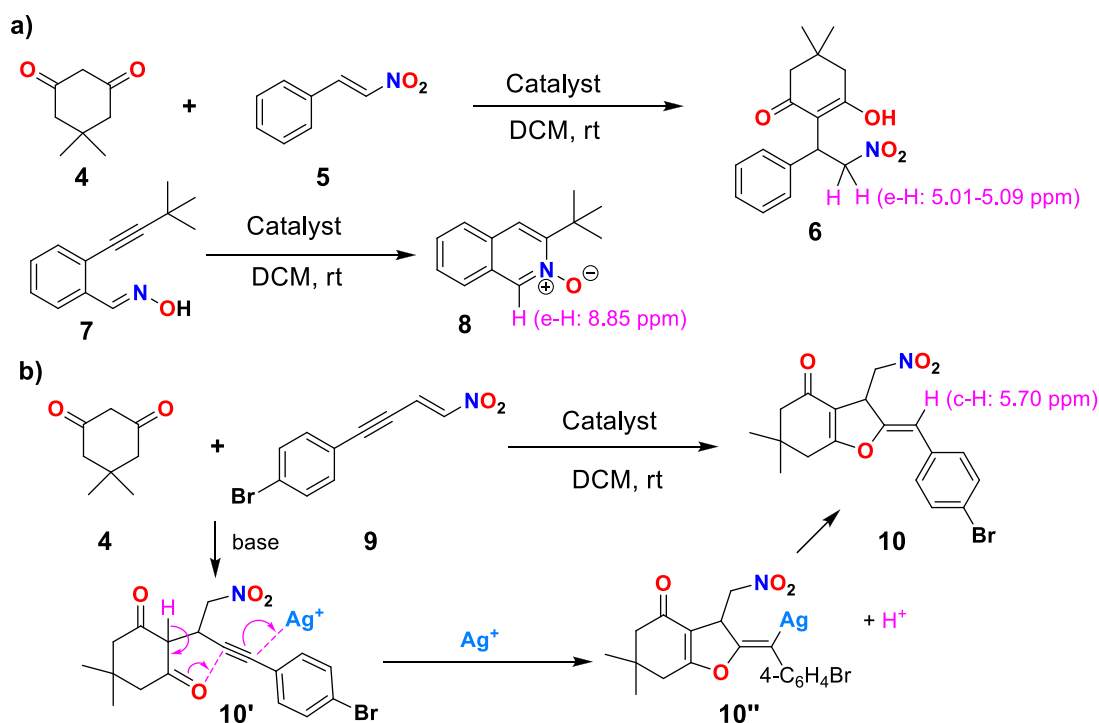


Figure S31. (a) Experimental and simulated ^1H VT-NMR (CD_2Cl_2 , 600 MHz) of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ of proton signal 4-H (red asterisk marked) and (b) Eyring plot for sliding exchange in $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$.

10. Catalysis

10a) Catalysis of model system: General procedure for catalysis



Scheme S4. a) Concurrent base-catalyzed Michael addition and silver(I)-catalyzed 5-*exo* cyclization reaction. b) Sequential Michael/hydroalkoxylation reaction⁷ catalyzed by [Ag₃(1)(2)(3)]³⁺.

All catalytic experiments were performed in CD₂Cl₂ directly in an NMR tube at rt (25 °C). The model catalyst was first generated, then the reactants were added. Product yields were determined using 1,3,5-trimethoxybenzene as an internal standard. In the ¹H NMR, product **6** shows up at 5.01-5.09 ppm as multiplet, product **8** exhibits a singlet at 8.85 ppm and product **10** shows up at 5.70 ppm as a doublet. The ¹H NMR was recorded after defined intervals of 2, 7 and 14 h.

a) [Ag(3)]⁺ (experiment **A** for two concurrent reactions)

In an NMR tube, **3** (367 μg, 1.03 μmol) was mixed with AgBF₄ (200 μg, 1.03 μmol) in 450 μL of CD₂Cl₂ to afford [Ag(3)]⁺. Dimesone (**4**) (1.44 mg, 10.3 μmol), β-nitrostyrene (**5**) (1.54 mg, 10.3 μmol), oxime **7** (2.07 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD₂Cl₂. After mixing, the ¹H NMR spectrum was recorded after 2 h (0% yield of **6**, 6%

yield of **8**), 7 h (6% yield of **6**, 38% yield of **8**) and 14 h (11% yield of **6**, 68% yield of **8**). The yield of **6** and **8** was calculated from the ^1H NMR spectra as shown in Figure S32.

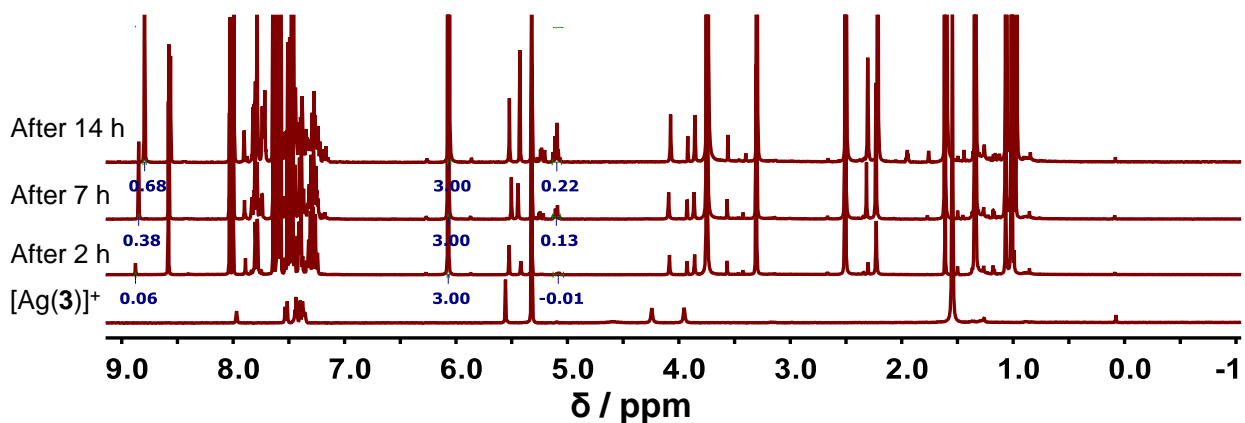


Figure S32. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the reaction of substrates **4**, **5** and **7** in the presence of catalytic amounts of $[\text{Ag}(\mathbf{3})]^+$ (10 mol%) at 25 °C in CD_2Cl_2 taken after 2, 7, and 14 h. Products **6** and **8** show up at 5.01-5.09 and 8.85 ppm, respectively.

b) $[\text{Ag}(\mathbf{3})]^+$ (experiment **B** for concurrent tandem catalysis)

Using the same conditions as in experiment **A**, **3** (367 μg , 1.03 μmol) was mixed with AgBF_4 (201 μg , 1.03 μmol) in 450 μL of CD_2Cl_2 to afford $[\text{Ag}(\mathbf{3})]^+$. Dimedone (**4**) (1.44 mg, 10.3 μmol), nitroalkenyne **9** (2.59 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD_2Cl_2 . After mixing, the ^1H NMR spectrum was recorded after 2 h (1% yield of **10**), 7 h (2% yield of **10**), 14 h (4% yield of **10**). The yield of **10** was calculated as shown in Figure S33.

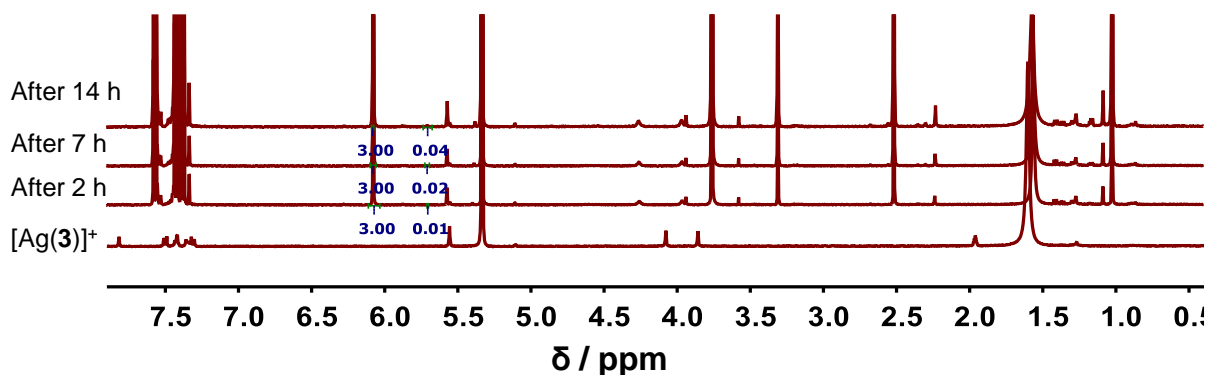


Figure S33. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the reaction of substrates **4** and **9** in presence of catalytic amounts of $[\text{Ag}(\mathbf{3})]^+$ (10 mol%) at 25 °C in CD_2Cl_2 after 2, 7 and 14 h. Product **10** shows up at 5.70 ppm.

c) $[\text{Ag}(\mathbf{3})_2]^+$ (experiment C for two concurrent reactions)

Using the same conditions as in experiment A, $\mathbf{3}$ (734 μg , 2.06 μmol) was mixed with AgBF_4 (200 μg , 1.03 μmol) in 450 μL of CD_2Cl_2 to afford $[\text{Ag}(\mathbf{3})_2]^+$. Dimedone ($\mathbf{4}$) (1.44 mg, 10.3 μmol), β -nitrostyrene ($\mathbf{5}$) (1.54 mg, 10.3 μmol), hydroxylamine $\mathbf{7}$ (2.07 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added. After mixing the ^1H NMR spectrum was recorded after 2 h (0.5% yield of $\mathbf{6}$, 0% yield of $\mathbf{8}$), 7 h (7% yield of $\mathbf{6}$, 2% yield of $\mathbf{8}$), and 14 h (13% yield of $\mathbf{6}$, 9% yield of $\mathbf{8}$). The yield of $\mathbf{6}$ and $\mathbf{8}$ was calculated as shown in Figure S34.

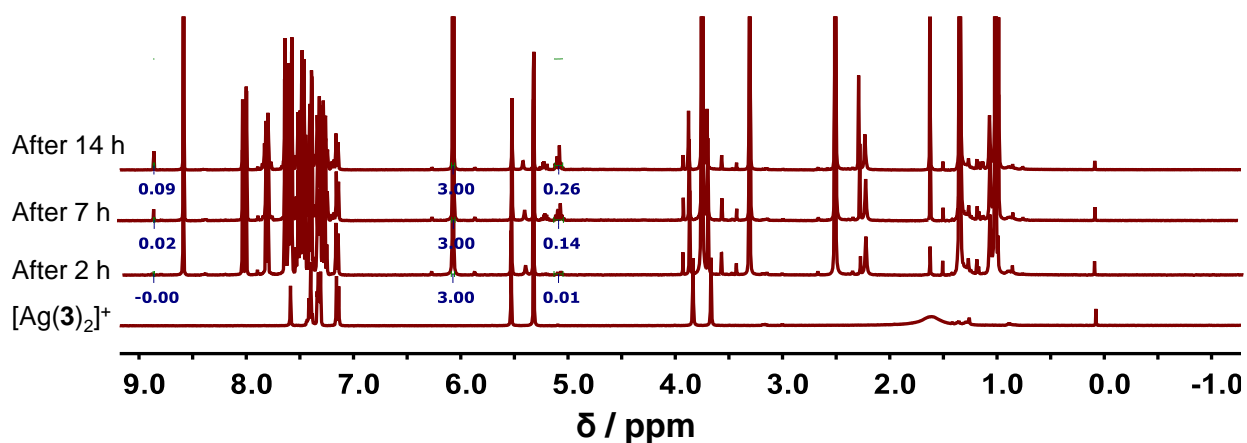


Figure S34. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the reaction of substrates $\mathbf{4}$, $\mathbf{5}$ and $\mathbf{7}$ in presence of catalytic amounts of $[\text{Ag}(\mathbf{3})_2]^+$ (10 mol%) at 25 $^\circ\text{C}$ in CD_2Cl_2 after 2, 7, and 14 h. Products $\mathbf{6}$ and $\mathbf{8}$ show up at 5.01-5.09 and 8.85 ppm, respectively.

d) $[\text{Ag}(\mathbf{3})_2]^+$ (experiment **D** for concurrent tandem catalysis)

Using the same conditions as in experiment **A**, **3** (735 μg , 2.06 μmol) was mixed with AgBF_4 (201 μg , 1.03 μmol) in 450 μL of CD_2Cl_2 to afford $[\text{Ag}(\mathbf{3})_2]^+$. Dimedone (**4**) (1.44 mg, 10.3 μmol), nitroalkenyne **9** (2.59 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD_2Cl_2 . After mixing, the ^1H NMR spectrum was recorded after 2 h (1% yield of **10**), 7 h (7% yield of **10**), 14 h (11% yield of **10**), and 40 h (17% yield of **10**). The yield of **10** was calculated as shown in Figure S35.

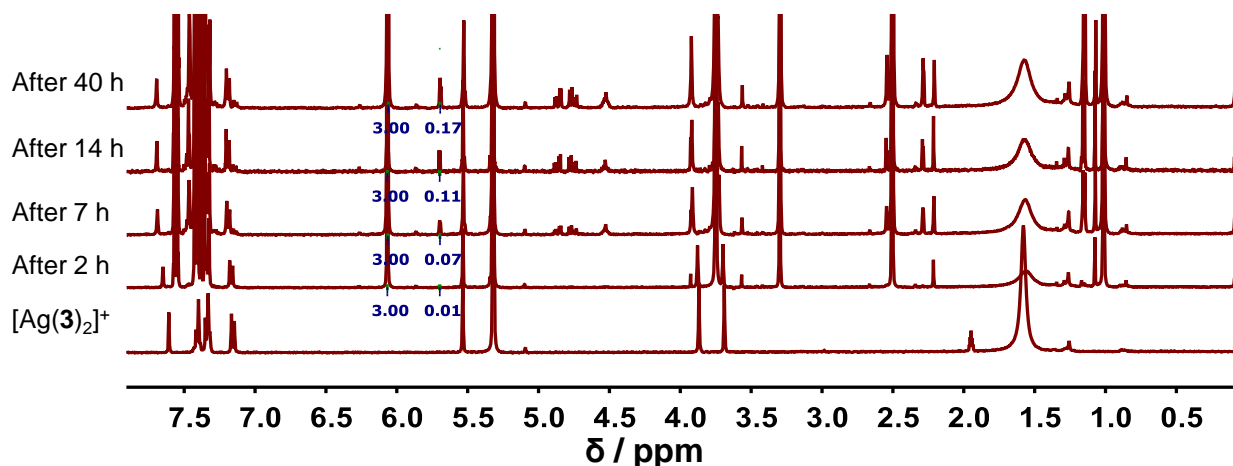


Figure S35. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the reaction of substrates **4** and **9** in presence of catalytic amounts of $[\text{Ag}(\mathbf{3})_2]^+$ (10 mol%) at 25 $^\circ\text{C}$ in CD_2Cl_2 after 2, 7, 14 and 40 h. Product **10** show up at 5.70 ppm.

e) $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+$ (experiment **E** for two concurrent reactions)

Using the same conditions as in experiment **A**, **3** (367 μg , 1.03 μmol), 2,9-dimesitylphenanthroline (**11**) (427 μg , 1.03 μmol) and AgBF_4 (200 μg , 1.03 μmol) were dissolved in 450 μL of CD_2Cl_2 to afford $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+$. Dimedone (**4**) (1.44 mg, 10.3 μmol), β -nitrostyrene (**5**) (1.54 mg, 10.3 μmol), oxime **7** (2.07 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD_2Cl_2 . The ^1H NMR spectrum was recorded after 2 h (0% yield of **6**, 1% yield of **8**), 7 h (0%

yield of **6**, 4% yield of **8**) and 14 h (0% yield of **6**, 8% yield of **8**). The yield of **6** and **8** was calculated as shown in Figure S36, Table S1.

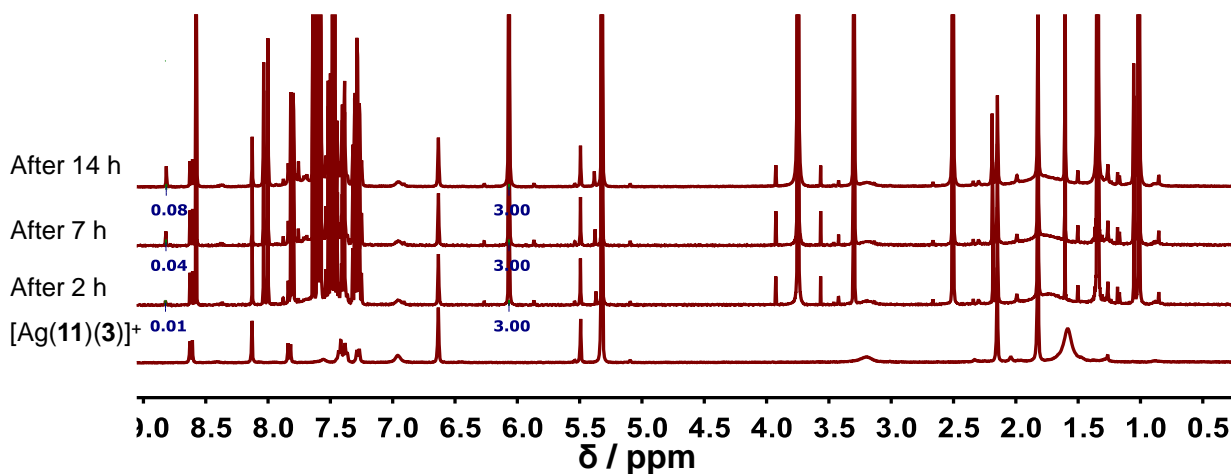


Figure S36. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the reaction of substrates **4**, **5** and **7** in presence of catalytic amounts of $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+$ (10 mol%) at 25 °C in CD_2Cl_2 after 2, 7, and 14 h. Products **6** and **8** show up at 5.01-5.09 and 8.85 ppm, respectively. For yield data, see Table S1.

f) $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+ + 2 \times [\text{Ag}(\mathbf{11})(\mathbf{12})]^+$ (experiment **F** for two concurrent reactions)

In an NMR tube, **3** (122 μg , 0.343 μmol), 2,9-dimesitylphenanthroline (**11**) (427 μg , 1.03 μmol), 4-iodopyridine (**12**) (141 μg , 0.690 μmol) and AgBF_4 (200 μg , 1.03 μmol) were dissolved in 450 μL of CD_2Cl_2 to afford $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+ + 2 \times [\text{Ag}(\mathbf{11})(\mathbf{12})]^+$. Dimedone (**4**) (1.44 mg, 10.3 μmol), β -nitrostyrene (**5**) (1.54 mg, 10.3 μmol), oxime **7** (2.07 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD_2Cl_2 . After mixing, the ^1H NMR spectrum was recorded after 2 h (0% yield of **6**, 20% yield of **8**), 7 h (0% yield of **6**, 50% yield of **8**) and 14 h (0% yield of **6**, 80% yield of **8**). The yield of **6** and **8** was calculated as shown in Figure S37, Table S1.

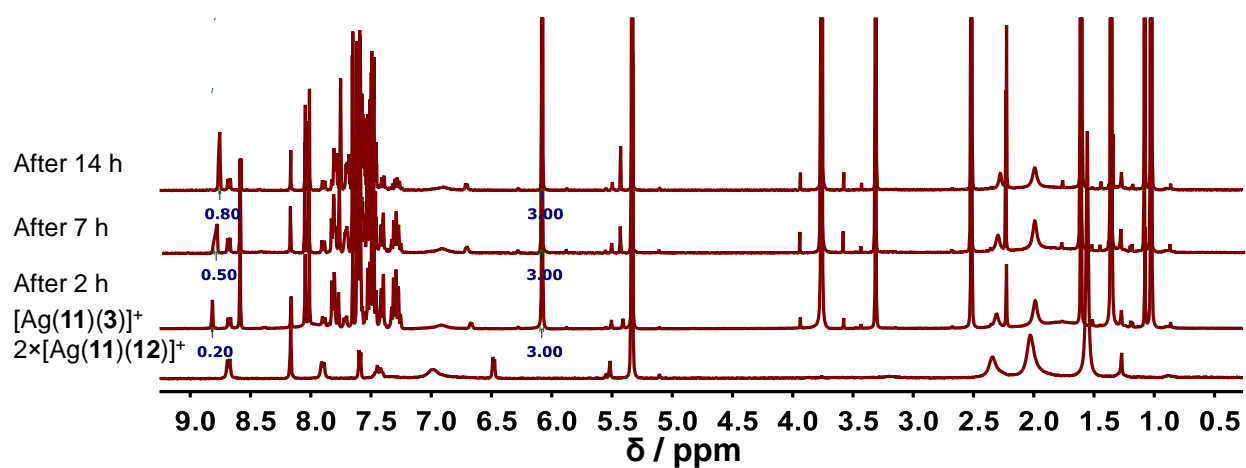


Figure S37. Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of the reaction of substrates **4**, **5** and **7** in presence of catalytic amounts of [Ag(**3**)(**11**)]⁺ + 2×[Ag(**11**)(**12**)]⁺ (10 mol%) at 25 °C in CD₂Cl₂ taken after 2, 7, and 14 h. Products **6** and **8** show up at 5.01-5.09 and 8.85 ppm, respectively. For yield data, see Table S1.

Table S1. Yield of products **6** and **8** formed by catalysis using [Ag(**3**)(**11**)]⁺ or 2× [Ag(**11**)(**12**)]⁺ + [Ag(**3**)(**11**)]⁺.

Complex	[Ag(11)(12)] ⁺		2× [Ag(11)(12)] ⁺ + [Ag(3)(11)] ⁺	
	of 8 (Ag ⁺ cat.)	of 6 (base cat.)	of 8 (Ag ⁺ cat.)	of 6 (base cat.)
After 2 h	0%	0%	20%	0%
After 7 h	3%	0%	50%	0%
After 14 h	7%	0%	80%	0%

b) Final catalytic system: General procedure for concurrent (a) and tandem (b) reactions.

All catalytic experiments were performed in CD₂Cl₂ directly in an NMR tube at rt (25 °C). The catalyst was formed first, then the reactants were added. Product yields were determined using 1,3,5-trimethoxybenzene as an internal standard. The ¹H NMR for model systems was recorded at intervals of 2 h.

a) Final catalytic system (experiment **E** for two concurrent reactions)

In an NMR tube, AgBF₄ (200 μg, 1.03 μmol), deck **1** (562 μg, 0.343 μmol), ligand **2** (139 μg, 0.343 μmol) and ligand **3** (122 μg, 0.343 μmol) were dissolved in 450 μL of CD₂Cl₂. Dimedone (**4**) (1.44 mg, 10.3 μmol), β-nitrostyrene (**5**) (1.54 mg, 10.3 μmol), oxime **7** (2.07 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD₂Cl₂. The ¹H NMR spectrum was recorded after mixing at 2 h intervals over 14 h. The yield of **6** and **8** was calculated from the ¹H NMR spectra (see Figure S38 and Figure S39).

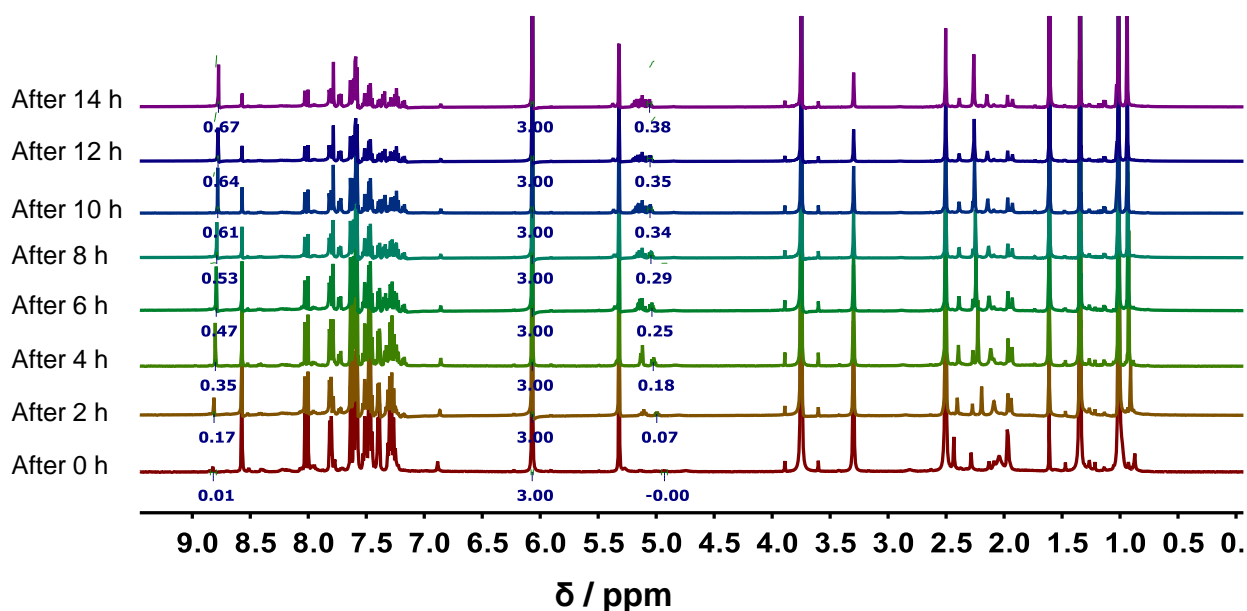


Figure S38. Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of the reaction of substrates **4**, **5** and **7** in presence of catalytic amounts of [Ag₃(**1**)(**2**)(**3**)]³⁺ at 25 °C in CD₂Cl₂ taken at 2 h intervals. Products **6** and **8** show up at 5.01-5.09 and 8.85 ppm, respectively.

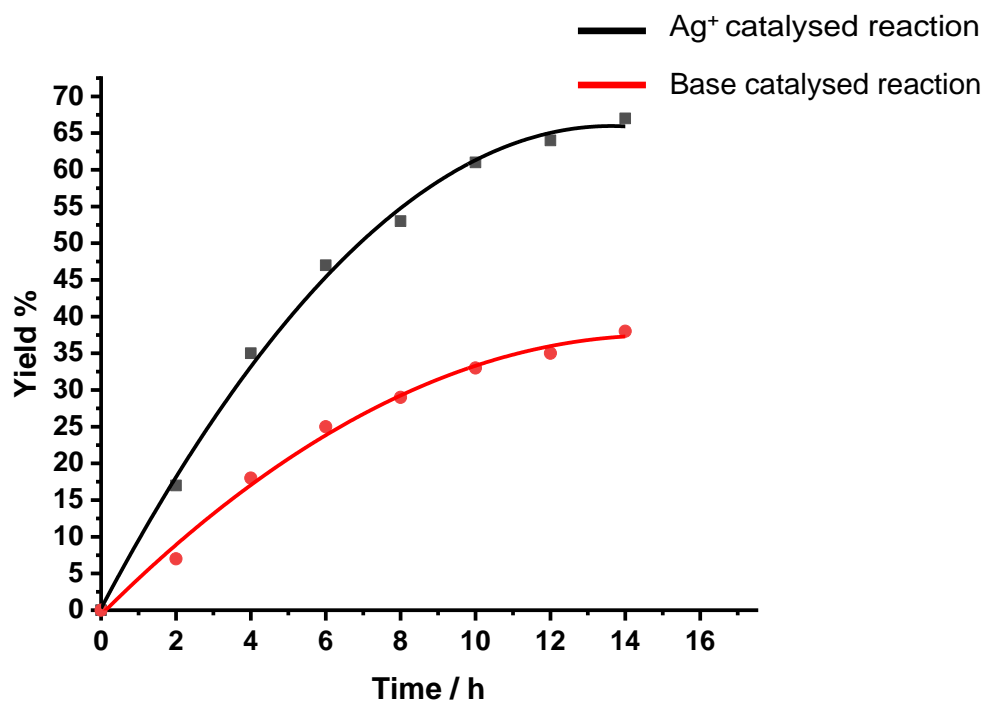


Figure S39. Base- and silver(I)-catalyzed formation of products **6** and **8** (yield vs. time).

Table S2. Base- and silver(I)-catalyzed formation of products **6** and **8** (yield vs. time)

Time / h	Base catalysis:	Ag ⁺ catalysis :
	Yield of 6 / %	Yield of 8 / %
0	0	0
2	7	17
4	18	35
6	25	47
8	29	53
10	33	61
12	35	64
14	38	67

b) Final catalytic system (experiment **F** for concurrent tandem catalysis)

In an NMR tube, AgBF₄ (200 μg, 1.03 μmol), deck **1** (562 μg, 0.343 μmol) as well as ligands **2** (139 μg, 0.343 μmol) and **3** (122 μg, 0.343 μmol) were dissolved in 450 μL of CD₂Cl₂. Dimedone (**4**) (1.44 mg, 10.3 μmol), nitroalkenyne **9** (2.59 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD₂Cl₂. The ¹H NMR spectrum was recorded after mixing at 2 h intervals. The yield of **10** was calculated from the ¹H NMR spectra (Figure S40).

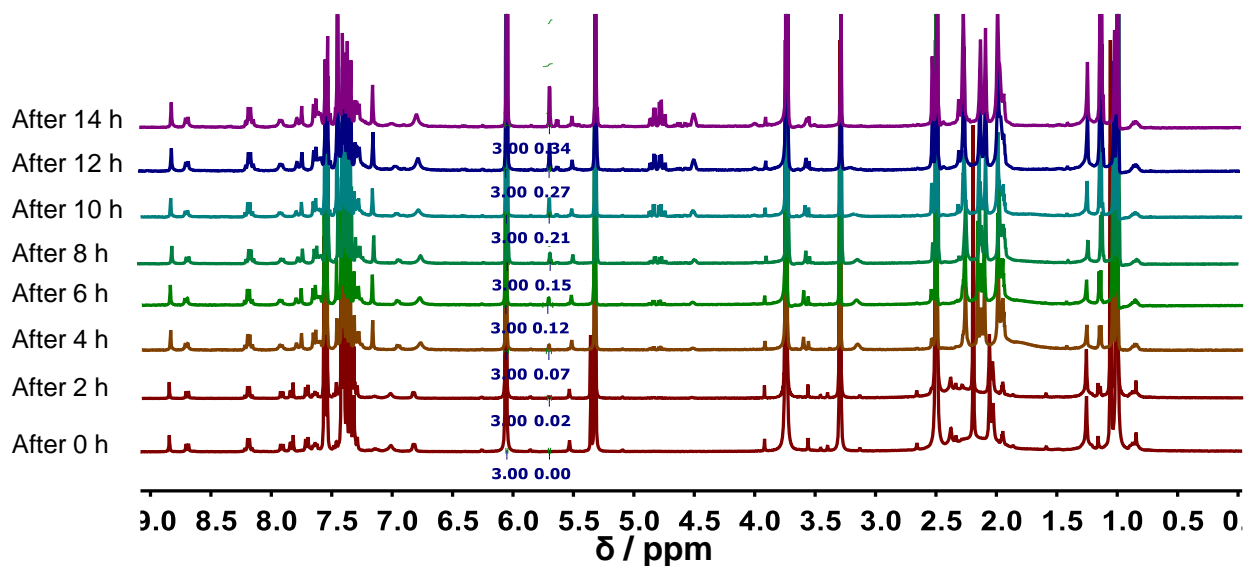


Figure S40. Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of the reaction of substrates **4** and **9** in presence of catalytic amounts of [Ag₃(**1**)(**2**)(**3**)]³⁺ at 25 °C in CD₂Cl₂ at 2 h intervals. Product **10** shows up at 5.70 ppm in the spectrum.

c) Final catalytic system (experiment **F** for concurrent tandem catalysis in presence of 1 eq. of **10**)

In an NMR tube, AgBF₄ (200 μg, 1.03 μmol), deck **1** (562 μg, 0.343 μmol), ligand **2** (139 μg, 0.343 μmol), ligand **3** (122 μg, 0.343 μmol) and product **10** (134 μg, 0.343 μmol) were dissolved in 450 μL of CD₂Cl₂. Dimedone (**4**) (1.44 mg, 10.3 μmol), nitroalkenyne **9** (2.59 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD₂Cl₂. The ¹H NMR spectrum was recorded after mixing at 2 h intervals. The yield of **10** (Figure S42, Table S3) was calculated from the ¹H NMR spectra (Figure S41).

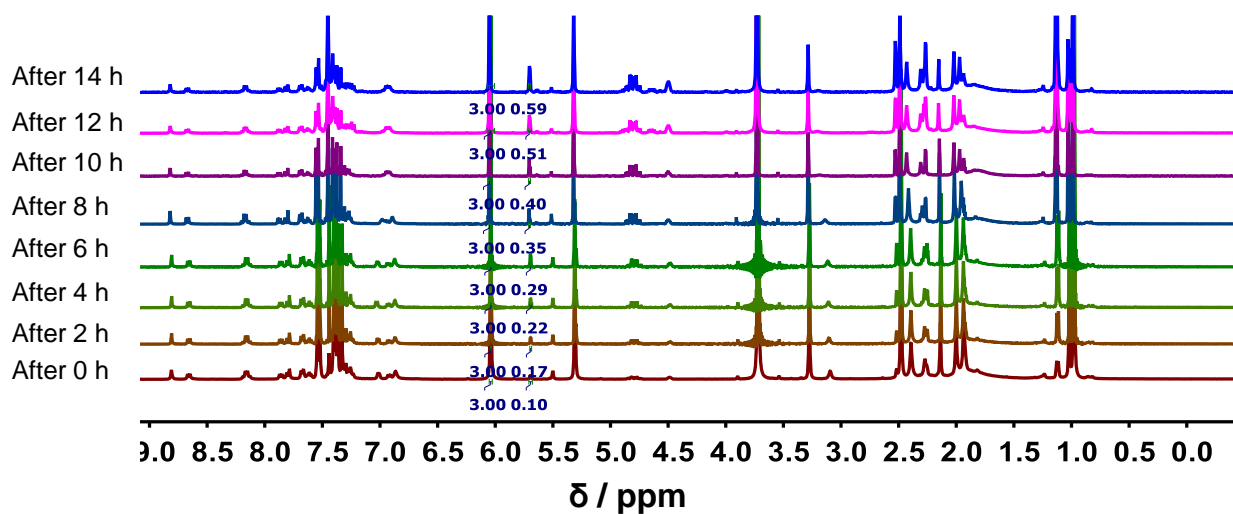


Figure S41. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the reaction of substrates **4** and **9** in presence of catalytic amounts of $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ at 25 °C in CD_2Cl_2 at 2 h intervals. Product **10** shows up at 5.70 ppm in the spectrum.

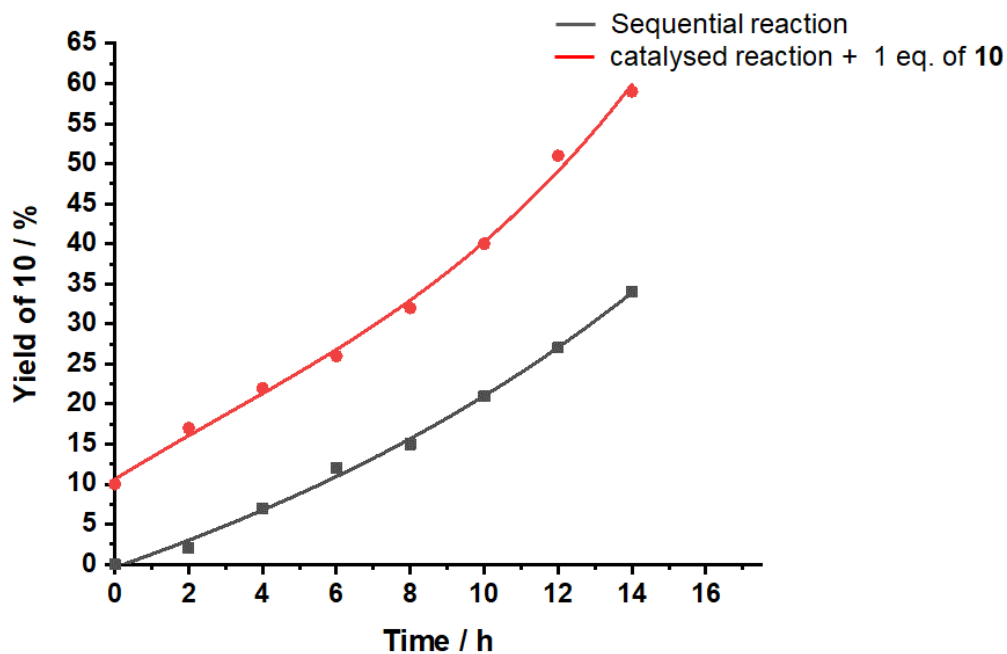


Figure S42. Yield of **10** catalyzed by $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ vs time in absence (black) and in presence of 1 eq. of **10** (red curve).

Table S3. Yield% of **10** catalyzed by $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ vs time in absence and in presence of 1 eq. of **10**.

Time / h	Yield of 10 / %	Yield of 10 / % (in presence of 1 eq. of 10)
0	0	10
2	2	17
4	7	22
6	12	26
8	15	32
10	21	40
12	27	51
14	34	59

d) Final catalytic system (experiment **F** for concurrent tandem catalysis, extended time)

In an NMR tube, AgBF₄ (200 μg, 1.03 μmol), deck **1** (562 μg, 0.343 μmol), ligand **2** (139 μg, 0.343 μmol) and ligand **3** (122 μg, 0.343 μmol) were dissolved in 450 μL of CD₂Cl₂. Dimedone (**4**) (1.44 mg, 10.3 μmol), β-nitroalkenyne **9** (2.59 mg, 10.3 μmol) and 1,3,5-trimethoxybenzene (1.73 mg, 10.3 μmol) were added in CD₂Cl₂. The ¹H NMR spectrum was recorded after mixing at 2 h intervals. The yield of **10** was calculated from the ¹H NMR spectra as shown (Figure S43)

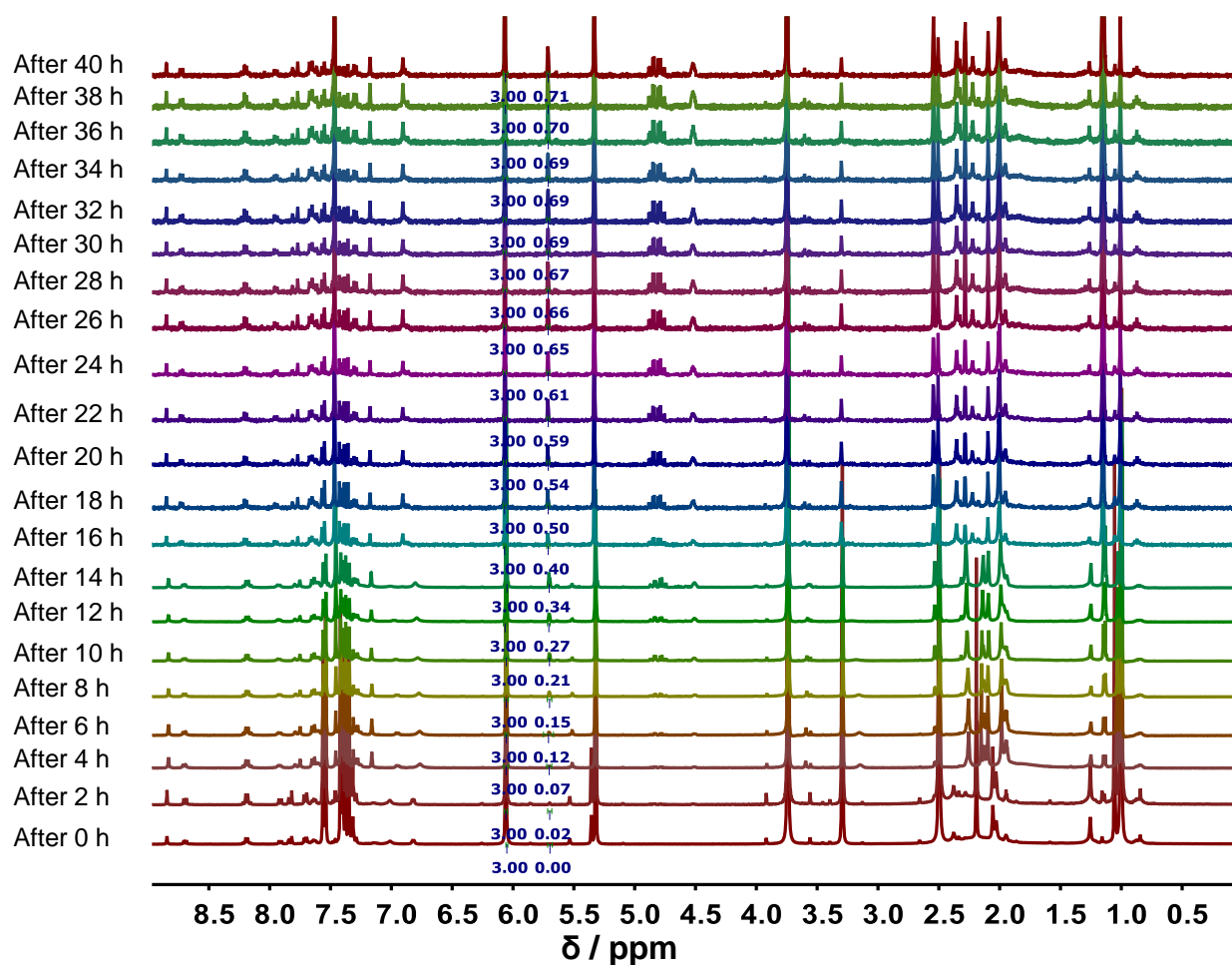


Figure S43. Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 298 K) of the reaction of substrates **4** and **9** in presence of catalytic amounts of [Ag₃(**1**)(**2**)(**3**)]³⁺ at 25 °C in CD₂Cl₂ at 2 h intervals over a period of 40 h. Product **10** shows up at 5.70 ppm in the spectrum.

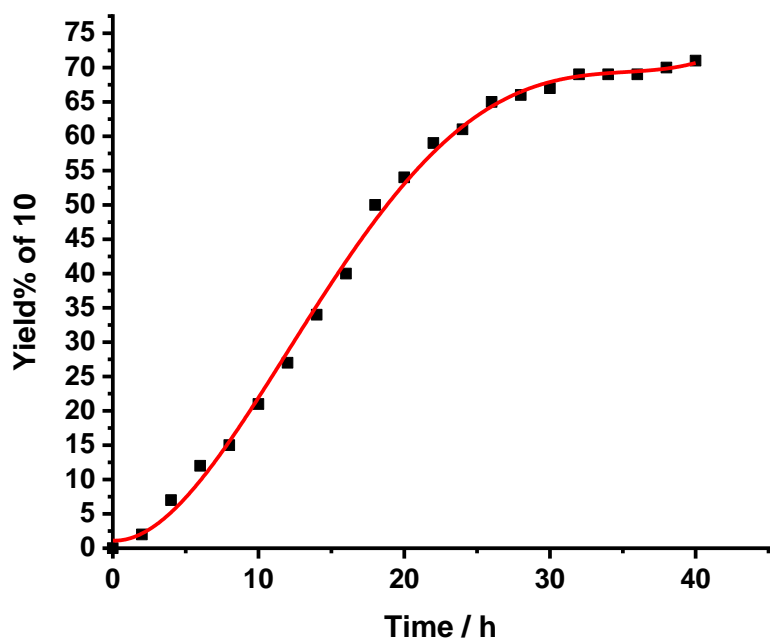


Figure S44. Time dependence of the yield of **10** catalyzed by $[\text{Ag}_3(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$.

11. Determination of $\log K$ of complex $[\text{Ag}(\mathbf{3})(\mathbf{11})]^+$

A UV-vis titration was performed to measure the binding constants between $[\text{Ag}(\mathbf{11})]^+$ and $\mathbf{3}$. A solution of $[\text{Ag}(\mathbf{11})]^+$ (1.3×10^{-5} M) was titrated with a 0.65×10^{-6} M solution of $\mathbf{3}$ in dichloromethane. The UV-vis response was analyzed by nonlinear curve-fitting using bindfit.⁸

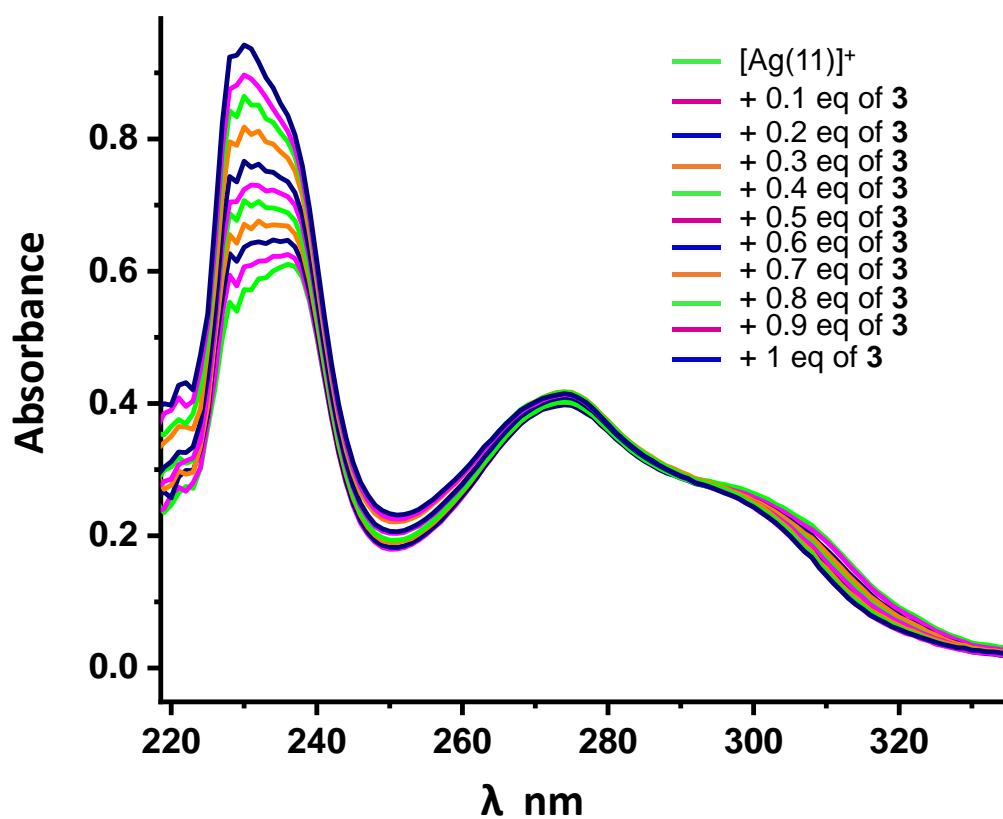


Figure S45. UV-vis titration of $[\text{Ag}(\mathbf{11})]^+$ (1.3×10^{-5} M) with $\mathbf{3}$ (0.65×10^{-6}) furnishing $\log K = 5.96 \pm 0.03$.

12. References

1. S. Saha, P. K. Biswas, I. Paul and M. Schmittel, *Chem. Commun.*, 2019, **55**, 14733–14736.
2. J. C. Anderson, A. S. Kalogirou, G. J. Tizzard, *Tetrahedron*, 2014, **70**, 9337–9351.
3. X. Zhao, W. Fan and Z. Miao, R. Chen, *Synth. Commun.*, 2013, **43**, 1714–1720.
4. S. Belot, K. A. Vogt, C. Besnard, N. Krause and A. Alexakis, *Angew. Chem. Int. Ed.*, 2009, **48**, 8923–8926.
5. I. Paul, N. Mittal, S. De, M. Bolte and M. Schmittel. *J. Am. Chem. Soc.*, 2019, **141**, 5139–5143.
6. H. J. Reich, NMR Spectrum Calculations: WinDNMR, Version 7.1.13; Department of Chemistry, University of Wisconsin.
7. U. Kaya, P. Chauhan, K. Deckers, R. Puttreddy, K. Rissanen, G. Raabe and D. Enders, *Synthesis*, 2016, **48**, 3207–3216.
8. a) <http://supramolecular.org>, b) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323, c) D. B. Hibbert and P. Thordarson, *Chem. Commun.*, 2016, **52**, 12792-12805.