Silver Chelation and Ethyne Interaction of 1,2-di(quinolin-8-yl)ethyne

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Supporting Information:

General Procedures

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise specified. Anhydrous pyridine and acetonitrile were obtained from Acros and Fluka respectively. All reactions were run under anhydrous conditions. Analytical thin-layer chromatography was performed on pre-coated silica gel aluminum-backed plates (Kieselgel 60 F_{254}, E. Merck & Co., Germany). Flash chromatography was performed using silica gel (230–400 mesh) from E.M. Science or Silicycle or neutral aluminum oxide (50–200 micron) from Acros. NMR solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). All NMR spectra were recorded on a Varian Mercury 400MHz instrument with chemical shifts reported relative to residual deuterated solvent peaks. Chemical shifts (δ) are reported in parts per million (ppm); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), or m (multiplet); coupling constants (*J*) are reported in Hertz. For 1,2-di(quinolin-8-yl)ethyne **3**, spectra are provided in CD_3CN and THF d_8 and DMSO d_6. Mass spectra were recorded at the UCSD Mass Spectrometry Facility, utilizing a LCQDECA (Finnigan) ESI with a quadrpole ion trap.

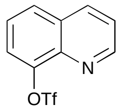
Spectrophotometric Experiments.

UV-Visible Experiments. UV-Visible experiments were carried out at ambient temperature in a quartz micro cell with a path length of 1.0 cm (Hellma GmbH & Co KG, Müllheim, Germany) on a Hewlett Packard 8452A diode array spectrometer.

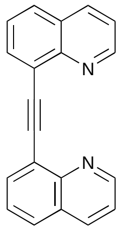
Fluorescence Spectroscopy. Steady State fluorescence experiments were carried out at ambient temperature in a micro fluorescence cell with a path length of 1.0 cm (Hellma GmH & Co KG, Mullenheim, Germany) on a Perkin Elmer LS 50B luminescence spectrometer.

Abbreviations used:
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

S.1 Synthesis of 1,2-di(quinolin-8-yl)ethyne

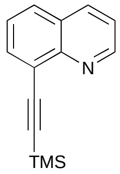


Quinolin-8-yl trifluoromethanesulfonate (2). To a solution of 8-hydroxyquinoline (8.6 g, 59.2 mmol) and anhydrous pyridine (25 ml, 309.1 mmol) in anhydrous dichloromethane (200 ml) at 0°C was added dropwise a solution of trifluoromethanesulfonic anhydride (12 ml, 70.9 mmol) in anhydrous dichloromethane (75 ml). The reaction solution was allowed to warm to room temperature. Water (150 ml) was added to the reaction solution and extracted with dichloromethane (3 × 80 ml). Resulting organic layers washed with water, 1M HCl, brine and dried over sodium sulfate. Solvent removed under reduced pressure resulting in an orange oil, where upon addition of a stir bar, product crystallized at room temperature. Product: orange solid (16.4 g, 59.2 mmol, 99% yield). ^{1}H NMR (400 MHz; $CDCl_3$) δ 9.05 (1 H, dd, *J* = 1.6 and 4.4 Hz, H-2), 8.22 (1 H, dd, *J* = 1.4 and 8.2 Hz, H-4), 7.86 (1 H, dd, *J* = 1.6 and 8.0 Hz, H-7), 7.62 (1 H, dd, *J* = 1.0 and 7.8 Hz, H-5), 7.56 (1 H, dd, *J* = 8.0 and 8.4 Hz, H-6), 7.52 (1 H, dd, *J* = 4.4 and 8.4 Hz, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 145.8, 140.7, 135.7, 129.6, 128.1, 125.8, 122.5, 120.9, 120.4, 117.2; ESI-MS *m/z* 277.92 ($C_{10}H_7F_3NO_3S$ $[M+H]^+$ requires 278.00).

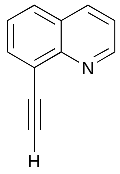


1,2-di(quinolin-8-yl)ethyne (3). To a solution of **2** (2.0 g, 7.2 mmol), tetrakis(triphenylphosphine)Pd (305 mg, 0.3 mmol) and copper(I) iodide (162 mg, 0.9 mmol) in anhydrous acetonitrile (15 ml) was added DBU (6 ml, 40.1 mmol). Reaction vessel was further degassed for 5 min with argon. A solution of cold trimethylsilyl acetylene (510 µl, 3.6 mmol) in anhydrous acetonitrile (15 ml) was degassed for 1 min and then cannulated into the reaction flask, followed immediately by the addition of deionized water (50 µl, 2.8 mmol). Reaction flask was again further degassed with argon for 5 min, covered with aluminum foil and heated to 60 °C for 3 h. Dichloromethane (150 ml) was added to the reaction and washed with water. Resulting organic layer was dried over anhydrous sodium sulfate. Solvent removed under reduced pressure, resulting in a black oil. The addition of hexane/dichloromethane (50/50) solution resulted in precipitation of an off-white solid. Solid collected and the resulting liquid evaporated followed by successive precipations until all product material was removed as an off-white solid. Resulting off-white solid was further purified via neutral alumina gravity column. Product: white solid (437.5 mg, 1.5 mmol, 43% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 9.02 (2 H, dd, *J* = 1.6 and 4.0 Hz, H-2), 8.36 (2 H, dd, *J* = 1.6 and 8.4 Hz, H-4), 8.10 (2 H, dd, *J* = 1.6 and 6.8 Hz, H-7), 8.00 (2 H, dd, *J* = 1.4 and 8.2 Hz, H-5), 7.65 (2 H, dd, *J* = 7.2 and 8.0 Hz, H-6), 7.57 (2 H, dd, *J* = 4.0 and 8.4 Hz, H-3); ^{1}H NMR (400 MHz, THF *d_8*): δ 8.99 (2 H, dd, *J* = 1.6 and 4.0 Hz, H-2), 8.27 (2 H, dd, *J* = 1.8 and 8.6 Hz, H-4), 8.10 (2 H, dd, *J* = 1.4 and 7.0 Hz, H-7), 7.89 (2 H, dd, *J* = 1.4 and 8.2 Hz, H-5), 7.57 (2 H, dd, *J* = 7.2 and 8.0 Hz, H-6), 7.48 (2 H, dd, *J* = 4.0 and 8.4 Hz, H-3); ^{1}H NMR (400 MHz, DMSO *d_6*): δ 9.03 (2 H, dd, *J* = 1.8 and 4.2 Hz), 8.47 (2 H, dd, *J* = 1.8 and 8.2 Hz), 8.10 (2 H, dd, J = 1.2 and 7.2 Hz), 8.07 (2 H, dd, *J* = 1.2

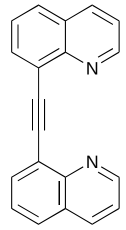
and 8.4), 7.68 (2 H, dd, *J* = 8.0 and 7.2 Hz), 7.64 (2 H, dd, *J* = 4 and 8.4 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ 152.3 (C-2), 137.9 (C-4), 135.3 (C-7), 130.3 (C-5), 129.8 (C-10), 127.6 (C-6), 123.4 (C-3), 94.3 (C≡C); ^{13}C NMR (100 MHz, THF d_8): δ 151.7 (C-2), 149.6 (C-9), 137.0 (C-4), 134.8 (C-7), 129.6 (C-10), 129.2 (C-5), 126.9 (C-6), 125.6 (C-8), 122.6 (C-3), 94.2 (C≡C); ^{13}C NMR (100 MHz, DMSO d_6): δ 151.1, 147.4, 136.7, 134.0, 129.1, 128.1, 126.3, 122.7, 122.2, 92.9; ESI-MS *m/z* 281.39 ($C_{20}H_{13}N_2$ $[M+H]^+$ requires 281.12). UV: λ_{max}(tetrahydrofuran)/nm 346 (ε/ dm^3 mol^{-1} cm^{-1} 19 200), 364 (16 400).



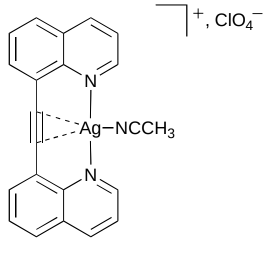
8-((trimethylsilyl)ethynyl)quinoline (4). To a solution of **1** (1.0 g, 3.6 mmol), copper iodide (50.3 mg, 0.3 mmol) and tetrakis(triphenylphosphine)Pd (208 mg, 0.2 mmol) in degassed piperidine (5 ml) was cannulated a briefly (1 min) degassed solution of trimethylsilyl acetylene (2.5 ml, 17.7 mmol). The reaction was heated to 90°C for 2hrs. Resulting solution was diluted with dichloromethane and washed with saturated aqueous ammonium chloride. Resulting oil was purified by flash chromatography (dichloromethane). Product: yellow oil (1.9 mmol, 429 mg, 52% yield). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.97 (1 H, dd, *J* = 1.8 and 4.2 Hz, H-2), 8.06 (1 H, dd, *J* = 2.0 and 8.0 Hz, H-4), 7.91 (1 H, dd, *J* = 1.2 and 7.2 Hz, H-7), 7.71 (1 H, dd, *J* = 1.2 and 8.4 Hz, H-5), 7.41 (1 H, dd, *J* = 7.2 and 8.0 Hz, H-6), 7.35 (1 H, dd, *J* = 4.2 and 8.2 Hz, H-3), 0.31 (9 H, s, Si-$(CH_3)_3$; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 147.9, 136.2, 134.9, 128.5, 128.0, 125.7, 123.0, 121.4, 102.5 (C≡C), 100.5 (C≡C), 0.0 (TMS); ESI-MS *m/z* 226.15 ($C_{14}H_{16}NOSi$ $[M+H]^+$ requires 226.11).



8-ethynylquinoline (5). To a solution of **4** (198 mg, 0.9 mmol) in methanol (4 ml) was added 1 M aqueous sodium hydroxide solution dropwise. The reaction was allowed to stir open to the atmosphere at room temperature for 15min. Water was added to the solution and the product extracted with dichloromethane (50 ml x 3). Organic layer was dried over anhydrous sodium sulfate and solvent removed under reduced pressure. Product: yellow solid (131 mg, 0.8 mmol, 99% yield). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.99–8.98(1 H, m, H-2), 8.08 (1 H, dd, *J* = 1.8 and 8.2 Hz, H-4), 7.90 (1 H, dd, *J* = 1.2 and 7.2 Hz, H-7), 7.74 (1 H, dd, *J* = 1.6 and 8.4, H-5), 7.44–7.36 (2 H, m, H-6 and H-3), 3.57 (1 H, s, C≡C–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 148.2, 136.3, 134.5, 128.8, 128.0, 125.8, 121.9, 121.5, 82.9 (C≡C), 81.2 (C≡C); ESI-MS *m/z* 154.18 ($C_{11}H_8N$ $[M+H]^+$ requires 154.07).



1,2-di(quinolin-8-yl)ethyne (3). Stepwise Procedure: To a solution of 8-bromoquinoline (190 µl, 1.5 mmol), tetrakis(triphenylphosphine)Pd (43 mg, 0.04 mmol), copper iodide (11.4 mg, 0.06 mmol) in degassed piperdine (2 ml) was cannulated a degassed solution of **5** (110 mg, 0.7 mmol) in piperdine (2 ml). Reaction was sonicated overnight. Resulting brown precipitate was filtered off and washed with water and hexanes. Resulting brown solid was purified by neutral alumina gravity column (hexanes/dichloromethane 50/50). Product: light yellow solid (50 mg, 0.2 mmol, 25 % yield); Spectral data is the same as seen for **3** above.



[Ag(3)(CH$_3$CN)](ClO$_4$) (6). To a concentrated solution of **3** (26 mg, 0.09 mmol) in chloroform was added 1eq of silver perchlorate solution (1ml of 94 mM) in acetonitrile. White solid precipitated upon addition of silver perchlorate solution. Solvent was removed under reduced pressure. Product: white solid, 99 % yield. ^{1}H NMR (400 MHz; CD$_3$CN) δ 9.14 (2 H, dd, *J* = 1.6 and 4.4 Hz), 8.60 (2 H, dd, *J* = 1.4 and 8.6 Hz), 8.34 (2 H, dd, J = 1.0 and 7.4 Hz), 8.16 (2 H, dd, J = 1.4 and 8.2 Hz), 7.82–7.76 (4 H, m); ^{1}H NMR (400 MHz, DMSO *d$_6$*): δ 9.20 (2 H, dd, *J* = 1.8 and 4.6 Hz), 8.76 (2 H, dd, *J* = 2.0 and 8.4 Hz), 8.40 (2 H, dd, J = 1.4 and 7.0 Hz), 8.28 (2 H, dd, *J* = 1.0 and 8.2), 7.92 (2 H, dd, *J* = 4.6 and 8.2 Hz), 7.85 (2 H, dd, *J* = 7.2 and 8.4 Hz); ^{13}C NMR (100 MHz, DMSO *d$_6$*): δ 153.9, 143.1, 139.6, 135.9, 130.8, 128.7, 127.1, 123.0, 118.8, 91.3;

S.2 2D NMR Data for 3 (NOESY, DEPT, HMQC and HMBC)

Figure S2.1 NOESY of 3
NOESY (400 MHz, CD_3CN) of **3**: Blue lines - ring 1 and red lines - ring 2.

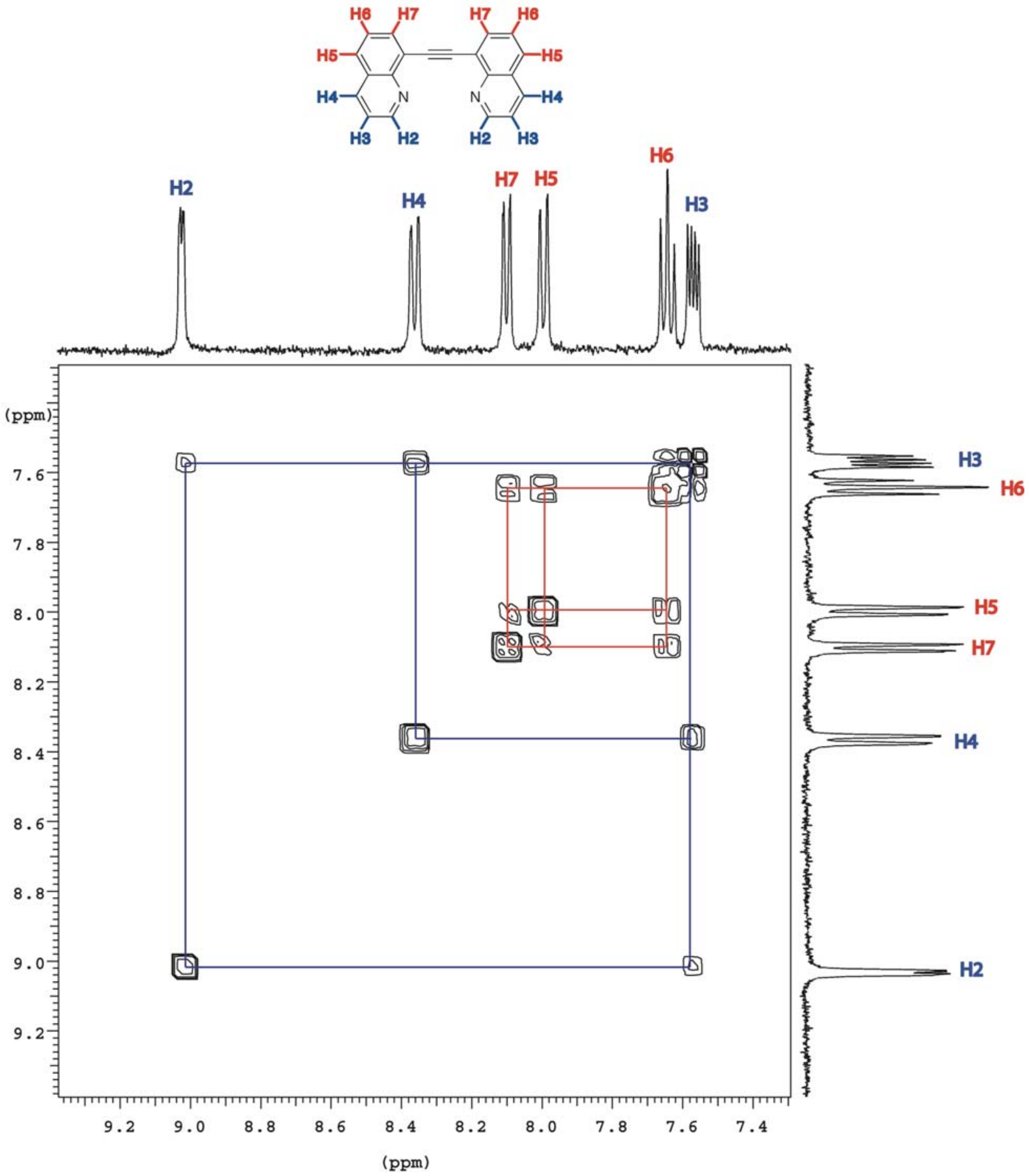


Figure S2.2 HMQC of 3
HMQC (400 MHz, THF *d*$_8$) of **3**: Blue lines - ring 1, red lines - ring 2, black lines - carbons 9 and 10, and green line – ethyne carbons.

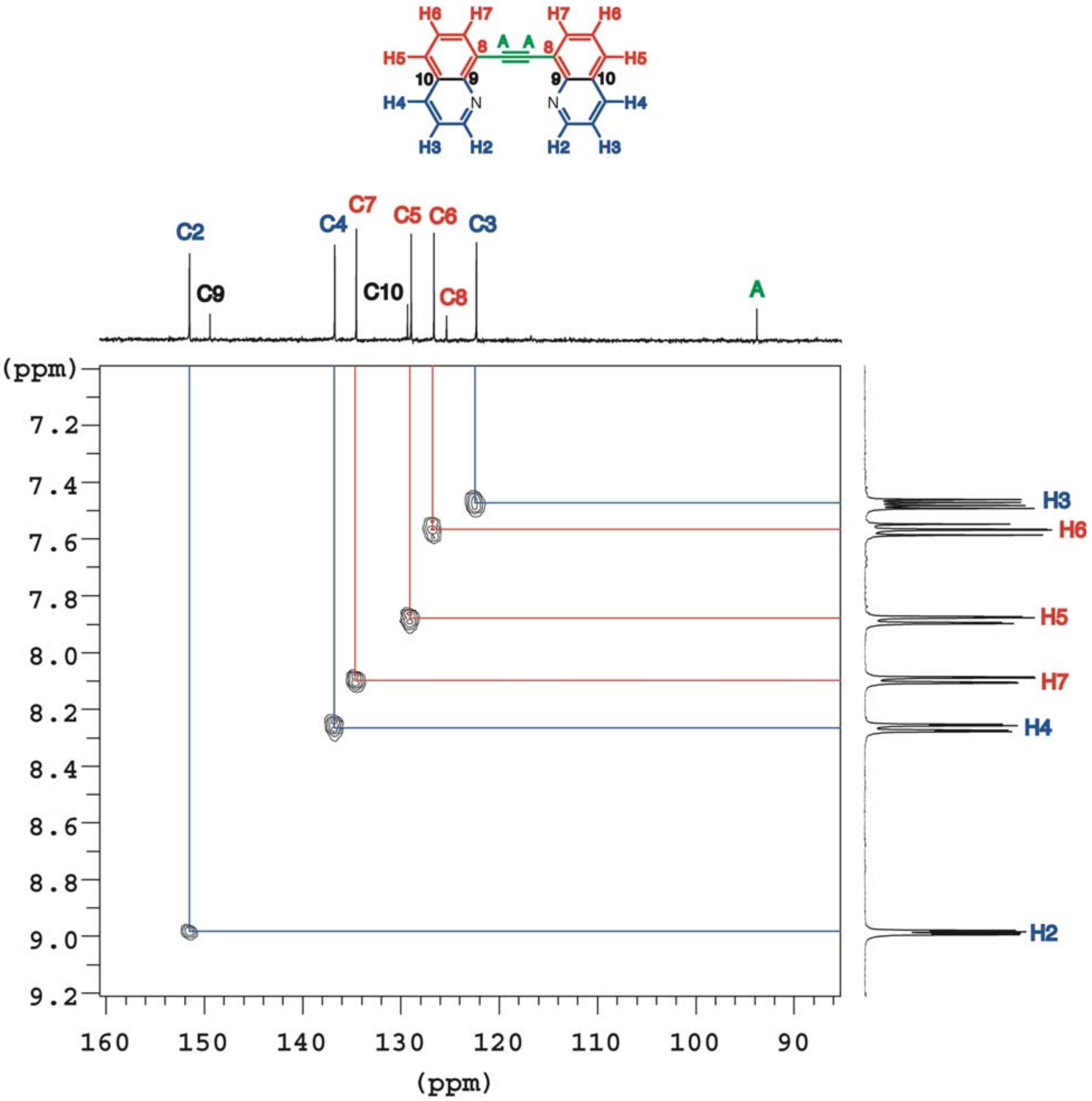
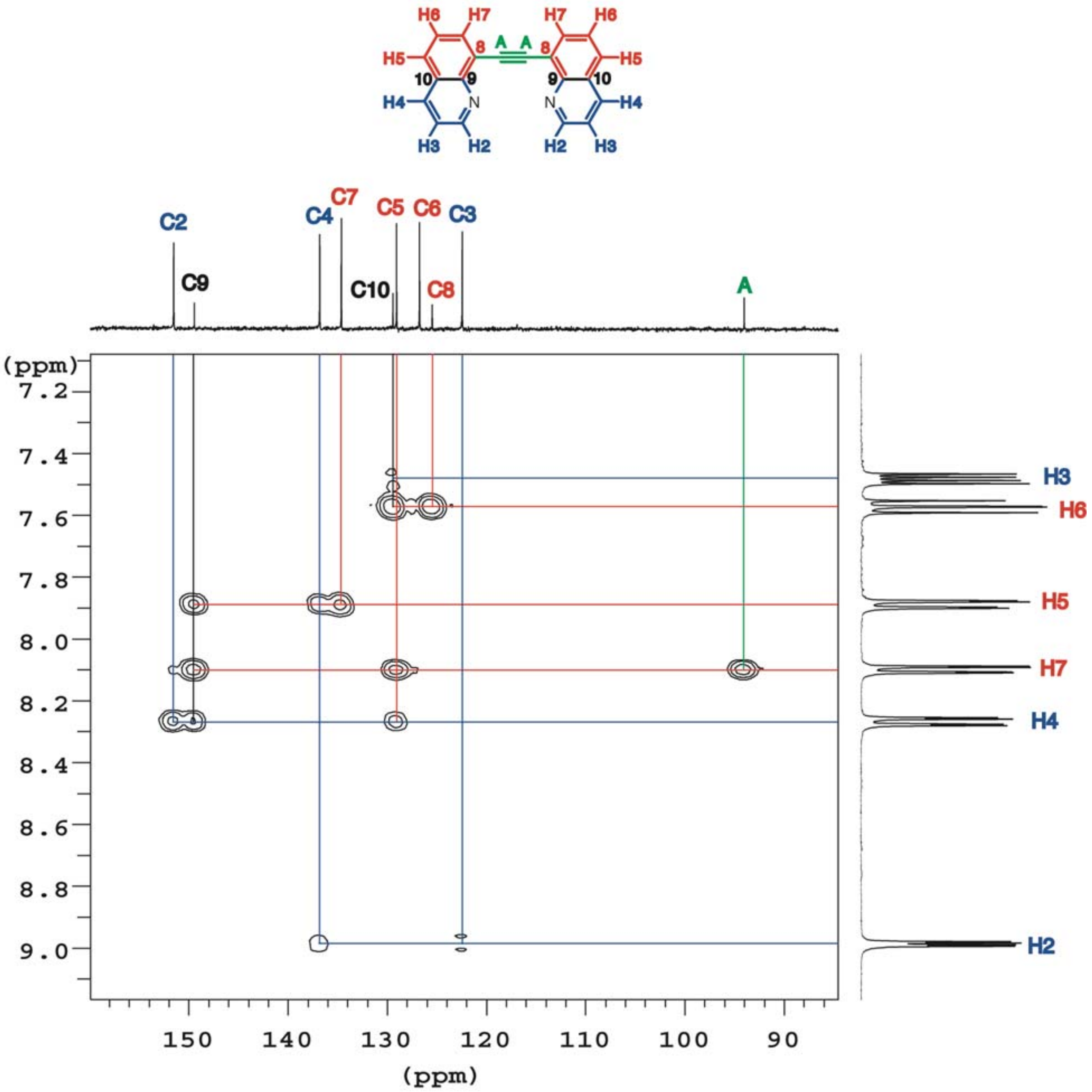


Figure S2.3 HMBC of 3

HMBC (400 MHz, THF d_8) of **3**: Blue lines - ring 1, red lines - ring 2, black lines - carbons 9 and 10, and green line - ethyne carbons.



S.3 NMR Titration of 3 with $AgClO_4$

Figure S3.1 NMR Titration (400 MHz, CD_3CN) of 3 (3 mM) with $AgClO_4$ - Straight View

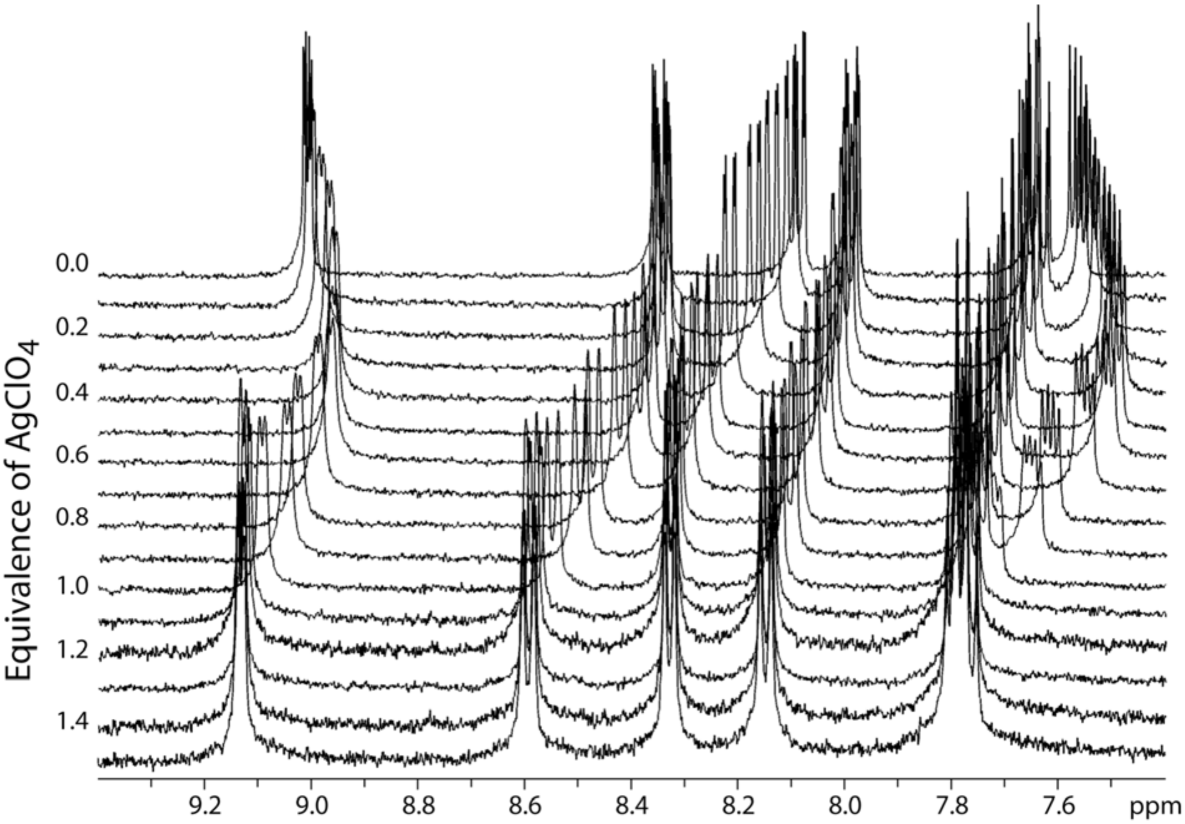
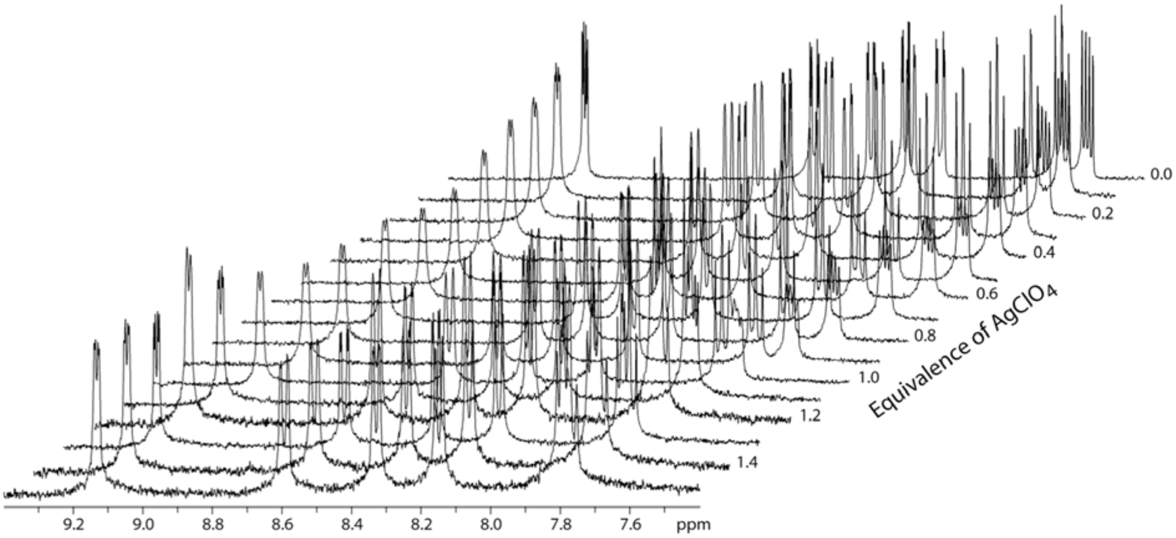


Figure S3.2 NMR Titration (400 MHz, CD_3CN) of 3 (3 mM) with $AgClO_4$ - Tilted View



S.4 ^{1}H and ^{13}C NMR of 3 and 6.

Figure S4.1 ^{1}H NMR (400 MHz, DMSO d_6) of 3 and 6.

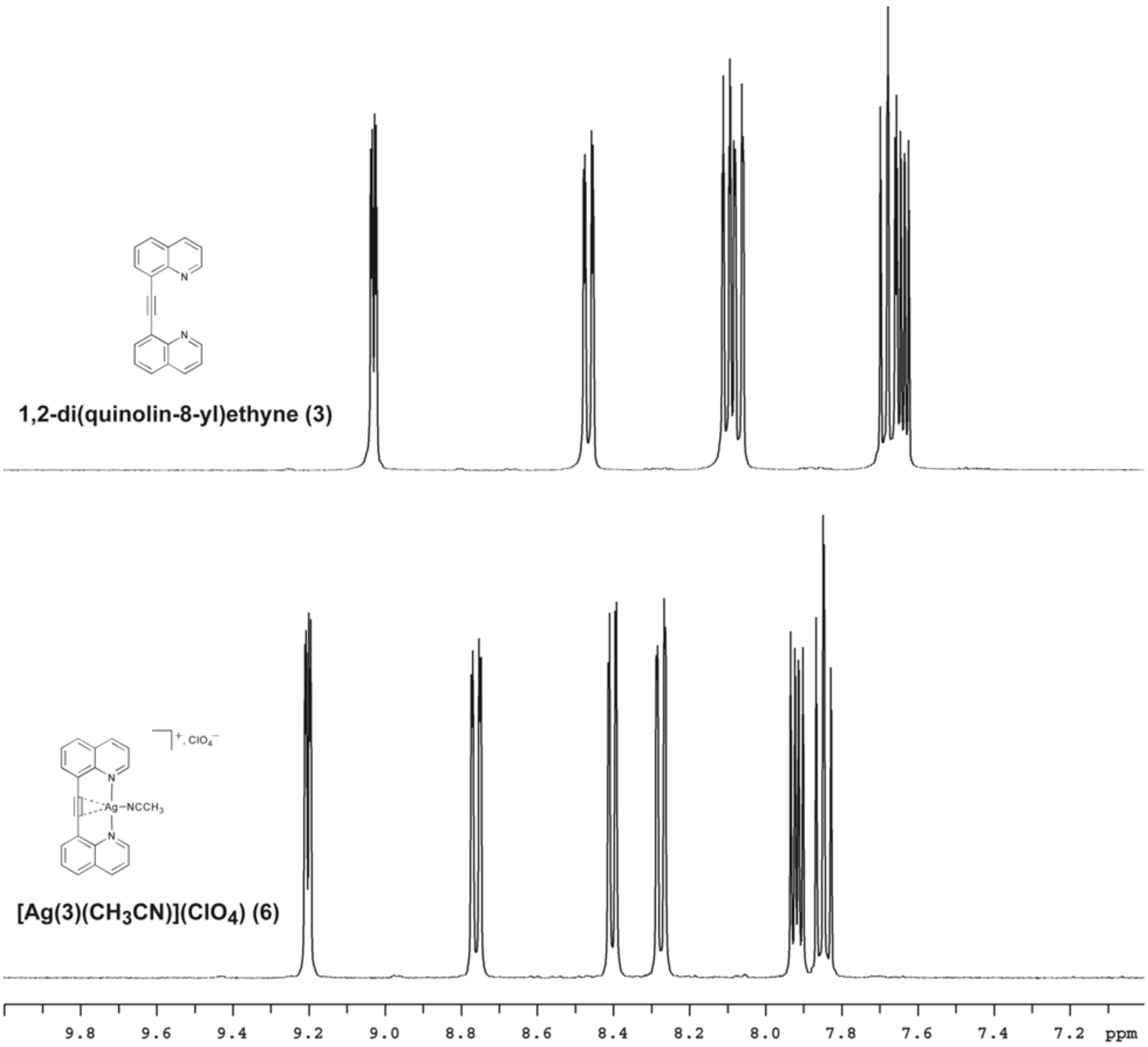
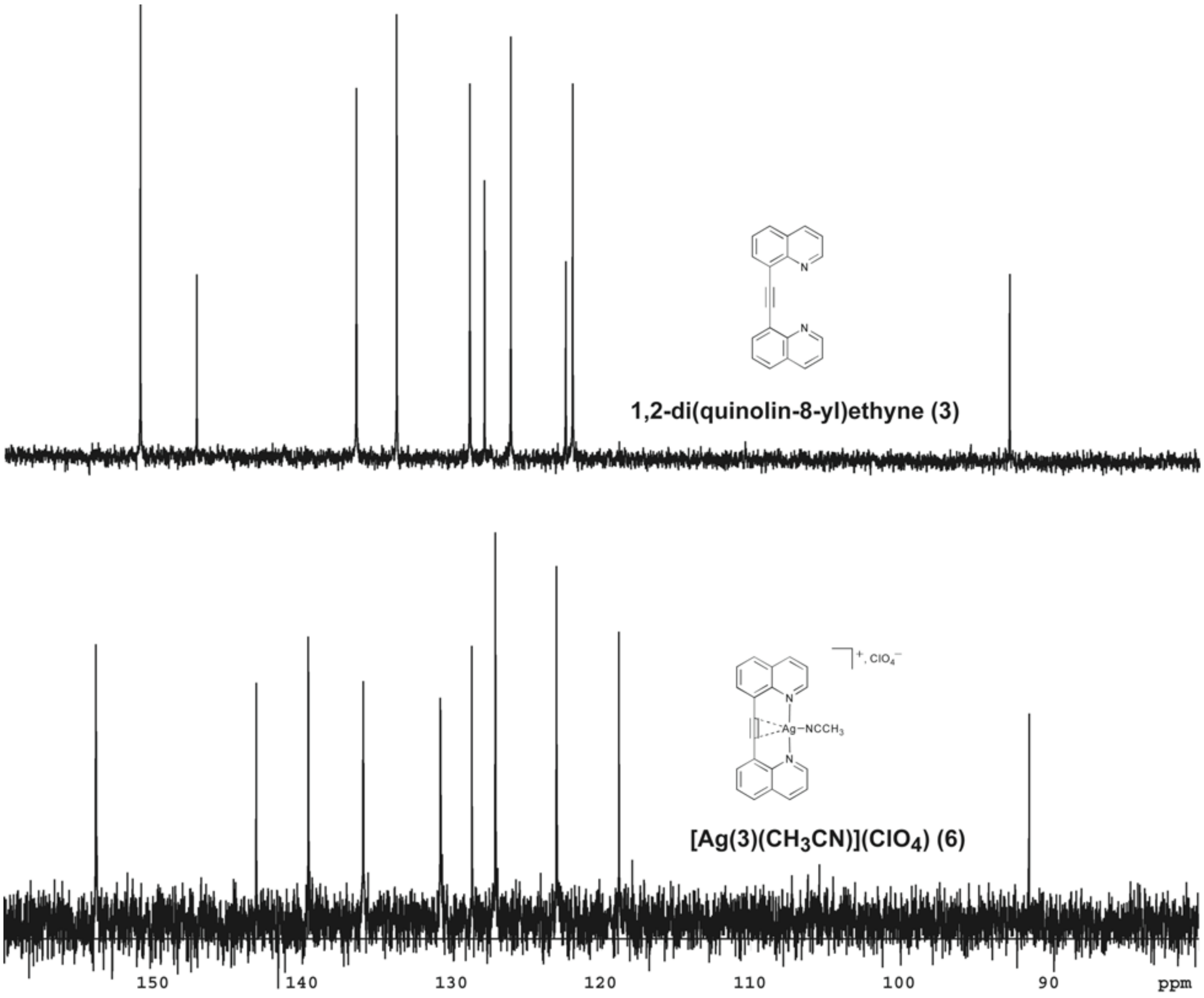
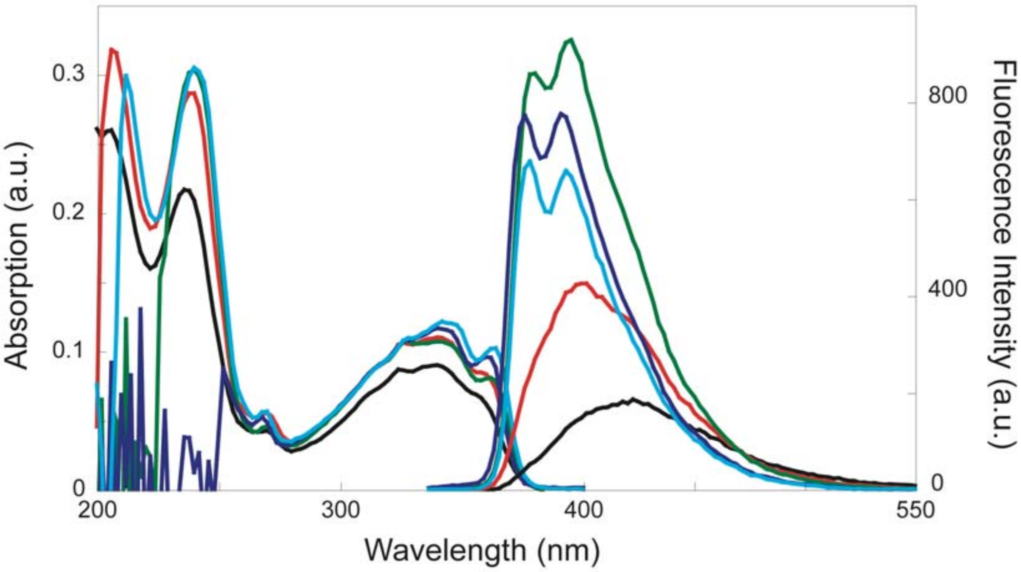


Figure S4.2 ^{13}C NMR (100 MHz, DMSO d_6) of 3 and 6.



S.5 Steady State Fluorescence and Absorption Spectra.

Figure S5.1 Absorption and Emission Spectra of 3 in Various Solvents



3 (5 μM) in Water (black), Methanol (red), Dichloromethane (green), Ethyl Acetate (dark blue) and Tetrahydrofuran (light blue). Excitation wavelength = 280 nm*, excitation slit = 2.9 nm, emission slit = 2.9 nm, scan speed = 300 nm/min, spectra averaged over three scans.

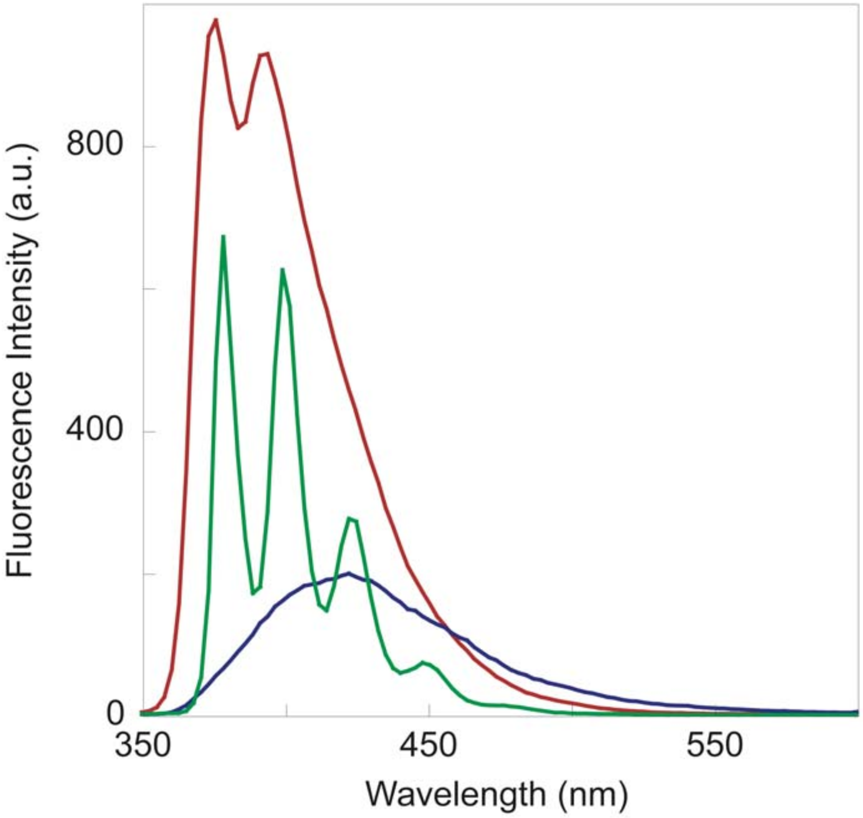
∗Note: excitation wavelength ≠ λ_{max} was used in order to view the emission and absorption spectra under equal concentrations.

S.6 Quantum Yield Determination.

Quantum yields were determined using the following equation where anthracence (Du, H.; Fuh, R. A.; Li, J.; Corkan, A.; Lindsey, J. S. *Photochem. and Photobiol.*, **1998**, *68*, 141−142) was the standard.

$\Phi_{F(x)} = (A_s/A_x)\ (F_x/F_s)\ (n_x/n_s)^2\ \Phi_{F(s)}$

Where s is the standard, x is the unknown, A is the absorbance at excitation wavelength, F is the area under the emission curve, *n* is the refractive index of the solvent and Φ is the quantum yield (Lavabre, D.; Fery-Forgues, S. *J. Chem. Educ.*, **1999**, *76*, 1260−1264).



Anthracene in cyclohexane Φ = 0.36 (green), **3** in water Φ = 0.23 (blue) and **3** in tetrahydrofuran Φ = 0.85 (red). All spectra are taken with equal absorption at the wavelength of excitation (340 nm).

S.7 Crystallographic Data for 1,2-di(quinolin-8-yl)ethyne - 3.

Empirical formula	$C_{20}H_{12}N_2$	
Formula weight	280.32	
Temperature	208(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 15.582(5) Å	α= 90°
	b = 8.095(3) Å	β= 117.362(4)°
	c = 12.481(4) Å	γ = 90°
Volume	1398.2(8) $Å^3$	
Z	4	
Density (calculated)	1.332 g/cm^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	584	
Crystal size	0.25 x 0.25 x 0.25 mm^3	
Theta range for data collection	2.92 to 28.07°	
Index ranges	−20<=h<=19, −10<=k<=10, −15<=l<=16	
Reflections collected	4647	
Independent reflections	1639 [R(int) = 0.0295]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9805 and 0.9805	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1639 / 0 / 100	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1236	
R indices (all data)	R1 = 0.0551, wR2 = 0.1321	
Largest diff. peak and hole	0.309 and -0.145 e $Å^{-3}$	

Figure S7.1 Thermal Ellipsoid Plot of 3

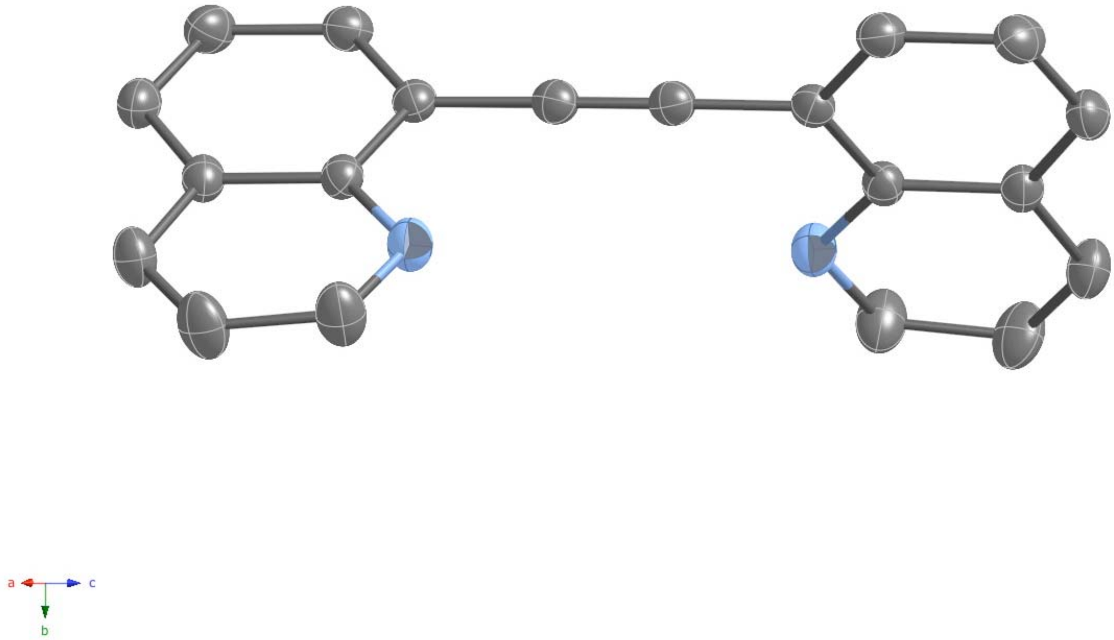


Figure S7.2 Thermal Ellipsoid Plot of **3** Packing Top View

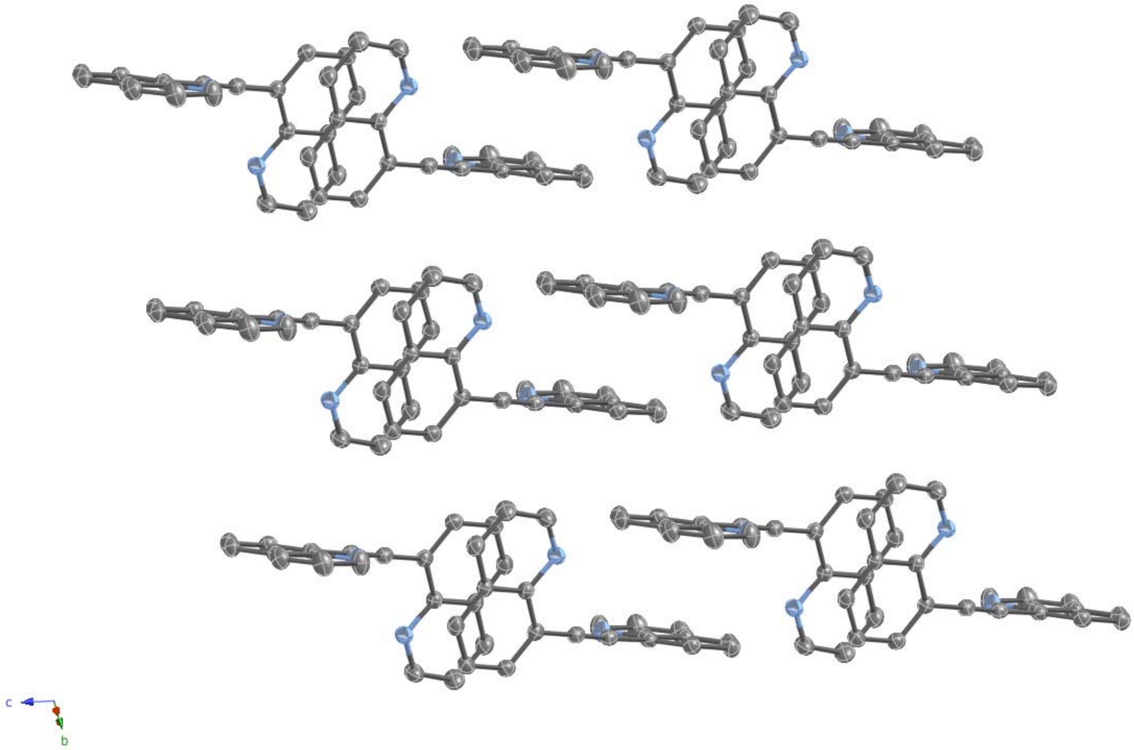
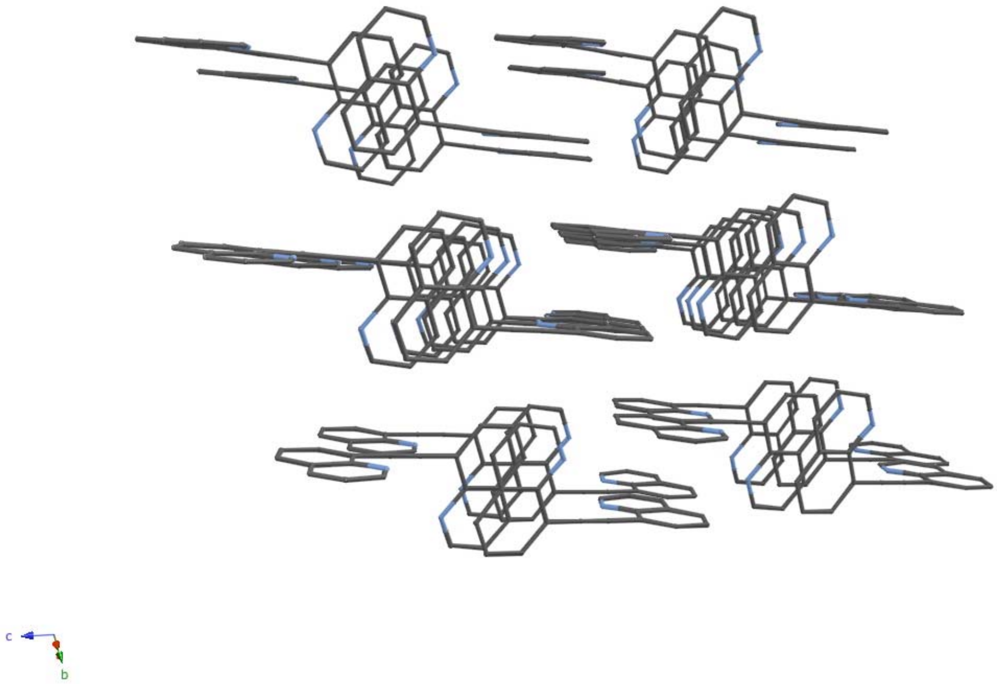


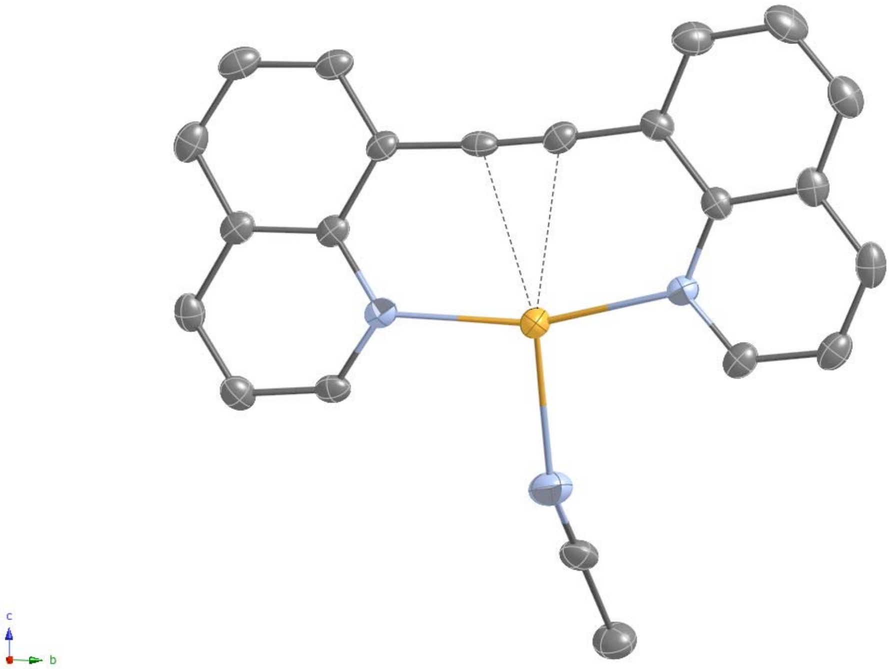
Figure S7.3 Plot of 3 Packing Top View with Perspective



S.7 Crystallographic Data for [Ag(3)(CH_3CN)](ClO_4).

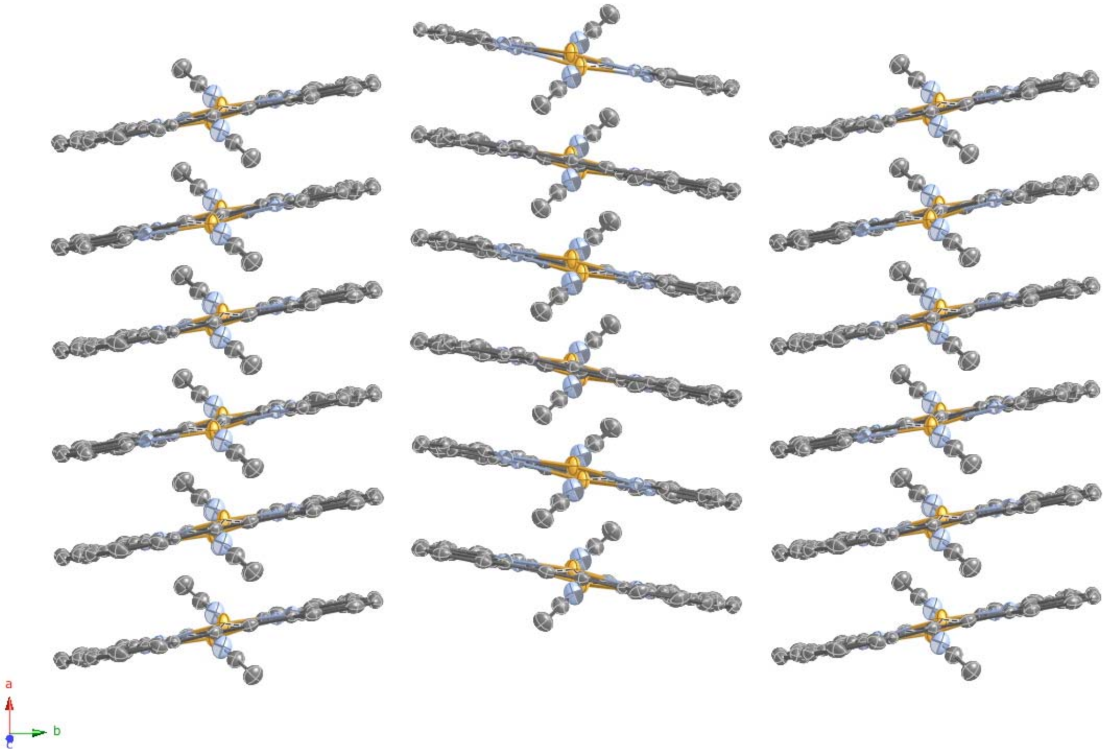
Empirical formula	$C_{22}H_{15}AgClN_3O_4$	
Formula weight	528.69	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.8416(17) Å	α= 90°
	b = 23.779(6) Å	β= 105.290(4)°
	c = 12.724(4) Å	γ = 90°
Volume	1996.7(9) Å^3	
Z	4	
Density (calculated)	1.759 g/cm^3	
Absorption coefficient	1.180 mm^{-1}	
F(000)	1056	
Crystal size	0.30 x 0.10 x 0.07 mm^3	
Theta range for data collection	1.71 to 26.00°	
Index ranges	−7<=h<=8, −28<=k<=29, −14<=l<=15	
Reflections collected	12985	
Independent reflections	3925 [R(int) = 0.0394]	
Completeness to theta = 26.00°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.9220 and 0.7185	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3925 / 0 / 280	
Goodness-of-fit on F^2	1.186	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1441	
R indices (all data)	R1 = 0.0725, wR2 = 0.1492	
Largest diff. peak and hole	0.949 and -1.057 e Å^{-3}	

Figure S8.1 Thermal Ellipsoid Plot of [Ag(3)(CH_3CN)](ClO_4) Top View



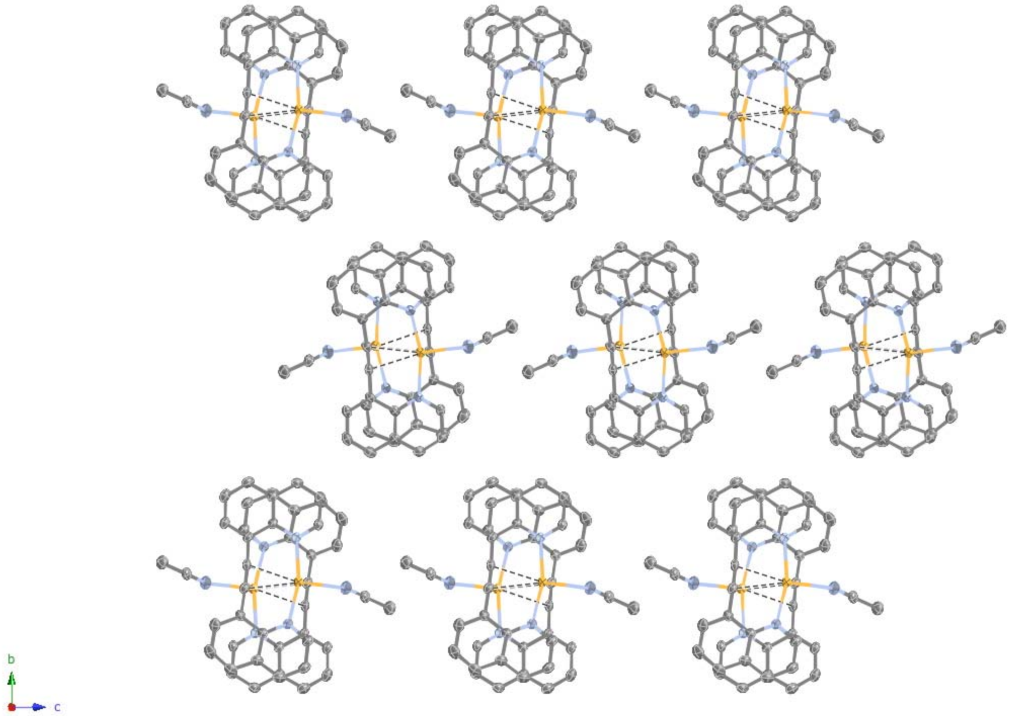
Perchlorate anions were removed for clarity.

Figure S8.2 Thermal Ellipsoid Plot of [Ag(3)(CH_3CN)](ClO_4) Packing Side View



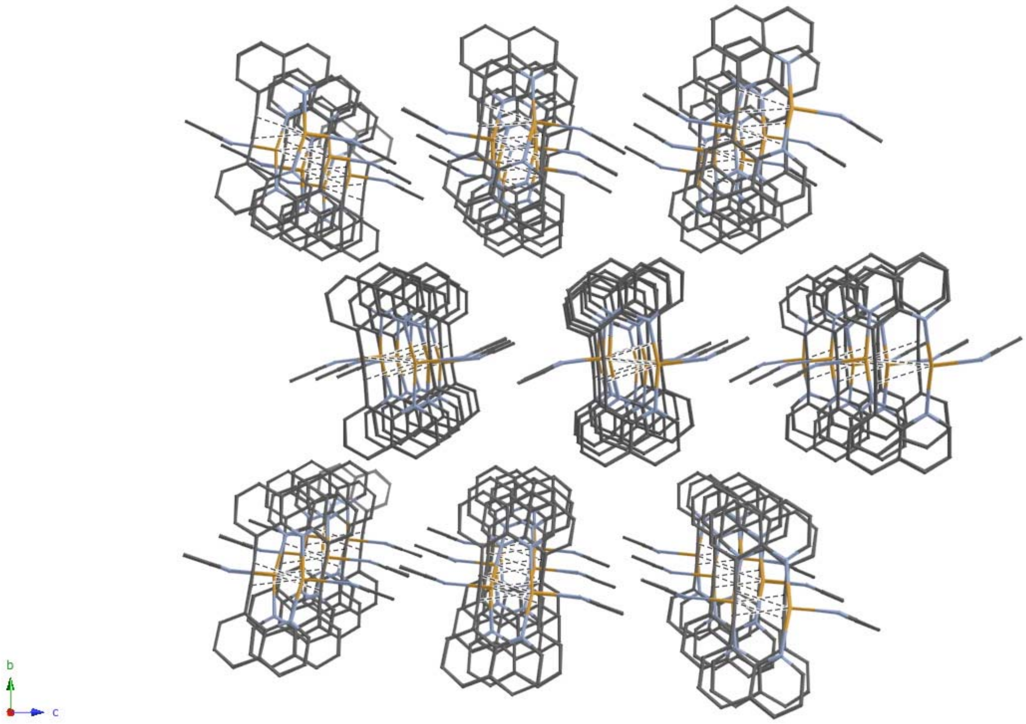
Perchlorate anions were removed for clarity.

Figure S8.3 Thermal Ellipsoid Plot of [Ag(3)(CH_3CN)](ClO_4) Packing Top View



Perchlorate anions were removed for clarity.

Figure S8.4 Plot of [Ag(3)(CH_3CN)](ClO_4) Packing Top View with Perspective



Perchlorate anions were removed for clarity.