Supporting Information Part 1 of 2 – Synthetic Procedures and Spectroscopy

Copper(II) complexes of *N*-propargyl cyclam ligands reveal a range of coordination modes and colours, and unexpected reactivity

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Contents

1. General Experimental

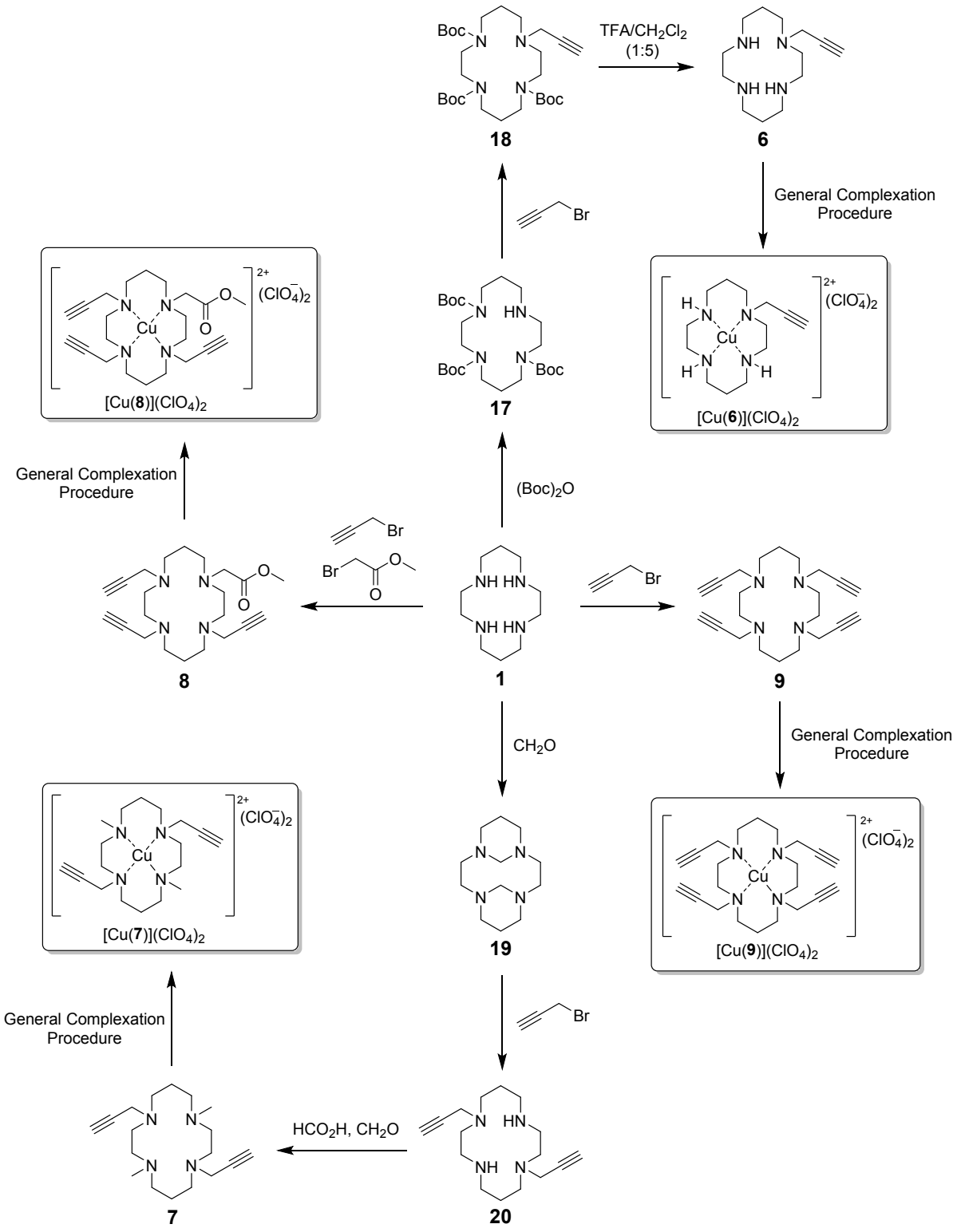
All reactions were performed in ordinary glassware. All reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, Matrix Scientific, Merck, or Ajax Finechem. Chemicals were used as received unless otherwise specified. Dichloromethane was distilled over calcium hydride prior to use. Chloroform was passed through a basic alumina column and stored over activated 4Å molecular sieves. Acetonitrile, methanol and tetrahydrofuran were collected from a PureSolv MD 7 solvent purification system fitted with anhydrous alumina columns.

For the monitoring of reactions, analytical TLC was performed on Merck TLC silica gel 60 F_{254} (0.2 mm on aluminium). Ninhydrin stain was used to visualise amines. Flash column chromatography was performed on Merck silica gel 60 (40-63 mm), under a positive pressure of N_2 gas to optimise solvent flow.

^{1}H and ^{13}C NMR spectra were obtained on either a Bruker AVANCE DPX200 (^{1}H at 200.13 MHz, ^{13}C at 50.32 MHz), DPX300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz), or DRX400 (^{1}H at 400.13 MHz, ^{13}C at 100.61 MHz). Chemical shifts (δ) are reported in ppm relative to either an internal standard (0.03% v/v TMS) or the non-deuterated residual solvent peak. Coupling constants (J) are reported in Hertz (Hz). Signal multiplicities are reported with the following abbreviations: s - singlet, d - doublet, t - triplet, q - quartet, qn - quintet, dd - doublet of doublets, dt - doublet of triplets, m - multiplet, br - broad. UV-vis spectra were obtained on a Varian Cary 4000 UV-Vis spectrophotometer, with temperature controlled by a Varian Cary PCB water peltier system. Attenuated total reflectance (ATR) infrared spectra were recorded on a Bruker Alpha-E FT-IR spectrometer. Unless a solvent is indicated, samples were analysed as solids. Low resolution mass spectrometry was conducted on a Finnigan LCQ Mass Spectrometer. High resolution mass spectra were obtained on a Bruker Apex 7T Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer. Ionisation of samples was achieved using positive electron spray ionisation (ESI). Melting points were recorded on an Optimelt Automated Melting Point System from Stanford Research Systems. Elemental analyses were performed either by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand, or the Chemical Analysis Facility, Department of Molecular Sciences, Macquarie University, Australia.

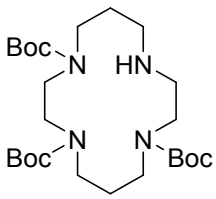
Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with caution.

2. Synthesis and characterisation



Scheme S1 – Synthetic route towards ligands **6-9**.

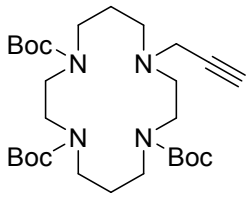
Tri-tert-butyl 1,4,8,11-tetraazacyclotetradecane-1,4,8-tricarboxylate **17**



To a solution of cyclam **1** (1.51 g, 7.54 mmol) and triethylamine (5.20 mL, 37.3 mmol) in anhydrous CH_2Cl_2 (300 mL) was added dropwise di-*tert*-butyl dicarbonate (2.95 g, 13.5 mmol) in anhydrous CH_2Cl_2 (90 mL) under N_2. After the addition was complete, the reaction mixture was cooled to -15 °C, and a second portion of di-*tert*-butyl dicarbonate (1.96 g, 8.98 mmol) in anhydrous CH_2Cl_2 (60 mL) was added. The reaction mixture was stirred at room temperature overnight and washed with 0.5 M Na_2CO_3 (2 × 150 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc ramping to EtOAc:CH_3OH = 9:1) to give **17** as a white foam (2.91 g, 77%).

$\boldsymbol{R_F}$ (EtOAc:CH_3OH = 9:1) 0.54. **m.p**. 46–47 °C. **IR** ν_{max}/cm^{-1} 2973, 2932, 2818, 1681, 1464, 1409, 1389, 1364, 1239, 1158. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 1.46 (s, 27H, 3 × C(CH_3)$_3$), 1.60-1.80 (m, 2H, $CH_2CH_2CH_2$), 1.80-2.10 (m, 2H, $CH_2CH_2CH_2$), 2.62 (t, 2H, *J* 5.6, CH_2NHCH_2), 2.78 (t, 2H, *J* 5.4, CH_2NHCH_2), 3.20-3.50 (m, 12H, 3 × CH_2N(Boc)CH_2) (one secondary amine proton signal (NH) not observed). **LRMS** (ESI+) *m/z* 501.3 [M+H]$^+$, 523.5 [M+Na]$^+$. The data are consistent with those previously reported.[1]

Tri-tert-butyl 11-(prop-2-yn-1-yl)-1,4,8,11-tetraazacyclotetradecane-1,4,8-tricarboxylate **18**

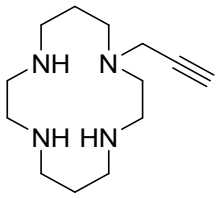


To a solution of tri-Boc cyclam **17** (437 mg, 0.873 mmol) in anhydrous CH_3CN (26 mL) were added Na_2CO_3 (370 mg, 3.49 mmol) and propargyl bromide (~80% in toluene, 156 μL, 1.05 mmol). The reaction mixture was heated at reflux under N_2 overnight. The insoluble salts were filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by

flash column chromatography (silica gel, EtOAc:hexane = 7:3) to give **18** as a white foam (446 mg, 95%).

$\boldsymbol{R}_{\mathbf{F}}$ (EtOAc:hexane = 7:3) 0.58. **m.p.** 47–48 °C. **IR** ν_{max}/cm^{-1} 3305, 3243, 2976, 2932, 2871, 2826, 1681, 1463, 1410, 1365, 1240, 1150. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 1.40 (s, 27H, 3 × $C(CH_3)_3$), 1.55–1.75 (m, 2H, $CH_2CH_2CH_2$), 1.75–1.95 (m, 2H, $CH_2CH_2CH_2$), 2.12 (s, 1H, C≡CH), 2.46 (t, 2H, *J* 5.4, $CH_2N(CH_2C{\equiv}CH)CH_2$), 2.55–2.70 (m, 2H, $CH_2N(CH_2C{\equiv}CH)CH_2$), 3.10–3.50 (br m, 14H, 3 × $CH_2N(Boc)CH_2$ & $NCH_2C{\equiv}CH$). **LRMS** (ESI+) *m/z* 539.4 $[M+H]^+$, 561.5 $[M+Na]^+$. The data are consistent with those previously reported.[2-3]

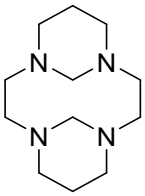
1-(Prop-2-yn-1-yl)-1,4,8,11-tetraazacyclotetradecane **6**



Propargyl-tri-Boc cyclam **18** (538 mg, 0.999 mmol) was deprotected in TFA/DCM (2 mL/10 mL) at room temperature for 3 days and concentrated under reduced pressure. The residue was dissolved in H_2O (1 mL), taken to pH 13-14 with 2 M NaOH and extracted with $CHCl_3$ (6 × 40 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give **6** as a pale yellow solid (221 mg, 93%).

m.p. 81–83 °C. **IR** ν_{max}/cm^{-1} 3279, 3215, 2925, 2881, 2816, 2096, 1688, 1465, 1120. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.68–1.78 (m, 4H, 2 × $CH_2CH_2CH_2$), 2.21 (t, 1H, *J* 2.1, C≡CH), 2.61–2.77 (m, 16H, $CH_2N(CH_2)CH_2$ & 3 × CH_2NHCH_2), 2.86 (br s, 3H, 3 × NH), 3.50 (d, 2H, *J* 2.1, $NCH_2C{\equiv}CH$). **^{13}C NMR** (75 MHz, CD_3CN) δ 26.7, 29.8, 40.7, 47.7, 49.0, 49.7, 49.9, 51.0, 52.2, 55.0, 74.5, 78.9 (one carbon signal overlapping or obscured). **LRMS** (ESI+) *m/z* 239.3 $[M+H]^+$, 277.1 $[M+K]^+$. **HRMS** (ESI+) *m/z* 239.22298 ($[M+H]^+$); calcd. for $C_{13}H_{27}N_4^+$ ($[M+H]^+$) 239.22302.

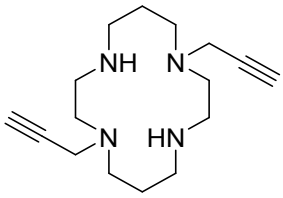
1,4,8,11-Tetraazatricyclo[9.3.1.14,8]hexadecane **19**



A solution of cyclam **1** (2.02 g, 10.1 mmo) in H_2O (100 mL) was cooled to -15 °C. Formaldehyde (37% in H_2O, 2 mL, 24 mmol) was added, and the solution stirred at room temperature overnight. The precipitate was filtered, washed with chilled H_2O (50 mL) and dried *in vacuo* to give **19** as a white solid (1.71 g, 76%).

m.p. 105–108 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.13–1.16 (m, 1H), 1.17–1.22 (m, 1H), 2.05–2.15 (m, 2H) (4H in total, 2 × $NCH_2CH_2CH_2N$), 2.30–2.46 (m, 4H), 2.62 (td, 4H, *J* 10.9 & 2.1), 2.78–2.86 (m, 4H), 2.90 (d, 2H, *J* 10.9, NCH_2N), 3.07–3.22 (m, 4H) (16H in total excluding peak at δ = 2.90, 2 × $CH_2NCH_2CH_2NCH_2$), 5.43 (dt, 2H, *J* 10.9 & 2.1, NCH_2N). **LRMS** (ESI+) *m/z* 225.1 $[M+H]^+$. The data are consistent with those previously reported.[4]

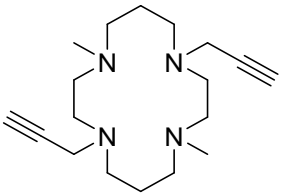
1,8-Di(prop-2-yn-1-yl)-1,4,8,11-tetraazacyclotetradecane **20**



To a solution of bridged cyclam **19** (1.49 g, 6.65 mmol) in anhydrous CH_3CN (50 mL) was added propargyl bromide (~80% in toluene, 3.70 mL, 32.7 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue washed with 3 M NaOH. The product was extracted from CH_2Cl_2 (3 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give **20** as a white solid (1.66 g, 90%).

m.p. 116–118 °C. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.73 (qn, 4H, *J* 5.3, 2 × $NCH_2CH_2CH_2N$), 2.16 (t, 2H, *J* 2.3, $NCH_2C{\equiv}CH$), 2.49–2.83 (m, 16H, 4 × CH_2NCH_2), 3.45 (d, 4H, *J* 2.3, 2 × $NCH_2C{\equiv}CH$). **LRMS** (ESI+) *m/z* 277.1 $[M+H]^+$. The data are consistent with those previously reported.[4]

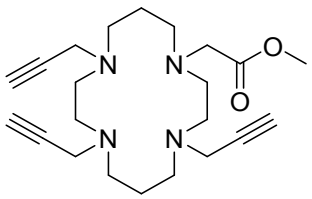
1,8-Dimethyl-4,11-di(prop-2-yn-1-yl)-1,4,8,11-tetraazacyclotetradecane **7**



To a solution of bis-propargyl cyclam **20** (739 mg, 2.67 mmol) in H_2O (4 mL) was added formic acid (6 mL) and formaldehyde (37% in H_2O, 4.00 mL, 48.0 mmol). The resultant mixture was heated at reflux for 24 hours. After cooling to room temperature, the product was extracted with $CHCl_3$ (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to give **7** as a white solid (736 mg, 90%).

m.p. 120–124 °C. **IR** ν_{max}/cm^{-1} 3290, 3163, 2941, 2781, 2080. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.59 (qn, 4H, *J* 6.4, 2 × $NCH_2CH_2CH_2N$), 2.10 (t, 1H, *J* 2.4, $NCH_2C{\equiv}CH$), 2.11–2.28 (br m, 6H, 2 × NCH_3), 2.28–2.47 (br m, 8H, 2 × $NCH_2CH_2CH_2N$), 2.47–2.68 (m, 8H, 2 × NCH_2CH_2N), 3.38 (d, 4H, *J* 2.4, 2 × $NCH_2C{\equiv}CH$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.7, 42.8, 43.4, 49.9, 54.0, 54.1, 72.9, 77.2, 78.7 (nine carbon signals overlapping or obscured). **LRMS** (ESI+) *m/z* 305.1 ($[M+H]^+$,100%). **HRMS** (ESI+) *m/z* 305.26982 $[M+H]^+$; calcd. for $C_{18}H_{33}N_4^+$ $[M+H]^+$ 305.26997.

Methyl 2-(4,8,11-tri(prop-2-yn-1-yl)-1,4,8,11-tetraazacyclotetradecan-1-yl)acetate **8**

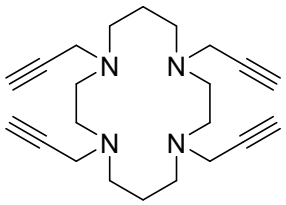


To a solution of cyclam **1** (1.00g, 5.02 mmol) and Na_2SO_4 (2.16 g, 15.2 mmol) in CH_3CN (350 mL), was slowly added propargyl bromide (~80% in toluene, 0.834 mL, 7.54 mmol) under N_2. The solution was heated at reflux overnight. After cooling to room temperature, a second portion of propargyl bromide was slowly added (~80% in toluene, 0.834 mL, 7.54 mmol) and the solution stirred overnight. Methyl bromoacetate (0.473 mL, 5.02 mmol) was slowly added, and the solution was heated at reflux overnight. Following cooling down to room temperature, the insoluble salts were removed *via* filtration and CH_3CN was removed *in vacuo*. The residue

was purified by flash column chromatography (silica gel, EtOAc ramping to EtOAc:CH_3OH = 9:1) to give **8** as a pale white solid (0.193 g, 10%).

m.p. 121–123 °C. **IR** ν_{max}/cm^{-1} 3291, 2946, 2819, 1736, 1680, 1462, 1410, 1364, 1241, 919, 803, 772, 646. **^{1}H NMR** (300MHz, $CDCl_3$): δ 1.57 (qn, 4H, *J* 6.6, 2 × $CH_2CH_2CH_2$), 2.04–2.15 (m, 3H, 3 × C≡C*H*), 2.24–2.72 (m, 16H, 4 × CH_2NCH_2), 3.30 (s, 2H, $NCH_2CO_2CH_3$), 3.35–3.40 (m, 6H, 3 × $NCH_2C{\equiv}CH$), 3.62 (s, 3H, CO_2CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.8, 24.1, 41.4, 41.6, 41.7, 48.5, 48.8, 48.9, 49.0, 49.1, 49.4, 49.7, 49.8, 50.2, 54.1, 71.8, 77.7, 171.0 (four carbon signals overlapping or obscured). **LRMS** (ESI+) *m/z* 387.1 $[M+H]^+$. **HRMS** (ESI+) *m/z* 387.27521 $[M+H]^+$; calcd. for $C_{22}H_{35}N_4O_2^+$ $[M+H]^+$ 387.27545.

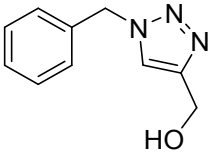
1,4,8,11-Tetra(prop-2-yn-1-yl)-1,4,8,11-tetraazacyclotetradecane **9**



Cyclam **1** (3.00 g, 15.0 mmol) and sodium hydroxide (6.12 g, 153 mmol) were dissolved in a solution of H_2O/CH_3CN (1:1, 250 mL). Propargyl bromide (~80% in toluene, 6.69 mL, 59.2 mmol) was added, and the resultant solution shaken vigorously at room temperature for 16 h. The precipitate was filtered, washed with chilled Et_2O (3 × 20 mL), passed through a silica gel plug (EtOAc), and concentrated *in vacuo* to give **9** as white prismatic crystals (3.84 g, 72%).

m.p. 135–137 °C. **IR** ν_{max}/cm^{-1} 3271, 3170, 2815, 2091, 1453, 1433, 1369, 1126, 1078, 990, 795, 748, 689, 649, 621, 554. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.59 (qn, 4H, *J* 6.6, 2 × $CH_2CH_2CH_2$), 2.16 (t, 4H, *J* 2.2, 4 × C≡C*H*), 2.55–2.61 (m, 16H, 4 × $CH_2N(CH_2C{\equiv}CH)CH_2$), 3.43 (d, 8H, *J* 2.4, 4 × $NCH_2C{\equiv}CH$). **LRMS** (ESI+) *m/z* 353.2 $[M+H]^+$. Characterisation accords with previously obtained data.[5]

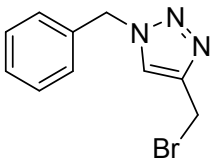
(1-Benzyl-1H-1,2,3-triazol-4-yl)methanol **21**



Benzyl azide **15** (628 µL, 5.03 mmol), propargyl alcohol (334 µL, 5.79 mmol), sodium ascorbate (953 mg, 4.81 mmol), DIPEA (1.74 mL, 10.0 mmol) and CuI (117 mg, 0.61 mmol) were dissolved in CH_3CN (5 mL), and the reaction mixture was stirred at room temperature for 21 h. H_2O (20 mL) was added, and the solution extraction with CH_2Cl_2 (4 × 20 mL). The organic phases were combined, washed with H_2O (2 × 15 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue taken up in a small amount of MeOH/CH_2Cl_2 (1:5) and passed through a short silica plug (50 g, eluting with 1–10% MeOH in EtOAc, 100 mL min^{-1}). Alcohol **21** was obtained following concentration of the filtrate under reduced pressure as white needles (756 mg, 80%).

m.p. 80-81 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.54 (s, 1H, O*H*), 4.77 (d, 2H, *J* 3.0, CH_2OH), 5.51 (s, 2H, Ar-CH_2-triazole), 7.26-7.44 (m, 6H, *J* 3.0, Ar-*H* & triazole-*H*). **LRMS** (ESI+) *m/z* 212.1 $[M+Na]^+$. The data are consistent with those previous reported.[6-7]

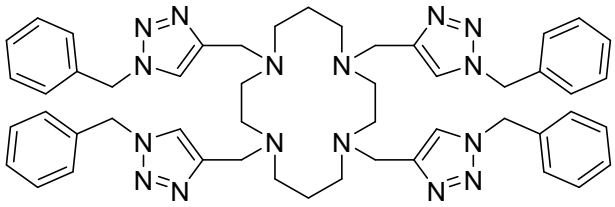
1-Benzyl-4-(bromomethyl)-1H-1,2,3-triazole **16**



Alcohol **21** (299 mg, 1.58 mmol), CBr_4 (802 mg, 2.42 mmol) and PPh_3 (619 mg, 2.36 mmol) were dissolved in CH_2Cl_2 (5 mL), and the solution was stirred at room temperature under N_2 for 18 h. Water (20 mL) was added, the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, washed with water (2 × 20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid residue was dissolved in CH_2Cl_2 (2 mL) and passed through a short silica plug (25 g, 1–10% EtOAc/CH_2Cl_2). Bromide **16** was obtained following concentration of the filtrate under reduced pressure as a white amorphous solid (304 mg, 76%).

m.p. 128-130 °C. **IR** υ_{max}/cm^{-1} 3117, 3074, 3027, 1455, 1341, 1214, 1129, 1051, 1031, 823, 745, 721, 700, 676, 649, 565. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.54 (s, 2H, CH_2Br), 5.52 (s, 2H, Ar-CH_2-triazole), 7.28-7.48 (m, 6H, *J* 3.6, Ar-*H* & triazole-*H*). **LRMS** (ESI+) *m/z* 301.1 $[M+Na]^+$. The data are consistent with those previously reported.[7]

1,4,8,11-Tetrakis((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1,4,8,11-tetraazacyclotetradecane
14

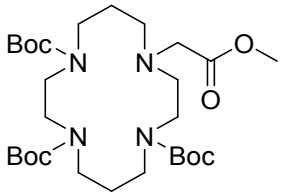


Synthetic Method 1: Tetra-alkyne **9** (105 mg, 0.30 mmol) and benzyl azide **15** (125 μL, 1.00 mmol) were added to a suspension of copper(I) iodide (78 mg, 0.41 mmol), sodium ascorbate (159 mg, 0.80 mmol), and DIPEA (348 μL, 2.00 mmol) in EtOAc (5 mL). The reaction mixture was stirred at room temperature for five days, filtered through Celite®, and washed with CH_2Cl_2 (60 mL). The filtrate was washed with an aqueous solution of Na_2(EDTA) (3 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was taken up in a small amount of CH_2Cl_2, passed through a short silica gel column (MeOH (containing 10% NH_3):CH_2Cl_2 = 1:50, ramping to 1:5), and recrystallised from EtOH to give **14** as fine white crystals (101 mg, 46%).

Synthetic Method 2: Cyclam **1** (61 mg, 0.30 mmol), bromide **16** (309 mg, 1.22 mmol) and sodium hydroxide (179 mg, 4.47 mmol) were dissolved in CH_3CN:H_2O (5 mL:5 mL), and the reaction mixture was shaken at room temperature overnight. The resulting precipitate was collected by filtration, washed with hexane (60 mL) and dried under vacuum. The crude product was dissolved in DCM, passed through a short silica gel column (MeOH (containing 10% NH_3):CH_2Cl_2 = 1:50, ramping to 1:5), and recrystallised from EtOH to give **14** as fine white crystals (190 mg, 71%).

m.p. 185–188 °C. **IR** ν_{max}/cm^{-1} 3327 (br), 1634. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55–1.65 (4H, m, 2 × $CH_2CH_2CH_2$), 2.40–2.46 (16H, m, 2 × $CH_2CH_2CH_2$ & 2 × NCH_2CH_2N), 3.43 (8H, s, 4 × NCH_2-triazole), 5.47 (8H, s, 4 × benzene-CH_2-triazole), 7.21–7.36 (24H, m, benzene-*H* & triazole-*H*). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.5, 49.5, 50.7, 51.4, 54.1, 122.7, 128.1, 128.8, 129.2, 135.1, 145.7 (thirty nine carbon signals overlapping or obscured). **LRMS** (ESI+) *m/z* 885.6 $[M+H]^+$. **HRMS** (ESI+) 885.52596 $[M+H]^+$; calcd. for $C_{50}H_{61}N_{16}^+$ $[M+H]^+$ 885.52577.

*Tri-tert-butyl 11-(2-methoxy-2-oxoethyl)-1,4,8,11-tetraazacyclotetradecane- 1,4,8-tricarboxylate **10***



To a solution of tri-Boc cyclam **17** (1.00 g, 2.00 mmol) in anhydrous CH_3CN (30 mL) were added Na_2CO_3 (422 mg, 3.98 mmol) and methyl bromoacetate (400 μL, 4.22 mmol). The reaction mixture was heated at reflux overnight. The insoluble salts were filtered, and the filtrate concentrated *in vacuo*. The oily residue was purified by flash column chromatography (silica gel, EtOAc:hexane = 1:1) to give **10** as a white foam (916 mg, 80%) following trituration with Et_2O.

m.p. 42–44 °C. **IR** ν_{max}/cm^{-1} 3291, 2946, 2819, 1736. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 1.38 (s, 27H, 3 × $C(CH_3)_3$), 1.59 (m, 2H, $NCH_2CH_2CH_2N$), 1.82 (m, 2H, $NCH_2CH_2CH_2N$), 2.56 (m, 2H, $CH_2N(CH_2CO_2CH_3)CH_2$), 2.74 (m, 2H, $CH_2N(CH_2CO_2CH_3)CH_2$), 3.15–3.30 (m, 14H, 3 × $CH_2N(Boc)CH_2$ & $NCH_2CO_2CH_3$), 3.60 (s, 3H, CO_2CH_3). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 27.4, 44.2, 46.1 50.2, 78.6, 154.5, 170.4 (twenty one carbon signals overlapping or obscured). **LRMS** (ESI+) *m/z* 573.1 $[M+H]^+$, 595.1 $[M+Na]^+$. **HRMS** (ESI+) *m/z* 573.38550 $[M+H]^+$, 595.36737 $[M+Na]^+$; calcd. for $C_{28}H_{52}N_4O_8$ $[M+H]^+$ 573.38579, $[M+Na]^+$ 595.36774.

3. Job's Plots

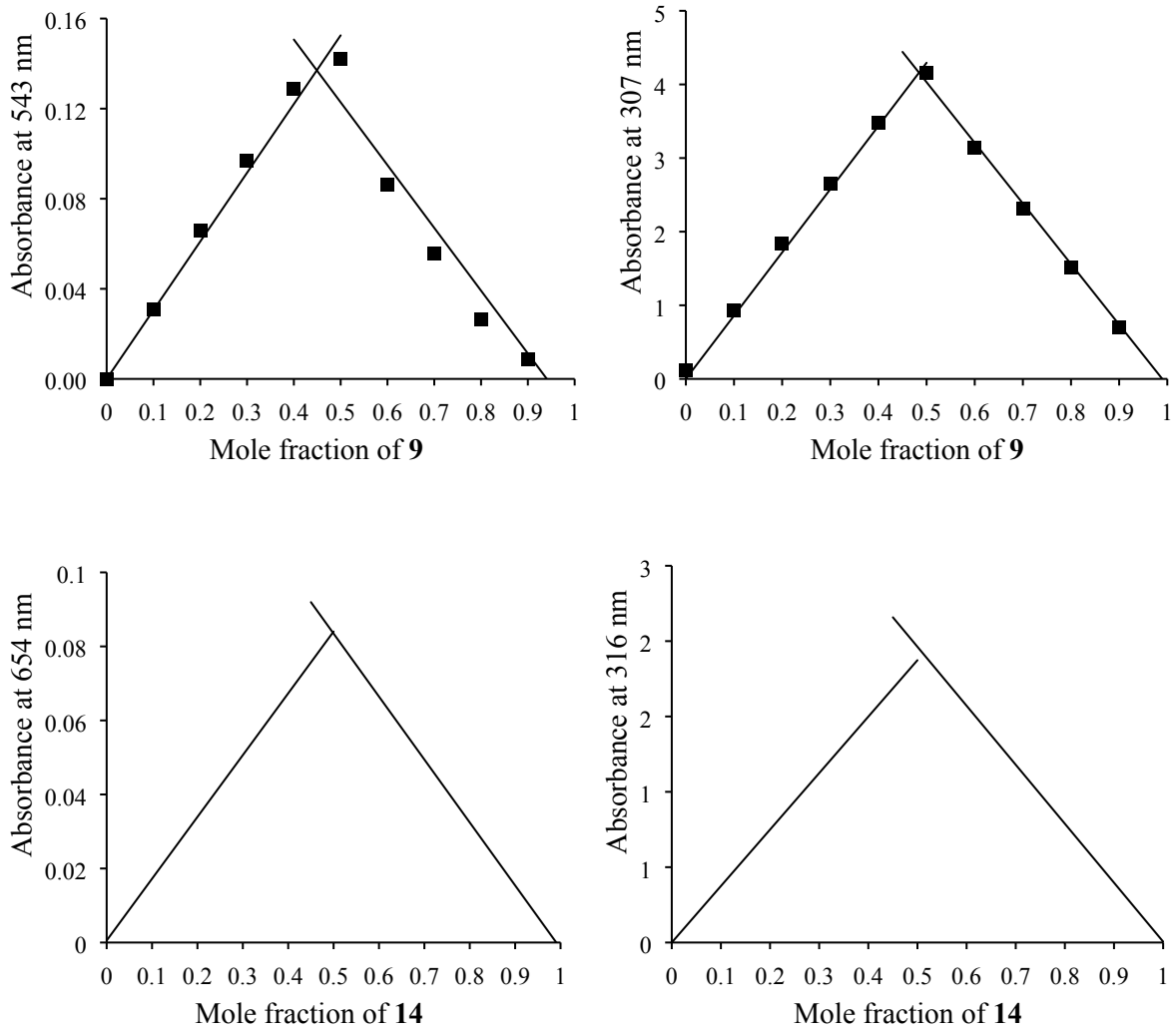


Figure S1 – *Job's plots* showing the 1:1 stoichiometry of the binding of ligands **9** and **14**, with $Cu(ClO_4)_2$.

4. ^{1}H and ^{13}C NMR Spectra of Novel Compounds

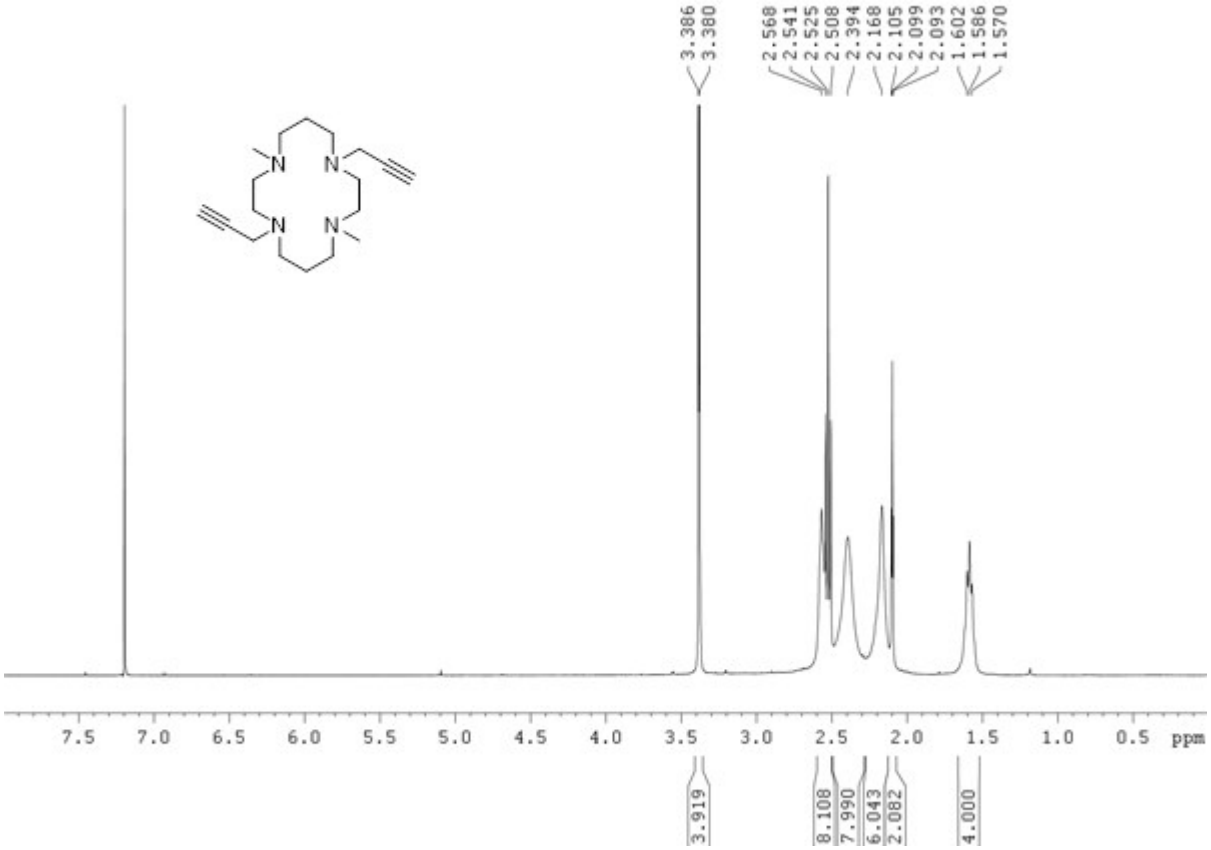


Figure S2 – ^{1}H NMR spectrum (400 MHz) of **7** in $CDCl_3$.

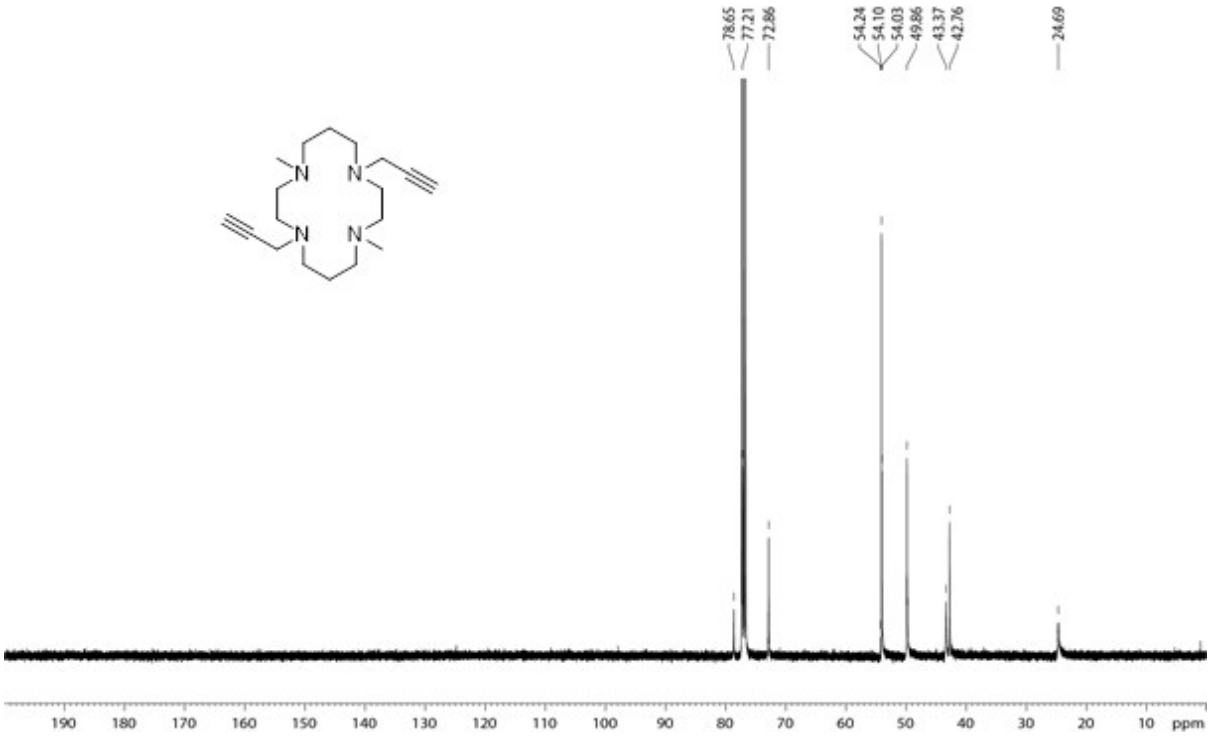


Figure S3 – ^{13}C NMR spectrum (100 MHz) of **7** in $CDCl_3$.

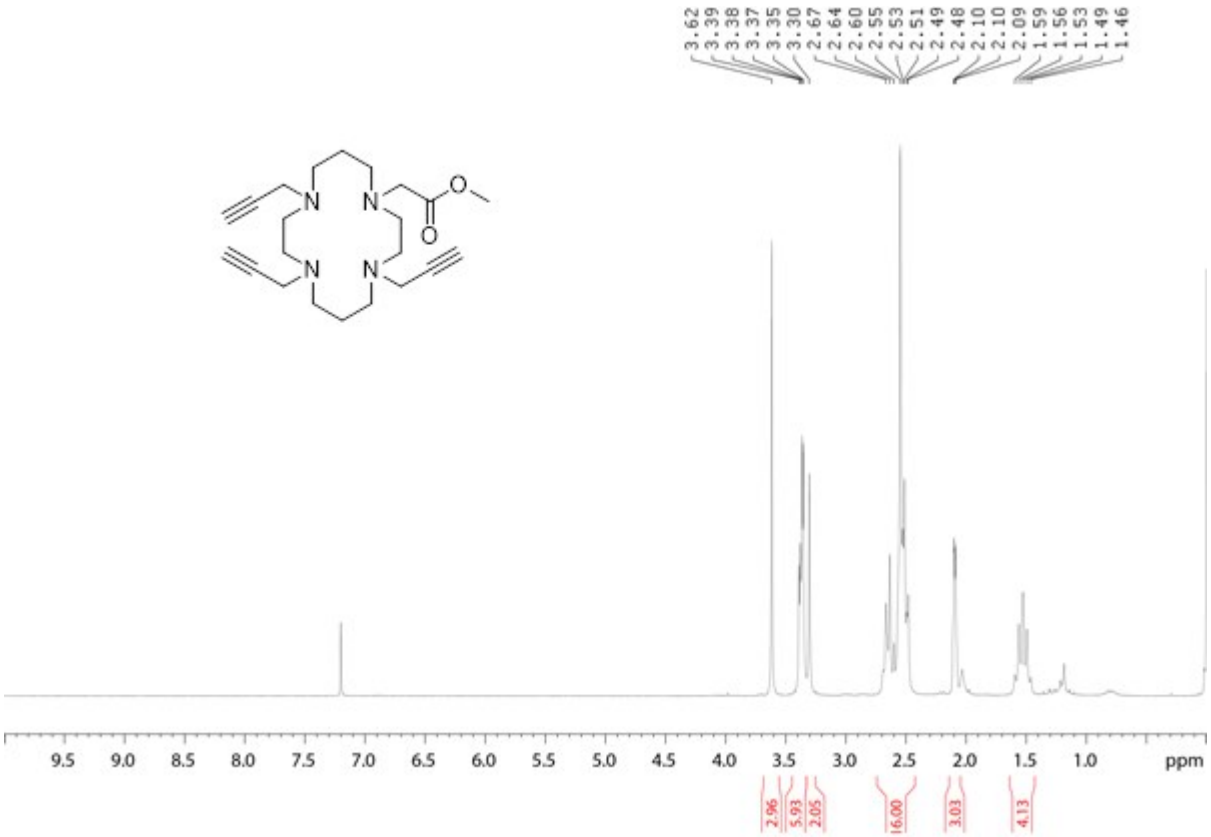


Figure S4 – ^{1}H NMR spectrum (300 MHz) of **8** in $CDCl_3$.

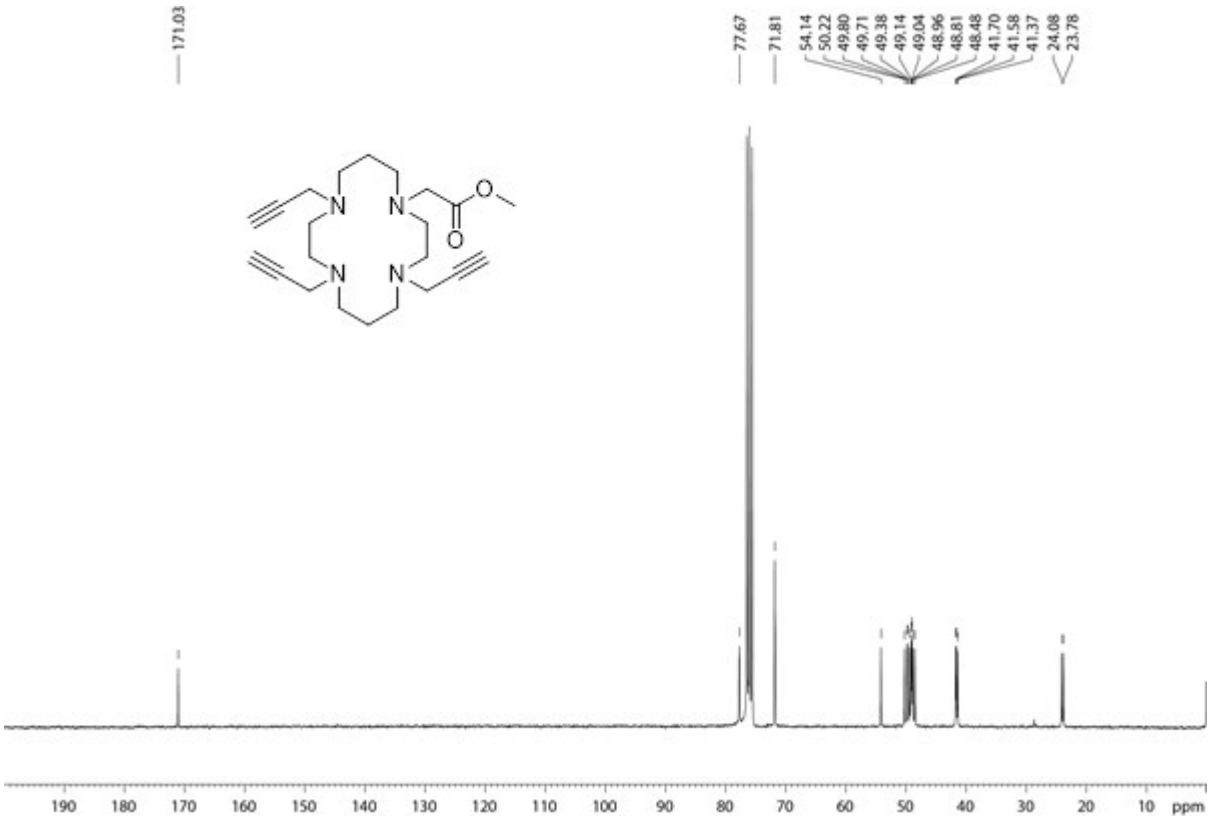


Figure S5 – ^{13}C NMR spectrum (75 MHz) of **8** in $CDCl_3$.

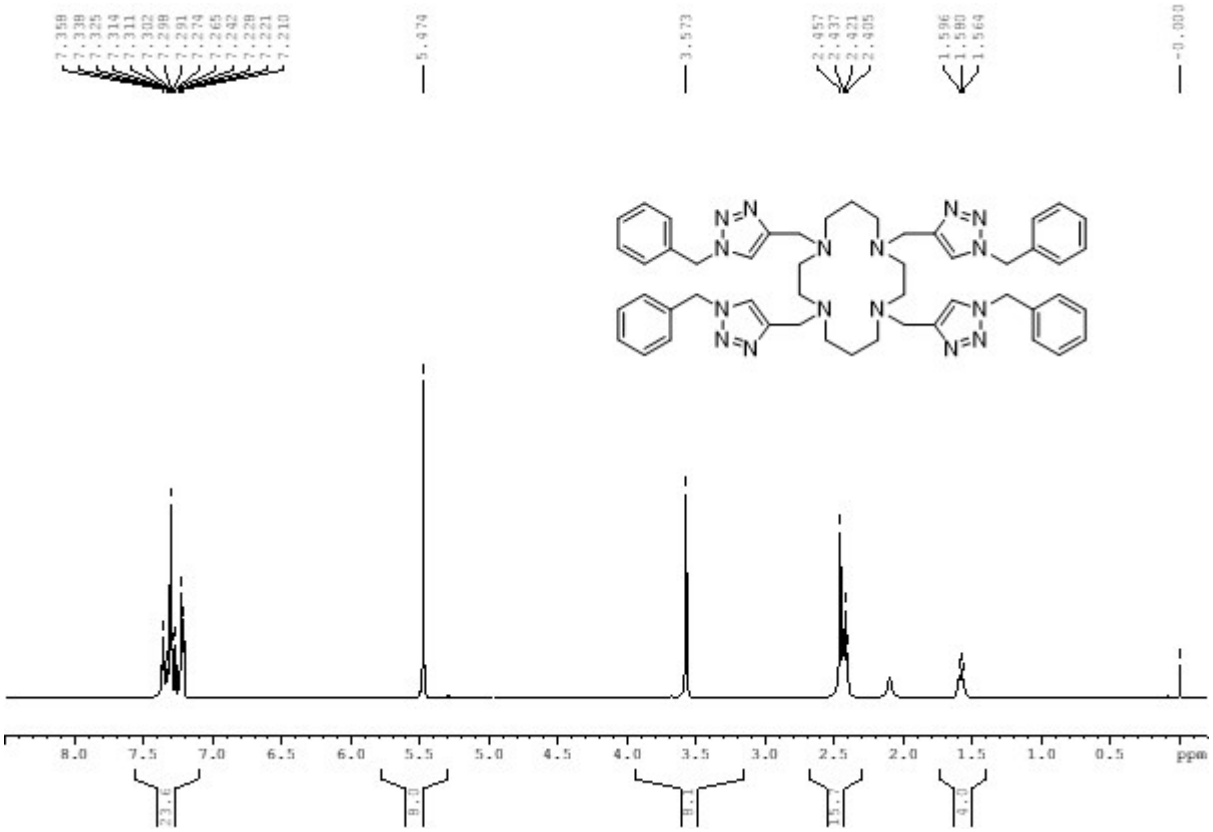


Figure S6 – ^{1}H NMR spectrum (400 MHz) of **14** in $CDCl_3$.

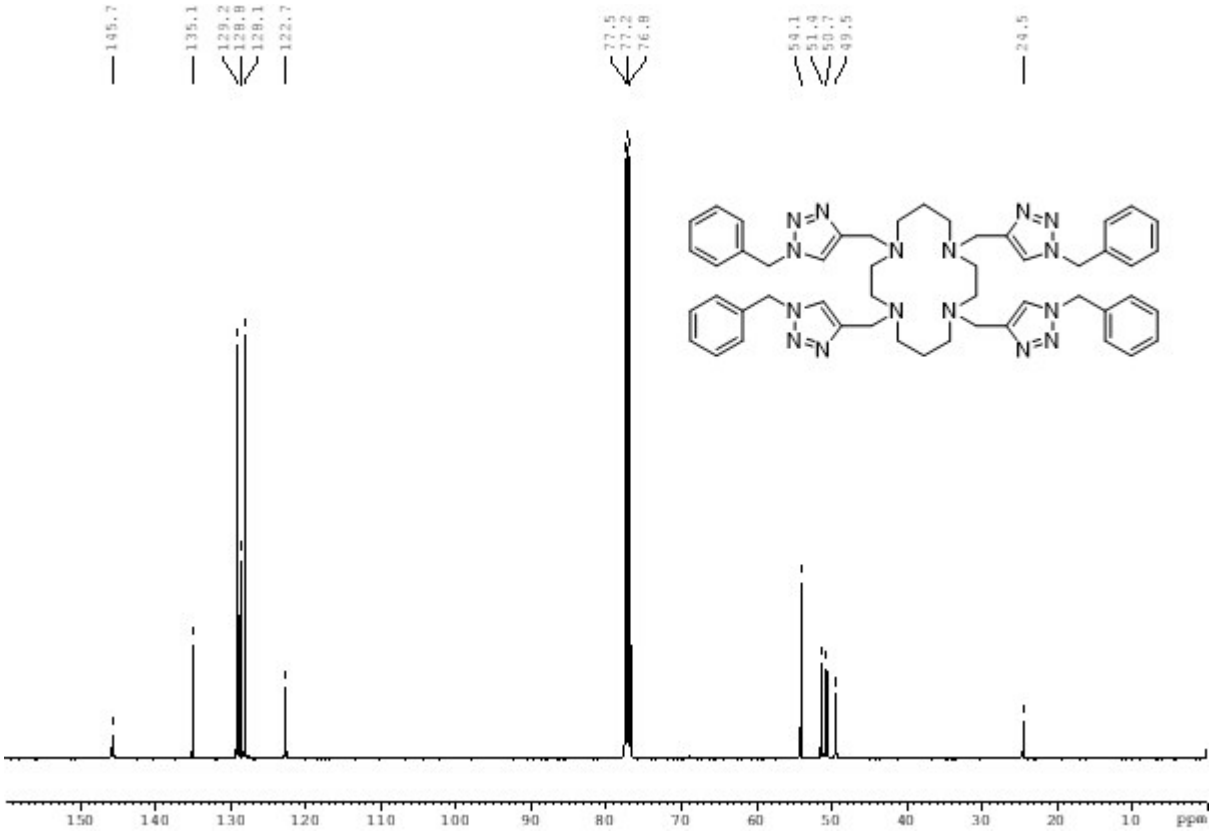


Figure S7 – ^{13}C NMR spectrum (100 MHz) of **14** in $CDCl_3$.

5. High Resolution Mass Spectra of Cu(13)

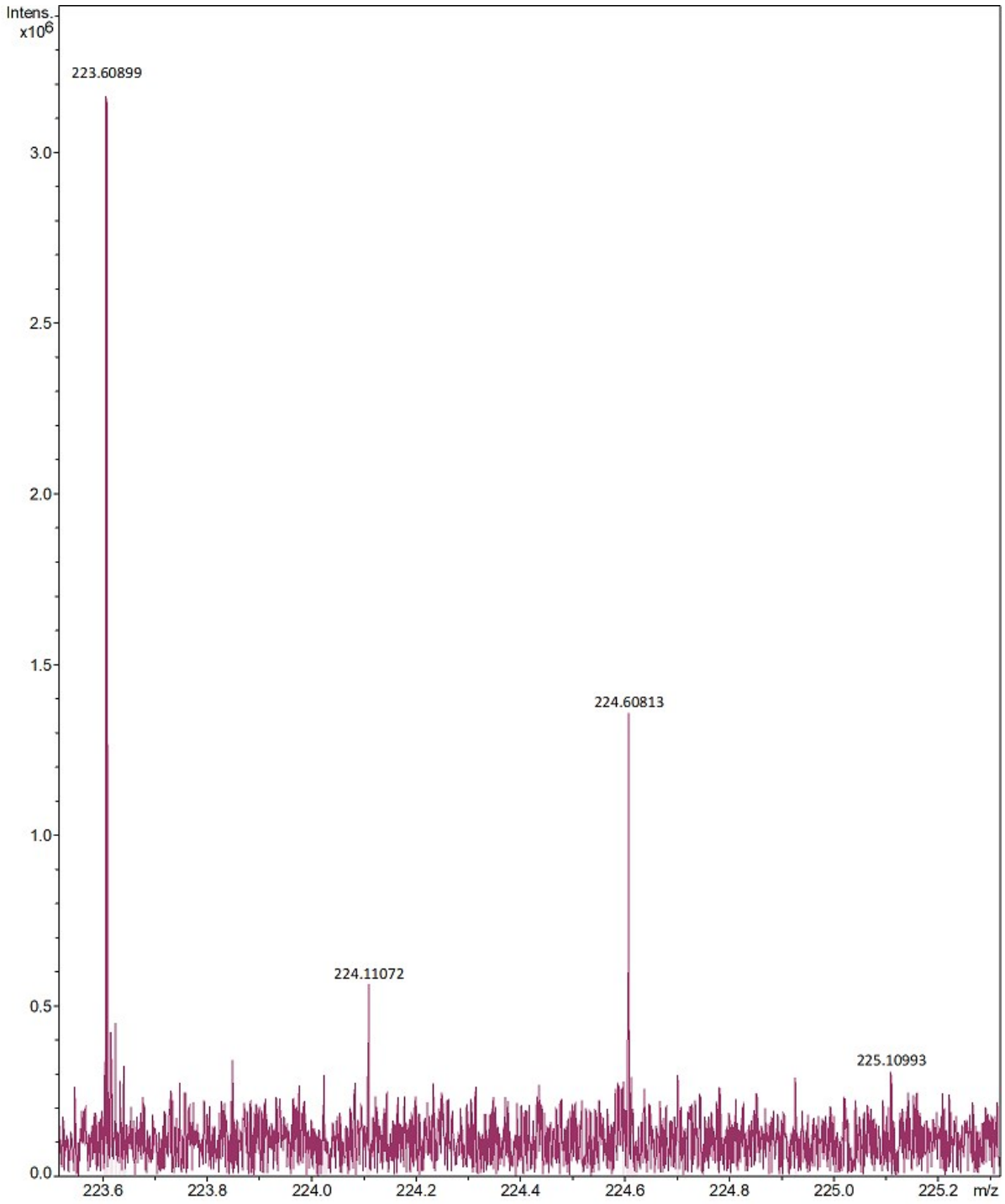


Figure S8 – High Resolution Mass Spectrum of Cu(**13**). Theoretical *m/z* distribution for $C_{23}H_{36}CuN_4O^{2+}$: 223.60871, 224.11039, 224.60780, 225.10948. Found: 223.60899, 224.11072, 224.60813, 225.10993.

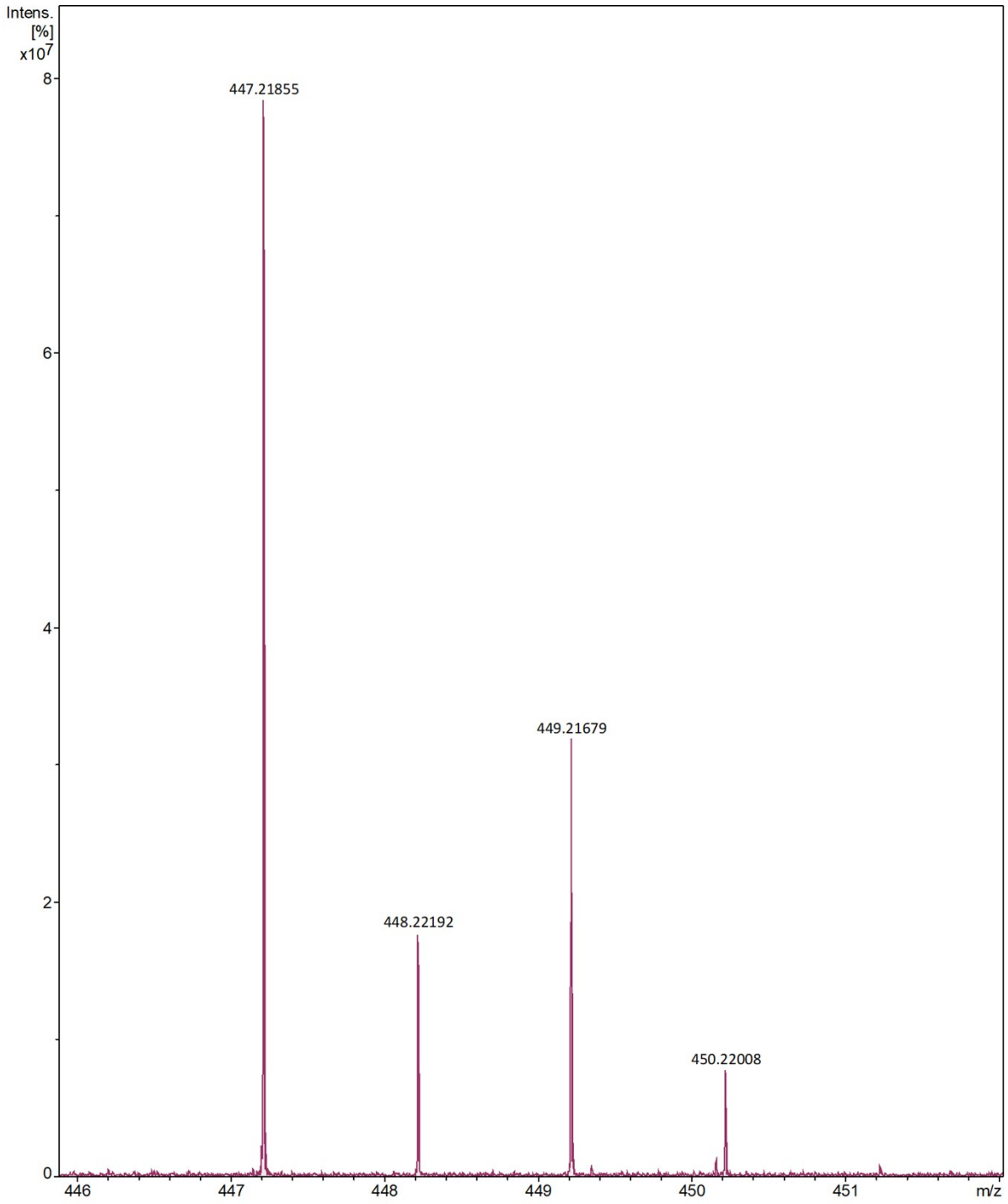


Figure S9 – High Resolution Mass Spectrum of Cu(**13**). Theoretical *m/z* distribution for $C_{23}H_{36}CuN_4O^+$: 447.21796, 448.22132, 449.21616, 450.21951. Found: 447.21855, 448.22192, 449.21679, 450.22008.

6. UV-*vis* spectroscopic assay of Cu(9)$(ClO_4)_2$ over time

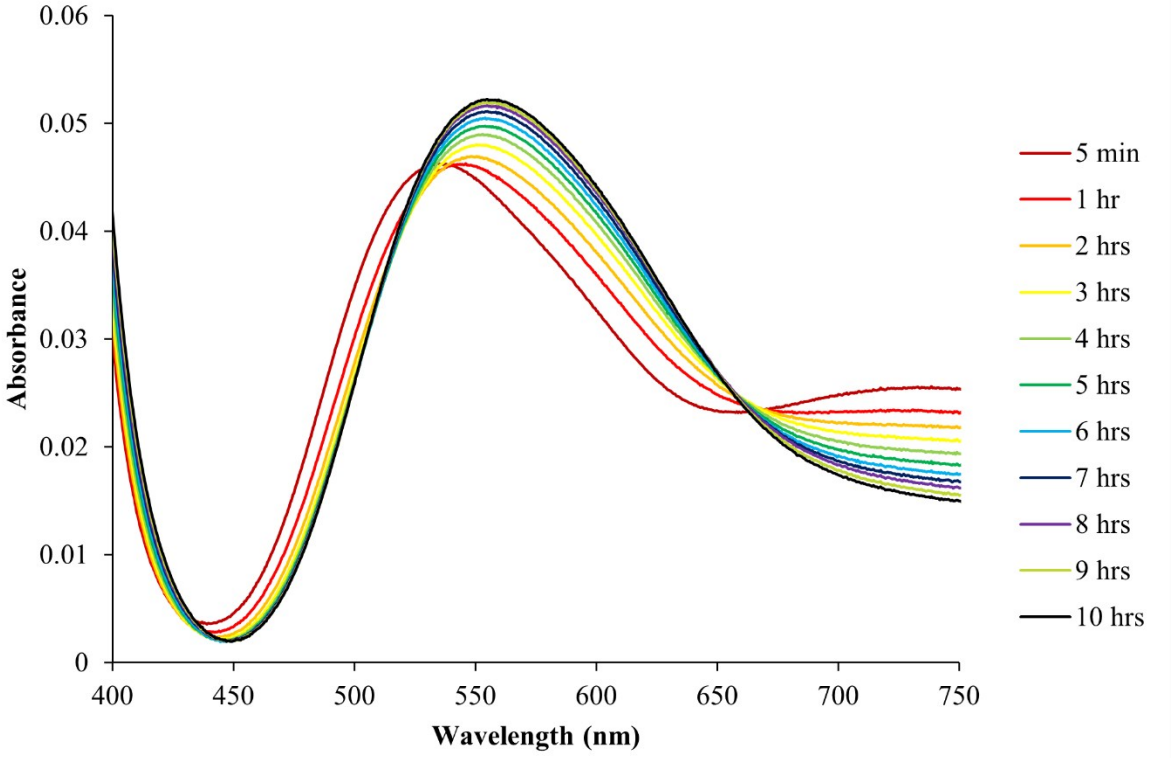


Figure S10 – UV-*vis* spectroscopic assay of Cu(**9**)$(ClO_4)_2$ (0.22 mM) in MeOH at 25 °C. Measurements taken in 1 hour intervals over 10 hours.

7. References

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