Organosilver(I) framework assembly with trifluoroacetate and enediyne-functionalized alicycles

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Supplementary Material

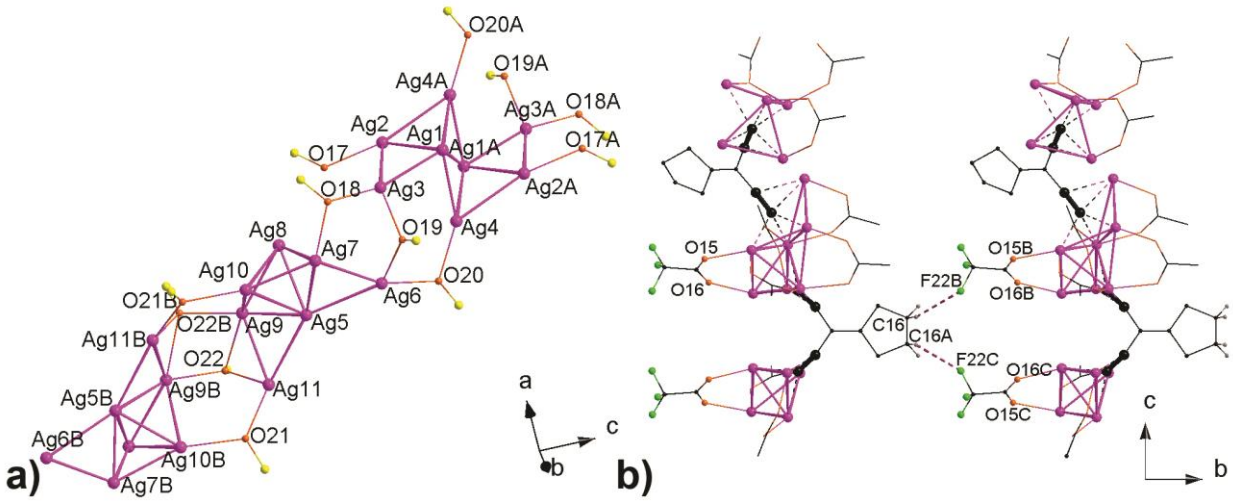


Figure S1. (a) Perspective view of the coordination silver-organic chain in (I). Symmetry code: A: 1.5–*x*, 0.5–*y*, 1–*z*; B: 1–*x*, *y*, 0.5–*z*. (b) Perspective view of the inter-association between adjacent silver-organic chains in (I). Symmetry code: A: 1–*x*, *y*, 0.5–*z*; B: *x*, 1+*y*, *z*; C: 1–*x*, 1+*y*, 0.5–*z*.

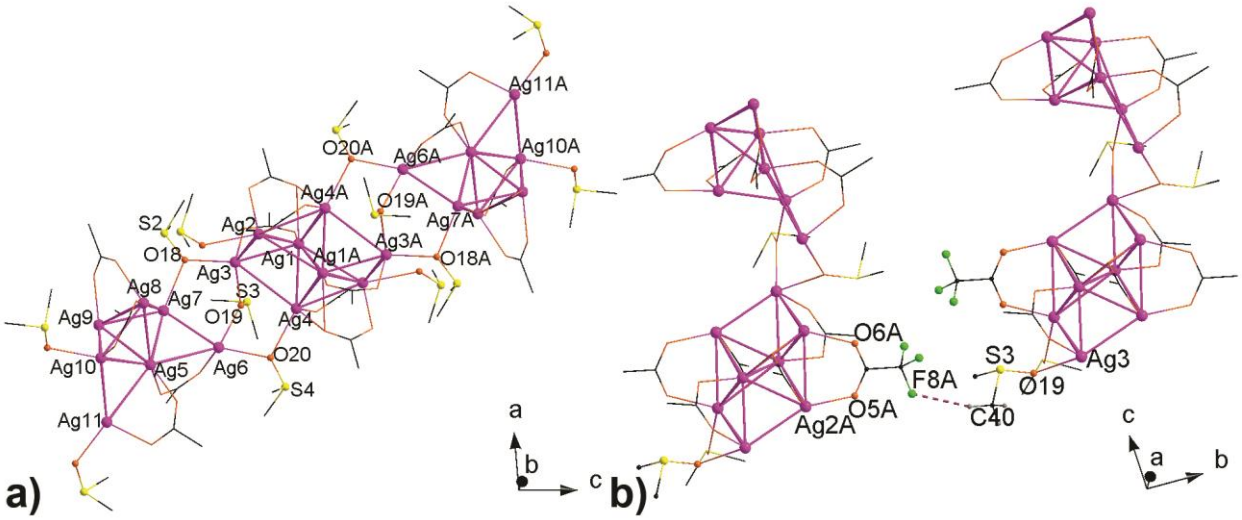


Figure S2. (a) Perspective view of the coordination silver-organic chain in (II). Symmetry code: A: 1.5–*x*, 1.5–*y*, 1–*z*. (b) Perspective view of the inter-association between adjacent silver-organic chains in (II). Symmetry code: A: *x*, –1+*y*, *z*; B: 1.5–x, 0.5–y, 1–z.

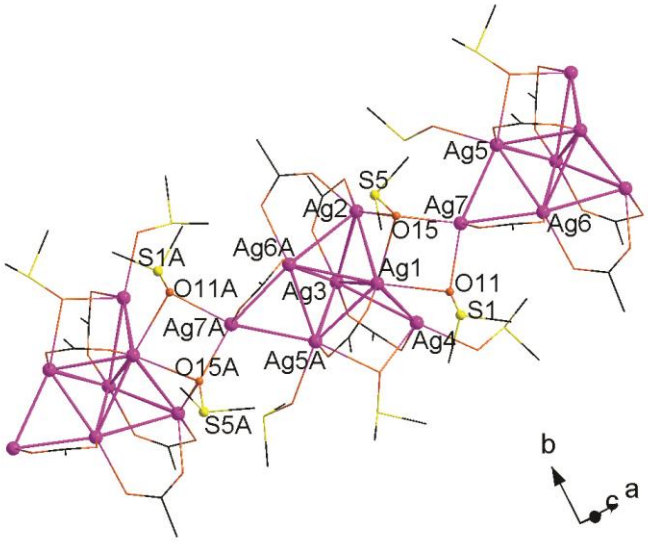


Figure S3. Perspective view of the coordination silver-organic chain in (III). Symmetry code: A: –0.5+*x*, 0.5–*y*, –0.5+*z*.

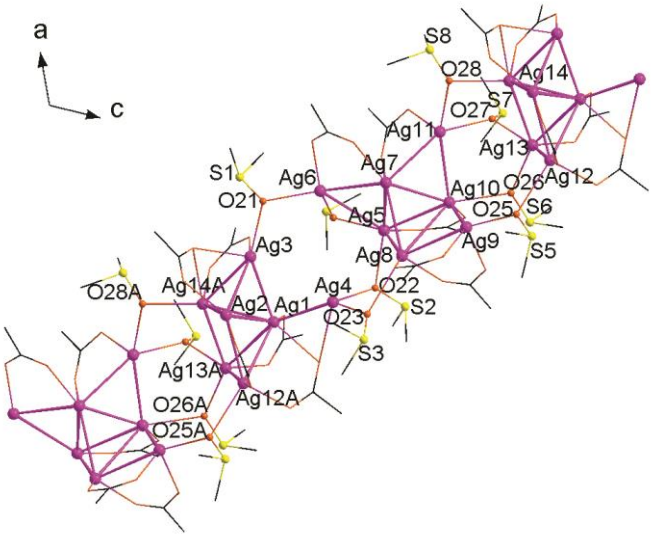


Figure S4. Perspective view of the coordination silver-organic chain in (IV). Symmetry code: A: –1+*x*, –1+*y*, –1+*z*.

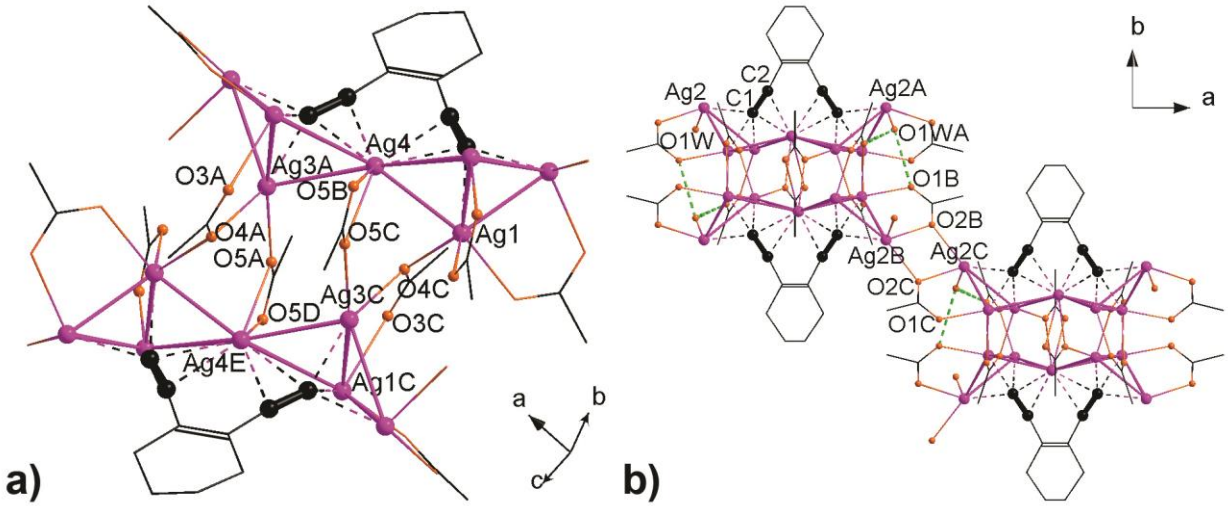


Figure S5. a) Perspective view of a portion of the coordination silver-organic chain along the *a*-axis in (V). Symmetry code: A: 1–*x*, *y*, 1.5–*z*; B: 1–*x*, –*y*, 1–*z*; C: *x*, –*y*, 0.5+*z*; D: *x*, *y*, 1+*z*; E: 1–*x*, –*y*, 2–*z*. b) Perspective view of the crystal packing in (V), showing all notable hydrogen bonds. Symmetry code: A: 1–*x*, *y*, 1.5–*z*; B: 1–*x*, –*y*, 2–*z*; C: 0.5+*x*, –0.5+*y*, 1+*z*.

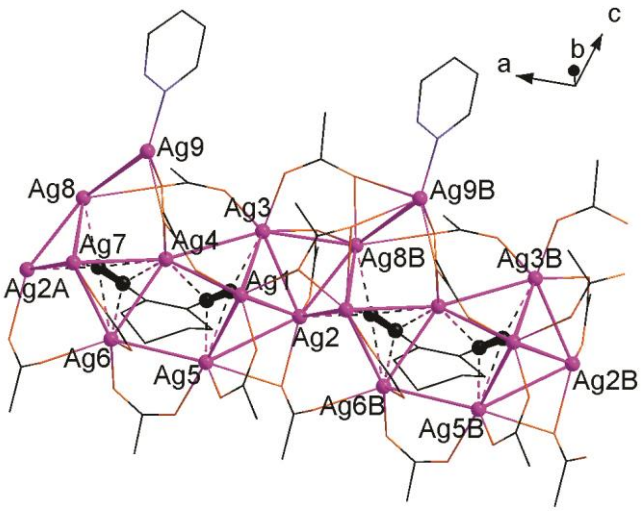


Figure S6. Perspective view of a portion of the 1-D silver chain in (VI) along the *a*-axis. Symmetry code: A: 1+*x*, *y*, *z*; B: –1+*x*, *y*, *z*.

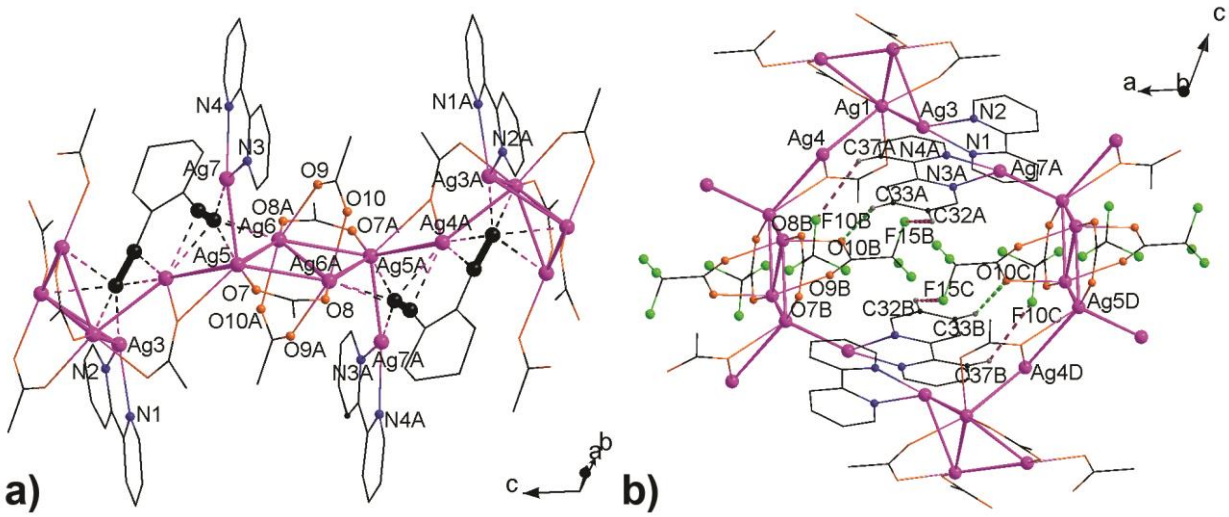


Figure S7. (a) Perspective view of a portion of the 1-D silver chain in (VII) along the *c*-axis. Symmetry code: A: –*x*, –*y*, 1–*z*. (b) Perspective view of the interconnection between adjacent silver chains in (VII) through H-bonds. Symmetry code: A: –1+*x*, *y*, *z*; B: –*x*, –*y*, 1–*z*; C: –1+*x*, *y*, *z*; D: –1–*x*, –*y*, 1–*z*.

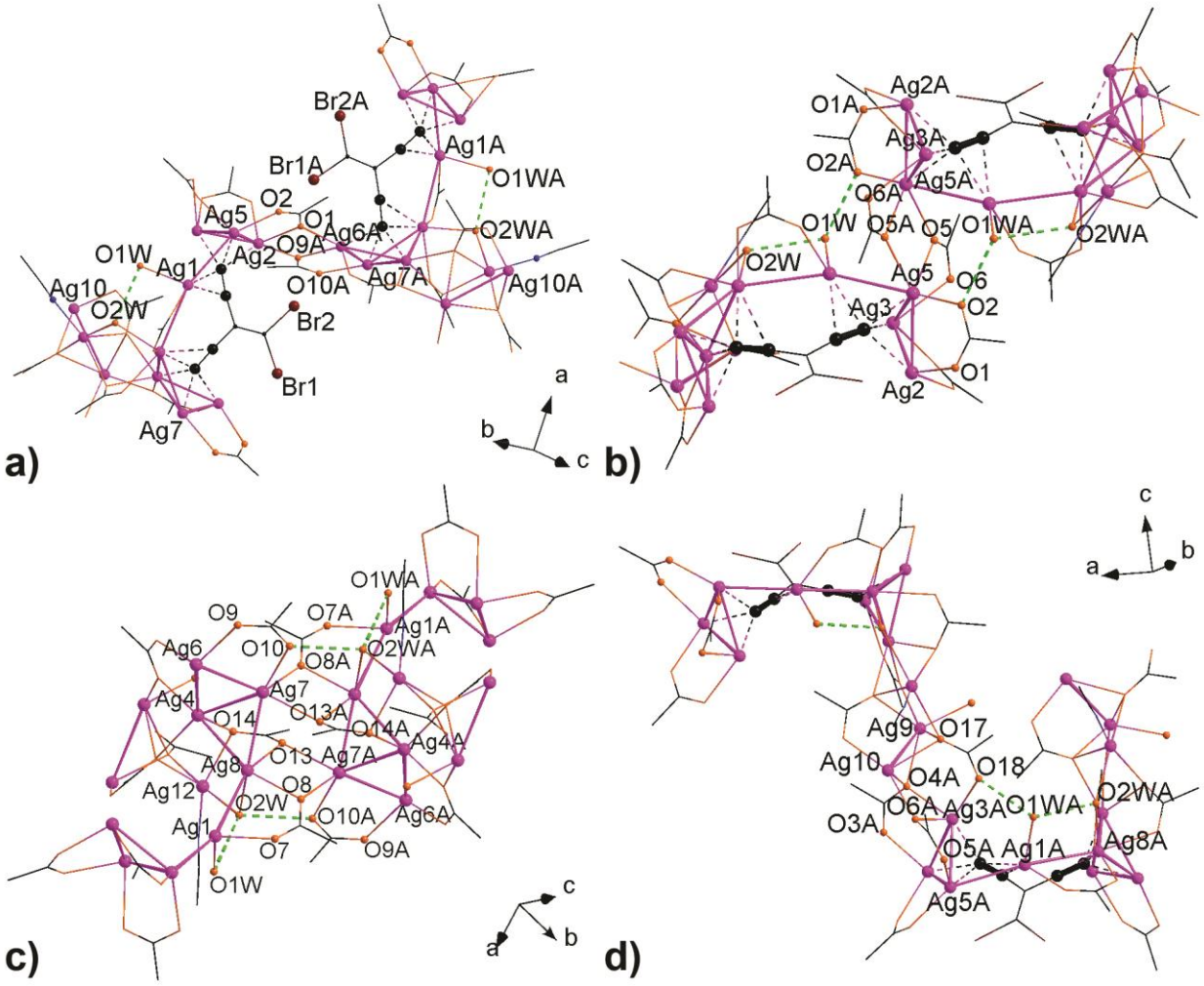
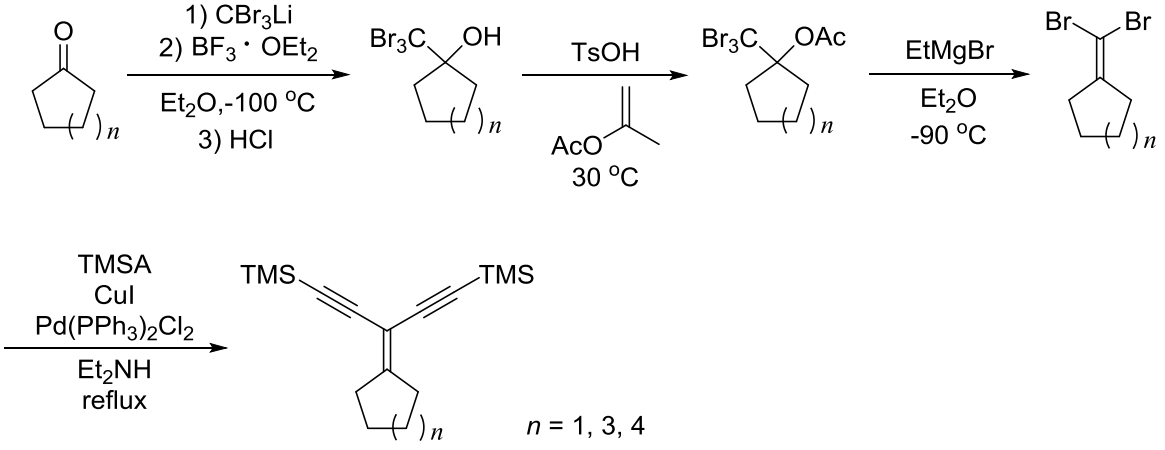


Figure S8. (a) Perspective view of a portion of the coordination network structure in (VIII). Symmetry code: A: 0.5+*x*, 0.5–*y*, 1–*z*. (b) Perspective view of a portion of the coordination network structure in (VIII). Symmetry code: A: 1–*x*, 1–*y*, 1–*z*. (c) Perspective view of a portion of the coordination network structure in (VIII). Symmetry code: A: –*x*, 1–*y*, 1–*z*. d) Perspective view of a portion of the coordination network structure in (VIII). Symmetry code: A: –0.5+*x*, *y*, 0.5–*z*.

Synthesis of ligands H_2L1-H_2L6

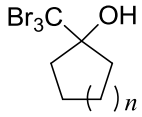
General Information

All reagents and solvents used were reagent grade. Further purification and drying followed the guidelines of Armarego[1] when necessary. Organic solvents were concentrated under reduced pressure on a rotary evaporator. Chromatographic purification of the products was performed on Macherey Nagel Kieselgel 60M (230-400 mesh). Thin-layer chromatography (TLC) was conducted on E. Merck silica gel 60 F254 (0.1 mm thickness) coated on aluminum plates. Visualization of the developed chromatogram was performed by a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. Melting points (uncorrected) were measured with a Reichert apparatus in degrees Celsius. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker ADVANCE-III NMR spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). All NMR measurements were carried out at room temperature in deuterated solution and were internally referenced to residual proton solvent signals (note: $CDCl_3$ referenced at δ 7.26 in 1H, and δ 77.16 for central line of the triplet in ^{13}C). Data for 1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, brs = broad singlet, dd = doublet of doublets, m = multiplet), integration, coupling constant (Hz) and assignment.



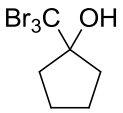
Scheme 1. Synthetic scheme of ligands trimethylsilyl-protected *L1*, *L3* and *L4* ligands.

1.1 General Procedure I for synthesis of 1-(tribromomethyl)cycloalkan-1-ol (n = 1, 3, 4)



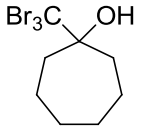
The synthetic procedure was according to the literature.[2] Anhydrous Et_2O (20 mL) was injected to a degassed 100 mL three-necked round bottom flask, followed by the addition of diisopropylamine (1.7 mL, 12.0 mmol) and the reaction mixture was cooled to –30°C. A solution of *n*-Butyl lithium (2.5 M in hexanes, 4.8 mL, 12.0 mmol) was added dropwise to the reaction mixture. The mixture was warmed to 0°C for 15 mins and then cooled to –100°C. After stirring at –100°C, $CHBr_3$ (1.05 mL, 12.0 mmol) was added dropwise over 15 mins. A solution of ketone (10.0 mmol) in anhydrous Et_2O (5 mL) was injected slowly, followed by the addition of $BF_3{\cdot}Et_2O$ (1.2 mL, 10.0 mmol). After reacting at –90°C for 4 hrs, aq. 1.0 M HCl (20 mL) was added and the reaction mixture was warmed to 23°C. The organic layer was first separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layer was sequentially washed with aq. 0.5 M HCl (15 mL), sat. $NaHCO_3$ solution (15 mL) and sat. NaCl solution (15 mL). After that, the organic layer was dried over $MgSO_4$ and concentrated in vacuo to provide the crude product for next step directly.

1.1.1 Synthesis of 1-(tribromomethyl)cyclopentan-1-ol



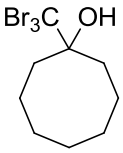
1-(Tribromomethyl)-cyclopentan-1-ol was prepared from cyclopentanone according to general procedure I. The isolated crude product is colorless oil (3.38 g). Yield: ~100%; R_f = 0.2 (DCM/*n*-hexanes, 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.71-1.84 (m, 6H), 2.25-2.29 (m, 2H), 3.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 37.5, 60.6, 92.7.

1.1.2 Synthesis of 1-(tribromomethyl)cycloheptan-1-ol



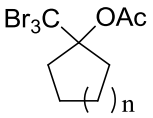
1-(Tribromomethyl)-cycloheptan-1-ol was prepared from cycloheptanone according to general procedure I. The isolated crude product is yellowish oil (3.94 g). Yield: ~100%; R_f = 0.5 (DCM/*n*-hexanes, 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.54-1.77 (m, 8H), 2.14-2.20 (m, 2H), 2.29-2.36 (m, 2H), 2.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.4, 28.7, 35.7, 67.6, 84.2.

1.1.3 Synthesis of 1-(tribromomethyl)cyclooctan-1-ol



1-(Tribromomethyl)-cyclooctan-1-ol was prepared from cyclooctanone according to general procedure I. The isolated crude product is yellowish oil (4.34 g). Yield: ~100%; R_f = 0.5 (DCM/*n*-hexanes, 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.51-1.87 (m, 10H), 2.28-2.42 (m, 4H), 2.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.7, 24.4, 27.7, 32.3, 67.9, 83.6.

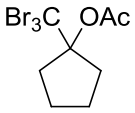
1.2 General Procedure II for synthesis of 1-(tribromomethyl)-1-acetoxycycloalkane (n = 1, 3, 4)



The synthetic procedure was according to the literature.[2] The crude 1-(tribromomethyl)-cycloalkan-1-ol (10.0 mmol) was first dissolved in isopropenyl acetate (45 mL). TsOH (5.5 g, 29 mmol) was added to the solution at 30°C. The mixture was kept stirring at 30°C until TLC indicating the absence of starting material (4 to 24 hrs). Isopropenyl acetate was removed under vacuum. Et_2O (30 mL) was added to the mixture and the solution was cooled to 0°C

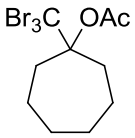
with stirring. Sat. $NaHCO_3$ solution (~ 100 mL) was added slowly until no effervescence was observed and the solution was stirred for another 30 mins at 23°C. The separated aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed sequentially with sat. $NaHCO_3$ solution (15 mL) and sat. NaCl solution (15 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexanes/dichloromethane (1:1) as eluent.

1.2.1 Synthesis of 1-(tribromomethyl)-1-acetoxycyclopentane



1-(Tribromomethyl)-1-acetoxycyclopentane was prepared from 1-(tribromomethyl)-cyclopentan-1-ol according to general procedure II. The product was purified as white solids (3.06 g). Yield: 81%; R_f = 0.8 (DCM/*n*-hexanes, 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.94-1.97 (m, 2H), 2.12 (s, 3H), 2.28-2.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.4, 27.6, 36.8, 55.4, 100.1, 169.1.

1.2.2 Synthesis of 1-(tribromomethyl)-1-acetoxycycloheptane

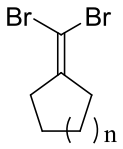


1-(Tribromomethyl)-1-acetoxycycloheptane was prepared from 1-(tribromomethyl)-cycloheptan-1-ol according to general procedure II. The product was isolated as pale yellowish solids (3.59 g). Yield: 88%; R_f = 0.9 (DCM/*n*-hexanes, 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.56-1.88 (m, 8H), 2.13 (s, 3H), 2.31-2.37 (m, 2H), 2.83-2.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.2, 24.1, 29.1, 35.4, 58.0, 94.8, 169.3.

1.2.3 Synthesis of 1-(tribromomethyl)-1-acetoxycyclooctane

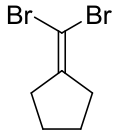
1-(Tribromomethyl)-1-acetoxycyclooctane was prepared from 1-(tribromomethyl)-cyclooctan-1-ol according to general procedure II. The product was purified as pale yellowish solids (3.7 g). Yield: 88%; R_f = 0.9 (DCM/*n*-hexanes, 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.56-1.95 (m, 10H), 2.11 (s, 3H), 2.28-2.33 (m, 2H), 2.96-3.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.6, 23.1, 23.7, 27.7, 31.2, 57.7, 93.4, 168.9.

1.3 General Procedure III for synthesis of (dibromomethylene)cycloalkane (n = 1, 3, 4)



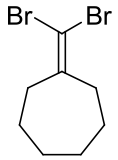
The synthetic procedure was according to the literature.[2] Freshly prepared ethylmagnesium bromide solution[3] (22.0 mmol in 20 mL Et_2O) was cooled to –90°C. A solution of 1-(tribromomethyl)-1-acetoxycycloalkane (5.5 mmol) in anhydrous Et_2O (5 mL) was slowly dropped to the reaction mixture. The reaction mixture was left stirring at –90°C for 30 mins. Aqueous 1.0 M HCl (15 mL) was added to quench the reaction. The mixture was then warmed to 23°C and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with sat. $NaHCO_3$ solution (15 mL) and followed by sat. NaCl solution (15 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexanes as eluent.

1.3.1 Synthesis of (dibromomethylene)cyclopentane



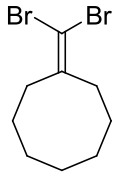
(Dibromomethylene)cyclopentane was prepared from 1-(tribromomethyl)-1-acetoxycyclopentane according to general procedure III. The product was purified as colorless oil (1.26 g). Yield: 65%; R_f = 0.8 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.78-1.81 (m, 4H), 2.30 (t, J = 0.018, 7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.3, 36.4, 78.5, 150.9.

1.3.2 Synthesis of (dibromomethylene)cycloheptane



(Dibromomethylene)cycloheptane was prepared from 1-(tribromomethyl)-1-acetoxycycloheptane according to general procedure III. The product was purified as pale yellow oil (1.53 g). Yield: 65%; R_f = 0.9 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50-1.51 (m, 4H), 1.63-1.64 (m, 4H), 2.43 (t, J = 0.015, 6.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.6, 28.9, 36.1, 85.1, 146.6.

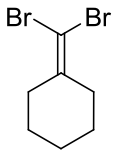
1.3.3 Synthesis of (dibromomethylene)cyclooctane



(Dibromomethylene)cyclooctane was prepared from 1-(tribromomethyl)-1-acetoxycyclooctane according to general procedure III. The product was purified as pale yellow oil (2.1 g). Yield: 84%; R_f = 0.9 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.43-1.53

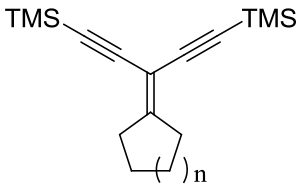
(m, 6H), 1.70-1.76 (m, 4H), 2.38 (t, J = 0.015, 6.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.3, 25.7, 27.2, 35.6, 84.5, 147.2.

1.4 Synthesis of (dibromomethylene)cyclohexane



(Dibromomethylene)cyclohexane was prepared according to the literature reported procedure.[4] Triphenylphosphine (10.6 g, 40.8 mmol) was dissolved in toluene (80 mL) and followed by the addition of carbon tetrabromide (6.8 g, 20.4 mmol). After stirred for 30 mins, cyclohexanone (1.0 g, 10.1 mmol) was injected to the reaction mixture and the mixture was heated to 80°C. After reacting for 15 hrs, the mixture was cooled and the mixture was diluted by hexanes (50 mL). The mixture was then subjected to filter through a silica gel pad and washed with two portions of hexanes (20 mL). Collected filtrate was concentrated and was purified by column chromatography using hexanes as eluent. The product was colorless oil (2.43 g). Yield: 95%; R_f = 0.9 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.55 (brs, 6H), 2.37-2.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.9, 26.9, 34.9, 82.0, 145.2.

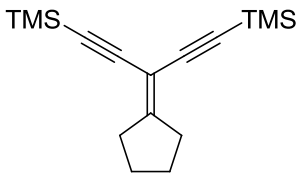
1.5 General Procedure IV for synthesis of (di((trimethylsilyl)acetynyl)methylene)cycloalkane (n = 1-4)



The synthetic procedure was according to the literature.[4] Diethylamine (20 mL) was added to the degassed mixture of (dibromomethylene)cycloalkane (5.0 mmol), $Pd(PPh_3)_2Cl_2$ (421 mg, 0.6 mmol) and CuI (228 mg, 1.2 mmol) at 23°C. The mixture was stirred for 5 mins and followed by the injection of trimethylsilylacetylene (1.8 mL, 12.5 mmol). The reaction mixture was refluxed for 24 hrs. After cooling to 23°C, the mixture was diluted with hexanes (30 mL) and filtrated through a silica gel pad, which was further washed with hexanes (2 ×

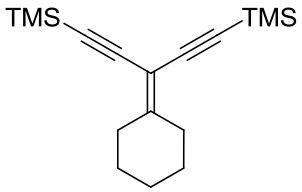
20 mL). The collected filtrate was concentrated and subjected to purification by column chromatography using hexanes as eluent.

1.5.1 Synthesis of (di((trimethylsilyl)acetynyl)methylene)cyclopentane



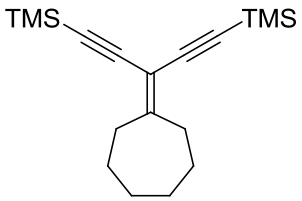
(Di((trimethylsilyl)acetynyl)methylene)cyclopentane was prepared from (dibromomethylene)cyclopentane according to general procedure IV. The product was purified as yellowish oil (700 mg). Yield: 49%; R_f = 0.5 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.19 (s, 18H), 1.71-1.75 (m, 4H), 2.49-2.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.2, 26.5, 34.2, 96.1, 97.6, 101.6, 171.3.

1.5.2 Synthesis of (di((trimethylsilyl)acetynyl)methylene)cyclohexane



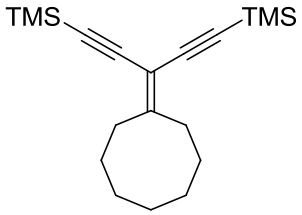
(Di((trimethylsilyl)acetynyl)methylene)cyclohexane was prepared from (dibromomethylene)cyclohexane according to general procedure IV. The product was isolated as yellowish solids (650 mg). Yield: 45%; R_f = 0.5 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.20 (s, 18H), 1.56 (brs, 6H), 2.49 (brs, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.15, 26.3, 27.6, 32.9, 96.3, 98.5, 101.3, 163.7.

1.5.3 Synthesis of (di((trimethylsilyl)acetynyl)methylene)cycloheptane

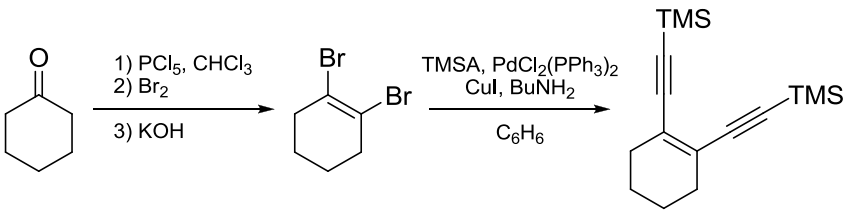


(Di((trimethylsilyl)acetynyl)methylene)cycloheptane was prepared from (dibromomethylene)cycloheptane according to general procedure IV. The product was purified as yellowish oil (734 mg). Yield: 61%; R_f = 0.4 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.19 (s, 18H), 1.51 (brs, 4H), 1.64 (brs, 4H), 2.60 (t, J = 0.015, 6.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.15, 26.9, 29.7, 34.5, 97.1, 101.3, 101.6, 167.3.

1.5.4 Synthesis of (di((trimethylsilyl)acetynyl)methylene)cyclooctane

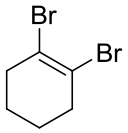


(Di((trimethylsilyl)acetynyl)methylene)cyclooctane was prepared from (dibromomethylene)cyclooctane according to general procedure IV. The product was isolated as yellowish oil (476 mg). Yield: 30%; R_f = 0.4 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.19 (s, 18H), 1.40-1.48 (m, 6H), 1.76 (brs, 4H), 2.52 (t, J = 0.015, 5.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.11, 25.7, 26.0, 27.5, 33.8, 97.1, 101.1, 101.8, 168.8.



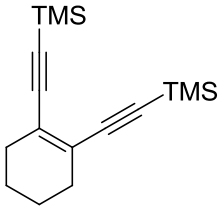
Scheme 2. Synthetic scheme of ligand trimethylsilyl-protected *L5*.

2.1 Synthesis of 1,2-dibromocyclohex-1-ene

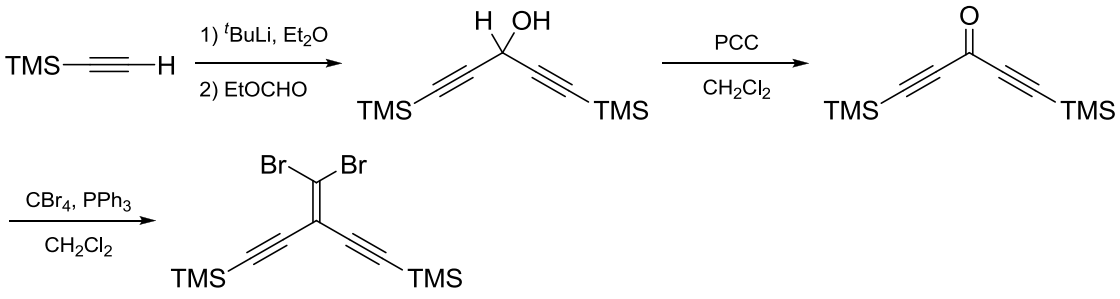


1,2-Dibromocyclohex-1-ene was prepared according to a literature reported procedure.[5] To a suspension of phosphorous pentachloride (21.6 g, 104 mmol) in chloroform (54 mL) was added cyclohexanone (10.3 mL, 100 mmol) in 30 mL of chloroform at 0°C over a period of 1 hr. The mixture was stirred for 2 hrs at 25°C and 2 hrs at reflux and poured onto 100 g of ice, followed by neutralization by adding solid $NaHCO_3$ (Caution! Extensive gas evolution!). The organic phase was separated, washed with sat. $NaHCO_3$ solution (100 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was dissolved in 10 mL CH_2Cl_2 and a solution of bromine (3.2 mL, 62 mmol) in CH_2Cl_2 (8 mL) was added dropwise at −5°C to the mixture. After the addition, the mixture was washed with $Na_2S_2O_3$ solution (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was distilled to give crude 1,2-dibromo-1-chlorocyclohexane as colorless oil, which was subjected to next step without prior purification. To a refluxing solution of KOH (2.2 g, 39 mmol) in methanol (10 mL), a solution of 1,2-dibromo-1-chlorocyclohexane in 10 mL of methanol was added slowly. The mixture was kept refluxing for another 3 hrs and then was cooled to 23°C. The mixture was neutralized with 6 M HCl solution and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried and filtered. After concentration, the residue was purified by column chromatography using *n*-hexanes as eluent to yield 1,2-dibromocyclohex-1-ene as colorless oil. Yield: 31%; R_f = 0.4 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.71-1.75 (m, 4H), 2.53-2.56 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.1, 37.3, 122.9.

2.2 Synthesis of 1,2-bis((trimethylsilyl)ethynyl)cyclohex-1-ene

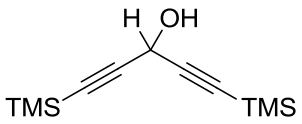


To a suspension of $PdCl_2(PPh_3)_2$ (134 mg, 0.19 mmol) and CuI (72 mg, 0.38 mmol) under nitrogen, a solution of 1,2-dibromocyclohex-1-ene (755 mg, 3.14 mmol) in benzene (6 mL) was injected. Subsequently, *n*-butylamine (2 mL, 20.1 mmol) was added. The mixture was kept stirring for 15 mins before the addition of trimethylsilylacetylene (2.4 mL, 16.7 mmol). The reaction mixture was allowed for stirring at 23°C for more than 16 hrs. TLC analysis indicated the disappearance of the starting materials. The mixture was diluted with *n*-hexanes (30 mL) and filtered through a pad of silica gel. After concentration under reduced pressure, the residue was purified by column chromatography (*n*-hexanes) to yield the desired product as pale yellowish oil. Yield: 76%; R_f = 0.3 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.20 (s, 18H), 1.56-1.59 (m, 4H), 2.20-2.21 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.25, 21.8, 30.1, 98.5, 105.5, 127.4.



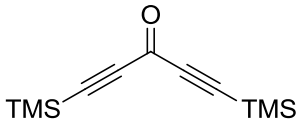
Scheme 3. Synthetic scheme of ligand trimethylsilyl-protected *L6*.

3.1 Synthesis of 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol



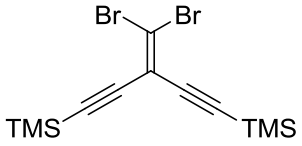
The preparation of 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-ol is followed according the reported literature procedure.[6] Trimethylsilane (4.0 mL, 28.6 mmol) was injected to a solution of Et_2O (70 mL) under nitrogen and the mixture was cooled to −10°C. A solution of ^{t}BuLi in pentane (1.3 M, 21 mL, 27.4 mmol) was dropped to the mixture slowly. The reaction mixture was continued to stir for another 15 mins. Subsequently, methyl formate (1.0 mL, 12.4 mmol) was injected and the mixture was allowed to warm to 23°C over 30 mins. Sat. NH_4Cl solution (30 mL) was added to quench the reaction and the ether layer was separated. The aqueous layer was further extracted by Et_2O (2 × 20 mL). The combined organic layer was washed with sat. brine solution (40 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography (*n*-hexanes/EtOAc, 20:1) to yield the pure pentadiynol as colorless oil. Yield: 50%; R_f = 0.4 (*n*-hexanes/EtOAc, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.19 (s, 18H), 2.20 (d, J = 7.4 Hz, 1H), 5.09 (d, J = 7.4 Hz, 1H).

3.2 Synthesis of 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-one



The preparation of 1,5-bis(trimethylsilyl)penta-1,4-diyn-3-one is followed according the reported literature procedure.[7] A solution of pentadiynol (2.9 g, 13.2 mmol) in CH_2Cl_2 (95 mL) at 23°C was added PCC (4.3 g, 19.8 mmol). TLC analysis was used to monitor the reaction, and oxidation to the ketone was typically complete after 3 hrs. The reaction mixture was passed through a plug of silica gel (CH_2Cl_2) to remove chromium waste and the solvent removed in vacuo to yield the ketone as pale yellowish oil, which is pure enough to proceed the next step. Yield: 95%; R_f = 0.5 (*n*-hexanes/EtOAc, 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.9, 53.5, 79.3, 160.2.

3.3 Synthesis of (3-(dibromomethylene)penta-1,4-diyne-1,5-diyl)bis(trimethylsilane)



The dibromo-olefination process is followed according the reported literature procedure.[7] Carbon tetrabromide (8.6 g, 25.9 mmol) and PPh_3 (13.6 g, 51.8 mmol) were added to CH_2Cl_2 (100 mL) and allowed to stir for 5 minutes at 23°C until the mixture turned bright orange. A solution of the ketone (2.9 g, 12.9 mmol) prepared previously in CH_2Cl_2 (5 mL) was slowly added to the CBr_4/PPh_3 mixture over a period of 1 min. The reaction mixture turned a darker red/orange color upon addition of the ketone. TLC analysis was used to monitor the reaction, indicating that dibromoolefination was typically complete almost immediately. Solvent was reduced to ca. 5 mL, hexanes added (100 mL), the inhomogeneous mixture filtered through silica gel and the solvent removed in vacuo. The residue is purified by column chromatography (*n*-hexanes as eluent) to provide the pure dibromoolefins as colorless oil. Yield: 90%; R_f = 0.5 (*n*-hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.5, 100.1, 102.7, 110.5, 114.3.

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